Polymer Reinforcement

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To my wife
Yuri S. Lipatov

Table of Contents

> No one scientific truth is given in direct experiment. The direct experiment itself is the result of speculation.
>
> Vladimir Solovjev

FOREWORD

Polymeric composite materials have been known since ancient times. To create modern composites, it is necessary to use the fundamental principles of organic and inorganic chemistry, polymer chemistry, physical chemistry, physics and mechanics of solid and polymers. In this monograph the author presents only one aspect of the problem, namely a physico-chemical one, as being the most general and typical of all the variety of modern composites. The materials included are polymers filled with particulate fillers, fiber-reinforced plastics, and polymer alloys and blends. The most common feature of all these materials is that they are heterogeneous multicomponent systems whose properties are not a sum of properties of constituent components.

For more than 35 years, the author of this monograph has developed and attempted to prove experimentally the ideas according to which the main role in properties of composite materials belongs to the surface phenomena at the polymer-solid interface. Author believes that all the development of the physical chemistry of filled polymers confirms this idea. This book is dedicated chiefly to the analysis of surface and interphase phenomena in filled polymers and their contribution to the physical and mechanical properties of composites. The advantage of such an approach is in its ability to describe the properties of all types of composites, namely those filled with disperse organic and inorganic fillers, reinforced by organic and inorganic, including metallic fibers, where the matrix is formed by rubbers, thermoplasts, elastoplasts and reactoplasts. The details of the mechanisms of reinforcement may be different in each case but the physico-chemical principles remain valid, since they are based on the analysis of the interfacial phenomena.

The above principles predetermined the structure of this book. Separate chapters are dedicated to the most fundamental principles of surface phenomena in polymers and to properties of the surface polymer layers at the interface with a solid. One can assert with confidence that fundamental principles of physico-chemical theory of filling of polymers include the theory of adsorption at the polymer-solid interface, adhesion to the surface, and the theory of behavior of surface or border polymer layers at the interface.

In this monograph, I have used both theoretical and experimental data presented in literature and experimental data and approaches developed by this author and his coworkers. Clearly, the development of any branch of science leads to the necessity to renounce some points of view developed earlier in order to formulate new, more precise theories. “In science, the only statements that have value are those which allow us to doubt their validity” - Valery Bryusov (1873 -1924). “For us, the freedom of the search of truth is the greatest value, even if it may lead to the collapse of all our ideals and beliefs”. Citing these words I would like to emphasize that other approaches and opinions are always welcome.

Finally, I wish to express my thanks and appreciation to many without whom this book could not be written. First to my wife, who, despite her own activity in polymer chemistry, helped, supported, and inspired me with her love and tenderness. Her advice to me has always been very fruitful and full of goodwill. My warmest thanks to my collaborators at the Institute of Macromolecular Chemistry, Prof. Valery Privalko, Dr. Anatoly Nesterov, Dr. Tamara Todosiychuk, Dr. Valentin Babich, and Dr. Valery Rosovitsky for numerous discussions. They provided many ideas, as well as the results, that are incorporated in this book.

My sincere thanks to Dr. S. Lipatov (Kiev) and Mr. P. M. Oleshkevych (Toronto) for their helpful assistance in preparing the computer version of this book.

Yuri S. Lipatov
Kiev, 1989-1994

INTRODUCTION

The reinforcement of linear and crosslinked polymers is a process of their compatibilization with various solid, liquid, and gaseous substances which are uniformly distributed in the bulk of polymer and have a pronounced phase border with polymeric phase (matrix). Polymers filled with solid particulate or fibrous fillers of organic and inorganic nature are classified as polymeric composite materials, PCM. In this book, we consider this class of polymeric materials but do not consider polymers filled with liquids (e.g., water) and polymeric foams. Filling or reinforcement of polymers to enhance some properties of the material is one of the most important and popular methods of production of plastics, rubbers, coatings, adhesives, etc., which must possess the necessary mechanical and physical properties for any given practical application. All these materials have the same common physico-chemical feature. They are heterophasic (consisting of two and more phases) polymer systems in which phases interact with one another. The appearance of new properties is determined not only by proportion of two (or more) different materials but also by the interphase phenomena.[1] On the basis of this definition, we relate to PCM the following systems:

- polymers, filled with particulate or fibrous mineral and organic fillers (talc, chalk, carbon black, fumed silica, disperse metals, glass spheres, monocrystalline whisker, polymeric powders, etc.)

- reinforced polymers where continuous reinforcing fibers are in a definite way distributed in polymer matrix. These fibers may be inorganic (glass, metal, boric, basalt) and organic (synthetic and carbon)
- polymer blends where polymer components are not thermodynamically compatible and form two-phase systems with a definite distribution of the regions of phase separation. These blends may be formed by both linear and crosslinked polymers (including semi- and full interpenetrating polymer networks).

Sperling[2] has proposed a classification of PCM which is more complex, and which considered details of a great number of compositions which we do not intend to discuss in our book. Having no claim to full classification, we would like to indicate that our classification, presented above, gives a rather comprehensive idea as to what materials should be related to PCM. Our principle is based, first of all, on the dimensional parameter of components introduced into polymer matrix: disperse particles, short cut fibers, anisotropic fibrous fillers, including fabrics and disperse polymeric particles.

From a theoretical point of view, fillers, introduced into the matrix, must be characterized by numerous parameters (shape, dimension, size distribution, orientation in matrix, composition, etc.); the mean particle size of disperse phase is the most convenient parameter. Here we use the word “phase” only to describe the reinforcing component, not the thermodynamic meaning of the notion as a structure, a uniform part of a substance. Many reinforcing fillers may be composed of heterogeneous multiphase systems. For the convenience of comparison, the mean values of particle sizes (in m), introduced into a polymer matrix to produce PCM, are given below:

colloid particles, metals, polymers	10^{-9} - 10^{-6}
phase domains in polymer blends	$5\text{-}50\times10^{-9}$
carbon black	10^{-8}
pigments and fine disperse fillers	10^{-8} - 10^{-5}
monocrystalline fibers (whisker)	10^{-5}
glass and synthetic fibers	10^{-8}
glass microspheres	10^{-6} - 10^{-4}

One of the most important characteristics of fillers, connected to their chemical nature, is the fundamental value of free surface energy. Because the conditions of the interfacial interaction between matrix and filler depend on the ratio between the free surface energy of filler and the matrix, it is acceptable to divide all the materials into two groups: of high (metals, oxides and other inorganic substances) and low (polymers, organic substances) surface energy. From this point of view, PCM also should be divided into two main groups: polymer matrices containing fillers of high surface energy and polymer matrices with fillers of low surface energy. The main factor for all cases, determining the contribution of interphase phenomena to the properties of PCM, is the total surface, S (per volume unit), of the phase border between two phases, i.e., the particle size or diameter. These values, together with the geometric shape of particles, determine the limiting load of polymer matrix with a filler. Taking into account these considerations, the structure of PCM may be represented as a continuous polymer phase (matrix) with inclusions of one or more disperse phases distributed in the matrix. In such a way, the very principle of formation of PCM consists of combination of two (or more) materials (at least two phases) and the technological method of their preparation. The resulting material may be isotropic or anisotropic, depending on the type of filler and its distribution in the matrix. The result of such a combination is the formation of material, physical and mechanical properties of which differ essentially from properties of initial components. The filler is first of all introduced to reinforce the matrix. The mechanism of reinforcing depends on the filler type, its amount, distribution and the chemical natures of a matrix and a filler. Introduction of filler also changes thermophysical, electric and dielectric, frictional, and other properties. This shows that introducing filler into a polymer matrix cannot be considered only as a method of modification of properties of polymers. It is a universal principle of creation of new materials with a complex mechanical and physical properties inherent only for these materials and caused both by micro- and macroheterogeneities of the system (see Chapter 4), and by the chemical and physical interactions at the polymer-solid interface. The physical chemistry of reinforcement of polymers differs, depending on the technological process of production (to produce PCM both polymeric substances and initial components used for their formation play role). However, in both cases, the processes at the interface play a dominant role. The necessary condition of efficiency of PCM is the ability of a binder to form strong adhesion bonds at the interface. These bonds allow us to realize the joint work of all elements of PCM, namely, filler and matrix, which is especially important for reinforced plastics. There also exists an optimum ratio of elasticity modulus of fibrous fillers and matrix which enhances the durability.[3] In such a way, the polymeric matrix should possess some definite properties to be used in PCM, including good ability of wetting the filler surface. The choice of fillers for PCM depends on the purpose of application and the necessity of changing some original properties of the material. Almost all the substances existing in nature, after a special treatment to reach the necessary size and shape of particles, can be used as fillers. The shape may be spherical, irregular, fibrous, etc. One may also use fibers, ribbons, platelets, roving, fabrics, thick felts, etc., which are distributed in a definite way in polymer matrix.[4] Filler choice is determined by the size of particles and their size distribution. The specific surface area of filler is its very important characteristic, which determines the effectiveness of filler action. The value of the specific surface is especially important in the cases where the filler surface is modified by surfactant, sizing agent, or any other chemical method. The shape of filler particles determines the manner of their packing in the matrix and therefore is also of great importance. Usually, to reach the minimum unoccupied volume in highly loaded composites, different sizes of filler particles are mixed in a predetermined way. The packing of larger particles determines the total volume of the filled system, whereas smaller particles fill the voids between larger ones. Introducing particulate fillers into a polymer matrix allows one to realize expected effects. The fillers, which improve mechanical properties of PCM, are usually termed as active fillers. From a chemical point of view, the choice of a filler is strongly dependent on its free surface energy, as mentioned above. The presence on the surface of various chemically-active groups, able to participate in chemical reactions with other substances, including polymeric binder, is of great importance. The fillers should have chemical and thermal stability in conditions of production and application of PCM. In some cases, the electrical, thermal, and optical properties of fillers are also emphasized. Polymeric composite materials or filled polymers (two-phase heterogeneous systems) have, as a rule, one continuous phase, namely, a polymer matrix (primary continuous phase, according to Richardson).[5] The phase distribution in PCM is a very important factor influencing its properties. Continuous fibers, threads, and fabrics form another, secondary continuous phase, whereas particulate fillers represent a secondary disperse (discontinuous) phase. Despite the great variety of properties and types of binders (matrices) and fillers, the common feature of all PCMs is the existence of a phase border between two main components and the formation of an interphase layer between them. The formation of the interphase layers and difference in properties between polymer in the interphase region and in bulk for the first time have been considered in some works summarized in monographs.[6,7] The concept of interphase layers is widely accepted now, although, up to now, the influence of these interphase regions on the properties of PCM is not yet quantitatively established.

According to Richardson,[5] their role should be neither overestimated nor underestimated. The formation of interphase layers is the most important result of an existing phase border between polymer and solid. It gives us the foundation to consider all the physical and chemical processes in PCM and physical chemistry of the reinforcement from one common point of view, based on the analysis of the influence of a polymer-solid interface on the properties and structure of surface layers and their contribution to the properties of filled polymers. In connection with the effects attained by introducing fillers into a polymeric matrix, there exists a classification dividing all fillers into two groups: active, or reinforcing (mainly improving mechanical properties) and inactive, which are introduced to attain a definite color of some materials or decrease their cost. The conventionality of such classification is evident, as the filler activity cannot be brought to change only one property. At the same time, the efficiency of active fillers may also be very different regarding their influence on the properties of filled polymers. According to Rhebinder,[9] all fillers may be divided from a colloid-chemical point of view into three groups:

- active fillers forming a stable suspension in the corresponding matrix
- inactive fillers capable of activation by surfactants, which form adsorption layers and have chemically bonded groups at the surface
- fillers inactive and incapable to activation, i.e., not able to form surface layers at the interface.

The filler activity in this case is determined by the molecular interaction between media and filler and by formation of solvated shells. This means that some part of the dispersion medium (polymer) forms these shells and transits into a two-dimensional state, which has higher mechanical properties, compared to the polymer in bulk. The fraction of the dispersion medium, in the state of shells, increases with increase in the degree of dispersity of a filler at a given volume concentration. The optimum of dispersity is situated in the region of the sizes of colloidal particles. At higher dispersity, the border between two phases disappears. Therefore, particles which form a liophilic disperse system in the dispersion media (liophilic suspension) may serve as active fillers. In highly polar media, only hydrophilic disperse fillers may be active, whereas in the media of low polarity, only oleophilic fillers (for example, carbon black as a filler for rubber) are active.[8]

It is also clear that activity of a filler should be related to any definite property of material. It was proposed[9] to introduce the concept of structural, kinetic, and thermodynamic activity of fillers. Structural activity of a filler is its ability to change the polymer structure on molecular and submolecular level (crystallinity degree, size and shape of submolecular domains, and their distribution, crosslink density for network polymers, etc.). Kinetic activity of a filler means the ability to change molecular mobility of macromolecules in contact with a solid surface and affect in such a way the relaxation and viscoelastic properties. Finally, thermodynamic activity is a filler's ability to influence the state of thermodynamic equilibrium, phase state, and thermodynamic parameters of filled polymers — especially important for filled polymer blends (see Chapter 7).

Introduction of these definitions is very important to understand the processes of reinforcement of polymers, although they cannot be used for quantitative description of filler influence. The degree of this influence, as shown below, depends not only on the chemical nature of a filler but on its concentration in a polymer matrix. In such a way, the same filler may be active in one polymer and inactive in another. The influence of a filler may be related to the change in properties per unit content of filler, which is another quantitative characteristic of filler. However, this assessment is very arbitrary, because the reinforcement is not linearly related to the filler concentration. Reinforcement can be related to the energy, A, used to rupture polymer under standard conditions, as measured by the area under the stress-strain curve:

$$A = \int_{L_0}^{L_r} \sigma dL$$

where L_r is the length of the specimen at rupture, L_0 is initial length, σ is the stress.

To bring the polymer into the state of a surface layer on the filler particles, it is necessary to contribute work to overcome the forces of surface tension. This work is expended for increasing the surface of the polymer, and it is a measure of the additional work necessary for rupture. The increase in the work of rupture, per unit of volume, by the incorporation of the filler, may be taken as a basic characteristic of the reinforcing action of fillers in polymers which are in the rubber-like state. Fillers which do not increase work of rupture are considered inactive, those which do increase are considered active. The magnitude of effect depends on the nature of the filler. To assess the reinforcement, one may use the relative reinforcement:

$$R = (\sigma_f - \sigma_p)/\sigma_p$$

where indices f and p refer to the filled and unfilled polymer. R also depends on the degree of reinforcement.

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1

THE BASIC THEORIES OF POLYMER ADSORPTION

The adhesion at the polymer-solid interface is the most important factor determining the properties of filled and reinforced polymers. Strong interaction is the necessary condition for improving and changing polymer properties by filler reinforcement. Polymer composite materials (PCM) are frequently formed from liquid compositions capable of curing and polymer formation, or because of solvent evaporation from concentrated solution. The primary act of formation of an adhesive joint is the polymer adsorption at the interface with a filler surface. This adsorption may proceed either from polymer solution or from liquid composition. The role of adsorption interaction with the solid surface is of special importance for multicomponent binders, where the selective adsorption of one of the components of the reaction mixture occurs. As a result of adsorption, the adsorption layers are formed at the interface with a solid. Their properties are different than properties of polymer in bulk. The formation of adsorption layers is a factor influencing adhesion of a polymer to the filler surface. Therefore, the theories of polymer adsorption are a very important constituent part of the theory of formation of PCM.

1.1 THE MAIN PRINCIPLES OF POLYMER ADSORPTION FROM DILUTE SOLUTION

Adsorption of polymers essentially differs from adsorption of low-molecular-mass substances. The difference is associated not only with macromolecular size of the molecules adsorbed from solution, but also because of different conformations of the macromolecular coil, the degree of interpenetration of the coils, and the degree of their aggregation, i.e., different shapes and sizes of the particles are adsorbed. With the exception of extremely dilute solutions, the effect of adsorption depends on concentration of the solution from which the adsorption occurs. There are many works and reviews where the modern theories of adsorption are discussed.[1-13]

The prevailing part of theoretical and experimental investigations was dedicated to studies of adsorption from dilute solution. Having in mind a great deal of various concepts of adsorption and the fact that most of them cannot be proved experimentally, in the present chapter, the basic theoretical statements concerning the adsorption from dilute solutions are only considered. More attention is given instead to adsorption from semi-dilute solutions, adsorption from polymer mixtures, and structure of adsorption layers - all important for understanding the properties of PCM and theory development which can describe the interphase regions in filled polymers.

The main findings in adsorption of polymers from dilute solutions regard observation that adsorption sharply increases at the initial stages, followed by pseudo-saturation at higher concentrations. The adsorbance, A, corresponds to 2 to 5 equivalent monolayers. The adsorption process strongly depends on the thermodynamic quality of the solvent. Adsorption from a “poor” solvent is more pronounced, compared with adsorption from a “good” solvent. As a rule, polymers with higher molecular mass are adsorbed, to a larger extent than low molecular mass polymers. This dependence is more pronounced for adsorption from poor solvents. It is important to note that desorption of macromolecules in dilute solutions practically does not occur.

These qualitative regularities have their theoretical substantiation in modern theories. Statistical theories considering the behavior of a single isolated chain in extremely dilute solution allow us to formulate the concepts describing the conformation of adsorbed chain, depending on the adsorption conditions. Figure 1.1 shows schematically the various conformations of polymer chain at the solid surface, including the case of an aggregative adsorption (see below). For flexible polymer chains, the formation of sequences of adsorbed segments (trains), loops, and tails is typical. The adsorbed loops and tails determine the configurational entropy of the polymer chain, whereas enthalpy of adsorption is determined by the direct interaction with the surface of the bound segments in trains.

Due to conformational limitations, brought about by the surface and statistical conformations of the macromolecular coils in the solution, the polymer chain is bound to the surface with a relatively small number of segments, p. It can be determined experimentally and calculated using the equation:

$$p = P_b/(P_b + P_s) \qquad [1.1]$$

where P_b and P_s are the numbers of segments connected and not connected with the surface, respectively, which are fundamental characteristics of adsorption. Hence, some segments of the polymer chain lie on the surface, whereas the remainder extend into the bulk of the solution in the form of loops with different configuration or free ends (tails). As a result of incomplete binding, the adsorption layers are formed having local concentrations exceeding the mean concentration of the polymer in solution. At a low equilibrium concentration of the solution after the initial binding of the statistical chain at one point, it is possible that the number of chain contacts with the surface will grow and the chain itself would sprawl because of the chain flexibility and thermal movement of molecules. However, the increase in concentration and the excluded volume effect result in changing conditions of interaction with the surface. Transition from the adsorption of molecules, having extended flat configurations on the surface, to adsorption in the form of sequences of bound segments (trains) and segments forming loops stretching into the solution takes place. The thickness of the adsorption layer (or the length of alternating sequences of bound segments and loops) and the conformations of macromolecules is determined by a number of free contact points with the surface, which is higher at a smaller degree of surface coverage. With the solution concentration increasing, the adsorption layer rearranges and the conformations of the adsorbed molecules change. With surface saturation, the adsorption layer is formed by statistical coils and is “monomolecular”. Accordingly, as the surface becomes saturated, the value of p diminishes. This qualitative description of the mechanism of adsorption does not take into account the polymer chain's own flexibility, molecular mass, the energy of the interaction of the polymer with the surface, or the nature of the solvent. The value p, the length of the sequences of bound and free segments, and the thickness of the adsorption layer depend on these factors.

The dependencies of the loop length and the fraction of bound segments as a function of the interaction energy were calculated elsewhere.[11] The following conclusions on the influence of the interaction energy with the surface during adsorption result from modelling: If a polymer molecule is sufficiently large, the contact with the surface is realized through the segments of macromolecule, which is divided into alternating trains and loops. The size and conformations of these sequences at the surface and chain fragments extending into solution, are determined only by the chemical nature and physical structure of adsorbent and they do not depend on the polymer molecular mass. If all active centers of the surface are capable of adsorption, segments are readily adsorbed, and the molecule is sufficiently flexible, then the loops will be short and the molecule will locate itself near the surface, even if the energy of adsorption is low. For a flexible molecule an energy of the order of kT is sufficient for about 70% of segments to establish contact with the surface. Varying the parameters that affect adsorption, the arrangements of the macromolecules on the surface, and in the layer adjacent to it, will change accordingly, and, as follows from the calculations for different models of adsorption, the segment density distribution in the surface layer will also change.

As a crude scheme, one can visualize the existence of two strata in the adsorption layer: one denser near the surface or on the surface and a remote, less dense layer consisting loops and tails and also chains bound to the surface with only one end, so-called anchor chains (their segments have no direct contact with the active centers on the surface). In the initial section of isotherm, the layer has a small thickness and a high polymer concentration.[12] With higher concentration, the solution and the layer structure undergo rearrangements; newly adsorbing molecules break already made links and as a result, the total number of binding points decreases, the layer thickness increases, and the concentration in the layer decreases.

Prigogine[13] identified three effects of adsorption from dilute solutions:

- entropy effect, determined by the possibility of attaining various conformations near the surface
- the first energy effect due to displacement of the adsorbed molecules of the solvent
- the second energy effect characterized by the difference in energies of pair interaction.

In describing the mechanism of adsorption, it is necessary to account for the nature of the solvent. The thermodynamic quality of the solvent is the main factor, determining the chain conformations. All current theories of adsorption from dilute solutions include the parameter of interaction between polymer and solvent. Temperature dependence of this parameter also determines the temperature dependence of adsorption and the characteristics of the adsorption layer (for more details see references 1-13).

It is worth noting that adsorption is a dynamic process, establishing the equilibrium in the system and may be described by the kinetic equations of the second order. The approach to the equilibrium state is very slow and the surface layer of a polymer at the interface in the presence of a solvent stays in the metastable state, which, however, does not prevent the establishment of the conformational equilibrium.[14]

1.2 ISOTHERMS OF POLYMER ADSORPTION FROM DILUTE SOLUTIONS

The properties of polymer solution and the solution of low molecular mass substance differ substantially. The adsorption isotherms obtained for low molecular mass systems cannot be applied to polymers. However, for very dilute solution, adsorption can be described by the Langmuir isotherm

$$\theta = A_p/A_{ps} = bc/(1+bc) \qquad [1.2]$$

where θ is the degree of surface coverage, A_p is the amount of polymer adsorbed at concentration c, A_{ps} is the adsorption at saturation, and b is a constant. Eq 1.2 is derived for solutions in which adsorbing molecules are spherical, do not interact with each other, and do not change their shape on adsorption. None of these conditions are valid for polymer solutions and therefore experimental isotherms coincide with those calculated using the Langmuir equation only at very low concentrations. For a wider concentration range, the polymer adsorption can be described by the empirical Freundlich isotherm:

$$A_p = \beta c^{\mu} \qquad [1.3]$$

where β and μ are constants. Eq 1.3, however, is not applicable at low concentrations. The applicability of the Freundlich equation over a wide concentration range can be explained by the mechanism of aggregative adsorption (see 1.8), in which aggregates of macromolecules, having independent kinetics or structural units, interact with the adsorbent surface together with individual molecules.[10] In this instance the adsorption mechanism is not as specific as for dilute solutions because the conformational effect is less important. Polymer adsorption isotherms for dilute solutions have been derived theoretically by Simha, Frisch and Eirich.[15,16] The polymer solution is assumed to be infinitely dilute, whereas a polymer molecule is regarded as a gaussian coil. Active centers are located regularly on the surface with the area of the active center corresponding to the surface of adsorbing segment, and each active center can bind only with one segment. In this instance, only monomolecular adsorption is taken into account. For this case, the adsorption isotherm assumes the form:

$$\left[\theta e^{2K_1\theta} / (1-\theta)^{\langle v \rangle}\right] = Kc \qquad [1.4]$$

where θ is the degree of the surface coverage, K_1 is a constant characterizing the interaction of polymer molecules with each other, K is a complex function of the molecular mass of the segment, solvent, temperature and other variables, $<\nu>$ is the mean number of bound segments of each molecule consisting of t segments; $<\nu> = pt$. The isotherm equation for $<\nu> = 1$, i.e., for full adsorption of all segments, becomes the Langmuir adsorption isotherm, as $K_1\theta << 1$. Although the derivation of the isotherm equation is based on simplified assumptions, the essential point is that at the stage of determination of values involved in the equation, one considers the interaction of polymer segments with each other, i.e., the concept of a reflecting barrier is introduced, due to which the already adsorbed segments hinder further adsorption. The magnitude of the barrier is characterized by a number of loops restricting access to adsorption centers and a function of the degree of surface coverage. Experimental data on the adsorption of polymers from dilute solutions, however, show that the value of equilibrium adsorption, as a rule, exceeds the values calculated for monomolecular adsorption.

Therefore, Frisch and Simha further assumed that one adsorption center can bind S layers of segments if the adsorption is carried out through individual loops; $\langle \nu \rangle$ equals the mean number of molecular bonds of each molecule in all layers. The equation of the adsorption isotherm can be derived in the following way. Let the surface contain N_s adsorption centers capable of binding one segment each. In the polymer solution, there are N molecules from t segments, of which ν segments are bound with the surface and N_o solvent molecules. The fraction of the surface occupied by polymer segments, θ, and molecules of solvent, θ_o, can be found from the equation:

$$\theta = \nu N'/N_s; \qquad \theta_o = N'_o/N_s \qquad [1.5]$$

where N' is the number of adsorbed macromolecules and N'_o is the number of adsorbed solvent molecules. The number of polymer molecules remaining in the solution of concentration, c, is $(N - N')$, whereas the number of the solvent molecules is $(N_o - N'_o)$ at the solvent concentration c_o. Let us consider the following equilibriums:[17]

a) macromolecule in the solution + ν free sites give N' adsorbed macromolecules bound by n segments (equilibrium constant $K_\nu = k_1/k_2$)
b) solvent molecules + 1 free site give N_1^o of adsorbed molecules of the solvent (equilibrium constant $K_o = k_1^o/k_2^o$).

The concentration of free sites on the surface is $(1 - \theta - \theta_o)$. Applying the law of mass action, we find an expression for the rate of the adsorption of the polymer:

$$_{r1} = k_1 c(1 - \theta - \theta_o)^\nu \qquad [1.6]$$

and the rate of desorption:

$$r_2 = k_1^o c_o(1 - \theta - \theta_o) \qquad [1.7]$$

Accordingly, the rate of the solvent adsorption is:

$$r_1^o = k_1^o c_o (1 - \theta - \theta_o) \qquad [1.8]$$

and the rate of desorption is:

$$r_2^o = k_2^o \theta_o \qquad [1.9]$$

In Equations 1.8 and 1.9, we equate r_1 and r_2 and divide both sides of the equation by $(1 - \theta)^n$:

$$(\theta/\nu)/(1 - \theta)^n = K_\nu c[1 - \theta_o/(1 - \theta)]^\nu \qquad [1.10]$$

where $K_\nu = k_1/k_2$. Taking $K_o = k_1^o / k_2^o$, we obtain:

$$\theta(1 - \theta) = K_o c_o / (1 + K_o c_o) = \beta_o << 1 \qquad [1.11]$$

Let us divide equation by $(1 - \theta)$. After a number of conversions, we find:

$$\theta/\nu(1 - \theta)^n = (1 - \beta_o^\nu) K_\nu c = K_c \qquad [1.12]$$

At $K_o \to 1$, the equation reduces to the Simha and Frisch equation, and at $K_\nu \to 0$ (i.e., $\theta \to 0$) to the Langmuir equation. The same equation may be obtained on the basis of statistical concept of the behavior of the flexible molecule in space. There are other approaches to derive the isotherms of adsorption based on the statistical physics of polymer. The equations obtained cannot be proven by experiment, due to a great number of unknown parameters.

A more perfect form of the adsorption isotherm was derived by Silberberg,[11] based on concepts of conformation of adsorbed chains and the structure of the adsorption layer formed by the sequences of bound segments and loops extending into the solution. According to Silberberg, the shape of the chain is determined by the adsorption energy and surface structure, i.e., by the character of the arrangements of active centers in it. Real isotherms of polymer adsorption strongly depend on the polymer polydispersity, due to various adsorbance of low and high molecular mass fractions.[11,18]

1.3 THERMODYNAMIC INTERACTION BETWEEN POLYMER AND SURFACE

The adsorption of polymers from solutions strongly depends on the thermodynamic quality of solvent and the interaction energy between polymer and surface. All theories of adsorption include the thermodynamic parameter of interaction of the Flory-Huggins theory χ_{12}. The thermodynamic interaction between polymer and solvent determines the conformation of macromolecules in solutions and thus the conditions of its interaction with the surface. The interaction between polymer and surface is characterized by the parameter of thermodynamic interaction, which was introduced by Silberberg,[19,20] χ_s, using the model of quasi-crystalline lattice of the surface layer, describing the properties of polymer solutions. This parameter may be determined as follows:

$$\Delta U_s = -\chi_s kT \qquad [1.13]$$

where ΔU_s is the change in enthalpy by adsorption, i.e., the difference between energies of contacts segment-surface and segment-solvent. The physical meaning of parameter is discussed below.[4] If a molecule of a solvent, adsorbed by the surface, is displaced by the segment of macromolecule, the interaction between segment and solvent is changed. It is assumed that the total number of contacts, z, of a given segment or molecule of solvent produces z′ contacts on the surface, and (z - z′) contacts are between neighboring solvent molecules and other segments in the bulk of solution. Parameter χ_s characterizes the total change in enthalpy (in kT units) in the course of exchange of the segment having 1/2(z \ z′) contacts with solvent molecules and 1/2(z - z′) contacts with other segments. The solvent molecules in solution have 1/2z contacts with other solvent molecules and 1/2z contacts with segments of macromolecules. It is supposed that adsorption sites on the surface have an equal number of contacts between segments and solvent molecules.

As a result of such an exchange, segment substitutes z′ contacts segment-surface (S-2) on 1/2 z contacts polymer-polymer (2-2) and 1/2 z contacts polymer-solvent (2 -1). The molecule of solvent losses 1/2 z′ contacts (1-2) and 1/2z′ contacts (1-1), and gains z′ contacts (S-1). Other (z-z′) segments are unchanged for solvent molecule and segments and do not contribute to the total enthalpy. The enthalpy of exchange will then be:

$$z'(H_{s1} - H_{s2} + 1/2\,H_{22} + 1/2H_{11}) \qquad [1.14]$$

or

$$\chi_{s} = z'(H_{s1} - H_{s2} + 1/2H_{22} + 1/2H_{11})/(kT) \qquad [1.15]$$

The value χ_s is positive if by interaction of polymer with adsorbent, there exists a critical value $\chi_s = (\chi_s)_{crit}$ at which adsorption is possible. This critical value is of the order some tenth per segment. Value $(\chi_s)_{crit}$ exists because the loss in conformational entropy, connected with segment adsorption, must be compensated by the decrease in free energy due to the formation of contacts segment-surface. When χ_s begins to exceed $(\chi_s)_{crit}$, the adsorption sharply increases with growth of χ_s. Such behavior distinguishes adsorption of polymers from adsorption of small molecules, which is possible at all positive values of χ_s and gradually increases with the growth of this parameter. The estimation of this value is of great importance. However, only recently was a general method of the determination of χ_s proposed.[21]

The method is based on the following theoretical premises. The lattice model for a regular solution in contact with an adsorbing surface is used. The physical meaning of value $-\chi_s/kT$ allows one to conclude that if the contact surface-solvent has a low free energy, value χ_s may be below critical value and adsorption of a polymer does not proceed. It means that there are such solvents which prevent adsorption. A mixture of two solvents allows us to bring about the desorption of previously adsorbed polymers. When the composition of mixed solvent is changed, the excess amount of adsorbed polymer, θ_{ex}^{p}, expressed as the number of equivalent monolayers, diminishes and eventually passes through the value $\theta_{ex}^{p} = 0$. At the critical composition of binary solvent, the adsorbed polymer is fully substituted by a more strongly adsorbing component of mixed solvent (solvent-displacer). In such a three-component system, three χ_s parameters play a role, one for each pair of components. Let us label each χ by two indices, specifying the respective component pair. Thus χ_s^{po} is the adsorption energy parameter for adsorption of polymer from solvent, χ_s^{pd} for polymer from displacer, and χ_s^{do} for displacer adsorbing from the solvent. Then there is a simple relation between the three parameters:

$$\chi_s^{po} - \chi_s^{pd} = \chi_s^{do} \qquad [1.16]$$

The preferential adsorption of displacer is characterized by the negative value of χ_s^{pd}. In the three-component system, the adsorption may be represented as an exchange process between each of the three-component pairs: polymer-solvent, polymer-displacer, and solvent-displacer. The free energy change of all three processes, which may be expressed by three χ_s and three χ_s parameters for six concentrations in the surface layers and in the bulk solution, must be zero. In order to describe the equilibrium in a three-component solution, it is sufficient to calculate the free energy of two exchange processes in which all three components participate.

In present theories,[22,23] it is considered a multilayer model for description of the interfacial region, i.e., a lattice consisting of many layers of sites parallel to the surface. Each lattice site may be occupied by either a solvent molecule, a displacer molecule, or a polymer segment. Each site has z nearest neighbors, fractions λ_o and λ_1 of which are in the same layer and in each of the neighboring layers, respectively. When the chain consisting r segments is adsorbed with the fraction of bound segments, p, that means that pz molecules of a solvent are displaced from the surface. The free energy change ΔG^{po} consists of several parts:

- the entropy of mixing per polymer chain, $kT\ln(\Phi_1 /F^*)$, where Φ_1 is the volume fraction of polymer in the adsorption layer, and Φ^* is the volume fraction of polymer in the bulk solution
- the mixing entropy for the pr solvent molecules, $-kTpr \ln(\Phi_1^o / \Phi_*^o)$, where Φ_1^o and Φ_*^o are the volume fractions of the solvent in the adsorption layer and in solution, respectively
- the change in conformational entropy per one chain. Its loss is equal to $kT(pr - 1)(\chi_s)_{crit}$, where $(\chi_s)_{crit}$ is a critical parameter equal to $\ln(1 + \lambda)$
- the adsorption energy with respect to the solvent, $-kTpr\chi_s^{po}$
- the mixing energy per chain, $pr\Delta H^{po}$. The last value determines the changes in the contact free energy in the case, when a polymer segment in solution is exchanged with a solvent molecule in the adsorption layer.

The final expression for the interaction parameter χ_s^{po} is:[24]

$$\chi_s^{po} = \ln\Phi_{crit} + \ln s + (\chi_s)_{crit} - \lambda_1\chi^{po} + [(1-\Phi_{crit})(1-\lambda_1) - \lambda_1]\Delta\chi^{do}$$
$$\Delta\chi^{do} = \chi^{pd} - \chi^{do} - \chi^{po} \qquad [1.17]$$

where $s = \exp(\chi_s^{do} + \lambda\chi^{do})$ is the initial slope of the displacer isotherm.

The experimental verification was presented for the adsorption of polyvinylpyrrolidone on silica,[24] and adsorption of PMMA on fumed silica.[25] The theory developed gives the possibility of experimental evaluation of the energetic factors and their role in adsorption.

Another experimental method of estimation of the energetics of adsorption is based on direct calorimetric determination of heat of adsorption.[26,27,28] The integral heat of adsorption is determined from the relation:

$$-\Delta H = n\Delta H_{ps} + n\Delta H_{so} + n\Delta H_{po} + \Delta H_{pp} \qquad [1.18]$$

where n is the number of surface sites covered by polymer segments, ΔH_{ps} is the enthalpy of bonding per a mol of monomeric units, ΔH_{so} is the heat of wetting per mole of active sites, ΔH_{po} is the enthalpy of desolvation per mole of adsorbed monomeric unit, and ΔH_{pp} is the energy of interaction of adsorbed polymer molecules. If the last term is neglected, it may be written:

$$-\Delta H = n(\Delta H_{ps} - \Delta H_{po} - \Delta H_{so}) \qquad [1.19]$$

where the adsorption enthalpy is proportional to the number of active sites on the adsorbent surface and constant enthalpy contribution (the term in brackets). The differential enthalpy of adsorption is:

$$D_A = -\partial\Delta H/\partial N = \partial H/\partial N\,(\Delta H_{ps} - \Delta H_{po} - \Delta H_{so}) \qquad [1.20]$$

where $N = A/M_m$ is the number of monomeric units of adsorbed macromolecules, A is the amount of adsorbed polymer, g, and M_m is the molecular mass of monomeric unit. In such a way, the value D_A may be considered as a measure of the fraction of segments bound with the surface.

1.4 THE STRUCTURE OF ADSORPTION LAYERS OF POLYMERS

For the following discussion, the definitions of adsorption and surface layers are introduced.[10] The thin surface layers of any condensed phase have different structure and physical properties as compared with the properties in bulk, and their thickness does not exceed the radius of correlation of structural long range interaction. These layers can be considered as interphase layers. Any liquid or solid body has an interphase layer. This interphase (border or surface) layer may be qualified as a layer in which, under the action of the surface force field, properties differ from those in bulk. The surface layer has an effective thickness beyond which the deviations of local properties from bulk are negligible.[29]

The introduction of such a definition is possible due to a small value of the radius of action of intermolecular forces, contributing to a fast decay of the influence of one phase on any property of a neighboring phase. In the adsorption layer, there exists direct molecular contact of two phases, i.e., the most intensive interaction between adsorbed molecules in surface layer and molecules of solid. The adsorption layer changes the Gibbs energy of liquid and solid surface. When we consider polymeric systems, we have to distinguish between surface layer of polymeric body of its own bulk and surface layer of polymer at the interface with solid (the interface layer). In modern theories of adsorption, one of the most important theoretical results is the estimation of a thickness of the adsorption layer and establishment of the distribution function of segments near the interface. These characteristics are important for understanding the properties of surface layers in filled polymers. In consideration of polymer chain conformation near the interface, one of the most essential tasks is establishing the dependence of the adsorption layer thickness on the energy of adsorption, which, together with chain flexibility, determines the length of adsorbed trains, loops, and tails.

The analysis of theoretical calculations[6] allows one to draw conclusions about the structure of adsorption layer. At a low energy of adsorption, the long loops and tails have extended conformations, stretched towards the solution and normal to the adsorbent surface. At high adsorption energies, the macromolecules form short loops and tails, and macromolecules are situated in the plane of the surface (Figure 1.1).

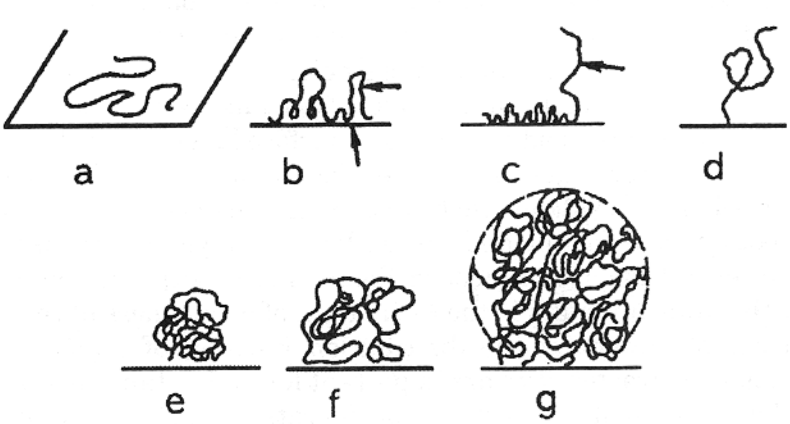

Figure 1.1. Schematic representation of conformations of adsorbed chains: (a) chain lying flat on the surface, (b) chain adsorbed with trains and loops, (c) adsorbed chain with free end, (d) anchored chain, (e) adsorbed coil, (f) adsorbed interacting chains, (g) adsorbed aggregates.

Corresponding to adsorption energy, the number of segments, bound to the surface, rapidly increases. The distribution of segments in the loops is an exponential function of the distance from the surface, whereas the distribution of tail segments is determined by the difference of two exponential functions and in such a way has a maximum at an intermediate distance from the surface. Establishing the concentration profile was the aim of a great number of theoretical investigations.[4,19,22,23,30-35] It is worth noting that the results of calculations strongly depend on the premises on which the calculations have been made.

As a rule, the adsorption layer may be subdivided into two regions:

- the first layer, consisting of segments in direct contact with the surface (trains)
- the second layer, consisting of the loops and tails.

Various theories propose different types of changes in segment density by transition from the first to the second layer. The general trend on the changes in conformation of macromolecules is that the fraction of bound segments increases and the layer thickness decreases with increasing energy of adsorption.

The variations of p values and mean maximum thickness of the layer, $<\delta_m>$, depend on the chain length (polymerization degree), and are expressed more obviously, if the energy of adsorption is low. The p and $<\delta_m>$ are less sensitive to the chain length as compared with adsorption energy, ε_a/kT. For example, at $\varepsilon_a/kT = -0.9$, the adsorbed molecule is densely spread on the surface and non-essential growth of p and diminishing $<\delta_m>$, with the growth in the chain length, indicate more pronounced ability of chain to align on the surface.[34] The application of a well-known scheme of adsorbed trains, loops, and tails to description the chain conformation gives the possibility to evaluate changes in their mean length, if we take into account the existence of free tails. The mean length of trains, loops, and tails, $<L_t>$, $<L_l>$, and $<L_e>$, respectively, is expressed in the number of segments as a function of energy. It was established that $<L_t>$ and $<L_l>$ are not essentially changed by increasing adsorption energy (the train length increases, whereas the length of loops diminishes). The changes in $<L_e>$ are greater, especially at low adsorption energy, where the thickness of the adsorbed layer is determined mainly by the length of tails. At $\varepsilon_a/kT = -0.8$, $<L_e>$ is twice as large as $<L_l>$ regardless of the chain length.

The analysis of distribution of the length of trains and loops has shown that it is very narrow, whereas for tails it is very broad. The $<L_t>$, $<L_e>$, and $<L_l>$ values may be used to determine the length of the “mean adsorbed chain”, i.e., the chain with these characteristics. The theoretically calculated distribution functions include some parameters which cannot be found experimentally, restricting the possibilities of experimental verification.

Some authors[4,22,36] calculated the distribution of loops and tails and mean-square thickness of the adsorption layer and mean lengths and number of trains, loops and tails. The mean-square of the thickness depends on the size of loops and length of tails. Contribution of tails was discussed earlier.[37] Tail segments are concentrated preferentially in the adsorption layer and their distribution is a function of concentration profile, parameters of thermodynamic interactions, χ^{po},χ^{ps}, and solution concentration. It was found that with increasing solution concentration, the total fraction of tail segments reaches a limiting value equal to 1/3 of the chain length. In this case, the adsorbed chain consists of two rather long tails and a short intermediate part, formed by trains and loops. It is essential that the effect of tail segments only slightly depends on the parameter χ_s, because after saturation of the first layer with segments, the distribution of tail segments depends not on energetic factors, but on translational and conformational entropy and osmotic effects.

More complicated theoretical calculations give a possibility to account for chain flexibility and its ability to align on the surface, using parameters χ_{12} and χ_s. According to Silberberg, accounting for the influence of solvent nature and its concentration makes any suppositions for the mechanism of adsorption unnecessary. It is not important, if the macromolecule is adsorbed in the form of a statistical coil or multilayer adsorption takes place. At the same time, in more concentrated solutions, the adsorption may be multilayer adsorption — thus the second layer of macromolecules is adsorbed on the first layer and has no more direct contact with the surface.

Theoretically, adsorption from diluted solutions may be described as the phase transition.[38,39] Silberberg explains[40] that adsorption of macromolecules is some kind of phase separation. In Chapter 6, this assumption is especially important for filled polymer blends, where this factor leads to the additional microheterogeneity of the interphase layer. Very often, polymer solutions are in close vicinity to phase separation and only entropy effects can prevent it, whereas energetic factors favor phase separation. The adsorption interactions with the surface induce phase separation, when the solution is close to θ-point. The closer is the system to θ-point (temperature of phase separation of molecules of infinitely high molecular mass), the greater is the thickness of the adsorption layer. In such conditions, the multilayer adsorption may take place and each layer will differ from another. Here, according to Silberberg and in accordance with the concepts developed by this author's group,[10] the total number of macromolecules bound to the surface exceeds the number of macromolecules adsorbed due to a direct contact with the surface.

Theoretical analysis of the process of adsorption and desorption in the framework of the concept of phase transition was already discussed.[41,42] The phase diagram in reduced coordinates $\varepsilon/\varepsilon_{crit} = \varepsilon N^{3/5}$ and $\phi/\phi^* = \phi N^{4/5}$ have been obtained, where ε is the energy of the chain attraction to the surface, ε_{cr} is the critical energy, N is the number of monomeric units in the chain, and ϕ and ϕ^* are concentrations of polymer in solution and cross-over, respectively. The latter work is important because cross-over concentration is considered — essential for adsorption from semi-diluted solution (see section 1.6).

The above discussion includes behavior of monodisperse polymers. In the case of adsorption of polydisperse polymer, the fractionating, according to molecular mass, proceeds. Theoretical and experimental works helped to establish[23,43,44] that long chains are preferentially adsorbed, and that shorter adsorbed chains are displaced by long chains. The analysis of adsorption from a binary mixture of monodisperse polymers of molecular mass A and B (B > A) shows[45] that the fraction B of a high molecular mass is preferentially adsorbed. The surface coverage, in the region of the plateau, is $\theta^m = \theta_A^m = \theta_B^m$, i.e. it is independent of molecular mass. Therefore, the sum of the surface coverage by fractions A and B, $\theta_T = \theta_A + \theta_B$, is always equal to θ^m, whereas the fraction of bonded segments is equal to p in the saturation region, at θ^m. This statement meets the experimental data.[44]

For the adsorption of polymer with bimodal molecular mass distribution, a model describing the structure of adsorption layer was proposed.[46] According to this model, the polymer chains of various length, N_L and N_S, are attached by their ends to the adsorbent surface with uniform distribution on the surface. It is assumed that the total surface density is sufficiently high for chains to overlap. In such a way, the adsorption layer has the structure of a brush and is divided into two layers: the first, nearest to the surface, consists of both short chains and part of segments of long chains. Their number is N_L^i. If the configurations of both chains are the same, the number of segments of long chains in the inner layer is $N_L^i - N_S$. The outer layer consists of $N_L - N_L^i$ segments of long chains. In the framework of such a model, the thickness of the adsorption layer is determined by the free energy of both inner and outer layers. The equilibrium structure is determined by both the energy of chain interaction, responsible for transfer of long chains from the inner layer to more diluted outer layer, and the elastic contribution to free energy, depending on conformations of long chains.

In polydisperse systems, where the polymer at the surface is in the state of an equilibrium with polymer in solution, the fractionating proceeds, and, as a result, the solution becomes enriched in low molecular mass fractions, whereas the surface in high molecular mass fractions. In the adsorption layer, the distribution according to molecular mass is shifted to a higher molecular mass and differs very markedly from the distribution in solution which is in equilibrium with adsorbent. Correspondingly, the thickness of adsorption layer from polydisperse polymers depends on the molecular mass distribution and on the general type of functional dependence of adsorption on a given adsorbent on molecular mass. It was shown[47] that the degree of displacement of low molecular mass fractions depends on the molecular mass distribution of previously adsorbed macromolecules. The thickness of the adsorption layer is changed accordingly. By adsorption from solution at θ- point, there is no full displacement of low molecular mass fractions by high molecular polymer. When considering the adsorption of polydisperse polymers, one should also have in mind the influence on adsorption of some degree of immiscibility of various fractions, which follows from the dependence of the parameters of interaction between fraction on the composition of the mixture of polymer homologues.[48,49] Partial immiscibility of fractions of various molecular mass leads to the formation of macromolecular aggregates, which can be adsorbed by the surface independently.[10]

For adsorption of polydisperse polymer, the dependence of adsorption on the ratio of the values of the adsorbent surface, S, and the volume, V, is an important factor characteristic of a system. Such dependence contradicts the very essence of the adsorption isotherm, which should be connecting two factors of intensity (i.e., concentration on the surface and in solution), and be independent of the intensity factor.

Such behavior is explained below.[4] If at any given amount of polymer in solution, the total surface of adsorbent is sufficiently low, only macromolecules with a high molecular mass can be deposited on the surface, and the amount of polymer adsorbed on the surface is very high. If at the same volume, a greater surface is available, both long and short macromolecules may be deposited on the surface. As a result, the mean molecular mass of adsorbed polymer, and therefore the amount of adsorbed substance, decreases. The isotherm of adsorption at low S/V ratios is situated higher, compared with isotherms at high S/V. Thus, the adsorption values on the macroscopic surfaces may not coincide with the results obtained for highly disperse adsorbents.

To characterize the structure of adsorption layer, it is very important to know the profile of density of segment distribution. In many works, the ultimate goal was to predict the concentration profile,$\phi(z)$, in the interfacial region as a function of the distance z from the interface. For many years, attempts were made to derive the structure of polymer layers from some theory.[22,50] In this case, each chain is submitted to an average potential which is a combination of short-range attractions, due to the adsorbing wall, and a long range repulsions, proportional to the concentration profile, $\phi(z)$. Scheutjens and Fleer[51] gave detailed numerical results on the repartition of the chain monomers between trains, loops, and tails, respectively. However, it was later established that the mean-field theory neglects important correlations, which considerably modify the interfacial profile. The scaling concept of adsorption was developed by de Gennes[52-55] for two regimes of adsorption solutions. If the adsorbed chain has large loops, stretched from the surface at a distance, D, for dilute solution, the theory gives the thickness of the adsorption layer formed by adsorption of a single chain as:

$$D = b\delta^{-3/2} \qquad [1.21]$$

where b is the effective length of segment, and δ is the thickness of the first adsorption layer. The value D happens to be independent of the number of segments in polymer chain and increases with decreasing δ. Value δ enters into the expression for the isotherm of adsorption as:

$$\gamma \approx b^3 C_B \exp(n\delta^{5/2}) \qquad [1.22]$$

where C_B is the concentration of solution, γ is dimensionless surface concentration of polymer, $\gamma = \Gamma b^2$, Γ is the amount of polymer adsorbed in segment unit per 1 cm^2. For the region of semi-dilute solutions the optimum thickness of the adsorption layer is equal:

$$D/b \approx (\delta - \gamma^2)^{-3/2} \qquad [1.23]$$

For the concentration range where the majority of chains is adsorbed (plateau region), the layer thickness is:

$$D = b(\gamma^5\delta^4) \qquad [1.24]$$

De Gennes developed the theoretical consideration for describing the equilibrium concentration profile for adsorption from semi-diluted solutions.[55] The surface is characterized by the “free energy of adhesion", f, which is negative for adsorption and positive for repulsion of the chain from the surface. For this case, scaling relations have been obtained connecting the thickness of the adsorption layer, formed by the loops, D, with a concentration profile:

$$\Phi(z) = \Phi_s g(z/D) \qquad (z >> a) \qquad [1.25]$$

where Φ_s is the fraction of polymer in contact with the surface. The relationship between the fraction of bonded segments, p, the adsorption energy, f, and the thickness of adsorption layer has been derived as:

$$p = \frac{\Phi}{D} \approx \left(\frac{|f|a^2}{kT} \right)^{3/2} \qquad [1.26]$$

The value D corresponds to two inequalities: $a << D << \xi_b$, where ξ_b is the correlation length in solution defined as $\xi_b = a\Phi^{-3/4}$. For semi-dilute solutions, when $\Phi_{b\,=}\,\Phi^*$ (Φ^* is the cross-over concentration) ξ_b corresponds to the size of a coil, $\xi_b = R_F$ (Φ_B is the fraction of polymer in solution). Theoretical profile of concentrations consists of three regions:

$z < a < D$
$D < z < \xi b$
$z > \xi_b$

The scaling approach allows one to predict that the structure of an adsorption layer weakly depends on the volume concentration of polymer, if the adsorption energy is not too high. De Gennes emphasizes that the relationships derived are only valid for an equilibrium adsorption, which, however, can hardly be attained due to hindrance of the reorientation of chains, bonded to the surface. The concentration profile, $\Phi(z)$, may also be estimated for semi-rigid chains near the solid wall.[56] In this case, the chain is characterized by its persistent length, L, whereas the profile is determined by the value of $\Phi_o(z)$ obtained in the mean-field theory, accounting for the value L,$\Phi(z) = \Phi_o(z + D)$.

The scaling approach is valid both for dilute and semi-dilute solutions.[57] The experimental verification of the theories of concentration profile is a very hard task because different methods are sensitive to various layers (i.e., ellipsometry is sensitive to the total value of the surface excess, and does not depend on the details of the profile, the hydrodynamic methods are more sensitive to the outer layer ($z = R_F$) not to the central region ($D < z < R_F$)). At higher degrees of the surface coverage, the fraction of bound segments is very low and chains are stretched from the surface into the solution.[58] Using a scaling approach, it was shown[59] that the width of the proximal layer in the immediate vicinity of the solid wall depends on the polymer system. The extension of the profile is usual of the order of the radius of gyration of macromolecule.[60]

It should also be noted that all theoretical and experimental data describe the static or equilibrium situation. The transition from statics to dynamics needs much more investigations.[61] For particulate filled polymers it is important how the particles, covered with an adsorption layer, interact with each other. This problem was only considered to solve the problems arising from steric or adsorption stabilization of colloid systems.[62] For stabilization, the concentration profiles are very important. From the scaling point of view, the question was discussed by de Gennes.[63] The interaction between two particles strongly depends on the form of the concentration profile. In equilibrium state both adsorption layers are attracted, and this effect depends on the nature of a solvent, degree of surface coverage, and the distance between particles.[64-66] The scaling approach can be used for estimation of the interaction between two flat surfaces with adsorption layer, when the surfaces are not fully covered by polymer (differs from saturated surfaces, where repulsion forces are operative, and the long-range forces separating surfaces play dominate roles).[67] The interaction between two surfaces, in which macromolecules are attached to the surface only by the tails, is determined by the concentration profile;[68] however, the structure of a layer strongly depends on the solvent nature. Below θ-point, the collapse of the layer proceeds in connection with coil-globule transition.[69] The theory of collapse of grafted chains[70] allows one to predict the dependence of the layer thickness, formed after collapse, on the solvent nature.

In relation to the equilibrium state of an adsorption layer, it is worth while to mention the latest theoretical results.[71] It was shown that at a strong interacting interface between polymer and solid, the quasi-two-dimensional structure is formed where chains have non-equilibrium conformations (see further discussion in Chapter 4). As compared with the weak interacting surfaces, in the case of strong interaction, macromolecules are oriented on the surface in such a way that they form few loops and tails, each chain is adsorbed in the non-equilibrium conformation. The adsorption layer, in this case, may be considered as quasi-two-dimensional for bulk glassy polymer. Temperature at which the chain mobility increases leading to the equilibrium structure, was considered from a theoretical point of view. The conclusion for the non-equilibrium state of the adsorption layer is that the structure should depend on its prehistory, including solution concentration. This conclusion is very important for understanding the structure of the surface layers in polymer composites.

1.5 EXPERIMENTAL ESTIMATION OF THE THICKNESS OF LAYERS

Numerous attempts to compare the results of theoretical calculations of the thickness of adsorption layer with experimental data were not satisfactory. The reason for the discrepancies is that assumptions made by theoretical calculations are not valid for real systems. For example, most of the calculations were done for an isolated chain, whereas in real systems we always deal with a great number of adsorbed chains. As a result, the chain conformations do not correspond to what is expected by theory. From the experimental point of view, the adsorption layer may be characterized by three parameters available for experimental determination. These are the adsorption energy (parameter χ_s), the fraction of bound segments, p, and the thickness of adsorption layer.

Value p was determined for a great number of systems (see ref. 6). The main methods used here are IR and NMR spectroscopies.[5,71] The data from these methods allow one to make some conclusions about the conformations of adsorbed chains. The NMR method is especially informative because the fraction of bound segments can be measured directly in the adsorption system without removing adsorbent.[72,73] The method of attenuated total inner reflection (ATIR) gives the best possibility to evaluate the concentration of polymer in adsorption layers of various thicknesses.[74] Having no aim to give the full analysis of the results of many authors who use these methods (see ref. 75), we would like to consider the results of one study.[76]

By addition to the adsorbent, saturated by adsorbed polymer, of an additional portion of the same adsorbent, there was observed an essential increase in the fraction of bound segments, p, as followed from the NMR measurements. This fact indicates formation of bridges between various particles of adsorbent, connected by macromolecules adsorbed on both particles simultaneously. This effect is supposed to be connected with transition of part of the segments from loops to trains due to the appearance of an additional free surface. The formation of a bridge leads to the transit of macromolecules from saturated particles onto an unsaturated one, leading in such a way to the growth in p.

Let us briefly discuss the data concerning the experimental determination of the thickness of the adsorption layer. This value is of great importance for understanding properties of surface layers in polymer composites. A review of the modern methods and results was published.[77] Typical values of the adsorption layer thickness are 10-1000 nm. For experimental estimation of the thickness, various methods are available. Among them are some methods giving information on concentration profile. Ellipsometric methods are well developed.[78] Ellipsometry gives not only the adsorbance and the overall coverage of the surface (number of monomer units per sq. cm), but also the concentration profile.[79] Using this method, it was established[80] that dependence of the adsorption layer thickness on the polymer concentration in solution at θ-temperature is characterized by a sharp increase in the region of low concentrations transiting to the plateau region. The initial slope of the curve depends on the molecular mass. The mean-square thickness of the layer is proportional to the square root of molecular mass.

Takahashi[2] summarized the dependencies of layer thickness, adsorbance, A, and the fraction of adsorbed monomer units per chain, p, on molecular mass. For the chain lying flat on the surface, $p=1$, $\delta \sim M^{o}$, $A \sim M^{o}$. For the chains forming loops and trains, $\delta \sim M^{0.5}$, $A \sim M^{a}$, $(0 < a < 1)$, for the chains with trains, loops and tails, $\delta \sim M^{0.5}$ in θ-solvent and $\delta \sim M^{2/5}$ in a good solvent, $A \sim M^{a}$ $(0 < a < 1)$. Measurement of surface forces acting between two polymer-covered plates also gives useful data for layer thickness.[81-83] It was shown that the effective thickness of the adsorbed layer depends on the molecular mass and the thermodynamic quality of solvent. The observed variation $\delta_{eff} \sim M^{0.43}$ is shown to be consistent with a scaling form for the extension of the polymer from the surface.

Methods based on the neutron scattering[84,85] give the concentration profile and the second moment of the profile, i.e., the mean square thickness of the layer. A neutron reflection[86-88] is also very useful for these studies. A comprehensive and coherent series of neutron reflectivity data of polymers adsorbed at the surface has been presented.[60,89] The data allow one to obtain the distribution function , $\Phi(z)$, using some realistic hypothesis, including independence of $\Phi(z)$

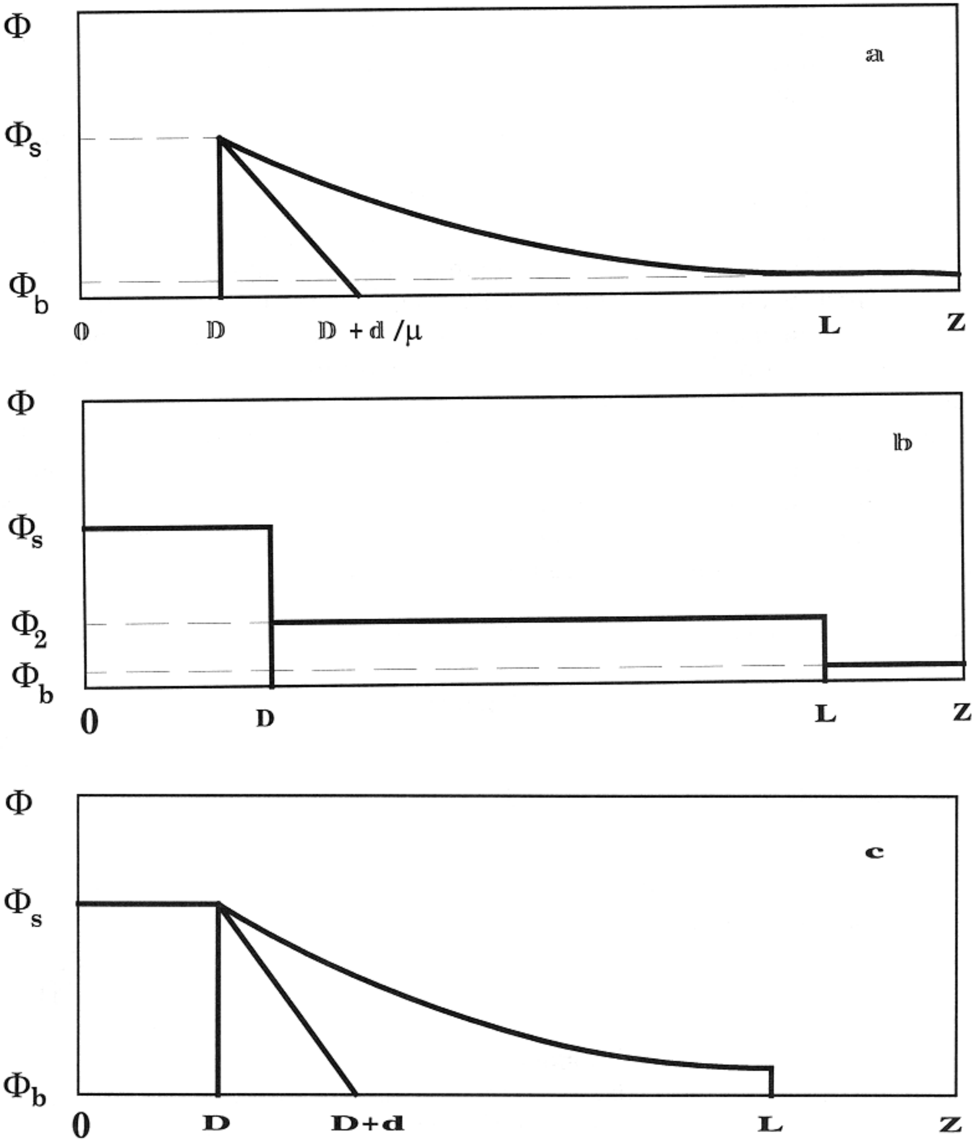

Figure 1.2. Representation of the power law profile (a), the two-layer profile (b), and the exponential profile (c).[60]

on the polymer molecular mass in the surface region over a distance at least equal to 30 Å. The experimental reflectivity curves may be modeled by three classes of concentration profile (Figure 1.2):

- power law profiles:

$$\Phi(z) = \Phi_s \qquad \text{if } z < D$$

$$\Phi(z) = \Phi_s\left[\frac{d}{(z-D)}\right]^{\mu} \qquad \text{if } D < z < L \qquad [1.27]$$

  where Φ_s is the volume fraction of monomeric units near the surface, D and d are distance characteristics (see Figure 1.2)

$$D = a/(3v\Phi_b)^{0.5} \qquad [1.28]$$

  where a is the size of monomeric units,
  v is the parameter connected to the excluded volume,
  μ is parameter characterizing the central part of profile

- Two-layer profile, where Φ_s and D do not depend on molecular mass, whereas Φ_s and D are dependent, and

- Exponential profile

$$\Phi(z) = \Phi_s \qquad \text{for } z < D$$

$$\Phi(z) = \Phi_s \exp\left[\frac{(z-D)}{d}\right] \qquad \text{for } D < z < L \qquad [1.29]$$

Experimental data allowed for the validation of several tested models. To determine the thickness of an adsorption layer, other methods also may be useful, among them: ESR,[76] sedimentation and hydrodynamics.[90-94] All methods have their own advantages and disadvantages. For example, the very convenient hydrodynamic method allows one to estimate the effective hydrodynamic thickness of the adsorption layer from viscometric measurements of particles dispersion in polymer solutions. The effective hydrodynamic volume of particles is increased, due to adsorption of polymer and formation of an adsorption layer. However, the determined value decreases with shear rate to a constant limiting value that is reached at a sufficiently high shear rate for a good solvent. In a θ-solvent, below the critical shear rate, effective thickness increases with increasing shear rate, and it decreases with shear rate above the critical shear rate. These effects are explained by the disentanglements of internal subloops and tails or detachment of weakly adsorbed trains.

To have insight into the structure of adsorbed layer and chain conformations, Killmann[95,96] used the method based on isotherms of layer thickness, polymer concentration in adsorption layer and adsorbed amount relative to solution concentration, and the same isotherms at saturation versus the molecular mass. The data can be obtained for the dependence of the thickness on the molecular mass, solution concentration, etc. It was established that, at rather high concentration of solution, the macromolecules are adsorbed in the form of coils.

New possibilities to evaluate the thickness of adsorbed layer were opened by using electrochemical methods.[97-99] The methods are based on the measurement of the ζ-potential of colloid particles covered with adsorbed polymer. Decrease in the value of ζ-potential with increase of polymer adsorption is determined by a shift of the sliding plane into the solution bulk as a result of the formation of the adsorption layer. From measurements of ζ-potential, the distance of the sliding plane from the surface may be calculated, which is taken as a measure of the layer thickness. In such a way the dependence of the layer thickness on the value of adsorption may be determined.

The direct comparison of results obtained by various methods is difficult. At the same time, the experimental data qualitatively meet the current theories of adsorption and theoretical predictions regarding dependence of the layer thickness on the adsorbed amount, molecular mass, nature of a solvent and adsorption conditions.[47] Corresponding dependencies in scaling form may differ by the critical exponents. It is also worth noting that the adsorption behavior of macromolecules is very specific for individual system polymer-solvent-adsorbent. It was shown[100] that adsorbance strongly depends on the structure of adsorbent surface (physical roughness, its characteristics, the existence of chemical impurities in the adsorbent, etc.). In this case, the behavior of the adsorbed chain differs from the adsorption on the flat surface.

1.6 ADSORPTION OF POLYMERS FROM SEMI-DILUTE SOLUTIONS

All theories of polymer adsorption were developed for adsorption from dilute solutions. It thus neglects the interaction between macromolecules in solutions and on the surface. Study of adsorption from semi-diluted and concentrated solutions is much more complex. It is necessary to account for the existence of a definite structure of solution, which has a pronounced effect on the adsorption. By increasing concentration of polymer solution, statistical coils begin to overlap, and as a result, the compression and decrease in coil size occurs.[101] In this region of concentration, two regimes exist, according to de Gennes:[52] semi-dilute and concentrated solutions. In semi-dilute solutions macromolecular coils begin to overlap, however the volume fraction of polymer, Φ, in solution is still low: $\Phi^* << \Phi << 1$.

$C = C^*$ (or in volume fractions, $\Phi = \Phi^*$), the coils begin to touch each other at the concentration corresponding to the threshold of overlapping. This threshold is not sharp and a region of crossover exists. Concentration C^* should be comparable with the local concentration inside the coil.

A generalized approach gives the possibility to consider the transition conditions from semi-dilute to concentrated solutions.[102] For statistical coils, the critical concentration of overlapping (cross-over concentration) is expressed as

$$C^* = (\Phi/N_A)(2^3/[\eta]) \qquad [1.30]$$

where N_A is the Avogadro number and Φ is the volume fraction of polymer in solution, and $[\eta]$ the intrinsic viscosity. C^* is inversely proportional to the intrinsic viscosity, related to radius of gyration. The transition from semi-dilute to concentrated solution means that entangled coils, dissolved in a good solvent, continue to contract towards an unperturbed size limit. The convergence of the hydrodynamic volume is a measure of the crossover between semi-diluted and concentrated regimes. In this case

$$C^{**} = 1/[\eta]^{**} \qquad [1.31]$$

where $[\eta]^{**}$ is the intrinsic viscosity corresponding to the limit molecular mass M^{**}, at which $[\eta] = [\eta]_\theta \sim (h^{**}/2)^3$. Here, h^{**} is the distance between chain ends at molecular mass M^{**} and C^{**}.

Adsorption of polymers on adsorbing particles of varying sizes is concentration specific. The analysis of such adsorption is very difficult, and to describe the experimental data, the first crossover concentration, where macromolecular coils begin to overlap and interact, can be used. Therefore we can use the simple criterion of transition from dilute to semi-dilute solutions:[103,104]

$$1 < C[\eta] < 10 \qquad [1.32]$$

or $\Phi^* = 0.12/[\eta]$. It is worth noting that these criteria have not been taken into account in all preceding investigations of adsorption.

In equilibrium solutions, together with isolated macromolecular level of dispersity), there exist structures of various types formed as a result of aggregation or association of macromolecules. These processes proceed in the concentration region both below and above C^*, which is connected with the dependence of the thermodynamic parameter of interaction polymer-solvent on concentration. The interaction between coils leads to the appearance of molecular aggregates, which are unstable structures formed by interactions of coils, having a definite lifetime. The type of aggregates and the number of coils depend on the intermolecular interaction between macromolecules, concentration and nature of a solvent. The thermodynamic reason for the formation of macromolecular aggregates is probably incomplete miscibility of polymer fractions of different molecular mass.[49] Therefore, by formation of aggregates some fractionating according to molecular mass may proceed. This idea, put forward by S. M. Lipatov in the early thirties,[105] assumes the dependence of the aggregation degree on molecular mass, connected with higher solubility of low molecular mass fractions. The aggregates of macromolecules are not colloid particles in a true sense of the word, but they may be considered as some kind of micelles, because their size is comparable with the size of colloid particles. Aggregates are not phase particles and they do not have a sharp phase border with the solvent. At the same time, the formation of aggregates is determined by the appearance of essential differences in local density in various parts of the system. The density fluctuations, as they are determined by the aggregate formation, may be

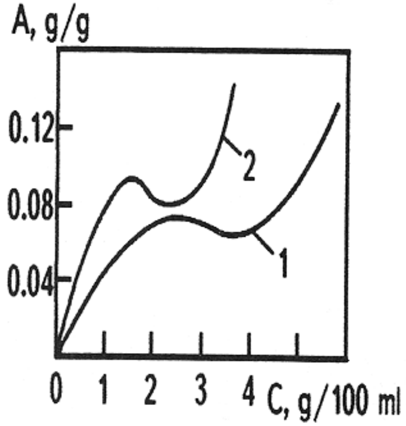

Figure 1.3. Isotherm of adsorption of oligoethylene glycoladipinate on carbon black (1) and fumed silica (2) from acetone solutions.

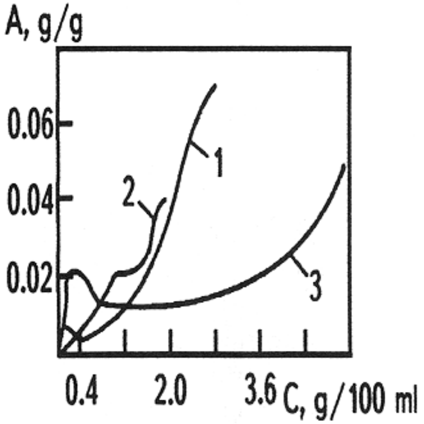

Figure 1.4. Isotherm of adsorption of polystyrene from toluene (1), cyclohexane (2), and polycarbonate from chloroform (3).

considered as the regions of higher concentration of polymer in a given solution as compared with an average density. It is important that these fluctuations of density exceed fluctuations typical for liquids, which can be described by the Boltzmann distribution.

It is worth noting that the size of aggregates strongly depends on solution concentration, temperature, and temperature dependence of the solvent properties. In polymer solutions, there exist equilibria between isolated and aggregated macromolecules. In definite conditions, the aggregates may serve as a nuclei of a new phase.[106,107] The system which contains aggregates is a one-phase stable system. The transition to a two-phase system proceeds only when the system happens to be in a metastable or unstable region of the phase diagram. There are many experimental results on the formation of aggregates in polymer solutions and methods of estimation of their size, number of molecules in an aggregate and size distribution.[108-114]

To prove experimentally the adsorption of aggregates, we have used the method of turbidity spectra,[115-119] which allow us to estimate the aggregate size and their number in solution. The comparison of these data with adsorbance shows that aggregates are transferred onto the adsorbent surface (their number

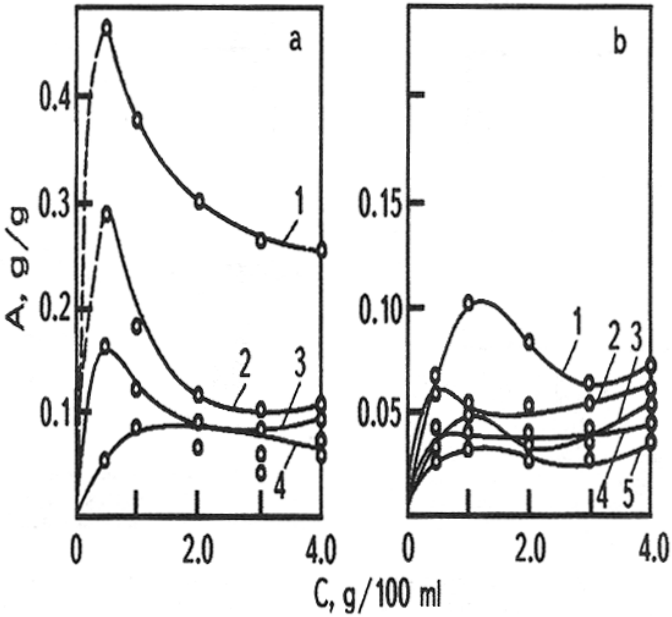

Figure 1.5. Isotherm of adsorption of polycarbonate (a) and polystyrene (b) by various amounts of adsorbent (fumed silica), (mg/ml of solution):1-5, 2-10, 3-20, 4-30, 5-40.

in the equilibrium solution diminishes after adsorption). The preferential adsorption of aggregates was explained by their lesser solubility as compared with isolated macromolecules and by analogy with decreasing solubility with growing molecular mass. The transition of aggregates onto the surface assumes weak bonding with the surface because only some molecules, forming an aggregate, interact directly with the surface (see Figure 1.2).

In this case, during desorption, adsorbed polymer is almost fully removed from the surface, which is different in adsorption from dilute solutions. The amount of the adsorbed polymer, which after aggregation is adsorbed on the surface, is much higher, compared with dilute solutions. Figures 1.3 and 1.4 show the adsorption isotherms for various systems. High amounts of adsorbed polymer are explained by simultaneous transition onto the surface both of aggregated and isolated macromolecules. The aggregate size increases with increased solution concentration. Correspondingly, the value of adsorption begins to increase at the same concentration, if marked aggregation proceeds. In some cases, isotherms have no saturation region or adsorption passes through a maximum.

It was established[120] that adsorption from aggregated solutions is characterized by the dependence of the adsorption value on the amount of the adsorbent in the system (Figure 1.5). The adsorption isotherms are situated lower, with increase in the amount of adsorbent due to decreasing adsorption. Maxima observed on the isotherms in formation of aggregates become less pronounced. Such behavior is explained by preferential adsorption of aggregates and, at the same time, by simultaneous adsorption of aggregates and isolated molecules. After establishing adsorption equilibria, a new equilibrium between aggregated and isolated molecules is established.

The number of aggregates in solution is considerably lower than that of isolated macromolecules. When all the aggregates are adsorbed, the higher the amount of adsorbent, the more pronounced is the adsorption of single molecules. As a result, the total value of adsorption diminishes.[118] The maximum on isotherms with the onset of strong structure formation in solution disappears, which may indicate the change in the equilibrium between aggregated and isolated macromolecules under the influence of adsorbent surface. The influence of temperature is determined by its effect on the equilibria between aggregated and isolated molecules, which, in turn, also depends on concentration.[118] With increasing temperature, due to thermal movement, the aggregates dissociate and their size diminishes. Increasing temperature leads to a shift of the onset of aggregate formation to higher concentrations, and their size diminishes. The concentration dependence of the aggregate size is more pronounced with increase in temperature. Thus, when considering the temperature dependence of adsorption, one should have in mind the change in the aggregation degree with temperature, which may result in diminishing adsorption.

It is also necessary to account for the influence of temperature on the interaction between various aggregates. Its diminishing facilitates the transit of aggregates to the adsorbent surface and as a result in some cases the aggregative adsorption increases with temperature. There are many factors influencing adsorption from semi-dilute and concentrated solutions, which may be explained now only on the qualitative level.

1.7 MOLECULAR-AGGREGATIVE MECHANISM OF ADSORPTION

The experimental data concerning adsorption from semi-dilute and concentrated solution allow for a general conclusion regarding the aggregative mechanism of adsorption.[1,2,10] This mechanism may be represented in the following way. During adsorption from solutions, where the aggregation of macromolecules proceeds, the aggregates are preferentially transferred to the adsorbent surface because they are less "soluble" as compared with isolated macromolecules. After equilibrium is established, the aggregates in solution are practically absent.[10] They reappear after some time necessary to attain a new equilibrium state between isolated and aggregated molecules. It was found that in solution, after some time the aggregates appear again. These data confirm the transition of aggregates onto the surface and explain the main peculiarities of adsorption from semi-dilute and concentrated solutions (extensive adsorption, inversion of the influence of the solvent nature, existence of maxima on isotherms, etc.).

Decreased adsorption, after the maximum is reached, may be explained by the formation of a physical network of entanglements in solution, which hinders and, after some concentration, prevents the transition of macromolecular aggregates and macromolecules onto the surface. Only such a supposition allows one to explain the absence of adsorption from solution after reaching some limiting concentration. At the same time, when explaining the adsorption isotherms, it should be remembered that, with increasing concentration, the aggregation constant diminishes. At each solution concentration a definite equilibrium between aggregated and isolated molecules is established. It is evident that the change of aggregation constant affects the distribution between aggregated and isolated molecules, which determines their ratio at the adsorbent surface. The preferential (but not exclusive) adsorption of aggregates is accompanied by the adsorption of isolated molecules. Their conformation is different than in dilute solution, as a result of coil overlapping.

The peculiarity of polymer adsorption, connected with its aggregative mechanism, consists in the fact that at each concentration of solution in adsorbent presence, a new state of equilibrium between isolated and aggregated molecules is established. To each point of isotherm corresponds another structure of adsorbing units (from isolated macromolecules up to aggregates of various size)

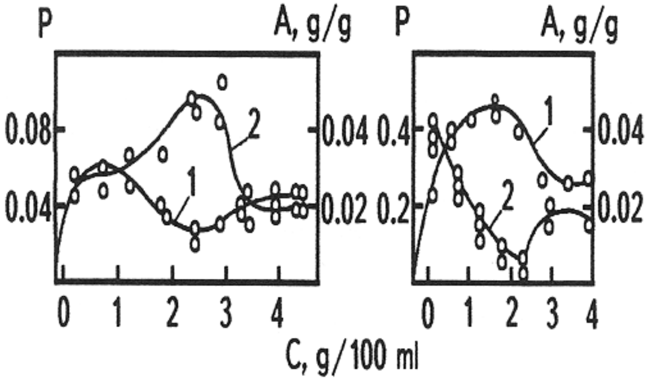

Figure 1.6. Isotherm of adsorption (1) and fraction of bound segments (2) for the system: polycarbonate-fumed silica-dichloroethane (a) and oligoethylene glycoladipinate-fumed silica-dichloroethane (b).

and their different distribution on the surface, depending on the solution concentration. The appearance of a maximum on the isotherms of adsorption is caused by diminishing of the number and size of aggregates with an increase in the solution concentration, i.e., change in the ratio between aggregated and isolated molecules at each point of isotherm. In this case, distinct from adsorption of low molecular substances, the adsorption value and the shape of the isotherm depends not only on concentration but also on the ratio of volumes of adsorbent and solution.

Studying adsorption of polystyrene, polycarbonate, and other polymers has shown that adsorption greatly increases after reaching some definite concentration of solution, which is accompanied by change in the shape of the isotherm and in a fraction of bound segments.[120, 121] Figures 1.6 and 1.7 represent the isotherms of adsorption and fractions of bound segments at various amounts of adsorbent. Increase of the amount of adsorbent leads to diminishing adsorption. Fraction of bound segments is changed non-monotonously and is higher at low values of adsorption as a result of transition on the surface of isolated macromolecules. The surface may influence the state of equilibria between aggregated and isolated macromolecules. Dependencies of the adsorption values and fraction of bound segments are opposite and the maximum of adsorption corresponds to the minimum of bound segments. All these data meet the concept

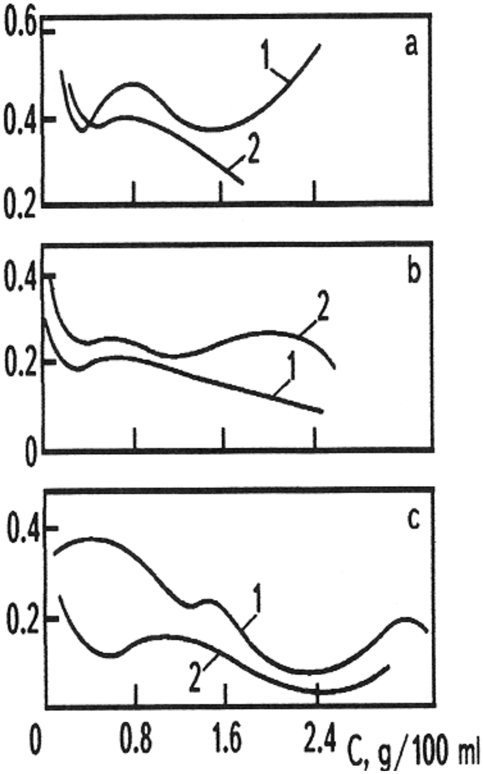

Figure 1.7. Fraction of bound segments of polybutyl-methacrylate from chloroform (a) and from mixture with polystyrene (b) at various amounts of adsorbent:1-20, 2-40 mg/ml.

of aggregative adsorption. Aggregative mechanism was discovered also for adsorption of some proteins onto the silica surface.[122]

It is evident that when this mechanism is operative, the structure and thickness of adsorption layers are determined by the structure and size of aggregates, and by the ratio between aggregated and isolated macromolecules in the layer. Killmann[123] calculated the thicknesses of adsorption layers of poly(methyl methacrylate) and some other polymers based on comparison of the amount of adsorbed polymer and surface of an adsorbent (adsorption from concentrated solutions (up to 56.0 g/l)). The values found are of the order of 0.7 mcm, which essentially exceeds the thickness of a monolayer. For solutions of isotactic polystyrene and other polymers on disperse powders, the thicknesses were found in the range of 1-8 mcm,[123] which may be explained by adsorption of aggregates. The thickness of adsorption layers of oligomeric epoxy resin on the glass powder was found to be 0.1 mcm.[125] This value is at least one order higher, as compared with adsorption from dilute solutions.

Molecular-aggregative mechanism of adsorption also explains a great difference between the fractions of bound segments adsorbed from dilute and semi-dilute and concentrated solutions. The fraction of segments of macromolecules, forming an aggregate and directly interacting with the surface, should be low, even at a high degree of surface coverage. As distinct from dilute solutions, where the fraction of bound segments monotonously decreases with increase in solution concentration, for adsorption from concentrated solution, value p is changed non-monotonously, similar to the value of adsorbed polymer. This value is also dependent on the thermodynamic quality of a solvent, from which the adsorption layer is formed. Transition onto the surface of large aggregates, increasing adsorbed amount, leads to the diminishing of the degree of their bonding with the surface. Thus, the conclusion may be drawn that transition of macromolecular aggregates onto the adsorbent surface results in formation of adsorption layer interacting with the surface to a lesser extent, compared with dilute solutions and aggregates which are not strongly attached to the surface.

The degree of aggregate bonding depends not only on the degree of surface coverage, but on the structure of solution, depending on solvent quality and solution concentration. The transition of aggregates determines to a greater degree the layer. The continuous change in the degree of aggregation with concentration has a strong influence on the structure of adsorption layers, obtained from solutions of different concentrations. However, the theoretical description of the aggregative adsorption has yet to be done.

1.8 ADSORPTION FROM SOLUTIONS OF POLYMER MIXTURES

Studying adsorption from solution of polymer mixtures is of great interest for the theory of PCM because many binders for composites are two-and more-component systems. The presence of two components determines the specificity of the properties of the boundary layers formed by two different polymeric molecules. From another point of view, as the large majority of polymer pairs is thermodynamically immiscible,[126] there may arise interphase layers between two components in the border layer at the interface. The selectivity of adsorption of various components, which is a typical feature of adsorption from mixture, leads to the change in composition of the border layer as compared with composition in the equilibrium solution. This fact, in turn, determines the non-homogeneity in distribution of components in the direction normal to the solid surface, i.e., creates some compositional profile. As compared with studying adsorption from solution of individual polymers, adsorption from mixture is studied insufficiently. The first investigations in this field were done[127-129] for immiscible pair PS-PMMA on silica surface, in conditions remote from the phase separation. It

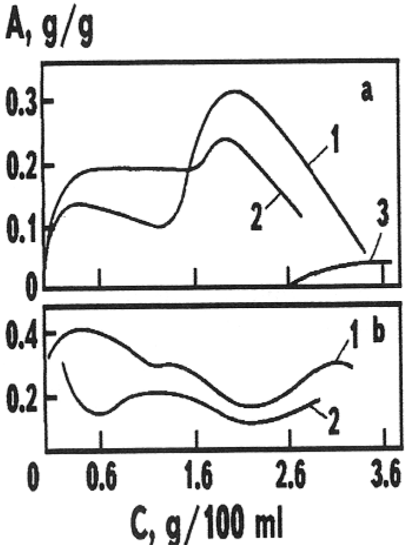

Figure 1.8. Isotherm of adsorption (a) and fraction of bound segments (b) for PBMA adsorbed from chloroform (1) and from mixture with rubber (2). [Adapted by permission from Y. Lipatov, L. Sergeeva, T. Todosijchuk, and V. Chornaya, *J. Coll. Interface Sci.*, **86**, 437 (1982)]

was found that adsorption of PS does not proceed until the end of the adsorption of PMMA, the presence of PS had no effect on PMMA adsorption. These results are indicative of the preferential adsorption of more polar polymer. If PS was initially adsorbed onto a silica surface, the addition of PMMA solution led to the rapid displacement of PS and full coverage of surface. Studying the adsorption of various systems (polyvinyl acetate-polyethylene vinyl acetate, ethylcellulose-PS and others) allowed to establish the series of affinity of polymers to the surface in conditions which are close to phase separation.[128] It was established that for the mixture of immiscible polymers, the presence of one polymer enhances the adsorption of another.

The quality of the solvent also influences the adsorption from mixture; as no solvent has the same thermodynamic quality for both polymers, adsorption is dependent on the solvent. For the system of polyvinyl acetate-PS, it was found that weakly adsorbing PVA may be fully displaced from the surface if PS molecules are adsorbed from a good solvent, forming a monolayer at the interface. PVA prevents the formation of the adsorption layer of PS, adsorbing from a poor solvent, due to a great difference in the conformations of adsorbed molecules.[130] For an immiscible pair in the definite region of concentration, a phase separation is possible. For this case, the adsorption was studied when adsorbent was mixed with a two-phase system.[131] The adsorption processes in such a system are very complicated and we believe that the investigations of this kind are hardly useful as the adsorbent is distributed between two phases and adsorption proceeds independently in each phase from one-phase solution (each separated phase is one-phase solution of the mixture).

The application of the model of the aggregative adsorption to polymer mixtures gives the possibility to establish some principal regularities of the adsorption. The adsorption was studied[132,133] from the system PBMA-PS-fumed silica and PBMA- butadiene-nitrile rubber-fumed silica. It was established that rubber is not adsorbed from the solution in the broad range of concentrations of PBMA (0.05-2.9 g/100 ml). At the same time, in the presence of rubber, the adsorption value and fraction of bound segments is changed. Figure 1.8 shows the adsorption isotherms (a) and fraction of bound segments (b) for adsorption of PBMA from chloroform and mixture with rubber in the same solvent. The inversion of the value of adsorption is observed, being dependent on the solution concentration. This inversion is determined by the worsening of the thermodynamic quality of the solvent by adding rubber.

It is known that the adsorption from dilute solutions in a poor solvent is higher as compared with good solvent, the fraction of bound segments is lower in a poor solvent due to the difference in the chain conformations. The reason for the increase of adsorption and decrease of p for adsorption of PBMA from dilute solutions may be explained on this basis. However, by increasing the solution concentration, adsorption of PBMA may be diminished, due to aggregation of its macromolecules in a poor "mixed solvent." The fraction of bound segments diminishes as a result of aggregative adsorption. At higher concentrations the adsorption of PBMA drastically diminishes and adsorption of rubber begins to proceed, i.e., some inversion of adsorption is observed. Figure 1.9 presents the adsorption isotherms of components at various ratios of adsorbent-solution and fractions of bound segments. At high content of the adsorbent in the system, only PBMA is adsorbed, whereas at low amount, both PBMA and PS are adsorbed. Thus, when adsorption proceeds from the mixture,with increasing amount of the adsorbent, adsorption of PBMA increases and PS level diminishes. It may be supposed that under the action of the adsorbent the degree of aggregation in solution changes as well. The complex behavior of polymer mixtures by adsorption from a common solvent[133] is determined mainly by the thermodynamic miscibility or immiscibility of the components in solution.

In analyzing the data on adsorption from a mixture, a solution of mixture of two polymers in a common solvent should be treated as a solution of polymer A in solution of polymer B and at the same time as a solution of polymer B in solution of polymer A. Accordingly, the thermodynamic quality of the "mixed" sol-

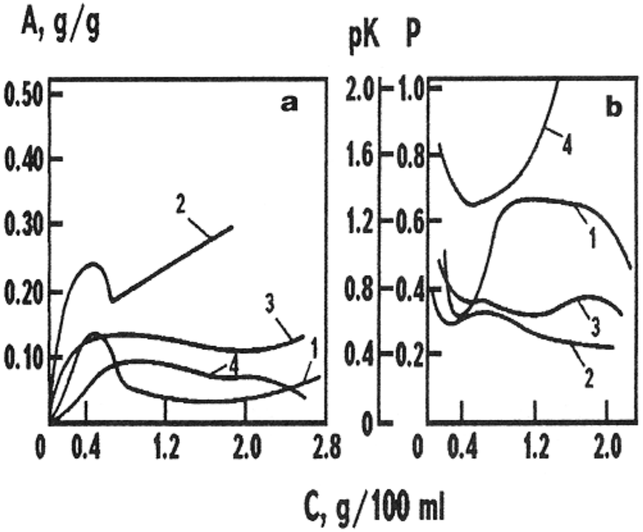

Figure 1.9. Isotherm of adsorption (a) and fraction of bound segments (b) for PBMA adsorbed from mixtures with PS in CCl_4 (1-3) and for PS mixture with PBMA (4) at various amounts of adsorbent: 1-10, 2-20, 3-30, 4-40 mg/ml. [Adapted by permission from Y. Lipatov, L. Sergeeva, T. Todosijchuk, and V. Chornaya, *J. Coll. Interface Sci.*, **86**, 437 (1982)]

vent (solvent + polymer) for either polymer will differ from that of a pure solvent. Adsorption of either polymer will depend on the effects exerted by the other polymer on the thermodynamic quality of the “mixed” solvent, with the result that the value of adsorption of each component depends not only on its affinity to the surface, but also on the ratio between the components in solution.

Thus, interpretation of the experimental evidence on adsorption from mixture is complicated by the thermodynamic quality of the solvent, and for either polymer, it differs from that for the other polymer and varies with the concentration of the latter. If the problem of adsorption of mixtures is approached on the basis of the concept of a dilute and semi-dilute solutions, then it is obvious that conditions of aggregation and adsorption should also depend on the critical concentration of overlapping of coils, i.e., on the concentration at which coils of the component macromolecules start touching and overlapping one another. It is clear that the values C^* for individual components in the solvent cannot be used here, since in the solution of a mixture, the thermodynamic quality of the “mixed” solvent differs from that of the pure solvent and depends on the concentration and ratio of components. For this case, we have proposed[134] the concept of an "averaged" critical concentration, determined from averaged intrinsic viscosity. We proposed to represent the averaged intrinsic viscosity and averaged critical concentration as:

$$[\eta]_{mix} = [\eta]_A \phi_A + [\eta]_B \phi_B \quad \text{and} \quad C_{mix} = 1/[\eta]^*_{mix} \qquad [1.33]$$

where ϕ_A and ϕ_B are volume fractions of components in their mixture ($\phi_A + \phi_B = 1$). It may be assumed that for a mixture of polymers A and B whether or not they are thermodynamically miscible, the crossover will be below C^*_A or C^*_B because a part of the solution volume has already been occupied by coils of A or B. In this case, the averaged concentration of the crossover is a function of the ratio between dissolved molecules of A and B.

Studying adsorption from various mixtures (polydimethylsiloxane-PS-ethyl acetate, polycarbonate-poly-ε-caprolactone-$CHCl_3$, PS-PBMA-CCl_4)[134,135] and investigating the form of aggregates in the same systems, allows us to draw some general conclusions. Figure 1.10 shows the dependence of the PDMS adsorption from its mixture with PS in a common solvent at various constant PS concentrations (below and above C^* for PS) in the A-(adsorption)-C/C^* coordinates. As seen, in the region of the crossover and above C/C^*, the adsorption decreases after its passage through a maximum, both in the case of pure PDMS and for mixtures containing different PS amounts.

Absolute values of the adsorption are very high, which corresponds to the concepts of an aggregative adsorption. As was shown earlier, the existence of a maximum on the adsorption isotherm is a typical sign of aggregative adsorption. The decrease in adsorption at concentrations over C^* corresponds to the same concept. As the PS content in the solution increases (the thermodynamic quality of the mixed solvent worsens), the magnitude of adsorption drops, while the maximum in the region of reduced concentrations over one (above the cross-over region) is retained. As has been noted, we relate this behavior to the worsening of the quality of the solvent for PDMS, which, by reducing the sizes of the coils, reduces at the same time the sizes of the aggregates. Thus the experimental evidence indicates the existence of an interrelation between the adsorption of polymer from mixtures, the thermodynamic miscibility of components in a solution, the variation of the thermodynamic quality of a mixed solvent, and the critical concentration of crossover for each component and the averaged critical concentration for the mixture.

The influence of the aggregation of macromolecules in solutions of mixture, caused by the above factors, on the adsorption in the concentration region above and below C^*, is evident as well. Since the formation of aggregates involves a change in the thermodynamic quality of solvent, it seems obvious that the presence of a second component, impairing the thermodynamic quality of the mixed solvent (regardless of whether a given pair of polymers is miscible in the solution), alters the conditions of formation and adsorption of aggregates when the thermodynamic quality is continuously changed. Passage through the cross-over region brings about changes in the solution structure because of the formation of a continuous network of entanglements and overlapping macromolecular coils. It was shown[134] that the aggregate formation begins at concentrations below C^* for a given polymer, and occurs also in a region above the crossover. It is quite obvious that aggregation processes occur also in solutions of mixture. Tendency toward aggregation of molecules of every kind should be more pronounced with lower thermodynamic compatibility and worse with the thermodynamic quality of the mixed solvent. The data on the average size of macromolecular aggregates in the PS-PBMA mixture, as a function of the composition of the mixed solvent, were given before.[136] It was shown that the presence of a second polymer, immiscible with the

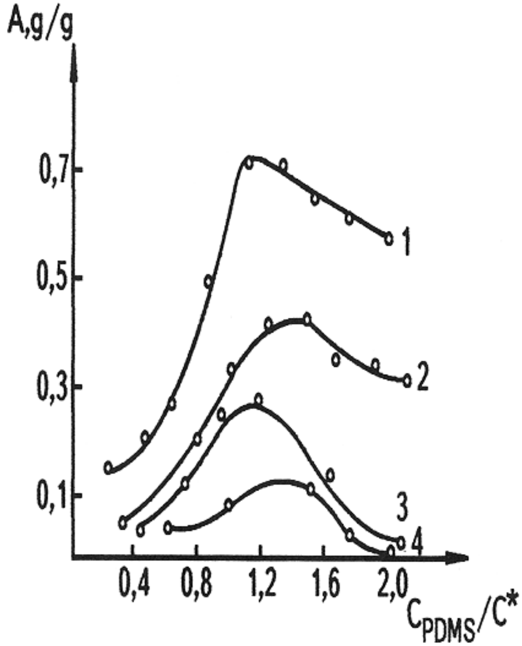

Figure 1.10. Dependence of PDMS adsorption from solution on C/C* ratio (1), and from its mixtures with PS in ethyl acetate on C/C* ratio at PS concentrations of 0.5 (2), 1.0 (3), and 2.5 g/100 ml (4). [Adapted by permission from Y. Lipatov, T. Todosijchuk, and V. Chornaya, *J. Coll. Interface Sci.*, **155**, 283 (1993)]

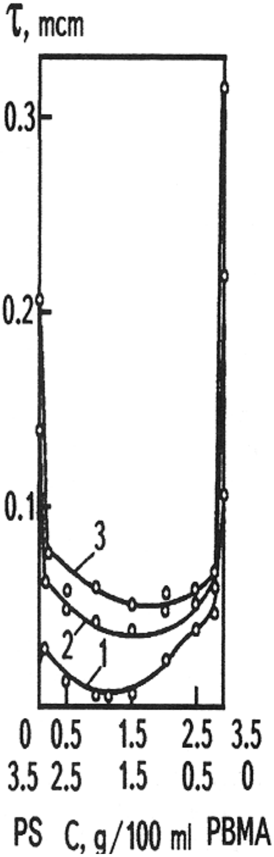

Figure 1.11. The average size of aggregates in the mixture PS-PBMA in CCl_4 at various temperatures: 1-283, 2-298, 3-333 K. [Adapted by permission from Y. Lipatov, V. Chornaya, T. Todosijchuk, and T. Khramova, *J. Coll. Interface Sci.*, **110**, 1 (1986)]

first one, leads to an appreciable decrease in the size of aggregates because of the worsening of the thermodynamic quality of the solvent.

Some additional information about adsorption from mixtures may be gained from determination of the fraction of bonded segments. The complicated dependencies of changing of p with concentration of the solution and with amount of the adsorbent present in the system, are the result of changing the aggregation constant, i.e., ratio between aggregated and isolated macromolecules. The comparison of the adsorption isotherms and data on p shows the existence of the inverse correlation between the adsorption magnitude and p. The dependence of p on the adsorbent amount corresponds to the change in the phase diagram of a polymer mixture under the influence of a solid surface,[137] and thus these effects may be determined by the deviations from the equilibrium phase state by introducing an adsorbent.

It is worth noting that in solutions of mixtures, the aggregates of both polymers are formed. Changing the mixture composition influences the aggregation processes. It is seen from Figure 1.11, in which the dependence of the average size of an aggregate in solution of the mixture PS-PBMA is presented as a function of the composition and temperature. The presence of either polymer diminishes the size of aggregates. These data allow for the conclusion to be drawn that structural rearrangements in solutions, caused by the concentration changes and temperature, are connected with the change in the thermodynamic compatibility. The peculiarities of adsorption from polymer mixtures determine the dependence of the adsorption layer thickness on the adsorbent nature.[121] For the mixture of polybutadiene rubber and epoxy resin, adsorbed from solution, it was shown that the thickness of the adsorption layer of epoxy resin, calculated from the isotherms, essentially exceeds the thickness of the monolayer, due to aggregative adsorption, dependent on the mixture composition and adsorbent nature. Adsorption and adsorption layer thickness also should be dependent on the molecular mass of the components because of different thermodynamic interactions between them.[138,139]

The molecular mobility of adsorbed macromolecules is characteristic of the structure of adsorption layer and connected with the mechanism of adsorption. The transition from adsorption of isolated molecules to adsorption of aggregates should be reflected in the molecular mobility. It was experimentally established for the mixtures PS-PBMA adsorbed from solutions.[140] The molecular mobility was estimated in conditions of an equilibrium state of the system: adsorbent-solution of mixture, i.e., at a different point of adsorption isotherm. NMR data allowed us to estimate the fraction p of hindered segments for the solutions of a given concentration in the presence of an adsorbent. These segments may be considered as immobilized by the surface and their amount does not directly correspond to the number of bonded segments determined from IR data. By IR measurements only, the fraction of segments directly bound to the surface is measured. The NMR estimation includes both segments in direct contact with the surface and hindered, or immobilized segments, which, having no direct contact with the surface, exhibit lower molecular mobility due to adsorption of adjacent segments tethered to the surface. This value determines the rigidity of the adsorbed chain and allows us to estimate the correlation length, i.e., the distance from the surface at which the molecular hindrances disappear.

It was established that the values of p, estimated from NMR measurements, are higher as compared with the corresponding values for pure components at the same conditions of adsorption. It means that each component is more strongly bound to the surface when both components are present in solution. The determination of p values for various points of isotherm of adsorption shows that a higher decrease in molecular mobility corresponds to a higher amount of the adsorbent in the system and to a higher value of adsorption. The analogous situation was observed for the same system when the amount of bound segments was measured, using IR spectra.[141] Studying the molecular mobility in the system at various amounts of the adsorbent allows one to find the degree of the mutual influence of either component on their ability to adsorption.

Increasing concentration of either component leads to the diminishing fraction of hindered segments of this polymer. Diminishing p is indicative of the preferential adsorption of aggregates, because for adsorption of aggregates only small part of segments interact directly with the surface. Thus the molecular mobility of adsorbed macromolecules strongly depends on the mechanism of adsorption. The common adsorption of both polymers from solution of their mixture leads to the appearance of some anomaly in the display of molecular mobility, due to the selective adsorption and arising from some concentration profile in the adsorption layer. It is worth noting that the structure of adsorption layers, estimated by various methods, in conditions when adsorbent with adsorbed polymer is removed from the adsorption system, is not the same as may be observed in conditions of unperturbed adsorption equilibrium.

As follows from some theoretical and experimental data, the adsorption layer in equilibrium with solution is a highly concentrated system, compared with a polymer solution. When solvent is removed from adsorbent with an adsorption layer, the structure of the layer may be drastically changed due to a collapse of concentrated gel of molecular aggregates, which is especially probable for immiscible polymers. Collapse of the adsorption layer follows from data[142] on the dependence of the thickness of the adsorption layer on the temperature below θ-point.

The data on molecular mobility obtained from NMR measurements may be used for estimation of the structure of the adsorption layer for adsorption from mixtures.[143] For the miscible system: polycarbonate-fractions of immobilized segments have been estimated for various concentration of solution, i.e., for various points on isotherm. To characterize the structure of the adsorption layer, we have used the fraction of immobilized segments, p, assuming that they correspond to the fraction of bound segments. In this way, we estimate the structure of an adsorption layer at various states of aggregation and structure of solution (various concentrations of solution). In the case of a molecular-aggregative adsorption, the isotherms exhibit an absence of saturation.

Figure 1.12 shows the dependence of p on concentration for polycarbonate adsorbed from pure solvent and from mixture with polycaprolactone. It is seen that the p value declines linearly with increasing concentration of the solution. It indicates that aggregates are bound to the surface by a smaller number of segments and that there is a continuous rearrangement of the adsorption layer itself. Despite an increase in adsorption with concentration, the fraction p declines continuously. A linear p decrease occurs both before and after the crossover point, but the variation rate (dp/dc) after the crossover declines. This agrees with the concept of a decrease in the passage of macromolecules and their molecular aggregates to the adsorbent surface at concentrations above the critical concentration. In fact, the crossover point corresponds to a maximum of pos-

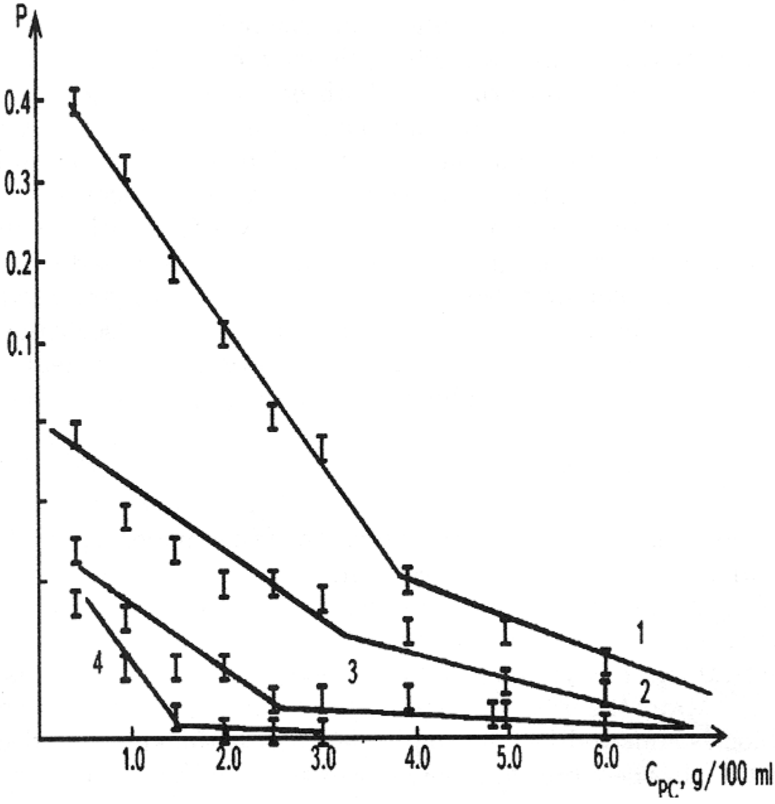

Figure 1.12. Dependence of p for polycarbonate on its concentration in solution (1) and its mixtures with polycaprolactone (2-4), concentration was 3.0 (2), 7.4 (3), and 10.0 (4) g/100 ml. [Adapted by permission from Y. Lipatov, T. Todosijchuk, and V. Chornaya, *Compos. Interfaces,* **2**, 53 (1994)]

sible adsorption under given concentration. The increasing amount of the second polymer in the mixture shifts the inflection point to lower concentrations, corresponding to the averaged crossover concentration. The same behavior was observed for the second polymer, oligocaprolactone.

To estimate the thickness of adsorption layer for adsorption from mixture, which is determined by adsorption of both polymers, taking into account the absence of saturation, it is reasonable to make the following assumption: since, for adsorption from dilute solution, the saturation already occurs at low concentration, then, for adsorption from semi-diluted and concentrated solutions, where the aggregative mechanism is operating, we deal with an already saturated surface, and a further growth of adsorption is associated with rearrangements of molecular conformations, ratio of isolated and aggregated molecules, etc. It follows that for the corresponding calculations, the adsorbent surface may be assumed constant, i.e., the problem of its coverage may be neglected. In this case the thickness of adsorption layer, δ_{mix}, are estimated from the equation:

$$\delta_{mix} = (A_1/\rho_1 + A_2/\rho_2)/S \qquad [1.34]$$

where A_1 and A_2 are the adsorbed amount of each component, ρ_1 and ρ_2 are their densities, and S is the specific surface of the adsorbent. Such calculations enable us to have an insight into the peculiarities of the structure of adsorption layers formed by two polymers simultaneously.[143]

The statistical thermodynamics of block copolymer adsorption was considered elsewhere.[144] Many theories[144-147] attempt to characterize adsorption by surface density, block segment distribution profile, and the thickness of adsorbed layer. As a rule, an adsorbed diblock copolymer has one block adsorbed on the surface in a rather flat conformation, whereas the other block, having a lower surface activity, forms dangling tails. Because of their freely dangling blocks, adsorbed diblock copolymers are often interpenetrated. The adsorption of block copolymers leads to the segregation of blocks in the adsorption layer. It was found[148] that both kinetic and equilibrium features of the block copolymer adsorption are intimately related to the phase behavior of the block copolymer solution. In particular, a very strong increase in the adsorbed amount is observed when the system approaches the phase boundary. As a consequence, a partial phase separation phenomenon may proceed in the surface zone.

From this point of view, the modelling of adsorption of block copolymers on heterogeneous surfaces is of special interest. The adsorption of copolymer of type AB was considered for a surface consisting of two strips of different chemical nature.[149] Block A has an affinity to the strip C(1), whereas block B has affinity to the strip C(2). Equations have been derived describing the density distribution of both blocks in various directions along the surface for different values of the interaction parameters $\chi_{AC(1)}$ and $\chi_{BC(2)}$. It was established that such a heterogeneous surface may induce phase separation. The structure of the chain determines its location at various domains of the surface, which allows changing the structure of the chain to vary the degree of the surface segregation. The properties of the adsorbed chain are dependent on the ratio of surfaces occupied by domains C(1) and C(2).[150] If we compare with adsorption of polymer mixtures, adsorption of block polymers have distinctive characteristics. However, the common feature consists of the role of the compatibility of two species in solution - for polymer mixture between two polymers and block copolymers between two blocks. An investigation of adsorption of block polymers has more importance for the steric stabilization of colloid systems,[152] but not for polymer composites.

1.9 ADSORPTION OF POLYMERS FROM MELTS

From a theoretical and practical point of view, it is of great importance to establish the nature of the adsorption interaction between solid and macromolecules in melt without solvent.[153] At first, it seems impossible to apply the definition of adsorption as an excess concentration of the substance at the interface to the system polymer melt-solid. However, any polymer is polydisperse material and may be considered as a solution of high molecular weight fractions in low molecular weight fractions. Sometimes the fractions of various molecular mass are not miscible in melt[48,49] and have different surface tensions.[154] In this case, the adsorption may be considered in a true sense of the word. Daoud[155] considered the adsorption of long chains made of N monomeric units that are dissolved in a melt of shorter chains with P units. It was assumed that both species are slightly different, but coexist, and that no phase separation occurs. Because of the difference in the species, there may be a difference in affinity to the surface, and it was assumed that the latter attracts the large species. In the situation discussed by Daoud, by increasing the molecular mass of the solvent from $P = 1$ to $P = N$, there proceeds a continuous transit from the dilute solution to a melt. The theoretical analysis was done using the concepts of blobs, and long chains were considered as a two-dimensional array of blobs. For the plateau regime, where long chains are saturating the surface, the concentration profile was estimated, which extends from the surface to a distance of the order of ξ, ξ is the screening length, $\xi \sim C^{-9/4}p^{1/4}$. Here C is a fraction of long chains in the mixture. Screening of the excluded volume interactions appears for concentration $C^* \sim N^{-4/5}p^{1/4}$ and corresponds to an overlap concentration, above which the long chains have large-scale screened behavior. The screening length is equal to $\xi(z) \sim \Phi(z)^{-9/4}p^{1/4}$. For larger distances, the concentration is constant and equal to its bulk value. The interfacial segment density profiles of end-anchored polymers in a melt was also considered in another source.[156] Using the method of neutron reflectivity, it was found that the adsorbed layer stretches out a distance, which is a few times the radius of gyration of the chain, and that its interphase with the unadsorbed polymer is rather broad. Experimentally, the adsorption of macromolecules from the melt may be evaluated by formation of a layer of a finite thickness at the interface. The analysis of molecular mass distribution at various distances from the surface after the contact of the melt with solid allows one to observe the

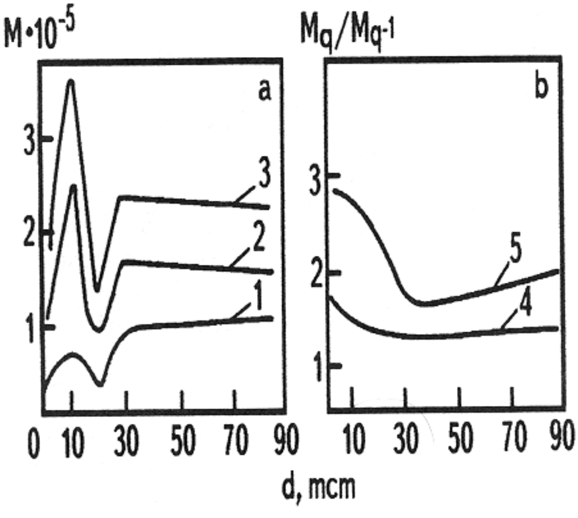

Figure 1.13. Dependence of molecular mass (a) and characteristics of distribution (b) on the distance from the surface: 1-M_n, 2-M_w, 3-M_z, 4-M_w/M_n, 5-M_z/M_w.

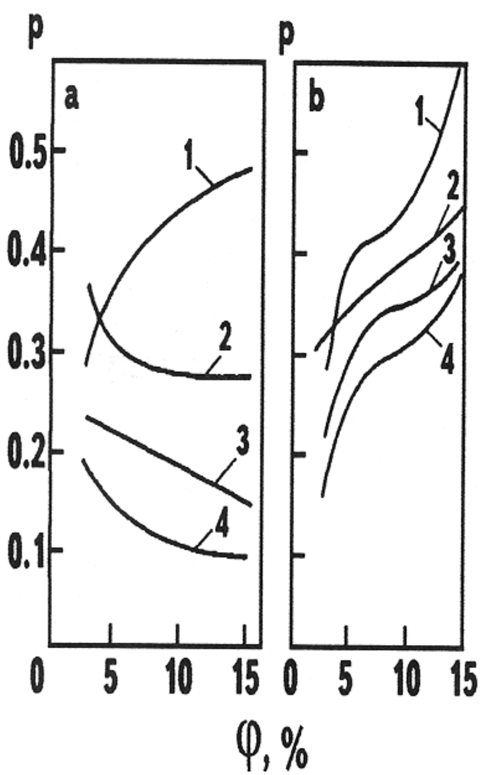

Figure 1.14. Fraction of bound segments as a function of fumed silica content, ϕ: (a) melts of PE and blends PE-PBMA at the PE content (%): 1-100, 2-756, 3-50, 4-25; (b) in melts of PBMA and blends at the content of PBMA: 1-100, 2-75, 3-50, 4-25. [Adapted by permission from Y. Lipatov, T. Khramova, T. Todosijchuk, and E. Gudova, *J. Coll. Interface Sci.*, **123**, 143 (1988)]

changes induced by adsorption.[157] Figure 1.13 shows the averaged molecular masses and ratio M_w/M_n and M_z/M_w for PS melt in contact with a glass. It is seen that, at the thickness of the surface layer of 20-30 mcm, near the surface, there is observed a complicated dependence of molecular masses and their ratios on the distance from the surface. The long range effect of the surface extends to rather large distances, which meets the theoretical and experimental data.[158] The data show that the fractions of low molecular masses are concentrated near the surface. At the distance of 10^{-13} mcm, the molecular masses are the greatest which may be accounted for by the shortage of low molecular mass fractions, due to their migration to the surface. The essential decrease of molecular masses, when approaching the surface, indicates their preferential adsorption and migration to the surface, due to their higher surface activity. For this kind of experiment, it is impossible to make any conclusion about the molecular mass distribution in the layer smaller than 2 mcm. However, the true adsorption layer is a part of this layer, and it is reasonable to suppose that low molecular weight fractions are preferentially adsorbed from the melt. Adsorption from the melts of polymer mixtures has importance for understanding the processes at the interface of polymer mixture (multicomponent binder) and solid. For filled binary polymer systems, which are formed in the melt state, the adsorption determines the structure of an adsorption layer and thermodynamic miscibility of polymers in this layer, because, due to the selective adsorption, the miscibility in the adsorption layer and in the bulk are not the same. The estimation of the selectivity of the adsorption interaction of mixture components in melt with solid can be based on the data on molecular mobility measured by NMR method.[159,160] Figure 1.14 gives the values of p for the melts of polyethylene and PBMA and for their mixtures in the melt for various ratios of components and different adsorbents (fumed silica) in the system. It is seen that values of p are increased with increasing amount of the adsorbent in the system, due to increasing number of contacts with the surface. Values of p for melts of mixture are lower than for individual polymers. These values are dependent on the ratio of components, and character of dependencies of p for PE and PBMA is different (Figure 1.14). However, at any ratio of components, increasing the amount of the adsorbent leads to the increase in p for PBMA and decrease for PE. With increasing volume fraction of PBMA in the mixture, p for PBMA also increases. It is therefore evident that PBMA preferentially interacts with the surface. For polymer mixtures, the additivity rule is valid, namely,

$$p_{mix} = p_{PBMA}\phi_{PBMA} + p_{PE}\phi_{PE} \qquad [1.35]$$

where ϕ is the fraction of the polymer in the mixture, and p is the fraction of bound (hindered) segments. When the selective adsorption of either component proceeds, the composition of the adsorption layer should differ from the composition in bulk. From the ratio of the surfaces under the NMR signals the fraction of the polymer in the adsorption layer may be found. It was established that with increasing amount of adsorbent, the PBMA fraction in the adsorption layer increases, i.e., the layer is enriched in PBMA. Only for the mixture with 75% of PE, this layer is enriched in PE if the amount of the adsorbent is below 3%. At 10% of an adsorbent, the fraction of PBMA in the adsorption layers increases again. Data on the fraction of bound segments allow one to calculate the thickness of the adsorption layer at the adsorbent surface separately for PBMA and PE. The calculations can be done using the following relation:

$$\delta = mp/\rho S \qquad [1.36]$$

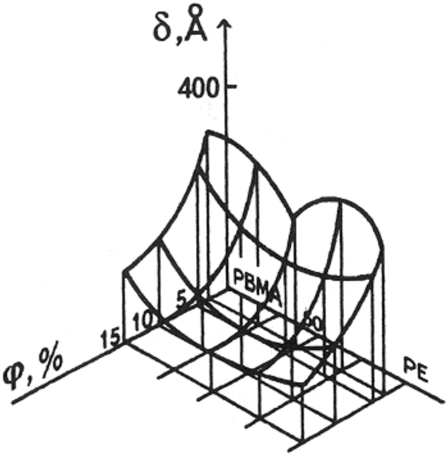

Figure 1.15. Dependence of the thickness of the adsorption layer on fumed silica content and ratio PE:PBMA in melts. [Adapted by permission from Y. Lipatov, T. Khramova, T. Todosijchuk, and E. Gudova, *J. Coll. Interface Sci.*, **123**, 143 (1988)]

where m is the amount of polymer, S is the specific surface of an adsorbent, and ρ is the polymer density. It was supposed that the fraction of a polymer in the adsorption layer can be found from the fraction of bound segments. The results of calculations are presented in Figure 1.15. It is seen that the thickness of the adsorption layer, for pure components, is 100-400 Å at 3-15% of the adsorbent in the system, which is much higher than the size of molecular coils. It means that the thickness of the adsorption layer in the melt is determined by the adsorption of both isolated and aggregated molecules, as in the case of semi-dilute solutions. At the same time, the diminishing thickness of the adsorption layers in mixtures may be related to immiscibility of polymers and compression of coils of both polymers in the mixture. It should be noted, however, that the values given (Figure 1.15) are probably underestimated, as the agglomeration of the fumed silica particles in viscous media of the melt, and consequently, the diminishing of the available adsorbent surface, cannot be avoided.

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2

ADHESION OF POLYMERS AT THE INTERFACE WITH SOLIDS

Adhesion of polymers at the interface with inorganic and organic solids is one of the main factors determining the properties of any PCM. The principles of adhesion are very complex, involving chemical, physical and mechanical aspects. There are many theories of adhesion discussed elsewhere.[1-9] However, no single theory presently allows one to calculate the real adhesion strength at the polymer-solid interface, and only qualitative predictions can be made. At the same time,*"one can stick anything to anything,"* as the late Professor Edwin Plueddemann used to say. That means that we are presently very far from a true understanding of the adhesion phenomena and can only explain isolated phenomena considering some aspects of an entire set of governing principles. The art of making an adhesive bond is older than physics and chemistry, wrote Bikerman,[8] and a large number of disconnected ideas, rules, and traditions have been accumulated by the many generations familiar with adhesives.

This chapter is devoted to a discussion of aspects of adhesion which are directly related to interfacial and surface phenomena at the substrate-adhesive interface (polymer-binder).

2.1 THERMODYNAMIC THEORIES OF ADHESION

Adhesion is a steady or firm attachment of two bodies, and as such it can be characterized by the thermodynamic work of adhesion, i.e., by the work which is needed to separate two different bodies in contact with each other under equilibrium conditions. The action of the molecular forces at an interface forms fundamental reasons for the adhesive forces between a substrate and an adhesive.[10]

Initial premises for the thermodynamic description of adhesion are the characteristics of two surfaces: their surface tension and interfacial tension at the interface between the two bodies in contact.[10] In the simplest case of two liquids with surface tension γ_{l1} and γ_{l2}, their surface tension at the interface (interfacial tension) is always lower than the highest surface tension at the interface with saturated vapor:

$$\gamma_{l1l2} = \gamma_{l1} - \gamma_{l2} \quad [2.1]$$

This empirical Eq 2.1 has been referred to as Antonov's rule. The separation of two surfaces (their breaking away from each other in the direction perpendicular to the interface) requires work per unitary surface area, W_a:

$$W_a = \gamma_{l1} + \gamma_{l2} - \gamma_{l1l2} \quad [2.2]$$

Eq 2.2 is applicable in any case, including the case when one of the components is a solid body. Accordingly, the cohesion energy is the work of destruction of a body, or the work needed to form a unitary surface area in this body. If the only result of the isothermal process here is the formation of 2 cm^3 of new surface area of the body, having surface tension, γ, the thermodynamic work of cohesion can be expressed as:

$$W_c = 2\gamma \quad [2.3]$$

On wetting, a droplet of liquid forms a definite contact angle on the solid. The state of mechanical equilibrium of the droplet on the surface is determined by

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\Theta \qquad [2.4]$$

where index s refers to the surface tension of solid, l to liquid, and sl to the interfacial tension at the interface.

The joint solution of Eqs 2.2 and 2.4 gives the thermodynamic work of adhesion between liquid and solid:

$$W_a = \gamma_l (1 + \cos\Theta) \qquad [2.5]$$

which is Dupre-Young's equation. At $\Theta = 0$, the behavior of droplet is determined by the condition

$$W_a = 2\gamma_l \qquad [2.6]$$

W_a can be greater than $2\gamma_{sl}$ if $\gamma_s > \gamma_{ls} + \gamma_l$, and in this case, the droplet of liquid spreads on the surface. The spreading condition occurs when $W_a > 2\gamma_l$, i.e., the liquid begins to spread on the solid surface when its adhesion becomes greater than its cohesion.

Continuing our discussion, we would like to emphasize the erroneous nature of the existing viewpoint that good wetting is a condition for providing good adhesion. Thermodynamically, it is high adhesion that determines good wetting.

Under conditions of complete wetting, the difference in surface tensions causes the droplet start to spread, which is given by

$$S = \gamma_s - \gamma_{ls} - \gamma_l \qquad [2.7]$$

The spreading coefficient, S, as follows from Eqs 2.4-2.7, is equal to the difference in the work of adhesion and cohesion of liquid:

$$S = W_a - 2\gamma_l \qquad [2.8]$$

The energy required for cohesive failure of the liquid should be $2\gamma_l$ and be equal to the adhesion, if $\Theta = 0$, i.e., if liquid completely wets solid. With incomplete wetting ($\Theta > 0$), failure of adhesion occurs more easily because $W_a < 2\gamma_l$.

In Eq 2.2 for solids, the surface tension of the solid is the energy of the solid-gas interface only after the liquid has been removed from contact with the solid. Only in this case is Eq 2.5 also valid. When the liquid is being removed from the surface, some part of it stays adsorbed and, consequently, liquid is not removed completely. Then, the interface solid-gas is composed of two areas: the unchanged initial solid and the solid with adsorbed layer. The latter possesses a lower surface energy and has an adhesion value corresponding to that obtained from Eq 2.2. A virgin surface is characterized by a higher energy, $\gamma_s + \pi$. This unknown value, taken into account when expressing the work of adhesion, as

$$W_a = \gamma_i(1 + \cos\Theta) + \pi \qquad [2.9]$$

can be obtained after Θ is measured for the interface of solid-gas, following the removal of the liquid, i.e., Θ corresponding to receding contact angle should be taken.

The difference between the works of adhesion of pure and covered surfaces cannot be measured directly and must be calculated from the adsorption isotherm of vapor on the solid. If Γ is the amount of vapor sorbed at pressure, P, the Gibbs equation gives:

$$\Gamma = \left(\frac{1}{RT}\right)\frac{d\Pi}{d\ln P} \qquad [2.10]$$

and hence

$$\Pi = RT\int_0^P \Gamma dP \qquad [2.11]$$

The above discussion concerns an ideal system. The work of adhesion is directly related to the strength of the molecular bonds at the interface and increases when the strength of the bond grows. In practice, one always seeks to attain maximum strength of the bond equal, in its limit, to the strength of the chemical bonds.

The thermodynamic approach to the description of adhesion has many advantages as compared with some other theories. It does not require knowledge of the molecular mechanism of adhesion but considers only the equilibrium processes at the polymer-solid interface. The approach to the problem developed by Zisman[11,12] is widely accepted. Zisman introduced the concept of the critical surface tension of wetting as a value which is found by extrapolation of the dependence of $\cos\Theta$ on γ to cos =1, i.e., when liquid fully spreads on the surface. The value γ_c found by extrapolation is considered as the critical surface tension of a solid. If the value γ_c is known, the equilibrium contact angle can be predicted for any liquid on any surface. If $\gamma_l < \gamma_c$, the contact angle equals zero and the liquid spreads on the surface.

According to Zisman, if liquid does not spread on a surface having high surface energy, it means that the surface is covered by an adsorption layer of a substance which decreases the surface energy of the solid to the level typical of a surface of low surface energy. Any liquid or gas may be adsorbed, forming a monolayer, and preventing the spread of another liquid. Such cases are of high importance in considering adhesion in PCM. According to Zisman any substance adsorbing at the interface should not decrease γ_c to a value lower than the surface tension of liquid adhesive.

The thermodynamic work of adhesion in the case of removal of a liquid from a surface covered by an adsorption monolayer may be found in the following way.

According to Zisman,

$$\cos\Theta = a - B\gamma_l \tag{2.12}$$

As γ_l approaches γ_c at $\Theta \to 0$,

$$\cos\Theta = 1 + B(\gamma_c + \gamma_l) \tag{2.13}$$

and

$$W_a = (2 + B\gamma_c)\gamma_l - B\gamma_l^2 \tag{2.14}$$

The maximum value of W_a can be found, provided that

$$\gamma = 1/B + 1/2\gamma_c \qquad [2.15]$$

Then

$$W_{a\,max} = 1/B + \gamma_c + 1/4\ B\gamma_c^2 \qquad [2.16]$$

Sometimes the value γ_2 is considered equal to γ_c.[13,14] However, from Eq 2.4, it tentatively follows that at $\cos\Theta = 1$, $\gamma_2 = \gamma_c$ only when the interfacial tension is zero. The value γ_c should be considered as an empirical value.

Another way to find the thermodynamic work of adhesion is to postulate a relationship between γ_2, γ_L and γ_{sL} (the Girifalko-Good equation):[15,16]

$$\gamma_{sL} = \gamma_s + \gamma_L - 2\Phi(\gamma_2\gamma_L)^{1/2} \qquad [2.17]$$

where Φ is an empirical parameter which can be calculated theoretically from molecular properties. Rewriting Eq 2.17 as

$$2\Phi(\gamma_s\gamma_L)^{1/2} = \gamma_s + \gamma_L - \gamma_{sL} \qquad [2.18]$$

and taking into account that the right-hand side of Eq 2.18 represents the thermodynamic work of adhesion, W_a, (Eq 2.2), Eq 2.17 can be written in a more convenient form:

$$W_a = 2\Phi(\gamma_s\gamma_L)^{1/2} \qquad [2.19]$$

Combination of Eqs 2.4 and 2.17 gives:

$$1 + \cos\Theta = 2\Phi\left(\frac{\gamma_s}{\gamma_L}\right) \qquad [2.20]$$

At Θ → 0, Eq 2.19 is transformed to:

$$\gamma_s = \frac{\gamma_L}{\Phi^2} = \frac{\gamma_c}{\Phi^2} \qquad [2.21]$$

The value of γ_2 depends greatly on the accepted value of Φ, which varies for different polymer-liquid pairs.[15,16] Such measurements have been done only for liquid systems. It was also found that:

$$\Phi = 1 - 0.0075\gamma_2 \qquad [2.22]$$

which is the same for a great number of solid polymers and liquids. Substituting Eq 2.22 into Eq 2.20, we obtain

$$\Phi = \frac{(0.015\gamma_{sL} - 2)(\gamma_s\gamma_L)^{1/2} + \gamma_L}{\gamma_{sL}(0.015(\gamma_s\gamma_L)^{1/2} - 1)} \qquad [2.23]$$

It can be seen that γ_c is only a part of the surface tension of a solid polymer, because, according to the experimental data, $\Phi < 1$. The non-conformance of individual, experimentally found, values of γ_c and γ_L and calculated according to Zisman can be explained by the difference of forces acting on the interface, and by the fact that γ_c is determined by wetting which reflects only part of the free surface energy influenced only by dispersion or polar interactions, depending on the liquid applied.

Behind this lies the Fowkes theory,[17] in accordance with which the total surface free energy is due to the action of dispersion and polar forces. The contribution of the latter in the free energy can be distinguished. It can be seen that the free surface energy of a liquid is given by

$$\gamma_L = \gamma_L^d + \gamma_L^h \qquad [2.24]$$

where d relates to dispersion and h to polar interactions, for example, hydrogen bonding. Fowkes assumed that interfacial tension between two liquids, such as hydrocarbon and mercury, is described by the relationship:

$$\gamma_{L1\,L2} = \gamma_{L1} + \gamma_{L2} - 2\left(\gamma_{L1}^d\gamma_{L2}^d\right)^{1/2} \qquad [2.25]$$

Eq 2.25 takes into account only the dispersive interactions of components, which in accordance with Reference 15 can be expressed as the geometric mean of dispersion components of both liquids. Eq 2.25 for a solid-liquid interphase has the form:

$$\gamma_{sL} = \gamma_s + \gamma_L - 2\left(\gamma_s^d \gamma_L^d\right)^{1/2} \qquad [2.26]$$

Eq 2.26 allows one to calculate the dispersive component for a liquid having free surface energy dependent on dispersive and polar forces based on values obtained for liquid determined only by dispersive forces. For example, for hydrocarbons $\gamma_L = \gamma_L^d$, and then for water $\gamma_L^d = 0.0218$ N/m.

Using the above relationships and Young's equation (2.4) for contact angles, one can predict the value γ_{sL} from:

$$\gamma_L \cos\Theta = -\gamma_s + 2\left(\gamma_L^d \gamma_s^d\right)^{1/2} \qquad [2.27]$$

For liquids having $\gamma_L > \gamma_s$, it follows from Eq 2.27 that:

$$\cos\Theta = -1 + 2\left(\gamma_s^d\right)^{1/2}\left(\frac{\gamma_L^d}{\gamma_L}\right)^{1/2} \qquad [2.28]$$

From the dependence of $\cos\Theta$ on $\left(\gamma_L^d\right)^{1/2}$, one can find the dispersive component of the surface tension of a solid, γ_s^d, measuring its contact angle. It is thus possible to determine γ_L^d for many liquids. Consequently, the values of γ_c found by Zisman for non-polar liquids correspond to their dispersion component, rather than to the full surface energy of a solid. Indeed, according to Zisman, at $\cos\Theta = 1$, $\gamma_L = \gamma_c$. For a non-polar liquid $\gamma_L = \gamma_L^d$, which modifies Eq 2.28 to the following form:

$$\gamma_L = \left(\gamma_L^d \gamma_s^d\right)^{1/2} \qquad [2.29]$$

and then $\gamma_s^d = \gamma_L = \gamma_c$. If dispersion and polar forces are operative on the surface, Eq 2.26 assumes the form:

$$\gamma_{sL} = \gamma_L + \gamma_s - 2\left(\gamma_s^d \gamma_L^d\right)^{1/2} - 2\left(\gamma_s^h \gamma_L^h\right)^{1/2} \qquad [2.30]$$

or

$$\gamma_{sL} = \left((\gamma_s^d)^{1/2} - (\gamma_L^d)^{1/2}\right)^2 + \left((\gamma_s^h)^{1/2} - (\gamma_L^h)^{1/2}\right)^2 \qquad [2.31]$$

where γ^h is determined by hydrogen bonding and dipole-dipole interactions. Eq 2.28 can similarly be written as:

$$1 + \cos\Theta = 2(\gamma_L^d)^{1/2}\left(\frac{\gamma_L^d}{\gamma_L}\right)^{1/2} + 2(\gamma_s^h)^{1/2}\left(\frac{\gamma_L^h}{\gamma_L}\right) \qquad [2.32]$$

Measuring γ_L^h, one can obtain equations for the calculation of γ_s^d or γ_s^h. Their sum gives the approximate full surface energy of a solid, γ_s.[18]

For the analysis, it is convenient to combine the Zisman equation: $\gamma_c = \gamma_s - \gamma_{sL}$ (at $\Theta = 0$) with Eq 2.32:

$$\gamma_c = \gamma_s - \left[\left((\gamma_s^d)^{1/2} - (\gamma_L^d)^{1/2}\right)^2 + \left((\gamma_s^h)^{1/2} - (\gamma_L^h)^{1/2}\right)^2\right] \qquad [2.33]$$

The term in parentheses is interfacial tension, γ_{sL} ,equal to γ_s - γ_c. Breaking into constituents, it serves as means of approximate evaluation of the surface layer structure.

The Fowkes theory played an important role in the evaluation of not only the free surface energy of polymers and its relation to γ_c, but also in the case of interfacial energy and determination of the relationship between adhesion of polymer solids and their surface energy. In this respect, it is essential to take into account, apart from dispersive forces, polar forces operating at the interface. Developing the approach considered above, some other theories have been proposed.[19-22]

Thermodynamic relationships describing adhesion can be used to substantiate the criterion of maximum of adhesion.[23] The maximum of adhesion strength is observed in these systems which have very low or equal zero interfacial tension, γ_{sL}. It means that such systems have equal surface tensions of adhesive and substrate. If these two values are not equal, the decrease in the adhesion strength is lower in systems having surface energy of substrate higher than the surface tension of adhesive. In this case the parameter Φ, can be presented as follows:

$$\Phi = 0.5(1+\cos\Theta)\left(\frac{\gamma_{sL}}{\gamma_s}\right)^{1/2} \qquad [2.34]$$

Parameter Φ depends on the contact angle and dimensionless ratio of surface tensions. Thus the value Φ cannot be considered as a constant. If liquid fully spreads on the surface, then $\cos\Theta = 1$, $\gamma_L = \gamma_c$ and $\Phi = \Phi_0$. In this case the expression:

$$\Phi_o = \left(\frac{\gamma_c}{\gamma_s}\right)^{1/2} \qquad [2.35]$$

may be considered as a constant for a given system. From the equations given above, it follows that:

$$\cos\Theta = 2\Phi\left(\frac{\gamma_s}{\gamma_L}\right)^{1/2} - 1 \qquad [2.36]$$

Because value Φ enters Eq 2.18 for thermodynamic work of adhesion, the latter is dependent on the factors influencing Φ. Eq 2.36 is valid for the case when Φ is constant and thus this value cannot correctly describe the situation when using Eq 2.35. In many cases, each point in the dependence of

$\cos\Theta = f(\Phi, \gamma_L)$ corresponds to another value of Φ. The critical surface tension of wetting, as shown by Gutowski,[23] is not a constant value which probably should be connected with various contributions in value γ_L of polar and dispersion constituents, Φ, which depend on them. Therefore, it is very important to find the correct form of the dependence of $\cos\Theta$ and γ_L.

To establish the physico-chemical criterion of maximum of adhesion, Gutowski[23] used the following relationships for linear dependence of $\cos\Theta$ and γ_L:

$$\cos\Theta = 2 - \left(\frac{\gamma_L}{\gamma_s}\right)\left(\frac{1}{\Phi_o^2}\right) \qquad [2.37]$$

for non-linear dependence:

$$\cos\Theta = 2\Phi\left(\frac{\gamma_s}{\gamma_L}\right)^{1/2} - 1 \qquad [2.38]$$

Denoting $\gamma_s/\gamma_L = a$ (a is the energetic modulus of the system), the following equations have been obtained for a linear dependence:

$$\frac{\gamma_{sL}}{\gamma_L} = a + \left(\frac{1}{a}\right)\left(\frac{1}{\Phi_o^2}\right) - 2 \qquad [2.39]$$

for non-linear dependence:

$$\frac{\gamma_{sL}}{\gamma_L} = (a+1) - 2\Phi_a^{0.5} \qquad [2.40]$$

Correspondingly for the first case the relative work of adhesion is:

$$W_a/\gamma_L = 3 - (1/a)(1/\Phi_o^2) \qquad [2.41]$$

and for the second:

$$\left(\frac{W_a}{\gamma_L}\right) = 2\Phi_a^{0.5} \qquad [2.42]$$

Maximum of adhesion, determined from the mechanical strength of an adhesion joint, corresponds to the minimum of interfacial energy:

$$a_{min} = \left(\frac{\gamma_s}{\gamma_L}\right) = \frac{1}{\Phi_o} \qquad [2.43]$$

At γ_{sL} approaching minimum, we have:

$$\left(\frac{\gamma_{sL}}{\gamma_L}\right)_{min} = \left(\frac{2}{\Phi_o}\right)^{-2} \qquad [2.44]$$

From these equations, the author concludes that the zero contact angle does not meet the condition of minimum interfacial energy and maximum of strength except for systems where $\Phi_o = 1.0$. The interfacial energy at the point where $\cos\Theta = 1$ is always greater than at the minimum point. Consequently, the expected strength at contact angle equals zero will be lower than the maximum strength attainable for a given system. The optimum contact angle corresponding to the minimum of the interfacial tension may be found from the equation:

$$\Theta_{opt} = \cos\Theta^{-1}\left(2 - (1/\Phi_o\right) \qquad [2.45]$$

The zero contact angle corresponding to full spreading of liquid meets the condition:

$$a_s = \frac{\gamma_s}{\gamma_L} = \frac{1}{\Phi_o^2} \qquad [2.46]$$

Gutowski's approach is based on the Girifalko-Good approximation, which postulates interrelations between values γ_s , γ_L and γ_{sL} not proven theoretically. This is a common shortcoming of all approaches to the description of adhesion based on the use of the above-mentioned postulate.

A new approach to the problem is based on the concept of acid-base interactions.[24-26] The theory takes into account the existence of acid or base properties of the filler surface and polymer adhesives.[27-29] For example, poly(vinyl chloride) or other chlorinated polymers have acid properties and are capable of interaction with fillers or polymers with basic properties (SiO_2, $CaCO_3$, polyesters etc). The enthalpy of adsorption of polymer with base properties B from one neutral solution on acid surfaces A is really the enthalpy of acid-base interaction ΔH^{AB}:

$$-\Delta H^{AB} = C_A C_B + E_A E_B \qquad [2.47]$$

where C and E are constants which may be found from measurements of the interaction between organic acids and bases.

Using the Fowkes concept regarding contribution of dispersion, polar components, and hydrogen bonds to adhesion, the adhesion between two substances 1 and 2 may be expressed as:

$$W_{12} = W_{12}^{d} + W_{12}^{ab} \qquad [2.48]$$

$$\gamma_1 = \gamma_1^{d} + \gamma_1^{ab} \qquad [2.49]$$

$$\Delta H_{12} = \Delta H_{12}^{d} + \Delta H_{12}^{ab} \qquad [2.50]$$

It is evident that in this case the dipole-dipole interactions are neglected. However, the acid-base interactions cannot be found from the geometric mean value equal to $2(\gamma_1^{AB}\gamma_2^{AB})^{1/2}$. The theory is based on the assumption that all interactions, which are determined by polar dipole-dipole interactions and by hydrogen bonding, may be quantitatively described as acid-base interactions. The value W may be estimated from the equation:

$$W_{12}^{ab} = W_{12} - W_{12}^{d} = \gamma_L(1 + \cos\Theta) - 2(\gamma_L^{d}\gamma_s^{d})^{1/2} \qquad [2.51]$$

The adhesion, according to Fowkes, depends on adsorption, determined by acid-base interactions. This statement is confirmed by the observation that polymers with basic properties have higher adhesion to acidic surfaces as expected from the adsorption data. The interactions between filler and matrix can be regulated by their acid-base properties - easily achieved by surface modification.

There is still another approach to the determination of the thermodynamic work of adhesion. The validity of Antonov's rule (Eq 2.10) is theoretically confirmed,[30] forming the base for thermodynamic calculations. Thermodynamic work of adhesion can be found from a value of thermodynamic work of cohesion, W_c. If the surface tension of polymer is γ_p, then $W = 2\gamma_p$.

Using Eq 2.1, one obtains:

$$W_a = 2\gamma_p = W_c \qquad [2.52]$$

This relation characterizes the thermodynamic state of a two-phase system with minimum free energy and is valid for the impermeable phase border between two immiscible bodies. Eq 2.52 is a condition of the minimization of the free energy of the system. A minimization of the work of cohesion of two phases W_{cs} and W_{cp} may be considered as an initial condition. From Eq 2.52, it follows that when any specific interaction at the phase border is absent, the thermodynamic work of adhesion is determined by the thermodynamic work of cohesion of the phase with lower cohesion energy. In this case, the adhesion may be enhanced by increasing cohesion strength of polymer.

To apply Eq 2.52, one needs to know the surface tension of adhesive. There are methods which allow one to estimate this value.[31,32] The methods are based on the measurement of contact angles. To find the surface tension of a polymer γ_p, using various liquids with surface tension, γ_L, the following equation is used:

$$2\gamma_s = \gamma_L(1 + \cos\Theta) \qquad [2.53]$$

It should be noted that the surface tension of a solid polymer is dependent on the surface tension of a wetting liquid. The experimental data, schematically presented in Figure 2.1, show that, at a contact angle close to 90°, a zone of invariable values of γ_p exists, whereas at other angles there is a linear dependence of γ_p on γ_L. The slope depends on the nature of polymer. This effect is determined by polarizability of molecules of both phases in the interphase region due to the changes in the surface force field of wetting of solid polymer by liquids having various surface tensions. The polarization, P, changes with field intensity, E:

$$\varepsilon E = E + 4\pi P \qquad [2.54]$$

where ε is a dielectric constant.

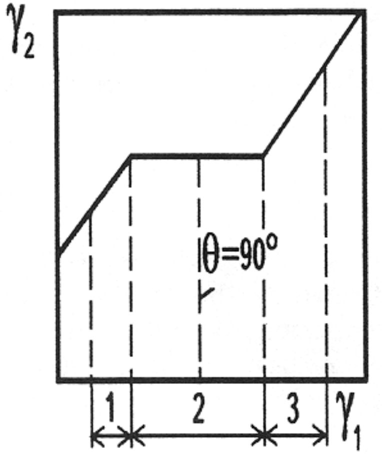

Figure 2.1. Schematic representation of the dependence of polymer surface tension γ_2 on the surface tension γ_1 of wetting liquid: 1-depolarization zone, 2-unperturbed zone, 3-zone of additional polarization.

The intensity of the surface force field is determined by the surface tension, and the polarization will not change as long as the surface tension does not change during the process of wetting of solid polymer by liquid. From Eq 2.4, it follows that this condition is fulfilled when the contact angle is close to 0 when $\gamma_s = \gamma_{sL}$. In this case, the surface force field does not change essentially, and as a result, a zone of values of γ_p independent on γ_L exists. However, if $\gamma_s >> \gamma_{sL}$, at low contact angles, then the surface field is also lower, leading to depolarization of molecules of solid polymer and to diminishing of its surface tension (depolarization zone). There is also a zone of additional polarization when $\gamma_s < \gamma_{sL}$.[33]

Let us now consider some consequences of the condition $\gamma_p = f(\gamma_L)$. The surface tension is an integral characteristic of the interphase layer:[34]

$$\gamma = \int_0^\delta (P_N - P_T)dz \qquad [2.55]$$

where δ is the thickness of the interphase layer, P_N and P_T are normal and tangential parts of pressure, z is the direction normal to the plane of an interface.

From this equation, it follows that by changing γ_p, other properties connected with γ_p are changed as well. In particular, from Eq 2.52, it follows that W_a for any polymer is not a constant value but changes in accordance with the dependence shown in Figure 2.1. When γ_p and γ_L are almost identical, the adhesion work is diminished, and, when the difference between these two values is relatively high, the adhesion increases. In the first case, $W_c > W_{ci}$ and in the second, $W_c < W_{ci}$ (index i denotes the interphase region).

From the analysis presented above, it becomes pertinent that when a polymer is in contact with a solid having higher surface tension, the increase in the surface tension of a polymer will be observed due to polarization. It is also evident that the value W_c should be considered as a cohesion energy of the interphase region but not of polymer in bulk. This value may or may not coincide with the cohesion energy of polymer far from the phase border. The same conclusion follows from the analysis of an interaction between solid and liquid along the ternary contact border.[30] The experimental data confirm a theoretical conclusion regarding an increase in the surface tension of polymers at a high interfacial tension. This means that under such conditions, the adhesion of a polymer to solid may be enhanced.

The main shortcoming of various approaches in problem-solving of adhesion is the use of surface tension of a liquid adhesive in all equations. According to Zisman, the reversible work of adhesion of cured adhesive should be close to the value calculated for liquid state, if the effects of inner stresses are not accounted for. Zisman believed that the forces acting at the interface are of short range and that the adhesion should not depend on the state of a substance. However, this point of view seems to be not quite correct. In reality, any thermodynamic phase transition (curing) in the system is accompanied by a change in its thermodynamic state and the values of its thermodynamic functions. From a purely molecular point of view, it seems hard to accept that liquid and solid will have the same strength of adhesion, due to the differences in their structure. Therefore, the transfer of concept of wetting by low molecular weight liquid to a high molecular adhesive has no substantiation.

From another point of view, the thermodynamic correlations (2.12 - 2.17), including surface and interfacial energies, do not depend on the aggregate or phase state of two contacting bodies. Therefore, it is possible to use these equations if we know the corresponding values for solid polymers. For example, it was shown that the correlation between the thermodynamic work of adhesion and adhesive joint strength can be attained if in Eq 2.5, instead of the surface tension of liquid, the corresponding value for cured adhesive is used and the contact angle values are taken from the data obtained in the course of its curing.[35] At the same time, in the same systems, no correlation was found when the work of adhesion was calculated using values for liquid adhesive.

This discussion explains the lack of correlations between thermodynamic work of adhesion and the data on the mechanical strength of adhesive joints. It also should be noted that all thermodynamic approaches only consider the equilibrium conditions at which the adhesive bonds were established, which is not the case in actual practice.

In real systems, one also should account for the dependence of surface tension on the molecular mass and polydispersity of polymeric binders. The low molecular mass fractions have lower surface tension and therefore during the formation of adhesive joints, separation, due to the molecular mass, is also possible in both the surface layers and in the bulk of a binder. For reinforcing fillers having high surface energy, the preferential concentration of fractions of higher molecular mass at the interface is observed. In the case of polymeric reinforcing fibres, because of the proximity of the surface tensions of fibres and binders, the low molecular mass fraction tends to migrate to the interface. Correspondingly, the polymer matrix in the bulk will be enriched or impoverished by the fractions of higher molecular mass.[36] As a result, in PCM two levels of the cohesion strength (cohesion energy) of polymer binder may arise: one corresponding to the surface layer and the other to the polymer bulk. The adhesion work will be determined by the cohesion energy of the surface layer, as was pointed out above.

Cases where the binder consists of two or more components are of great importance. The introduction of filler leads to the redistribution of fractions of both components between the surface layer and bulk. It was shown[36] that filler incorporation into a two-component binder essentially changes the dependence of binder surface tension (determined from their respective contact angles) on the composition. This effect is connected with the above-mentioned redistribution of components between the surface layer and bulk.

Concluding the thermodynamic analysis, we would like to note that all the approaches are based on the general principles of thermodynamics and they do not account for specific features of polymer behavior used to explain properties of polymer solutions, adsorption, mechanical properties, etc. We believe that the science of adhesion should be transformed from general and qualitative descriptions to the quantitative analysis of the interphase phenomena based on statistical theories. It is also desirable to distinguish between adhesion at various phase borders such as non-polymeric solid-polymer, polymeric adhesive-another polymer (in any phase or aggregate state).

2.2 THEORIES OF ADHESION

Many theories of adhesion have been proposed which can describe some features of the formation of adhesive joints and their properties. The thermodynamic analysis of adhesion, discussed above, is sometimes identified with the thermodynamic theory of adhesion.[36] However, it cannot be recognized as an independent theory, as it is an application of fundamental thermodynamic principles to the description of interfacial interactions. In adsorption theory,[3,37] adhesion is considered as a result of molecular interaction forces acting between molecules of adhesive and substrate in physical contact. Molecular interactions proceed by a formation of contact between heterogeneous surfaces. However, Berlin also was correct[3] to emphasize that the statement indicating that molecular interaction is the origin of adhesion hardly means anything.

Unfortunately, problems of the adsorption or molecular theory of adhesion are in most instances solved exclusively at the qualitative level and are limited to consideration of a role of the polarity of components in adhesion (the so-called polarity rule: high adhesion cannot be achieved between a polar substrate and apolar adhesive, and *vice versa*). It is very unfortunate that in many books on adhesion the description of adhesion is not given at the molecular level, which is now accessible for the description of intermolecular interactions in liquids and solids. At the same time, it is obvious that from a physical point of view the adsorption theory presents a rather correct concept of interfacial phenomena and agrees with thermodynamics. Within this context, adhesion can be regarded as a particular case of adsorption, inasmuch as the formation of molecular bonds at the interface and the transfer of polymer molecules from the bulk to the interface are phenomena typical of adsorption.

The existing theories of adsorption (see Chapter 1) and ideas about the structure of adsorption layers provide us with the concept of the character of the interactions which occur during adhesion. If we consider adsorption as an excess concentration of the component at the interface, this definition is applicable to adhesion because the study of the structure of polymer surface layers on solid surfaces shows that redistribution of different components of adhesive resulting from selective adsorption is taking place. With a prolonged adhesive contact under conditions ensuring the required molecular mobility (above the glass transition temperature) molecules redistribute, in the course of time, according to their molecular mass and surface activity.[38] However, one cannot draw a parallel between the adsorptivity of polymers from solutions and adhesion, as there is none, and a direct connection between them cannot exist. The absence of this connection is explained by difference in conditions of interaction and conformation of molecules in the polymer solution and in the solventless polymeric adhesive.[39]

Adsorption theory also considers chemisorption and formation of primary valent bonds between the surface and adhesive if some specific groups are present at the surface. Evidently, there are several bases on which the adsorption theory can be criticized[40] - among them, it cannot explain the mechanical response of a system of materials in which volume deformations occur.[40] The electric theory of adhesion, developed by Deryagin and associates,[1] postulates that all adhesion phenomena can be explained in terms of the transfer of electrons through the interfacial border, leading to the formation of an electrical double layer. This theory treats the adhesion joint as though it were a capacitor, charged due to the contact of the two materials composing the joint. In contrast to other theories of adhesion, this theory interprets phenomena taking place during the separation of the adhesive from the substrate on the basis of the concepts of the electrical double layer. The latter interferes with destruction of the adhesion joint at dynamic loads and increases the work of separation. Electrical phenomena not only accompany film separation, but also act as an important factor determining the resistance of film to failure even when it regards adhesive of mixed character (adhesive and cohesive failure simultaneously).

Without diminishing the role of electrostatic phenomena in adhesion, it should be noted that their influence is greatest in the course of adhesion joint failure and depends on the conditions of separation (especially its rate). In most instances, PCM are used under conditions, far from failure and separation, where the electric theory can be applied.

In evaluation of the significance of the electrical double layer at the boundary of two amorphous bodies due to the donor-acceptor bond, the authors of the theory proceeded from the fact that the near-surface layer of one of the contacting bodies is saturated with donor molecules and the other with acceptor molecules or functional groups. A double layer is formed only when the free energy of the system decreases in this process. These provisions bring the electrical theory of adhesion and adsorption (molecular) theory closer to each other. The electrical theory has often been criticized. Authors usually mention it but almost nobody accepts it. Wake[36] criticized the theory and particularly emphasized that the nature of the origin of charges on the surface of polymer remains unclear. Crushing arguments against this theory were given by Bikerman.[41]

Recently, the theory was criticized again by Sharpe,[40] one of whose arguments considers that electrically conductive materials should not form adhesion joints, because they could not support separation of charge (however, they do). The generalized thermodynamic discussion on the surface energy of solids, including polymer materials, as suggested by Fowkes, and accounting for polar, donor-acceptor, acid-base interactions, includes, among possible interfacial interactions, the donor-acceptor interactions to which is attributed (by the Deryagin theory and to our mind unjustifiably) the underlying role in adhesion. In fact, various forces act at the interface, depending on the nature of contacting bodies, including purely ionic and chemical interactions. It is thus more reasonable to describe them within the framework of a unified molecular approach, i.e., in terms of molecular theory of adhesion.

The diffusion theory of adhesion of two heterogeneous polymer bodies was proposed by Voyutsky.[42] The theory is based on the concept of a mutual diffusion of segments to the interface with the formation of a transition layer responsible for the strength of the adhesion joint. When applied to polymer pairs, this theory has been well corroborated experimentally, largely with regards to the influence of the conditions of the formation of adhesive contacts on adhesive strength.

This theory is mainly applicable when both polymers are at a higher temperature than their glass transition temperature, and when there is a possibility to achieve a high molecular mobility of the macromolecules. The main condition for the formation of an adhesion joint on contact of two polymers is their thermodynamic compatibility. However, the most important question of what this compatibility should be in order that diffusion processes can ensure a sizable contribution to adhesion remains open. Because most polymeric pairs are incompatible and many of them have the lower critical solution temperature (LCST), other processes leading to the formation of the transition layer should be responsible for adhesion (for example, pure rheological factors - see Chapter 7). Therefore, it would be valid to say that it is unreasonable to refer to a special "diffusion theory of adhesion". One can only refer to the role of diffusion processes in the adhesion of some polymeric systems, since theoretical considerations for the time being have only a qualitative character.

The first attempt to theoretically describe mutual diffusion at the interface was made by Helfand[43-45] who also took into account the thermodynamic affinity of polymers. As a result of theoretical calculations, it was established that the thickness of the transition layer formed on diffusion is negligibly small and does not correspond to the concept of the diffusion theory.

In considering the above theories, one has to admit that the most useful concept of adhesion stays within the boundaries of the molecular theory and the thermodynamics of interfacial phenomena. At the same time, no one theory of adhesion can predict the real adhesion between solid and polymer or adhesion joint strength. A large number of theoretical ideas on adhesion do not refer to the phenomena of adhesion but rather to the processes of failure of adhesion joints and their description. A clear distinction between the processes of adhesion and the formation of adhesion contact and failure is a key to understanding this complex set of phenomena, referred to for convenience as adhesion.

2.3 THE THEORY OF WEAK BOUNDARY LAYERS

Among many theories describing the phenomenon of adhesion, the theory of weak boundary layers developed by Bikerman[8,46,47] plays a special role. Strictly speaking, it is not a theory, but in considerable degree a display of a pragmatic common sense. Bikerman believed that his concept was a very practical one but should be cleverly applied to give a practical result. Bikerman had written: *"If an adhesive joint (adhint) is weak, is weakness present or is strength absent? The tradition leaned toward the latter opinion; it was believed that the breaking stress of an adhint was small when the molecular forces between the adherent and the adhesive were not strong enough. We now prefer the former alternative; when a joint is weak and breaks apparently in adhesion, a week boundary layer is likely to be present."*

According to Bikerman, for mechanical breaking of the adhesion joint, some stresses should be applied or some work done. It is important to know how these stresses are distributed. Each adhesion joint consists of some components (in the simplest case, two components: adhesive and substrate). Between them, some other layers, having different properties, might be present. Therefore, the statement implying that during the breaking the adhesion joint it is only necessary to overcome the molecular forces is not correct. In reality, the breaking strength is not equal to adhesion. Physically, it may be shown that the true interfacial failure rarely, if ever, occurs in the breaking of a joint by purely mechanical means. The surface of a real adherent is generally a highly irregular, three-dimensional contour, relative to atomic dimensions. On the probability grounds, one should not expect failure to occur along this predetermined, highly irregular path in response to some external loading. As a rule, the breaking of a joint has a mixed adhesion-cohesion character. Therefore, the experimentally found strength of an adhesion joint is not really its strength. The failure, as Bikerman stated, takes place not along the interface but at some distance from it, and correspondingly the breaking stress does not characterize the adhesion joint strength. The main, but not the only reason, for failure is the existence of weak boundary layers. According to Bikerman, the assumption of the existence of weak boundary layers is as important for the modern theory of adhesion joints as a denial of the sharp failure along the phase border.

In most cases, failure cracks arise in the weak boundary layers. Bikerman distinguished many groups of weak boundary layers according to their origin. Similar to the formation of the adhesion joint, three phases usually participate in failure: adhesive, substrate and air (or other medium). Various admixtures form a weak boundary layer, being concentrated at the phase border. The defects in the structure of the substrate and adhesive and admixtures determine the formation of these weak layers. The general conclusion is that the failure proceeds in the zone of weak material (in the interphase). The concept of weak boundary layers gives a possibility for critical estimation of the very problem of adhesion joints and establishing of the failure location. This leads to the conclusion that true molecular adhesion has nothing in common with the resistance to shear, peeling, breaking, etc. The Bikerman concept seems to be physically valid if we neglect the molecular nature of adhesion and the chemical and polymeric nature of adhesives. Having put forward some substantiated ideas on the rheological theory of adhesive joints, Bikerman neglected thermodynamic factors, the influence of the polymer chemistry, the nature of the surface on adhesion, and some other factors. Sharpe[40] believes that Bikerman's theory should not be considered because it applies only to the breaking strength of a joint. It should rather be thought of as a theory of mechanical response of a joint. Despite some one-sideness of Bikerman's theory, it should be appreciated because it is very simple and practical.

The detailed analysis of the interphase phenomena in polymeric systems[36] has allowed the discovery of some additional, but strictly thermodynamic, reasons in favor of the formation of weak boundary layers during the formation of adhesion joints (see Chapter 6). Distinct from the reasons considered by Bikerman, which are mostly purely technological ones, the thermodynamic and structure factors of the formation of weak layers are related to the physico-chemical processes proceeding at the interface. These processes lead to the formation of the microheterogeneous structure of the boundary layer with different levels of cohesion energy. The approaches developed by us and presented in the following chapters may be considered as theoretical substantiation of the existence of weak boundary layers. Their appearance cannot be prevented by any technological means.

2.4 MECHANISM OF ADHESION JOINT FORMATION

To understand the properties of the adhesion joints one should consider the mechanism of their formation. The latter consists of several stages:

- spreading of the adhesive on the surface of a solid body and its wetting

- equilibrium establishment (which is not always possible) of the adhesion contact, depending on the viscosity of the adhesive and on the processes of diffusion and adsorption
- formation of the chemical or physical structure of the adhesive on curing, accompanied by the emergence of a surface layer distinguishable in its properties from the bulk. This stage also includes the setting of the adhesive, possible crystallization, evolution of new phases, etc.

The emergence of forces of molecular interactions responsible for adhesion is possible only under conditions under which the molecular contact occurs at the adhesive-substrate interface. This process is dependent on the physical relief of the surface. The process of the formation of adhesive joints also depends on the kinetics of spreading, which, in turn, depends on the rheological properties of adhesive. As we have already noted, the state of true thermodynamic equilibrium in many cases cannot be achieved.

The spreading of liquid adhesives on a surface is determined by the general regularities for the impregnation of porous and disperse solids.[48] Roughness of the surface affects wetting and the contact angle on the real surface Θ' is determined by the Ventsel-Deryagin relationship $\cos\Theta' = K\cos\Theta$, where Θ is an equilibrium contact angle and K is the roughness coefficient, i.e., the ratio of the true surface area to the apparent surface. If $K > 1$, spreading can take place only at $\Theta > 0$. One can show that:

$$\Delta\Theta = \gamma_L(K\cos\Theta - 1) \qquad [2.56]$$

i.e., the increase in the roughness of the surface, K, contributes to the spreading of liquid having a contact angle close to, but always less than, 90°. It is also known that the equilibrium value of the contact angle of wetting is attainable over a very long period of time, similar to the establishment of the equilibrium value of the surface tension of polymer system during their curing.[36]

There is a theory describing the kinetics of surface wetting due to the action of capillary forces in relation to the surface tension predicted by a Laplace equation.[48] One can calculate the rate of liquid flow into a narrow or wedge-like slot, or a round hole. The theory takes into consideration the rheological properties of liquids. In particular, it can be applied to viscoelastic liquids, which include polymer adhesives. In this case, the wetting depends on the polymer structure. With an increase in temperature of melt or polymer solution, the intermolecular interactions become weaker and molecules assume the most probable conformations. The rate of change of the molecular arrangement and interaction with a surface determines the kinetics of adhesion development due to chain flexibility and intermolecular interactions in the polymer system and also the energy of the interaction with the surface. With the penetration of the adhesive due to possible orientation of molecules during flow, the viscosity may increase. The relationship between the wetting rate and the relaxation time affects the structure of the adhesion joint formed, which cannot be predicted by the thermodynamic theory because it does not account for the non-equilibrium properties of a system. If the adhesive viscosity is high or it is increased rapidly during the process of wetting, defects are likely to occur on account of incomplete wetting. Limiting strengthening of the adhesion joint can be accomplished by maximum filling of microdefects in the substrate surface. High viscosity of the adhesive, features of the surface topography, an insufficient duration of the plastic state, and other causes, result in pores and cavities found in the adhesive layer. As a result, the area of actual contact with the adhesive decreases and potential sources of adhesion bond failure appear.

The molecular description of the formation of an adhesive layer does not take into account the polymeric structure of adhesives either. It is based on determination of the number of adhesion or molecular bonds, n, per unitary area of a true contact surface and the energy of a single bond between two surfaces.[49] During the formation of such bonds the adhesion strength, A, can be expressed by a specific work spent on the destruction of the adhesive joint:

$$A = S_t \Sigma n_i U_i \qquad [2.57]$$

where n_i is the number of adhesion bonds of the i-th order per unitary area of the true contact surface, S_t, and U_i is the energy of these bonds. The true surface area may be calculated as follows:

$$S_t = 2n_1 \frac{n_i}{\cos\alpha} + \left(2n_1 \frac{n_i}{\cos\alpha}\right)\left[n_2\pi^2 d^2 (Pt / \eta)^{1/2}\right] \qquad [2.58]$$

where n_1 is the number of groves on the surface having a depth, h_i, and half of the angle at the apex of the triangle formed by the section of furrow, α, d is the pore diameter, n_2 is the number of pores per cm^2, t is time of contact, η is the melt viscosity, and P is the pressure under which the melt flows into microdefects. Because work of adhesion, irrespective of the nature of the bonds, is proportional to the true contact area, we can derive:

$$A = 2x_1 n_1 \frac{h_i}{\cos\alpha}\left[1 + n_2\pi^2 d^2 (Pt / \eta)^{1/2}\right] \qquad [2.59]$$

where x_1 is the average energy of a single bond multiplied by the number of adhesive joints per cm^2 of the true contact area.

The appearance of the maximum number of bonds, determined by the surface relief and adhesive rheology, is one of the most essential conditions for the formation of contacts and increase in adhesion strength. Microrheological effects include adsorption interactions with the surface and are determined by the flexibility of chain and molecular mobility in the adsorption layer.

A valid molecular-kinetic treatment of the formation of adhesive bonds has been given by Voronin and Lavrentyev.[50,51] When discussing the mechanism of formation and failure of adhesion joints, it is assumed that for segments of the polymeric chain in the boundary layer there are two possible states:

- segments bound with the surface active centers with the number of bonds n_2
- segments bound with similar ones with the number of bonds, n_1.

In this instance, $n_1 + n_2 = n_0 = const$. The rate of change of the number of bonds is:

$$\frac{dn_2}{dt} = -n_2\nu_2 + n_1\nu_1 \qquad [2.60]$$

where ν_1 and ν_2 are the frequencies of the formation and destructions of the bonds of kinetic units of the polymer with the active centers of the substrate. In a general form:

$$\nu_1 = \nu_{i0}\exp\left[\frac{-U_\alpha}{kT}\right] \qquad [2.61]$$

where U is activation energy of the formation or destruction of adhesive joints. Under conditions of equilibrium:

$$\frac{dn_2}{dt} = 0; \quad n_2 = \frac{n_o}{1 + \nu_2/\nu_1} \qquad [2.62]$$

Then, adhesion strength in a simplified form can be expressed as:

$$A = n_2 f_{av;} \quad f_{av} = \frac{n_2 \sum n_{2i} f_i}{\sum N_{2i}} \qquad [2.63]$$

where $\Sigma n_{2i} = n_2$, n_{2i} is the number of bonds between polymer segments and active centers on the surface, f_i is the energy of binding. When loads are applied to the adhesion joint, some bonds, prior to failure, will pass with average frequency from state 1 into state 2, i.e., the number of active bonds will be less than n_2. Therefore, the experimentally determined value of A is $A = n_3 f_{av}$, where $n_3 = n_2 - n_2\nu\alpha$, and α is a coefficient depending on the rate of loading. In a general form:

$$A = \frac{n_o f_{av}}{(1 + \nu_2/\nu_1)(1 - \alpha\nu)} \qquad [2.64]$$

From a molecular-kinetic concept, it follows that n_1 and f_{av} have an important effect on the strength of the adhesion joint. Depending on n_1, the density of the polymer boundary layer, directly adjacent to the solid surface, varies.

All these approaches enable us to get some relationships to establish the durability of adhesion joints, accounting not only for adhesive but also for cohesive failure of an adhesion joint.

2.5 THE STRENGTH OF ADHESION JOINTS

The strength of adhesion joints determines the main properties of PCM. When evaluating the adhesion strength one should take into account many factors, including the processes of crack development, distribution of stresses in the system, the existence of inner stresses, etc. These questions are thoroughly discussed elsewhere.[4] In our analysis of the adhesion strength we give more emphasis to the relationship between thermodynamic evaluation of adhesion and adhesion joint strength, which have no direct correlation. One has to distinguish between two definitions: thermodynamic work of adhesion as an equilibrium value which does not depend on the conditions of test, application of adhesive to a surface, roughness of the surface, etc. This value, as as has been shown, depends only on the thermodynamic characteristics of adhesive and adherent. The adhesion strength, similar to the strength of any solid, is a kinetic value depending on the conditions of failure, defects in the material structure, weak boundary layers, etc.

It is known that the theoretical strength of a solid does not correspond to the real strength. The first is determined by the molecular forces, whereas the second depends on the structure of the material. The deformation of a solid is a non-equilibrium process dependent on energy dissipation. The lack of correlation between thermodynamic work of adhesion and strength of adhesion joints is a direct consequence of the non-equilibrium failure. It may be predicted that the correspondence between these two values may only be reached if the strength was determined in the thermodynamically equilibrium conditions, i.e., at deformation with infinitely low rate.

The thermodynamic work of adhesion is an invariant value determined only by the nature of interacting surfaces, whereas the strength of a joint depends on many factors. From this point of view, only thermodynamic evaluation may have physical meaning. However, thermodynamics does not take into account nonelastic deformations, defects at the phase boundary, the inner stresses in the adhesion joints which arise during the joint formation, concentration of stresses connected with the difference in modulus of the adhesive and adherent, and many other factors.

According to Bikerman,[8,47] the failure of adhesion contact never has a pure adhesion character. Depending on the conditions, various types of failure may be observed:

- adhesive in which a full separation of adhesive from substrate occurs
- cohesive failure where the destruction of adhesive contact proceeds either in adhesive or in the solid phase
- mixed failure where partial destruction of contact takes place in both phases.

Only adhesive failure should characterize adhesion, even though it is a rather rare case.

It is evident that the theory of failure of adhesion joints should be based on the general principles of solid destruction. However, the transfer of the classical concept of Griffith's theory to two-phase systems is very complex.[52] The difficulties are related to determination of two main parameters in the equation for critical stress of fracture:

$$\sigma_f = K\left(\frac{EG_c}{l}\right)^{1/2} \qquad [2.65]$$

where E is elastic modulus, G_c is the work of deformation of a crack, and l is its length. The work of crack deformation is stored as a free surface energy of a solid, γ_s, and energy, ψ, needed for other processes which accompany the crack propagation:

$$G_c = 2\gamma_2 + \psi \qquad [2.66]$$

For a two-phase system, it is necessary to introduce two new parameters, δ_1 and δ_2, which characterize the thickness of two border layers in adhesive and adherent where the process of the energy dissipation proceeds. Good[52] proposed the form of functional dependencies for some cases of fracture at various values and signs of ΔG and ΔE, which allow one to draw some conclusions regarding adhesion in two-phase systems. If ΔG and ΔE have the same sign, and if the forces acting along the interface are sufficiently high, the most probable place of crack origin is in one of the contacting phases. If ΔG and ΔE have the opposite signs and ΔlogG > ΔlogE, and interface forces are sufficiently high, the fracture proceeds near the surface in the phase with lower G. At ΔlogG< ΔlogE the fracture takes place near the surface in the phase with either lower G or E. This case includes the results which can be explained from the point of view of weak boundary layers. In the case when the interface forces are weak, as a rule, true adhesion fracture proceeds. The fracture is determined by the nature of forces acting at the interface. In strong interfacial interactions, the fracture begins in the phase with lower G, whereas in weak interactions, it begins at the phase border.

Gutowski[53] proposed a very interesting model to describe the adhesion strength which takes into account the surface properties of materials involved. The force of interaction F_{12} between two materials can be estimated based on the energy function, U(r), relating the energy of interaction to the separation distance, r:

$$F_{12} = \frac{dU_{12}(r_{12})}{dr_{12}} \qquad [2.67]$$

The energy of interaction between two materials can be estimated from the Eq 2.2. The total thermodynamic work of adhesion and thus the interaction energy comprises three main contributions: dispersive component, acid-base interaction term, and dipole-dipole interaction term. In order to apply the thermodynamic relationship to estimate the interaction forces, the surface energy of materials 1 and 2 should be described in terms of their bulk properties, including the equilibrium separation on distances r_1 and r_2, pertinent to these materials. This becomes possible due to the fact that the surface energy of any material is given by:

$$\gamma = \frac{\overline{h}\,\overline{\omega}_o(2)}{32\pi^2 r_o^2} \qquad [2.68]$$

where $\bar{h}$ is the Planck constant, $\bar{\omega}_o$ is the specific adsorption frequency, and r is the equilibrium separation distance. Considering the values of surface energies of materials 1 and 2 for the energy of interaction, we obtain:

$$U_{12} = \frac{\bar{h}\bar{\omega}_o(2)}{32\pi^2}\left[\frac{3}{r_o^2(2)} - \frac{r_o^2(1)}{r_o^4(2)}\frac{\bar{\omega}_o(2)}{\bar{\omega}_o(1)}\right] \quad [2.69]$$

This equation describes the energy of interaction as a function of bulk properties of the matrix and filler and the relevant separation distance specific to these materials.

The resultant force of interaction (per unitary area), or adhesion between the matrix and reinforcement is given by the following expression:

$$F_{12} \propto \frac{\bar{h}\bar{\omega}_o(2)}{32\pi^2}\left[\frac{6}{r_o^3(2)} - \frac{r_o^2(1)}{r_o^5(2)}\frac{\bar{\omega}_o(2)}{\bar{\omega}_o(1)}\right] \quad [2.70]$$

or alternatively by:

$$F_{12} \propto \gamma_1\left[\frac{3}{(\gamma_1/\gamma_2)^2} - \frac{2}{\psi_1^2(\gamma_1/\gamma_2)^3}\right] \quad [2.71]$$

where $\psi_1 = [\gamma_c(1)/\gamma_1]^{1/2}$.

Eq 2.71, expressing the interaction force as a function of surface energy of the filler and the ratio of surface energies of filler and matrix, is applicable to the systems adhering through physical interactions typically failing at the filler-matrix interface.

The value G_c in Eq. 2.65 may be presented as $G_c = W_c + W_p$, where W_c is the energy of cohesion and W_p is the energy of viscoelastic losses. Taking this into account, Gutowski proposed the following expression for the force of adhesion (stress) between the filler and a matrix:

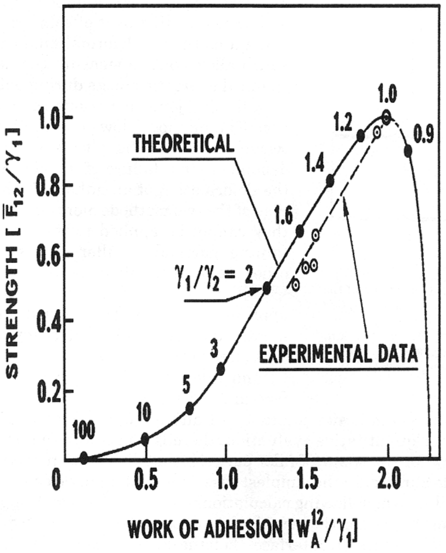

Figure 2.2. The theoretical relationship between the relative strength of adhesion, $\overline{F}_{12}/\gamma_1$, and thermodynamic work of adhesion, W_A^{12}/γ_1. [Adapted by permission from W. Gutowski in **Controlled Interphases in Composite Materials, Ed. H. Ishida**, *Elsevier*, New York, 1990, p.

$$F_{12} \propto \gamma_1 \left[\frac{3}{(\gamma_1/\gamma_2)^2} - \frac{2}{(\gamma_1/\gamma_2)^3} \right] \Phi_v(\dot{a},T,\varepsilon) \qquad [2.72]$$

where $\dot{a}$ is the rate of crack propagation, T is temperature, ε is strain, and Φ_v is the viscoelastic loss function. Gutowski has shown that the total fracture energy G_c is always proportional to the intrinsic fracture energy $G_c = W_A^{12}$, which in turn depends upon the surface properties (surface energy) of the matrix and filler. It was also shown experimentally that adhesion in terms of strength of adhesive bonds increases up to some maximum value with the increase of W_A^{12} and then begins to decline along with any further increase in W_A^{12} (Figure 2.2).

It is well known that when evaluating the peel adhesion strength, only a part of mechanical work is consumed for real fracture of the adhesion bonds, whereas energy balance is spent on various by-processes. The part of energy spent on the deformation of polymer film during peeling is of special importance.

This example indicates that it is necessary to know the individual processes leading to adhesion joint failure. These factors should be taken into account when determining the so-called quasi-equilibrium work of adhesion.[54] The method is based on the analysis of the dependence of the peeling force on time at a given rate of peeling (Figure 2.3). Continuous increase of force (part AB) is observed, then force remains almost constant (part BC). The constant force corresponds to the peel stress at a given rate of detachment P. The work of adhesion of coating is determined from the average stress value at detachment relative to the unitary width of the film, and it depends on the film thickness and deformation rate. However, if at point C the peeling is stopped, the stresses created in the film lead to a further detachment of the film from the substrate surface as a result of the relaxation of stresses created in the film.The peeling process proceeds till the stresses in the film are not balanced by the adhesion forces (part CD). At this point, the peeling process stops (point D). The value of the residual stress at the point D serves as a quasi-equilibrium value of adhesion strength, since this value does not depend on the rate of peeling nor film width. The mechanical work of adhesion bond failure and corresponding heat effects can be recorded using a method of deformational calorimetry,[55] which allows one to measure the heat and mechanical energetic effects during deformation of an adhesion joint at various rates of deformation. The method allows one to distinguish between the energetic effects at the interface dependent on a failure of interfacial bonds and the deformation of an adhesive. The disadvantage of the two methods mentioned above is that they cannot be applied to the composites containing particulate filler. For such systems, other methods should be used.

Photoelectron X-ray spectroscopy is one of applicable methods. The method comprises ele-

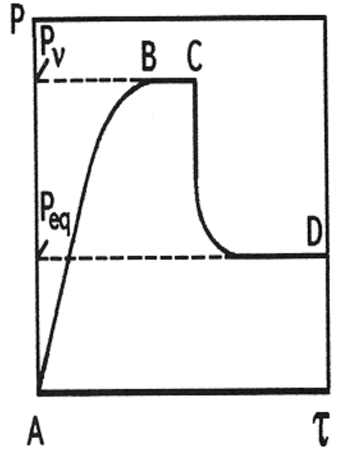

Figure 2.3. Dependence of the peeling force, p, on time, τ, (see the text). [Adapted by permission from A. N. Kuksin, L. M. Sergeeva, and Y. S. Lipatov, *J. Adhes.*, **6**, 275 (1974)]

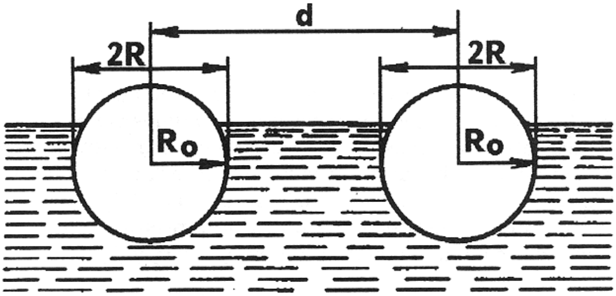

Figure 2.4. Scheme of the fractured surface of composites containing particulate filler (for explanation see the text).

mental analysis of thin surface layers. From the data on the intensity of spectral lines of polymer, I_p, and filler, I_f, it is possible to evaluate the fracture surface occupied by filler particles. In cohesive failure of adhesion joints, $I_p = 1$ and $I_f = 0$; in adhesive failure, $I_p = 0$ and $I_f = 1$. For quantitative evaluation, there is a need to use a model capable of accounting for the shape of filler particles and distribution of stresses at the filler particle surface. In the simplest case, when filler particles are spherical in adhesion failure, the following calculations can be performed. Suppose that the tensile strength of a matrix exceeds the adhesion strength, $\sigma_p > \sigma_a$ from the interfaces into the bulk of a polymer matrix. The surface of the fracture is represented in Figure 2.4.

If the filler particles are placed in the cubic lattice having period, d, the following expression is obtained:

$$\gamma = \frac{I_f}{I_{fo}} = \frac{\pi R_o^2[1-(\sigma_a/\sigma_p)^2]}{2d^2} \qquad [2.73]$$

From the equation, it follows that

$$\sigma_a = \sigma_p\left[1-(2\gamma/\pi)(d/R_o^2)\right]^{1/2} \qquad [2.74]$$

If the volume fraction of a filler, is $\phi = 4\pi/3(R_o/d)^3$, we obtain:

$$\sigma_a = \sigma_p \left[1 - (2\gamma/\pi)(4\pi/3\phi)^{2/3}\right]^{1/2} \qquad [2.75]$$

The quantitative data obtained from these relationships can be considered only an approximation because the simple model assumes pure adhesive failure. Also, there is no proof that all bonds in the cross-section are destroyed simultaneously. The method allows evaluation of the relationship between adhesion and cohesion failure, which is its main advantage.

To establish the character of failure (adhesion or cohesion), microscopic methods and visual analysis of the fracture surface are used.[53] Also, methods based on the electron scattering (β-rays) are used because scattering depends on the surface composition.[58] If the sample is composed of, for example, metal and adhesive film, current arising when β-rays are scattered is connected to free metal surface. The fraction of adhesion failure, A, can be estimated from:

$$A\,(\%) = (C_\beta - C_a)/(C_m - C_a)100 \qquad [2.76]$$

C_a and C_m are counts of β-rays, respectively for the surface of adhesive and metal, and C_β is an averaged count for a great number of regions of fracture. There exists a linear relationship between the breaking stress of the adhesive joint and the fraction of bonds destroyed at the interface. Using this technique, the profile of the stress distribution was evaluated,[58] which allows us to establish a correlation between the breaking stress and the fraction of the surfaces with cohesion and adhesion failure θ_c and θ_a:

$$\sigma_f \approx K[\theta_a \sigma_a^c + \theta_c \sigma_p^c] \qquad [2.77]$$

where σ_a^c and σ_p^c are the average stresses for adhesion and cohesion failure and K is proportionality coefficient. This equation may be presented in a more convenient form:

$$\sigma_f \approx \theta_a(\sigma_a - \sigma_p) + \sigma_p \qquad [2.78]$$

where σ_a and σ_p are values proportional to σ_a^c and σ_p^c. From the linear dependence of σ_f and θ_a, the characteristics of adhesion and cohesion strength for mixed character of the failure of adhesion joints can be found by extrapolation. The use of this approach allows one to estimate the characteristics of various layers of an adhesion joint (weak layer formed by impurities, polymer layer, oxide layer, etc.).

The above-mentioned methods are based on the analysis of the fracture surface, which may not be always convenient and possible. Also, analysis of fracture surface assumes a simultaneous break of bonds over the whole area of the adhesion contact, which is not the case with dispersed fillers. The strength of the adhesion contacts on the filler particle surface determines the mechanical stress in the interphase region at the binder-filler interface, at which the filler particles begin separating from the binder resulting in formation discontinuities.[59] To estimate this stress, various methods were proposed, including determination of changes in the sample volume by ultrasound waves to detect discontinuities in the deformed composition.

The analysis of the change in the modulus of elasticity of the material as a result of a sample preloading is still another technique which can be used.[60] The modulus is determined twice: in the initial sample, and after a fraction of the existing adhesion bonds in the material is broken. Such an approach ensures a linear viscoelasic behavior of the binder and provides the possibility to analyze the interrelation between the modulus of elasticity and the volume concentration of separated filler particles, based on two known facts: increasing the filler concentration proportionally increases Young's modulus of a composite if there is sufficiently strong adhesion bond between the binder and a filler (see Chapter 6); conversely, Young's modulus is decreased if the adhesion bond is absent or is not sufficiently strong. In the latter case, the binder is separated from the filler surface determination during elasticity modulus determination even at low stress.[61,62] After the adhesion contact in filled polymer is partially destroyed, the Young's modulus of the composite decreases. The effect is well-known as Mullin's effect, used for estimation of adhesion strength. The decrease in the Young's modulus of a filled polymer after a preset mechanical action can be used as evidence that separation of binder from a fraction of filler particles has occurred. If change of the Young's modulus for varying concentration of separated filler particles, ϕ_x, is determined, then the fraction of separated particles can also be determined from the Young's modulus change. For this purpose, Zgaevsky[62] proposed the relation, derived theoretically:

$$\frac{E_f}{E_o} = \frac{2}{3}(1-\phi_f) \qquad [2.79]$$

where E_o is the Young modulus of the binder, E_f is the modulus of filled polymer, and ϕ_f is the concentration of the filler which not bonded to the filler. It should be noted that this relationship poorly describes the experimental results in the region of low filler concentration. The experimental results can be much better approximated by the empirical equation:[60]

$$\frac{E_f}{E_o} = e^{-3}\phi_f \qquad [2.80]$$

It can be expected that when some filler particles are separated from binder in the course of a mechanical action, the remaining filled polymer with unbroken adhesion bonds serves as a "binder". Eq 2.80 can be applied to predict the properties of such a system. When a polymer filled with adhesively bonded particles is treated as a binder characterized by the modulus E_f, then, in the presence of such "binder", the same relation should exist between the composite modulus E_x and filler concentration, ϕ_x:

$$\frac{E_x}{E_f} = e^{-3}\phi_x \qquad [2.81]$$

The value of E_f can be determined experimentally in an initial sample; hence equation 2.81 makes it possible, in principle, to calculate the concentration of the separated-off filler.

The volume concentration of debonded particles or the fraction of the debonded filler, $\phi_o = \phi_x/\phi_f$ can be determined by measuring the Young's modulus of a filled elastomer before and after preloading that breaks adhesion contacts. When studying the filler separation in the model samples, it was noted that not all particles debond simultaneously, and that the number of debonded particles depends not only on the magnitude of the disturbing stress, but also on the time

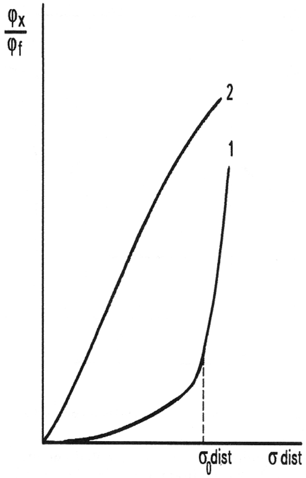

Figure 2.5. Typical form of the dependence of debonded filler concentration on average stress in sample. See text for explanation of both curves. [Adapted by permission from Y. Lipatov, V. Babich, and T. Todosijchuk, *J. Adhes.*, **35**, 187 (1991)]

of duration of the disturbing load, s. It was found that an increase of s results in a decrease of the E_x/E_f ratio, i.e., in a growth of ϕ_x.

Consequently, ϕ_x is a function of disturbing stress, $\sigma_{o\ dist}$. An analysis of the form of the function can be useful in calculating the strength of adhesion, σ_a. Possible dependences of ϕ_x and $\sigma_{o\ dist}$ are shown in Figure 2.5. Curve 1 characterizes the case of filler separation when a certain σ is reached, followed by catastrophic failure. A characteristic point of the curve is that corresponding to the $\sigma_{o\ dist}$ value at which a sharp increase in the separation rate occurs. Proceeding from the assumption that the entire sample's resistance force is concentrated solely at the cross-sectional area of all the filler particles in the sample cross-sectional plane, one can calculate σ_a from the formula:

$$\sigma_a = \sigma_{o\ dist} / 2\phi_f^{2/3} \qquad [2.82]$$

where $\sigma_{o\ dist}$ is the stress corresponding to the beginning of the catastrophic separation of the filler. The dependence shown by curve 2 is observed as well. One of the causes of such a behavior may be a nonuniformity of the stress-strain state of binder interlayer; as a result, the filler debonding occurs at locations where the

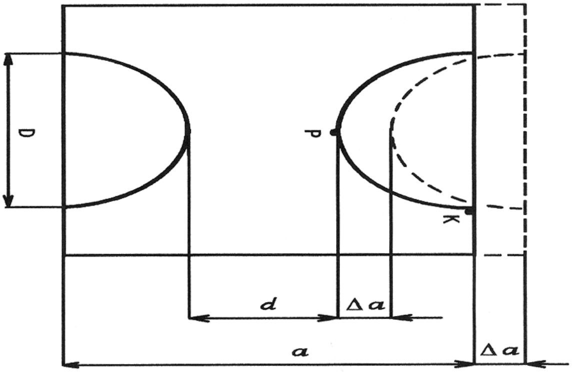

Figure 2.6. Elementary cell of filled polymer. [Adapted, by permission, from Y. Lipatov, V. Babich, and T.Todosijchuk, *J. Adhes*., **35**, 187 (1991).]

stress has reached the level of the adhesion or cohesion strength. With $\sigma_{o\ dist}$ increasing, more such sites are created and an increasing number of filler particles debond. To evaluate the adhesion strength of such a case, consider the simplest model of an elementary cell of a filled polymer, illustrated in Figure 2.6. The cell is a polymeric cube with an edge length, a. Filler particles of a spherical shape have a diameter, D. The shortest distance between particle surface is d. If such a cell is deformed, the absolute deformation is Δa; then the strain in polymer at point K is $\varepsilon = \Delta a/a$. The absolute deformation of the polymeric interlayer at point P is also Δa because filler is a high-modulus material and, therefore, it practically does not deform. The strain at point P is also $\varepsilon = \Delta a/a$, hence:

$$\varepsilon_p / \varepsilon_f = \Delta a / d; \quad \Delta a / a = a / d \qquad [2.83]$$

Since a > d, then, from Eq 2.83, the deformation, a, in sites where particles come closest to each other, and, consequently, the stress in the same sites in the binder interlayer, are appreciably greater than in material bulk. A purely geometric analysis shows that the volume concentration of the filler is $\phi_f = \pi D^3/6a^3$, and:

$$a = D\left(\frac{\pi}{6\phi_f}\right) \text{ and } d = a - D = D\left[\left(\frac{\pi}{6\phi_f}\right)^{1/3} - 1\right]$$ [2.84]

This allows the a/d ratio to be expressed in terms of the filler concentration, ϕ_f:

$$\frac{\varepsilon_p}{\varepsilon_x} = \frac{a}{d} = \left(\frac{\pi}{6\phi_f}\right)^{1/3}\left[\left(\frac{\pi}{6\phi_f}\right)^{1/3} - 1\right]^{-1}$$ [2.85]

i.e., the higher the ϕ_f, the greater the non-uniformity of the deformation. From Eq 2.84 it is pertinent that the $\varepsilon_p/\varepsilon_f$ ratio can reach an appreciable value at sufficiently high ϕ. This means that in some locations, the strain of the polymeric interlayers, and, consequently, the stress, is much greater than the average values even at low average stresses. The ratio $\varepsilon_p/\varepsilon_f$ may be presented as:

$$\frac{\varepsilon_p}{\varepsilon_f} = \frac{a + \Delta a}{d + \Delta a} = \frac{\beta(1 + \varepsilon_f)}{\beta(1 + \varepsilon_f) - 1}$$ [2.86]

where $\beta = (\pi/\phi_f)^{1/3}$. If the magnitude of stress in the most strained site of the interlayer is assumed proportional to the magnitude of the strain, then the following equation can be proposed to calculate the adhesion bonding strength, σ_a, for the case of a smooth increase of the concentration of the debonded filler (curve 2, Figure 2.5) :

$$\sigma_a = \sigma_{dist(i)}\frac{\varepsilon_\pi}{\varepsilon_{fi}} = \sigma_{dist(i)}\frac{\beta(1 + \varepsilon_{fi})}{\beta(1 + \varepsilon_{fi}) - 1}$$ [2.87]

where ε_{fi} are strains of the composite, corresponding to $\sigma_{dist(i)}$. Apart from an increase in the distance between particles, straining of samples also involves a decrease in the sample cross-sectional area. Due to this, the true stress can greatly exceed the average stress calculated for the initial cross-section of the sample. Moreover, a redistribution of stresses in the binder occurs when fractions of filler particles continue to debond. The kinetics of these processes complicates the calculation of the strength of the adhesion bonding of particles to the binder. Therefore, the magnitude of the disturbing stress at which the concentrations of debonded filler are identical, rather than adhesion bonding strength itself, can be compared in analyzing adhesion characteristics of different binder-filler systems. Again, using this approach we cannot determine with certainty if the debonding has an adhesive or cohesive character.

There are some other physical methods of estimating the beginning of the continuity loss in sample. These methods are based on the analysis of the dependence $\sigma = f(\varepsilon)$ and the data on volume changes during deformation, change in the Poisson ratio, damping of ultrasound waves, etc.[59,62,63] The common disadvantage of all these methods is that we do not know exactly the mechanism of failure of adhesion bonds (adhesion, cohesion, or mixed character). The non-simultaneous failure of adhesion bonds during deformation, analyzed in the previous case, is also a very important factor to be included in analysis by these methods.

Among the methods of special interest is the acoustic emission at fracture of adhesion contact, which can be used to estimate adhesion in rigid polymeric composites.[64-66] This method can be applied both to the fiber- and particulate-reinforced plastics. The acoustic emission manifests itself by the appearance of acoustic signals during material deformation. The dynamic local rearrangement in the material structure is the source of this emission. The data on acoustic emission enable one to characterize the process of crack formation and propagation, in particular, the failure of adhesion joints. We have used the method of acoustic emission[67] to evaluate the adhesion in rigid composites with particulate filler. During the deformation, the accumulation of elastic energy of deformation, due to the difference in the elastic properties of a filler and a matrix, occurs preferentially in the filler and in the interlayer of matrix near the filler, where the modulus of a matrix is higher compared with the modulus in bulk. This leads to the local non-homogeneities of main stresses and deformations and in the deformation work. The appearance of the microcracks is accompanied by the acoustic emission. The number of signals depends on the number of the signal sources (i.e., the number of filler particles) and the energy of each signal (the energy accumulated before formation of microcrack). This energy is proportional to the particles' volume and their size. In the case of a strong adhesion interaction between filler and matrix, the accumulated energy is substantially higher at low adhesion. The formation of microcracks during deformation is thus accompanied by a signal of high energy and amplitude. The count of signals allows the comparative estimation of adhesion. Recorded as the main parameters are the total count of acoustic emission signals, the count rate, the amplitude distribution of the signals and their frequency characteristics, as well as the dependence of these quantities on the stress applied to the sample and straining time. It was observed that increase in the adhesion bond strength results in raising the total acoustic emission over the whole filler concentration range. The effect of the filler dispersity on the above-listed parameters also can be ascertained. The maximum of the acoustic emission signal count rate can be used for the calculation of the adhesion contact strength. The results of amplitude distribution of signals gives the best possibility to characterize the energetic parameters of microcrack formation. A decrease in the filler-matrix adhesion results in a shift of the maximum of the amplitude distribution signals towards the lower amplitude values, which is an evidence that acoustic emission signal energy declines with decreasing strength of the adhesion contact. The dependencies of the acoustic emission total count on mechanical stresses are close to linear in a logarithmic coordinate system and are approximated by two straight-line segments. The load corresponding to the point of their intersection, corresponding to an abrupt change in the relative count rate, is the load corresponding to the maximum signal count rate, which characterizes the maximum of the break of adhesion contacts of the filler with the most probable size (i.e., it corresponds to the maximum of the filler particle size distribution curve). This makes a quantitative determination of the adhesion bond strength possible.

There are many non-destructive methods of adhesion strength evaluation.[68-77] These methods give indirect evaluation of adhesion interaction based on the change of the interphase layer properties. The analysis of propagation of ultrasound waves is one of the most widely used methods.[74] The application of the surface ultrasound waves was described for evaluation of adhesion.[75] The principle of the method is based on the observation that the surface waves formed in the support are transformed into the interfacial waves which provoke the shear stresses near the interface. Their magnitude strongly depends on the properties of the adhesion joint. These waves may be used to study very thin layers, whose thickness, d, is relative to the shear wave length, l, according to the relationship: 2 d/l <0.01. Usual longitudinal waves are not sensitive to the existence of a thin surface layer at the interface . The method may be also used to study the processes of adhesive curing.[75] Taking into account that the viscoelastic properties of an adhesive vary with the layer thickness, the multilayer model was proposed[75] which accounts for both adhesive layer and weak boundary layer, having varying density, shear modulus, m, and thickness, h. According to this model, the shear modulus of an adhesive, calculated from the measurements of the velocity of propagation of ultrasound waves, is an effective magnitude characterizing the effective viscoelastic properties of the multilayer adhesion system. If the contact between adhesive and substrate is poor, the velocity of propagation of an interfacial wave diminishes and the effective shear modulus is lower than the real modulus of adhesive. Their ratio may serve as a measure of the adhesion strength. The model proposed[75] also enables one to calculate properties of the interphase. The physical basis for the correlation between parameters of the interfacial wave and adhesion strength is the following: At any point of the wave propagation, its velocity and damping are determined by the properties of the adhesion joint and by the elastic properties of adhesive. The damping velocity is the result of the averaging of the velocities for two regions, one with a good adhesion and the second with a poor adhesion, where the velocity is lower. Correspondingly, the total velocity diminishes as compared with that of pure cured adhesive. The mechanical test of the adhesion joint is done in the direction perpendicular to the direction of wave propagation. Because the interphase regions of poor adhesion have a lower shear modulus, the critical stress of fracture is reached earlier, compared with pure adhesive. The transfer of stresses from one of the bonded surfaces to another is controlled by the effective shear modulus and therefore the correlation between the adhesion strength and the wave velocity exists.[75] This method, although very interesting, does not allow us, however, to characterize the real conditions of the fracture and gives only correlations similar to all non-destructive methods.

2.6 HOW THE ADHESION AT THE INTERFACE MAY BE ENHANCED?

The enhancement of adhesion at the interface of a polymer-solid is very important for PCM properties. It depends on two main factors: the state of the solid surface and possibility of modification of both the substrate and adhesive. The state of the surface determines its wetting and the probability of the formation of weak boundary layers, i.e., the appearance of defects serving as centers of fracture. The cleanliness of the surface is a very important factor and during production of PCM it is desirable to remove all impurities from the surface. It is especially important in reinforcing fibres which, treated with various substances, have decreased surface tension. The degree of roughness of the surface also plays an essential role, as well as chemical uniformity. In particulate fillers, it is well established[78] that some degree of microheterogeneity of the surface can be a positive factor of reinforcement, due to which the structural network is formed around the filler particles. From this point of view, some degree of non-uniformity of the surface also may be desirable. According to Kuleznev, to have the compositions with optimal properties it is desirable to reach some degree of non-uniformity of the surface, because it improves the mechanical properties of composites due to the changing conditions for stress redistribution during deformation.[79]

When considering polymeric fibres as reinforcing elements in PCM, the heterogeneity of the fiber structure may also improve the properties of composite, due to the difference in the surface tension of the fiber on its surface. The surface tension is increased, with fiber diameter diminishing and with an increase in the spinning speed, which is related to the degree of orientation on the surface layers of the fiber. The mutual influence of the binder and organic fiber leads to the change in the structure of fiber and in its orientation degree.[36] In the surface layers of a fiber some processes proceed leading to the formation of an intermediate layer. As a result, there is no sharp phase border between the reinforcing fiber and binder, and in some cases it results in improved adhesion (diffusion mechanism of adhesion; see above).

Another solution can be derived from the modification of the filler surface using physical and chemical methods. The purpose of such a modification is to improve the adhesion between filler and binder. The surface modifiers have various functions. First of all, they should change the adhesive interaction between two components, i.e., create a good contact between adhesive and adherent. If the wetting is not complete, some voids and microvoids may arise at the interface, leading to the formation of weak layers. A review of the methods of surface modification of fillers is available elsewhere.[80] Physical methods of modification are based on the adsorption of some substances at the interface, which enhance the interaction between components of PCM. Chemical methods have as their main aim the creation of new chemical groups at the interface, increasing adhesion or forming chemical bonding between filler and binder. The surface modification is also very important for elimination of agglomerates of filler particles in viscous polymeric media to create better conditions for interaction between the surface and the polymer. In many cases, the agglomeration of filler particles prevents the realization of the filler activity.

The essence of chemical modification consists of surface treatment with the substances capable of chemical interaction with the reactive chemical groups on the filler surface. Such methods of coupling are described in many works.[6,81-84] The surface treatment allows one to change both the chemical nature of the surface and its ability to wet. Organosilanes are the most widely-used substances for these purposes. They are capable of chemical interaction with hydroxyl groups at the glass fiber surface and with other functional groups. Various functional groups (vinyl, acrylic, epoxy, amino-, imino etc) are available in the coupling agents which allow them to form chemical bonding with filler surface and surrounding binder. As a result, the chemical interaction between coupling agent and a binder proceeds and binder becomes chemically bound to the filler surface. The coupling agent forms, in this case, an intermediate layer between the surface and a binder; this layer plays also a role of a damper and decreases the stress at the interface. The chemical bonds which appear between the filler surface and a binder change the conditions of the formation of the cured binder structure.[85,86]

Coupling agents also improve wetting of the surface by a liquid binder, which contributes to improved adhesion.[87] There are many methods of surface modification by coupling agents.[89-91] However, the question remains open regarding the mechanism of the action of coupling agents. The question is: whether functional groups of coupling agents bound to the surface are able to improve adhesion, and how? It was found[92,93] that coupling agents containing vinyl groups can react with a corresponding binder, but the degree of such reaction in the surface layers at the interface was so low that this reaction could have played any role in adhesion enhancement. Adequate conditions should be chosen for such reaction to realize the full potential of adhesion improvement due to the formation of the chemical bond. According to Wake,[6] the contribution of chemical bonding in adhesion is limited. For example, if on the surface there exists a chemical bond between coupling agent and a binder, during failure of the adhesion bond, the destruction of C-C or Si-C bond should occur. In both cases, the energy of the bond is close to 240 kJ/mol, which corresponds to the surface energy of the order 1.4 J/m. However, the adhesion work does not exceed 0.15 J/m. This discrepancy is explained by the fact that, in reality, only a small number of vinyl groups of the coupling agent are chemically bound to the surface. At a low number of chemical bonds for the surfaces with critical surface tension γ_c=25.10 N/m, the work of adhesion should be approximately 0.1 J/m. From these data, it may be shown that the maximum number of vinyl groups reacting with the binder is about 3%. Wong[94] makes a conclusion that chemical bonds cannot play a determining role in the properties of glass-reinforced plastics. It is evident that the possible chemical interaction between the coupling agent and a binder depends strongly on the surface concentration of functional groups of coupling agent and on changes in their reaction ability on the surface, which is not the same as in bulk. However, the coupling agents cannot be considered only as substance enhancing the chemical interaction. In some cases, a coupling agent is able to improve the compatibility of filler and binder.[95] The chemical theory allows one to explain many effects of improving properties of PCM when coupling agents are used.[96-99] In the use of coupling agents, two factors should be taken into account: the chemical bonding of the coupling agent with the surface and formation of monomolecular layer of the same agent chemically not bound with the surface. The latter changes the wetting and mechanical properties. With increasing amount of chemisorbed coupling agent, the mechanical properties may become worse.

Some other effects are also responsible for improving properties when applying coupling agents.[100-103] It is proposed that at the interface, the interpenetration of molecules of coupling agent and molecules of binder proceeds, leading to their mixing on molecular level. This effect is equivalent to the formation of an interpenetrating polymer network (see Chapter 6). There are two possible effects: penetration of the matrix molecules into the chemisorbed layer of silane and migration of physically sorbed silane into the matrix. In this case, in the silane phase, the copolymerization with binder does not take place.[102] An interpenetration of this kind, together with chemical bonding, may be an important factor in enhancing an adhesion bond. However, the question regarding the mutual solubility or compatibility of silane and polymer binder is unanswered and needs additional verification.[103]

A new approach to the problem is in the search for conditions in which the improvement of adhesion can be reached when an interpenetrating polymer network is created in the surface layer of the organic reinforcing fibre.[104] If the fiber is capable of swelling in the oligomeric composition which serves as a binder, oligomeric molecules diffusion into the surface layer of a fiber may lead to the formation of the semi-interpenetrating network during curing.

It is worth noting that coupling agents may be applied not only to reinforcing fibres but also to particulate fillers. Here the most efficient are organo-titanium coupling agents.[82] Their general formula is $(RO)_nTi(OX\text{-}R\text{ -}Y)_{4\text{-}n}$, where RO is the group capable of hydrolysis, Y is organic functional group reacting with the binder (acrylic, methacrylic, epoxy etc), and OX is the group giving some additional properties (increasing compatibility, heat resistance, plasticization, etc.). In many cases, the polymeric coupling agents can also be used (phenolic resins, copolymers of vinyl acetate and vinyl butyral, poly (vinyl acetate) latex, etc.). The mechanism of action of polymeric agents may be explained in the following way: these agents, which are, as a rule, elastomers, decrease the inner stress arising in the course of the binder curing and form an elastic interlayer between the surface and cured binder.[105] The inner stress relaxation leads to improvement of the adhesion strength. The data available allow the conclusion that at the polymer-solid interface, when the surface is modified, both chemical and physical bonds may be formed. However, their role in the improvement of the PCM properties seems not to be well established. It is possible to think that to attain the reinforcement, some strong bonds must be formed at the interface. These bonds may be chemical or physical. The nature of these bonds perhaps plays no important role. The problem is not in the nature of these bonds but in their number and strength which give the best properties. When the number of bonds is high, the molecular mobility in the surface layer is strongly diminished, inner stresses arise, and the conditions favorable for the formation of a weak boundary layer appear. However, up to now, the strength of the bonds at the interface is not analyzed in current theories of reinforcement.

There is also another possibility to create the chemical bond between filler and polymeric binder, the grafting of polymeric molecules to the solid surface. For the first time, the possibility of grafting on solid surfaces has been shown.[107] Later it was demonstrated[108-110] that the mechanical dispersion of a solid in the presence of monomers may lead to the graft polymerization. The reason for this reaction is the formation of a juvenile surface on which, due to its high surface energy, the reaction-able atoms are present. As a result, such a surface enhances its ability to chemisorption, i.e., to the formation of chemical bond between the surface and molecules adsorbed. If some monomers are present in the system, one can expect direct interaction between some sites of unsaturated surface with active centers of ionic or radical type and molecules of organic monomer. As a result, the reaction of polymerization may proceed. Such methods cannot be applied to fiber reinforcing agents, for example, to glass fibres. However, on the surface of a glass fiber, compounds may be formed which serve as a center of grafting. These centers may be created due to a high activity of hydroxyl groups on the glass surface. In such a way, the same principle is used as in coupling agents. However, in this case, the surface treatment serves as a means to create the centers of grafting. Such centers may be formed if the glass surface is treated with hydrogen peroxide which is the initiator of radical polymerization.[111] The radical polymerization and grafting are possible on such surfaces. The chemical activity of the glass surface allows us to treat it with the catalysts of polymerization, such as chlorides of metals of transient valency ($TiCl_4$, $SnCl_4$, BF_3).[112-114] These compounds are active catalysts of cationic polymerization and are able to form complexes with active centers on the glass surface. These complexes are the centers of grafting. Using such an approach, polystyrene, epoxy resin and poly-dimethacrylate-bis-(triethylene glycol phthalate) were grafted on the glass surface. The processes of graft polymerization may be of special importance for organic reinforcing fibres. The peculiarity of these fibres is that the grafting is accompanied by a change in the fiber structure dependent on the initial structure of fibre.[115,116] Grafting on the surface of carbon fiber is of special interest.[117-122] The analysis of data on polymer grafting on the surface of organic, glass, and carbon fibres allows a general conclusion to be drawn. In all cases, the grafting proceeds non-uniformly on the fiber surface, i.e., only some part of the surface contains rather high amounts of grafted polymer. It is also evident that only a small part of a polymer is directly bound to the surface, whereas the rest is connected with the grafted molecules, due to strong cluster formation. Therefore, the surface of a fiber is covered by a non-uniform, cluster-like regions alternating with regions covered only by a thin grafted layer. As a result, the properties of grafted fibres depend on the ratio between grafted and non-grafted chains. The thickness of the grafted layer depends on the energetic non-uniformity of the fiber surface. Due to this non-uniformity on the surface there are regions of various activity which determine the alternation of grafted regions. It is worth noting that grafting of organic and inorganic fibres, resulting in some cases in their strengthening, takes place, due to the structural rearrangements and healing surface defects by grafted polymer.

To improve adhesion of binders to fibres, including carbon fibers, methods of surface treatment by cold plasma were developed.[123-127] In the course of such treatment, the removal of a weak border layer of the fiber proceeds and the contact between the surface and a binder is improved. At the same time, the number of active centers capable of chemical interaction with a binder increases and the wetting becomes better. It may be expected that polymerization under plasma action may also serve as a tool adhesion improvement at the phase border. In spite of the existence of many ways of surface treatment of the reinforcement surface, no model of interaction was proposed which is effective in predicting the type of reinforcement by surface treatment of a given filler-matrix combination. According to Drzal,[83] the major reason for this lack of theoretical developments is in the over-simplification of the composition and nature of the filler-matrix interface.

Up to this point, we have only considered ways to improve adhesion by filler treatment. However, from the thermodynamic consideration, presented in this chapter, it follows that improving adhesion also may be reached by modification of a matrix, in particular, by increasing its cohesion strength. There are some colloid-chemical ways which should be taken into account as part of the solution. We have already mentioned that adsorption interaction of a polymer with a solid leads to the redistribution of molecules according to their molecular mass and surface tension. It is important both for polydisperse polymers and multicomponent binders. Two ways of adhesion improvement can be envisioned, based on the above-mentioned concept of increasing the cohesion energy. The first method consists of the introduction into the matrix of a second filler having an affinity to the matrix component and which differs in affinity to the main reinforcing agent. In such a system, there are two kinds of surfaces and two kinds of surface layers.[128,129] The existence of two surfaces with different surface energies leads to the redistribution of the matrix component between two surfaces.[130] Due to the selective adsorption of fractions or components, the matrix in the surface layer of main reinforcement (fiber) may have different cohesion energy, as compared with bulk.

The strengthening of a matrix is also possible by introducing another polymer in a small amount. In this case, the low molecular weight fraction will be concentrated at the interface with added polymer, the bulk will consist of a fraction of higher molecular mass and higher cohesion energy.[128] In accordance with thermodynamics, this should lead to an increase in the work of adhesion. The application of mixtures of two incompatible polymers as a matrix[131] has its advantage in the formation of an excess free volume, facilitating the relaxation of inner stresses.

New possibilities are given by the use of interpenetrating polymeric networks.[132] The curing of each constituent of the network proceeds at a different rate. If the curing of one of the networks is much faster compared with the other, a system is formed where the cured network determines the initial strength of the adhesion joint, whereas the second, non-cured network plays a role of plasticizer, decreasing the inner stresses. In the second stage of curing, a second network is formed where, due to the low rate, inner stresses are virtually absent. As a result, such IPN has higher adhesion to the reinforcement as compared with individual networks. It was also shown in this case that at a definite ratio between two networks, their tensile strength has a maximum. In such a way the increasing cohesion strength is also achieved, which is one of the conditions of increasing adhesion strength.

Finally, to improve adhesion, some reactive surfactants can be used. It is known that improvement of wetting leads to an increase in adhesion. The use of surfactants is one of the ways of improving adhesion.[133] However, introducing surfactants into the adhesive increases the adhesion only in a very narrow concentration interval, beyond which polymolecular layers of surfactant are formed on the surface. These layers have a very low cohesion strength (weak layers), and as a result, the adhesion may decrease. The problem may be solved on the basis of the following concept.[134] The adhesive may include a surfactant that would act as an agent improving wetting and spreading only in the initial stages of formation of the adhesive joint. Subsequently, the surfactants should lose their properties, following a chemical reaction with the adhesive, and participate in the formation of a cross-linked polymer. For this reason, the initially-formed adsorption layer of the surfactant becomes part of the cured adhesive.

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3

SURFACE LAYERS OF POLYMERS AT THE INTERFACE WITH SOLIDS

3.1 DEFINITIONS

The structure and properties of surface (boundary, interfacial) layers at the interface with a solid are important factors determining the properties of PCM. Thin surface layers of any condensed phase, whose thickness does not exceed the correlation radius of structural long-range interactions, have a different structure and different physical properties than the matter inside the phase. They can be considered as transitional or interfacial layers. It is known that every liquid or solid has a characteristic transition layer. A boundary or surface layer of solid matter can be considered as a layer whose properties vary under the action of the surface force field, and they differ from the properties in bulk.

The boundary or surface layers possess an effective thickness, beyond which the deviation of local properties from their bulk values become negligible.[1] The introduction of such a concept is possible due to a small radius of effective action of intermolecular forces, which causes a rapid decrease in the influence of one of the phases on any property of a neighboring phase. At the same time, in polymeric systems, the experimentally found thickness of the surface layer may be rather high due to the chain structure of polymer molecules which determines the specifics of behavior of polymers, compared with low molecular mass substances.

The surface layers are not uniform in their structure and properties. One may distinguish the adsorption layer, namely, the layer in which macromolecules are in direct contact with the surface (see Chapter 1). All segments directly bound to the surface, and segments forming loops and tails, belong to the adsorption layer. However, the distance from the surface, at which the surface layers exist, is much higher compared to the thickness of an adsorption layer.[2] The surface layers have a rather complicated structure with properties depending on the distance from the interface. The function, connecting the properties of a polymer in surface layers, is generally determined by three variables: surface energy of solid, surface energy of polymer, and chain flexibility.

It is worth noting that the surface layer has no definite border with bulk polymer and its thickness is not a constant value. The thickness depends on the properties under consideration and may change within predetermined limits. Any given property can be determined by the behavior of chain segments treated as independent kinetic units, macromolecular coils, macromolecular aggregates, etc. Therefore, the thickness of the surface layer should be defined as an effective or apparent value. The peculiarities of the structure and properties of surface layers are the subject of discussion in this chapter.

Recently, Sharpe[3,4] noted a fundamental difference between two definitions: interface and interphase. He asked the question: *what plays the major role in determining ultimate properties of an adhesion joint and its behavior? Is it interface?* Evidently, it is not, because a two-dimensional array of atoms or molecules, such as an interface, is impossible to measure, whereas interphase has a sufficiently large assembly of atoms or molecules to have a modulus, strength, etc. According to Sharpe,[4] interphase is *"a region intermediate to two (usually solid) phases in contact, the composition and/or structure and/or properties of which may be variable across the region and which also may differ from the composition and/or structure and/or properties of either of the two contacting phases."*

Using the same concepts,[2] Theocaris[5] introduced the term "mesophase" to describe the surface layer of polymer at the interface with a filler. According to Theocaris, mesophase is a region covering the filler particles or the fiber surface, which may be considered as isotropic and homogeneous with a finite thickness. Its existence is determined only by defects of poor adhesion bonds, by the presence of cracks, stresses, etc. For a "perfect" adhesion, the mesophase disappears. This point of view can hardly be accepted because it neglects the physical essence of the processes at the interface and contradicts the experimental verifications of the surface layer concept.

In prevalent cases, the conditions of formation of the surface layers, in filled polymers, coatings, etc., do not allow the possibility of isolating these layers and determining their characteristics separately. Many conclusions have been drawn on the basis of those changes which surface layers contribute to the properties of a filled polymer if compared with the unfilled polymer. It is also worth noting that the properties of the surface layers of polymers depend on the nature of the interface. Two kinds of surface layers should be distinguished:

- layers at the interface with a solid
- layers at the interface with air.

The properties of the latter differ from the properties in bulk, due to the difference in the energetic state of macromolecules in the bulk and at the interface, and due to conformational restrictions imposed on macromolecules by the polymer-air interface which acts as a limiting or reflecting barrier.[6] In the surface layer, the polymer molecules cannot take the same number of conformations as in the bulk. Therefore, an equilibrium state will be attained, either due to the interaction with adjacent chains or as a result of the redistribution in the surface layer of different conformers and their transformation into a more stable state. In the latter case, conformational stabilization is achieved as a result of an energy gain. As a rule, the state of a chain in the surface layer is less statistically probable, and the entropy of the chains is lower. Some properties of the surface layers of polymers at the polymer-air interface are described elsewhere.[7]

Heterogeneous polymeric compositions include most commercially important materials. All these systems are two-phase systems in which heterogeneity is inherent in the very principle of production of these materials. Polymeric blends and alloys are noted for a two-phase structure (see Chapter 6) in which both phases are continuous, and for this reason it is impossible to determine which phase is the dispersion medium and which the dispersed phase (of course, this depends on the ratio of components). In contrast to blends, polymers, filled with polymeric fillers (including fibers), comprise systems which are characterized by a specific nature of distribution of one component in the other. Despite such demarcation, the physico-chemical properties of the latter two types of systems are similar. In considering the properties of heterogeneous systems, they can be divided into two main groups:

- in which the dispersed phase inclusions (fibers, particulate fillers, etc.) are virtually incompressible as compared with the bulk
- in which both components possess approximately the same compressibility.

These two types of systems also differ in the structure of the transition region between the two phases. As already mentioned, the first type, due to the adsorption interaction of the polymer with the solid surface, is characterized by the appearance of a surface layer of varying thickness whose properties differ from the properties in bulk.[2]

The second system is characterized by the appearance of a transition region in which the structure and properties of both phases undergo changes because of the interaction of the components; the latter changes depend on miscibility of a given polymer pair. The difference in the structure of the two types can be schematically presented, as in Figure 3.1. In both cases, the interaction of polymeric molecules with a solid surface (including polymeric one) should lead to the redistribution of intermolecular bonds in the surface or transition layer and to the formation of additional physical junction points in physical network of any polymer with the surface.

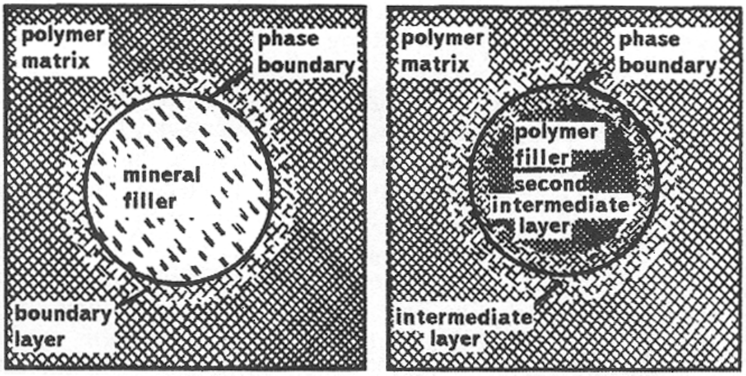

Figure 3.1. The scheme of two types of filled systems. [Adapted by permission from Y. S. Lipatov, *Adv. Polym. Sci.*, **22**, 2 (1977)]

It is also worth noting that for the surfaces of both high and low surface energy, the main contribution in changing properties of surface layers belongs to the conformational restrictions, not to the energetic interaction of macromolecules with a solid. If it were not so, we could not observe effects of changing properties at distances rather remote from the surface, as only a very small part of the macromolecules in the surface layer has direct contact with the surface.

In order to explain the long-range surface effect, one should naturally assume that the influence of the surface on molecules that interact directly with it, owing to intermolecular forces and formation of these or other supermolecular structures, extends to neighboring molecules that are not in contact with the solid surface directly. This point of view is supported by the data on aggregative adsorption (see Chapters 1 and 2). The fact that the long-range interactions stem from the influence of intermolecular contacts is confirmed by the fact that the long-range effect is greater, the higher the energy of cohesion of polymer being considered, i.e., the stronger are the intermolecular interactions.

The surface influence is explained by the theory of adsorption and the structure of the polymer adsorption layer. However, one should not think that this factor is prevailing, as the thickness of the adsorption layer is low compared with the thickness of the surface layer, as it will be shown below.

3.2 CONFORMATIONS OF MACROMOLECULES AT THE POLYMER-SOLID INTERFACE

The conformational characteristics of macromolecules at the polymer-solid interface are one of the main factors determining not only the structure and properties of the surface layer, but the structure and properties of a filled polymer as a whole. Theoretical concepts, which can explain chain conformations in the surface layers, are based on adsorption theories. At the same time, it is evident that conclusions of the adsorption theory have more theoretical meaning because the real conditions of production of filled polymers are very far from those in which adsorption layers are formed. The main concept describing the conformational properties at the interface is as follows. The surface of a solid serves as a protecting barrier that does not allow macromolecules to take the same number of conformations as in the bulk. Limitations of molecular mobility in the surface layers due to conformational restrictions are connected with an entropy factor, i.e., with the depletion of the conformational set of macromolecules near the interface. This permits a satisfactory explanation of a poor dependence of the effects of a chemical nature and the rigidity of chains on surface mobility. In fact, the conformational set of macromolecules, already limited in its initial state, cannot vary as strongly near the interface as in flexible polymer. As a result, the effects for rigid-chain polymers will be less pronounced.

The main statements of the theory of polymer adsorption may be used for the analysis of conformations of macromolecules in filled polymers.[8] For this case, a very simplified model of a filled polymer was used, according to which the density of a polymer between filler particles does not change. It was assumed that conformations of chains do not change, due to the interaction with a solid, and that the conformational states depend only on the entropy effects. For such a system, some general conclusions, based on the theoretical calculations, can be reached concerning the conformations in a filled system. It was established that in the border layer of a thickness $\delta \approx 2R_g$ (R_g is the radius of inertion of gaussian coil), the coils are flattened and have anisotropy, which is determined by the existence of an interface. The number of contacts of chains with a flat surface of a filler depends on the distance from the surface. The average length of the chain segments bound to the surface does not depend on the number of links in the chain and is of the order of several links, whereas more than half of the links are situated at a distance from the surface. The thickness of the border layer is comparable with the chain dimensions in the bulk (or in Θ-solvent) and growth proportional to $M^{0.5}$, being for flexible chains of the order of hundreds of Å.

According to the developed approach, the main contribution to the change of the structure of the layer is made by the conformational restrictions. Such a conclusion has already been reached earlier on the basis of experimental data[2,7] and is of interest as one of the first attempts to describe the effect from the theoretical point of view.

To describe the microscopic structure and thermodynamic properties of a polymer near the interface with a solid lattice, a theory was developed[9] based on the theory of solutions. However, as distinct from a solution, the system analyzed consists of a great number of chains. It is assumed that in the surface layer, various orientations of chain links are realized, which deviates from the isotropic one only in a very narrow region near the interface (approximately 6 lattice lines or 25 Å). In such conditions, the shape of polymeric chains near the interface becomes flat, whereas at a definite distance the chain has its unperturbed dimension. In properties of the polymer near the interface, the detail of molecular structure of a polymer plays a critical role in determining the conformations. Effects connected with entropy loss due to the reflecting barrier and those determined by the energy of interaction at the interface should be taken into account, and especially effects connected with the difference in the interactions between segments of various chains and between segments and the surface.

Theoretical analysis in the framework of the mean field theory[9] allows the conclusion to be drawn that the idea, according to which the density in the surface layer sharply changes, is over simplified. The density profile is sensitive to the chemical nature as much as the structural peculiarities near the interface. Immediately at the interface, the structure is determined by the interaction of segments with the surface atoms, all effects being strongly dependent on chain flexibility. Thus the theoretical calculations based on the general principles of conformational statistics of polymers meet the experimental data very well (which we believe the author forgot to mention) concerning the structure and properties of surface layers, which will be discussed below.

However, the problem of chain conformations in the filled polymers may be analyzed more simply, based on the principles of thermodynamics, without any simplifying assumptions about the structure of the surface layer. The approach is the following.[10] The heat of dissolutions of filled and unfilled polymers may be easily determined. The heat of the interaction of filled polymer with the solvent, ΔH_{13}, may be determined from the relationship:

$$\Delta H_s = \Delta H_{13}(1-\varphi) + \Delta H_{23}\varphi \qquad [3.1]$$

where ΔH_{23} is the heat of wetting of a filler with a solvent, φ is the volume fraction of a filler, and ΔH_s is the integral heat of interaction. Value ΔH_{13} consists of two terms:

$$\Delta H_{13} = \Delta H_q + \Delta H_p \qquad [3.2]$$

where $\Delta H_q = -\Delta C_p(T_g - 303)$ is excess in relation to the equilibrium melt enthalpy of glassy polymer, ΔC_p is the difference of heat capacities of a polymer in a melt and a glassy state,

$$\Delta H_p = \Delta H_r + \Delta H_v + \Delta H_c \qquad [3.3]$$

is the heat of interaction of an equilibrium melt with a solvent, ΔH_r is the heat of mixing for a regular solution, ΔH_v is contribution of the volume change by mixing,

$$\Delta H_c = [4\Delta\varepsilon\sigma^{2/3}(\sigma^2 + 1)]\left[\frac{(1-\alpha^2)}{(1+\alpha^2\sigma^2)}\right] \qquad [3.4]$$

is the configurational contribution which is determined by the expansion or compression of the coil during its transition from the state in a bulk into solution, α is the expansion coefficient, given by $\langle \overline{h}^2 \rangle^{1/2} / \langle \overline{h}_\theta^2 \rangle^{1/2}$, $\sigma = \langle \overline{h}_\theta^2 \rangle^{1/2} / \langle \overline{h}_o^2 \rangle^{1/2}$ is the parameter of thermodynamic flexibility, $\langle \overline{h}_\theta^2 \rangle^{1/2}$, $\langle \overline{h}^2 \rangle^{1/2}$, and $\langle \overline{h}_o^2 \rangle^{1/2}$ are mean-square distances between the chain-ends in ideal, non-ideal solvent, and for the model of the freely-joined chain, Δε is the difference in energy between two rotational isomers.

Using these equations, polystyrene, PS, filled with fumed silica was studied. It was found that calculated values $\Delta H_p < 0$, and they decrease with increasing amount of filler until they reach some constant value, $\Delta H'_p$. It means that the heat of interaction between polymer and a filler, $\Delta H_{12} = \Delta H_p - \Delta H'_p$ found experimentally, reaches its limiting value, which corresponds to the saturation of interactions at the interface due to realization of a maximum number of contacts of chain segments with active centers, N*, of the surface. The number of contacts may be calculated as:

$$N^* = \frac{\Delta H_{12}}{S\Delta H^*} \qquad [3.5]$$

where $S = S_0\varphi$ is the surface available for interaction, S_0 is the specific surface of the filler, ΔH^* is the energy of a single contact. Calculations have shown that the fraction of PS segments interacting with the surface is about 15-20% of the total number of segments. Therefore, the majority of segments is present in the surface layer as loops. It is easy to establish that the thickness of the surface layer (i.e., the height of the loops), $\delta \approx \langle R_g \rangle$, is of an order of radius inertion of an unperturbed chain. The value may be considered for a filled system as a half-thickness of the interlayer between two filler particles (at saturation), $\delta = \langle L \rangle / 2$. Calculation of α shows that macromolecules in the surface layer have more extended conformation, compared with the bulk, which may be the result of realization of the maximum possible number of polymer-filler contacts. This effect should depend on the chain flexibility, which determines the possibility of changing conformations in the surface layer. Such a simple experimental approach allows one to make some qualitative conclusions concerning the conformation of chains at the interface.

More detailed information may be gained from application of the method of the attenuated total inner reflection in IR-region (ATR). It is known that for attenuated total inner reflection, the depth of penetration of radiation, ΔP, into the sample depends on the indices of refraction of element and sample, n_1 and n_2, and on the wavelength of radiation, λ, and angle of incidence, θ:

$$dP = \frac{\lambda}{2\pi n_1 \left[\sin^2\theta - \left(\frac{n_2}{n_1} \right)^2 \right]^{1/2}} \qquad [3.6]$$

In such a way, changing the angle of incidence, θ, and λ at constant n_1 and n_2 it becomes possible to investigate the polymer structure at various distances from the surface.

For thin layers of PMMA on the surface of crystal KRS-5, it was established that at changing depths of radiation penetration, the spectra vary in regard to the intensity of some bands. Complex changes in spectra and the intensity of conformation-sensitive bands are observed at the distances of 1.5-2 μm from the surface. The analysis of spectral data allows us to understand that in the surface layer a narrowing of conformational set of macromolecules takes place and a more regular arrangement of some chain fragments arises. The solid surface stabilizes a more stable conformation of the ester group of PMMA, which leads to the densening of a polymer and to the redistribution of conformations in such a way that in the surface layer, the concentration of more stable conformers increases. For polymers capable of crystallization, the isomeric composition of macromolecules in the surface layers also changes.[12,13] The structure of surface layers of polypropylene was studied using this method.[14] It was found that the structure of a layer is heterogeneous. At the surface, macromolecules are in a conformationally-regular state, whereas at some distance from the surface the structure is more irregular. Application of the ATR method has shown[14] that the degree of the conformational ordering in amorphous regions near the surface increases. The perfection of packing of macromolecules is higher, the closer the layer is to the surface.

The degree of the order of macromolecules in the surface layers depends on the nature of the polymer. For polymers capable of crystallization, the range of changes is broader compared with amorphous polymers, and the degree of perfection of packing is higher. The latter may be explained by the formation of one-dimensional or two-dimensional isomorphic structures. All peculiarities of the conformational state of macromolecules in the surface layer depend on the conditions of the layer formation. Therefore, by changing these conditions, one can vary the degree of conformational ordering of macromolecules in amorphous regions. The phenomenon of epitaxy is of special interest, i.e., the oriented growth of crystalline structures on the surface of crystalline substrate. The surface having a regular structure may induce the orientation. In this case, the surface directly influences conformational changes and the ordering. The investigation of the epitaxial crystallization of some polyurethanes[14-18] has shown that changes in the structure of a polymer are observed in layers up to 4 μm and have their essential representation in IR-spectra, due to conformational restrictions. As distinct from the free films of the same polymers, for epitaxial films the half-width of the adsorption bands in IR-spectra depends on the film thickness. It was also established that during epitaxial crystallization in surface layers changes take place in the orientation of macromolecules in relation to the plane of a solid, macromolecules being oriented preferentially, perpendicular to the surface.

Table 3.1: Cohesion energy density and flexibility

Polymer	E, J/cm	σ
PMMA	556.4	2.14
PS	305.0	2.22
PDMS	322.6	1.47

3.3 MOLECULAR PACKING IN SURFACE LAYERS

When a filler is incorporated into a polymer, the conditions of molecular packing worsen and packing density diminishes because of conformational restrictions described above. The polymer transforms to a less stable state, from a thermodynamic point of view. It seems proven that the loose packing is the result of the retardation of relaxation processes during the formation of a filled polymer. The retardation depends on the nature of solid and polymer. The main factors determining the retardation of the relaxation processes are the energy of interaction between a filler and a polymer (adhesion energy), cohesion energy of a polymer (intermolecular interactions in the polymer matrix), and the flexibility of polymeric chains. The statement validity was experimentally evaluated[19,20] for three polymers having different chemical structure - PS, PMMA and poly(dimethyl siloxane) (PDMS). Two of these polymers (PS and PMMA) have almost equal values of the parameter of the thermodynamic flexibility, σ. At the same time, polymers have various cohesion energy densities, E_c. The other selection - PS and PDMS - have almost the same cohesion energy density but different flexibility, as follows from data in Table 1.

Such choice of polymers gives a possibility to establish contributions to the changing density packing in the surface layer at the expense of chain flexibility and the chemical nature of a polymer, i.e., the presence of some functional groups capable of interaction with the surface. The density of packing was investigated by the method of molecular probe.[19,20] Figure 3.2 presents the data on the dependence of the density of a polymer in the layer ρ_s and in the bulk ρ_p on the distance from the surface. The density ratio was calculated from the experimental data based on the spectral shift of probe molecules, whereas the distance

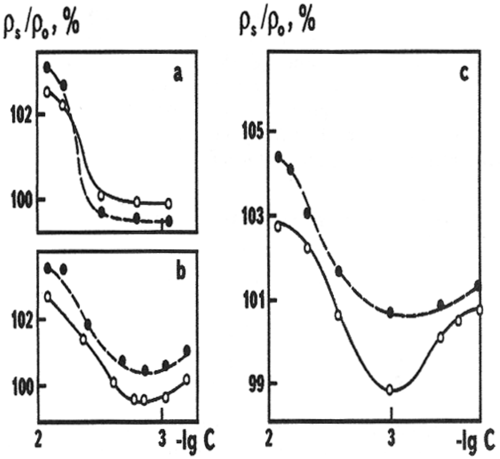

Figure 3.2. Changes in the packing density in surface layers with distance from the surface: PDMS (a), PS (b), PMMA (c). Dotted lines - layers on poly(tetra-fluoroethylene), solid lines - on quartz. [Adapted by permission from Y. Lipatov, E. Moisya, and G. Semenovich, *Polymer*, **16**, 582 (1975)]

from the surface was estimated from the concentration of probe molecules, which according to the theory is proportional to the layer thickness or to the distance from the surface.

Two surfaces have been taken as supports: quartz (high surface energy) and poly(tetra-flouroethylene) (Teflon^{TM}) (low surface energy). It is seen that for all polymers there is some increase observed in the packing density in layers adjacent to the surface, independent of its surface energy. This effect may be attributed to the orienting action of the surface. The increase in density in this layer is of the order of 3-5% for all polymers. The difference in the surface influence on the packing density for supports of high and low surface energy is the greatest for PMMA having higher E_c and σ and is very low for PDMS. From the comparison of these data, it is seen that the difference in value E_c and σ determines the character of macromolecular packing. The density ratio, the layer thickness, and the degree of the influence of the surface energy of support are functions of these two parameters.

It was found that the structural rearrangements in the surface layer for films formed at the Teflon surfaces is restricted by the formation of a more dense layer near the interface. The thickness of this layer for PDMS is 2-3, for PS and

PMMA, 3-4 μm. For more flexible PDMS on both surfaces, the orienting influence of the surface diminishes at thicknesses larger than 2-3 μm, and density of packing becomes equal to that for the polymer in bulk. On the contrary, for PS and PMMA, the structure of a layer on a substrate with high surface energy is rather complex. The regions of high density near the interface are replaced by the region with the same density as in bulk (transition layers), followed by the region where the packing density is lower compared with bulk (loose packing). The total thickness of the surface layers on the support of high surface energy, where the changes in density are observed, is 30 μm for PS and 60 μm for PMMA. These data show that under the influence of a solid, surface layers are formed having a complex structure and a definite density profile. The character of this profile depends on the three parameters: chain flexibility, cohesion energy of a polymer, and surface energy of a support. However, in all cases the layer nearest to the surface has higher density, compared with bulk.

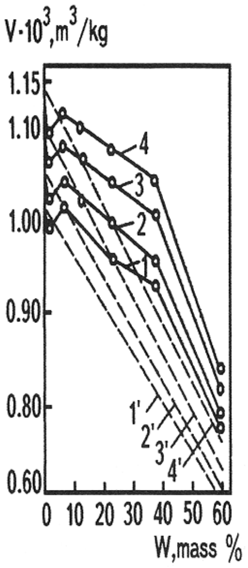

Figure 3.3. Dependence of specific volume, v, of filled PS on the filler amount, W, at various temperatures (K): 1-297, 2-365, 3-425, 4-471. 1'-4'- corresponding additive dependencies.

The non-homogeneous structure of the surface layers follows also from the data on the dependence of the specific volume of the system on the filler concentration.[21,22] Figure 3.3 shows such dependence for a PS-glass powder system. It is seen that specific volume, v, for highly loaded samples exceeds the additivity rule. This effect cannot be the result of the formation of voids in loose-packed aggregates of filler particles which are not available for polymer molecules. The extrapolation of the linear part of the dependence of v on volume fraction of filler, φ to $\varphi = 1$ gives the value of $v = 0.420 \times 10^{-3}$ kg/m, which coincides with the specific volume of a glass. Thus the character of the changes of v in dependence on the filler concentration confirms the transition of PS into the state of a loose-packed surface layer. In the region, $\varphi > 0.3$ all polymer may be considered as being in the state of a surface layer. The value of φ corresponds to the effective thickness of the interlayer between two filler particles, which is about 1.5×10^{-6} m.

It may be postulated that the change of the structure in filled polymers (change in the packing density) is connected with formation of disjoining pressure in the interlayers of a polymer between filler particles. According to definition,[23] the disjoining pressure, P_d, is an excess of a phase pressure in the thin liquid film near the interface, P_{ph}, in relation to the pressure in the bulk, P_0, i.e., $P_d = P_{ph} - P_0$. Disjoining pressure is a result of the change in the free energy of a film during the approach of two restricting surfaces (i.e., with diminishing film thickness, h), thus:

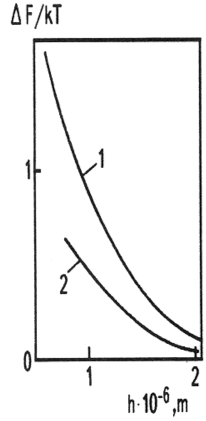

Figure 3.4. Dependence of the relative free energy, ΔF/kT, for filled PS (1) and PMMA (2) on the effective thickness, h, of the polymer interlayer.

$$P_d = \frac{\left(\frac{\partial F}{\partial h}\right)_{T,\nu,S}}{S} \qquad [3.7]$$

where S is the interphase surface and F is the Helmholz free energy.

The curves of dependence of the relative free energy of PS and PMMA filled with glass powder on the effective thickness of the interlayer between two filler particles are given in Figure 3.4. The values ΔF/ kT were calculated according to the formula:

$$\frac{\Delta F}{kT} = \frac{-\nu_D}{\nu_h \sigma} \qquad [3.8]$$

which includes parameters of Eq 3.7. The monotonous increase in the free energy with decreasing h (Figure 3.4) reflects the repulsion of particles due to the positive disjoining pressure. A quantitative assessment of the change in the structure of the polymer which takes place in the processing of the polymer in the presence of a filler can be made based on the determination of the specific surfaces and pore volumes, which makes assessment of packing density of macromolecules possible.[24] For this purpose, the isotherms of the sorption of vapor of the solvent (inert in relation to polymer) may be measured.[25]

Figure 3.5 shows isotherms of sorption of methyl alcohol vapor (p_1, the pressure of vapor over the solution, and p_0 the pressure of the saturated vapor) by films of PMMA containing varying amounts of filler. The isotherms for filled PS have the same shape. It may be seen that the addition of filler leads to an increase in adsorption which grows as filler content increases. Calculation shows that the rise in adsorption cannot be due to sorption of vapor on the filler and is governed, consequently, by changes in the packing density. It was also shown that specific surfaces and pore volume calculated using the BET method increase with incorporation of the filler. These data indicate a powerful influence of the filler on the processes of structure-formation taking place in the processing of a polymeric material in the presence of a filler.

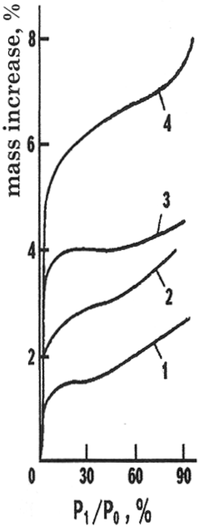

Figure 3.5. Isotherms of sorption of methyl alcohol by films of PMMA prepared from solutions: 1-pure PMMA, 2-PMMA with 10% of filler, 3-with 30%, 4-with 50%.

Moreover, the reduction in the packing density in the presence of a filler is considerably more marked with the specimens cast from solution than those prepared by molding. This is because in the processing of a polymeric material the interaction of the polymer molecules or aggregates with the surface of the filler alters the conditions under which relaxation occurs. Because of the interaction of the chains with the surface, there is a limitation in the mobility of the chains, leading to loose packing. It is quite evident that in this case, where relaxation processes in the filled polymer are facilitated, the filler will have less effect on the density. Some thermodynamic problems connected with sorption of vapor by filled polymers are discussed below (Chapter 4).

For crystalline polymers, the incorporation of filler also leads to changes in density of the amorphous phase of polymer. If the density of disordered regions in filled semi-crystalline polymer, ρ_d, is an additive sum of the density of the disordered region in the bulk, ρ_o, and in the surface layer, ρ_s, then we have:

$$\rho_d = \rho_s \nu + \rho_o(1-\nu) = \rho_o - (\rho_o - \rho_s)\nu \qquad [3.9]$$

where ν is the fraction of a polymer in the surface layer. This value is connected with the volume fraction of a polymer in the filled system:

$$\left[\frac{(r+\delta)}{r}\right]^3 - 1 = \nu\varphi(1-\varphi) \qquad [3.10]$$

where r is the radius of a filler particle, δ is the thickness of the surface layer, and φ is the volume fraction of a filler. From Eqs 3.9 and 3.10 we have:

$$\rho_d = \rho_o - \frac{K(1-\varphi)}{\varphi} \qquad [3.11]$$

where

$$K = (\rho_o - \rho_r)\left[\frac{(r+\delta)}{r}\right]^3 \qquad [3.12]$$

If these assumptions are correct, then the dependence of ρ_d on the ratio of $(1-\varphi)/\varphi$ should be a straight line with a slope K which cuts off, on the ordinate axis, the value ρ_0 corresponding to the density of unfilled amorphous polymer. Such dependence is presented in Figure 3.6 for filled polyethylene. From this dependence, the following values were calculated: ρ_0 = 880±15 kg/m^3 and K = 4400±100 kg/m^3. The value of ρ_0 corresponds to the density of amorphous regions in unfilled polyethylene.

It is important to evaluate the thickness and the density of the surface layers in filled polyethylene. The dependence of ρ_s/ρ_0 on δ/r is presented in Figure

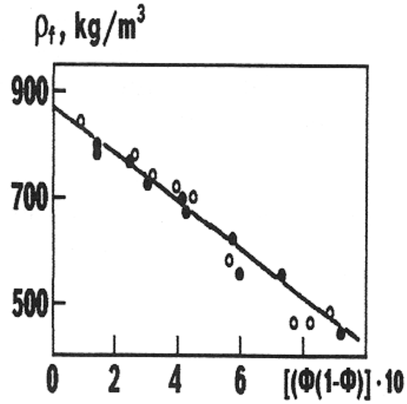

Figure 3.6. Dependence of the density of distorted regions in polyethylene, ρ_f, on the amount of fumed silica: ○ - initial samples, ● - heat treated samples.

3.7. It is seen that at high value of δ/r, the ratio ρ_s/ρ_0 asymptotic approaches unity, whereas at $\delta/r < 3$ that ratio sharply decreases. Because, as follows from Figure 3.7, the inequality $\rho_s/\rho_0 > 0$ is valid, the ratio δ/r is more than 1. More correctly, these values may be estimated if we assume the additivity of densities of surface layers around filler particles and polymer density at the condition that the distance, L, between filler particles is $L \le 2\delta$. The L may be calculated from the relation:

$$L = 2\delta = 2r\left[\frac{\varphi_M}{(1-\varphi)^{1/3} - 1}\right] \qquad [3.13]$$

where φ_M is the volume fraction of a filler at maximum dense packing of filler particles in the polymer (for polydisperse particles $\varphi_M = 0.81$). Because, as follows from Figure 3.6, Eq 3.11 is valid at fumed silica content up to 10 wt%, using value $(1 - \varphi)/\varphi = 0.01$ and $\varphi_M = 0.81$, we find from the above relations that $\delta/r=1.2$, which corresponds to the thickness of the surface layer ~150 Å, if the diameter of the fumed silica particle is 250 Å. From Figure 3.6, we also find that at $\delta/r=1.2$, the ratio $\rho_s/\rho_0 = 0.5$. Finally, from Eq 3.10, it follows that $\nu = 0.1$.

In a previous publication,[27] the kinetics of the isothermal crystallization of oligoethyleneglycol adipate, filled with glass powder, was studied and the reduced packing densities V_a/V_{as} (V_a and V_{as} are specific volumes of amorphous phases in bulk and surface layers) calculated, based on the average distance between the filler particles, L (Figure 3.7). It was found that in the investigated range of L values, the regions with varying density arises, i.e., alternations of more dense and less dense regions are observed. Such picture can be explained by the non-equilibrity of the surface layers (see below). It may be predicted that a real profile of the curve of reduced packing density consists of alternating max-

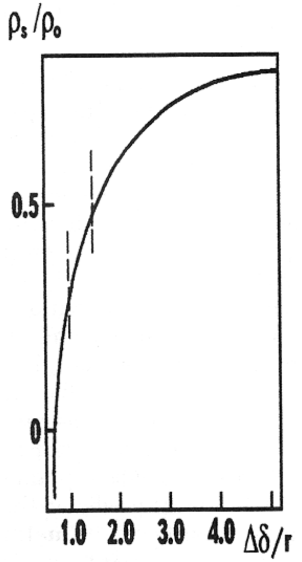

Figure 3.7. Dependence of ρ_s/ρ_o on $\Delta\delta/r$ (dotted lines denote the more probable region of reduced values).

imum and minimum, with step-wise decrease in their intensity with increasing L.

The thicknesses of the surface layers of some elastomers are 100 Å and depend on the surface nature.[28] For elastomers the formation of more dense and less dense layers was also observed. The loose layer has the greatest thickness. The values determined by the ellipsometry method depend on temperature, because with growing temperature the molecular mobility of chains increases, and because of the increase in the surface of the molecular contact, the density of the layer increases. Much less data are available on packing density in filled crosslinked polymers. For cured epoxy resin it was found[29] that the properties of the surface layer at the interface with a solid depend on the curing conditions. The ordered surface layer has a thickness of $0.5\text{-}0.6\times10^{-3}$ m, which is by one order higher when compared with linear polymers.

3.4 METHODS OF EVALUATION OF THE FRACTION OF SURFACE LAYERS IN FILLED POLYMERS

The content of the surface layers in filled polymer is very important because, due to the changes of properties in these layers, all properties of the filled polymer are changed. Empirical methods of estimation of the surface layer fraction can be divided into four groups.[30]

1. Experimentally, it was found[31] that an increment of the Newtonian viscosity of melts of filled oligoesters, η/η_0 (η_0 is the viscosity of unfilled material) increases with the increase in the amount of a filler more rapidly than predicted from hydrodynamic theories of the flow of suspension. Such behavior testifies to the apparent increase of the fraction of the dispersed phase in the system, due to the formation of surface layers on the particles, these layers forming a shell incapable of deformation. The fraction of oligomer in the surface layer, ν, is esti-

mated from experimental data, assuming that the filler fraction, φ, in theoretical equations, is a sum of the fraction of solid particles plus adsorbed layer of oligomer, i.e., $\varphi = \varphi_o + \nu$. For various systems, it was established that the value ν changes with φ_0 in such a way that the thickness of the surface layer is the same for different values of φ_0. The same approach may be used for the systems which are characterized by the anomaly of viscosity.[32] In this case, value φ may be estimated from the values of viscosity extrapolated to the infinite shear stress, τ. It may be supposed that for the systems capable of both Newtonian and non-Newtonian flow, the calculated values of ν will not coincide. The length of the surface layer should be the greatest for Newtonian flow, where the structure of the melt does not depend on the shear stress. With transition to the non-Newtonian flow, the length of the surface layer should diminish as a result of destroying the initial structure of the filled melt.

2. As it was shown above (Figure 3.3), the dependence of the specific volume, v, on the filler content, φ, is linear. The extrapolation to the $\varphi = 1$ gives the specific volume of a filler, v_f, (if the agglomeration of filler particles is absent). If we assume that the linear part of the dependence corresponds to the transition of the polymer into the state existing in the surface layers, with specific volume, v_s, then the fraction of the surface layers may be estimated from the additivity rule:

$$v = v_f \varphi + [v_s \nu + (1 - \nu) v_0](1 - \varphi) \quad [3.14]$$

(v_o is a specific volume of unfilled polymer). This method assumes a homogeneity of the surface layer, which is not true.

3. Assuming the additivity of contributions of filler (f), polymer (o) and surface layer (s) into the thermal expansion,

$$\alpha = \alpha_f \varphi + \alpha_s \varphi_s + \alpha_o \varphi_o \quad [3.15]$$

($\varphi + \varphi_s + \varphi_o = 1$), it was proposed[33] that the fraction of a polymer in the surface layer, ν, can be evaluated as follows:

$$\nu = (\alpha - \alpha^*)/(\alpha^* + \alpha_o - \alpha) \quad [3.16]$$

where α^* is the experimental value of the expansion coefficient of the filled polymer. Values ν, calculated from Eq 3.16, for epoxy resin filled with metal powder, show the inadequacy of the proposed equation which manifests itself in varying dependence of ν on φ. It may be proposed that this inadequacy is connected with the influence of the prehistory of the filled sample related to the thermal stresses in the sample and expansion coefficients, rather than a real effect of a long-range action of the solid surface on the structure of a layer.

4. The experimental values of the specific heat capacities for filled polymers are additive in the range of the glassy state. It was proposed[34,35] that this phenomenon be explained by the fact that some macromolecules do not participate in the cooperative process of the vitrification, due to their transition into the surface layers where their segmental mobility is hindered. The fraction of surface layers in this case may be calculated as:

$$\nu = 1 - \Delta C_f / \Delta C_o \qquad [3.17]$$

where ΔC_f and ΔC_0 are the changes in the heat capacity, at the glass transition temperature, calculated for polymer of filled and unfilled samples. The values calculated according to Eq 3.17 increase with φ, which corresponds to the permanent effective thickness of the surface layer. The shortcoming of this method is the assumption that segmental mobility in the surface layer is fully depressed.

From the above discussion, it follows that the fraction of the surface layer, estimated according to one of the listed methods, depends on the sensitivity of the measured macroscopic property to the change in the structure state of a polymer near the interface. Therefore, these methods should be considered only as qualitative, not quantitative, characteristics of the influence of the surface on the structure of a polymer.

In analysis of the experimental data, those methods are preferable which give the thickness of the surface layer, independent of the filler amount.

3.5 MOLECULAR MOBILITY OF MACROMOLECULES NEAR THE INTERFACE

The restriction of molecular mobility, when filler is introduced into the polymer, is due to the adsorption interaction at the interface. It manifests itself

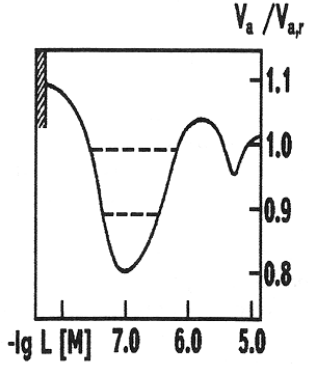

Figure 3.8. Dependence of reduced packing density on the effective thickness of the polymer interlayer between fumed silica

both in the change of relaxation behavior and in glass transition temperature (see Chapter 4). Again, judgment about the change in molecular mobility is usually made from the data on the total change in the system properties, as it is impossible to isolate the surface layer. To explain a long-range action of the interface on the molecular properties, it should be assumed that the mechanism, which we call a relay-race mechanism, is operative. It consists of the transition of the surface influence from the macromolecules directly connected with the surface to more remote layers, due to the forces of the intermolecular interaction. This is why the cohesion energy is so important in the effects of the solid influence (see Section 3.3). The molecular restrictions imposed on the conformations by the surface are transferred to the molecules not bound with the surface. This may be the result of formation of some supermolecular structures like aggregates, etc. The greater the cohesion energy, the higher the transfer of surface influence.

The influence of the interface on molecular dynamics was considered in some theoretical works.[36-38] It was shown that the presence of the interface has a great effect on the molecular mobility of chains and their diffusion. The molecular mobility diminishes, compared with the bulk, by a factor of approximately 0.5. There are many experimental data regarding the change of molecular mobility in filled polymers. These data are collected and discussed in two works.[2,7]

The data available allow the conclusion that the change of molecular mobility in the surface layers may be connected both with conformational restrictions imposed by the surface and energetical interactions between the macromolecules and surface. The contribution of both factors to the restriction of molecular mobility may be estimated from the data on activation energy of the relaxation processes. For this purpose, the following expression is used:

$$\tau = \tau_o \Delta F / RT; \quad \Delta H = -RT^2 \delta \ln \tau / \delta T; \quad \Delta S = -\delta[RT\ln(\tau/\tau_o)]\delta T \qquad [3.18]$$

where ΔF is free energy of activation, H is enthalpy, and S-entropy, τ is average relaxation time which may be easily found from experiment.[2,7] Consideration of the dependence of ΔH and ΔS on the thickness of the surface layers shows that in the surface layers, the entropy of activation increases, compared with the bulk, while the enthalpy decreases to an insignificant extent. This observation confirms once more that the main contribution to the change in the properties of the polymer in the surface layers is the entropy factor.

The increase in the entropy of activation of filled polymers is explained by the fact that, for the transfer of segments from one arrangement to another in the relaxation of chains whose effective rigidity is raised, a greater change in the number of possible conformations is required as compared with analogous movements taking place within the bulk. Here we must stress also that the main contribution in the activation energy of relaxation is the enthalpy component, but, on the other hand, in the change of activation energy, with transfer in boundary layers, the main role is played by the entropy factor.

It was also shown[7] that the molecular mobility in adsorption layers changes non-monotonously with the layer thickness. This effect is determined by the dependence of the adsorption layer structure on conditions of the interaction between the polymer and the surface and the shape of the concentration profile (see Chapter 1).

The data on molecular mobility allows us to draw some very important conclusions as to the heterogeneity of the surface layers. For example, the molecular mobility of styrene-methyl methacrylate-acrylonitrile copolymer filled with fumed silica was studied by the dielectric relaxation method.[39] It was found that, at loading of 24% and more, an additional maximum of tanδ appears in the temperature region of 338-353 K, whereas for unfilled copolymer the main maximum is observed near 383 K. This new broad maximum seems to be determined by the segmental mobility of chains in looser regions where molecular mobility is higher. In such a way, one can conclude that in the surface layer, the splitting of the main maximum proceeds. This fact may indicate the complicated structure of the surface layer. At high loading, the position of the main maximum does not depend on the amount of the filler because the polymer has already passed into the surface layer. In this case, the second maximum appears. That means that despite the transition of polymer into the surface layer, with increasing filler amount, some structural rearrangements in this layer continue to proceed, and a decrease in packing density of the surface layer continues.

This result seems to be rather unexpected, as in a thin layer one could expect more dense packing. However, the long-range action of the surface on the relaxation processes plays the prevailing role in the formation of the structure, which increases with a ratio of filler surface to its volume.

The discovering of the separate segmental relaxation in denser and looser layers allows the fraction of polymer segments, p, in the loose part to be estimated. For this purpose, either the areas under the corresponding maxima of ε'' or the product of the width of maximum by the height of the maximum of ε'' should be compared (Figure 3.9). If we assume that the chain segments in the surface layer are distributed between the denser and looser parts proportionally to the maximum area, the following relation may be obtained, in which ε''_{md} (the maximum of the dense part), and ε''_{ml} (the maximum of the loose part) are used:

$$\frac{(\varepsilon''_{ml} - \varepsilon''_{bl})m_l}{(\varepsilon''_{md} - \varepsilon''_{bd})m_d + (\varepsilon''_{ml} - \varepsilon''_{bl})m_l} = \frac{P_l}{P_d + P_l} = p \qquad [3.19]$$

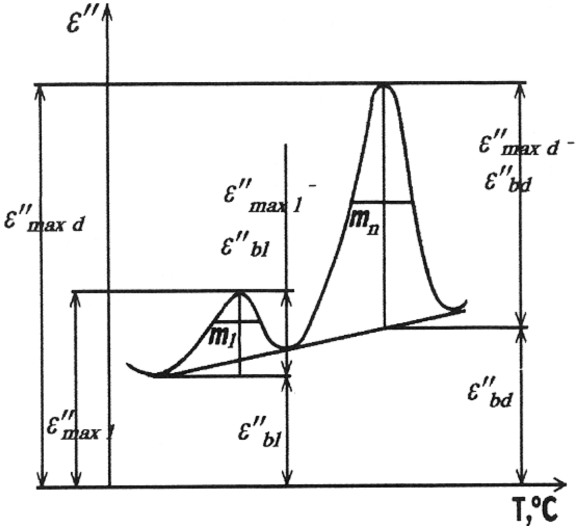

Figure 3.9. Representation of two relaxation processes for the surface layer (see text).

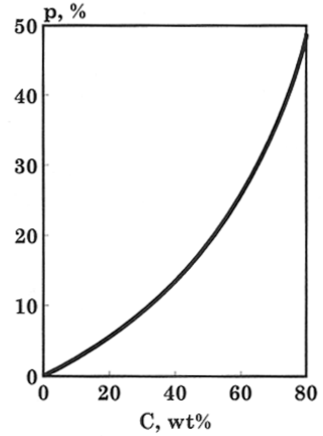

Figure 3.10. Dependence of the fraction of segments in less dense layer on the filler content.

where ε''_{bd} and ε''_{bl} are the background losses for the corresponding maxima, m_l and m_d are the widths of maxima, P_l and P_d are numbers of segments in the looser and denser areas of the surface layer. Value p represents the fraction of segments in the surface layer belonging to the loose part.

In Figure 3.10, value p increases with the increase in the filler content and at the maximum filler amount, it rises to ≈60%. It is important to note that the fraction of the loose part increases with a growth in the filler amount, whereas the position of the main maximum is unchanged, indicating the permanent restriction of molecular mobility. The widths of maxima for the loose part increases with filler content. With diminishing thickness of the surface layer, the packing density in the surface layer begins to increase, because the more dense the packing, the greater the width of the maximum. (The loose packing facilitates relaxation and leads to a sharper maximum and smaller width.)

Another approach to the characterization of the molecular mobility in the surface layers may be based on the measurements of the heat capacity of filled polymers.[34,40] The increase in the specific heat capacity at the glass transition, ΔC_p, is linked with the molar cohesion energy of the polymer, W_c, and the molar energy of formation of the holes, ε_h, by the relationship:

$$\Delta C_p = (W_c / T_g)(\varepsilon_h / RT_g)\exp(-\varepsilon_h / RT_g) \qquad [3.20]$$

The molar hole volume, ν_h, is determined by the following formula:

$$\nu_h = \varepsilon_h / V_c W_c \qquad [3.21]$$

where V_c is a molar volume of polymer at T_g.

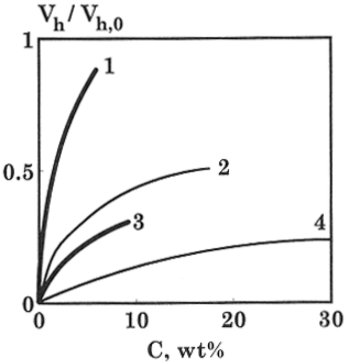

Figure 3.11. Dependence of $\nu_h/\nu_{h,0}$ on fumed silica content for PS (1), polyurethane (2), PMMA (3), and PDMS (4)

The experimental data show that the main contribution to the value ε_h comes from the energy of intermolecular interactions. By introducing filler, both values, ε_h and ν_h, always increase. The increase in ε_h with increasing amount of a solid phase indicates the growth of the energy required for transition from glassy to elastic state related to the restrictions in molecular mobility in the surface layer. However, increase in ν_h is connected with more loose packing of macromolecules.

Let us consider the dependence of the properties of a polymer in the boundary layer on the chemical structure of the polymer. Figure 3.11 shows the dependence of $\nu_h/\nu_{h,o}$ (where the subscript, o, refers to the unfilled polymer). The increase in the looseness of packing in a filled system on the filler content is presented. All plots have an initially more or less rapid rise and subsequent flattening, but the slopes of the curves and the absolute values of $\nu_h/\nu_{h,o}$, at saturation significantly depend on the nature of the polymer.

It is interesting that there is a qualitatively similar character in the plots of the dependence on T_g, and also on the fraction of polymer in the surface layer, ν, on the filler concentration. The absence of a linear relation between T_g, in the filled system, and the amount of filler is usually explained by the fact that with an increase in the fraction of solid phase there is an aggregation of the solid particles and reduction in the effective surface of contact with the polymer phase. At the same time, we may expect there is a certain linear dependence of the properties of filled polymer (e.g., T_g and $\nu_h/\nu_{h,o}$) on the fraction of polymer in the surface layer. Plots of these dependencies are shown in Figure 3.12.

It is readily seen that both T_g and $\nu_h/\nu_{h,o}$, for filled systems, are approximately proportional to ν. Analytically, this may be represented by the formulae:

$$T_g = T_{g,o} + \Delta T \nu \qquad [3.22]$$

Table 3.2: Properties of various polymers

Polymer	ΔT, K	ε_h / ν_h, J cm^{-3}	A	B
Polystyrene	0	304.8	0.95	1.72
Polymethylmethacrylate	105	552.6	1.00	1.48
Polyurethane	14	477.3	1.00	1.17
Poly(dimethyl siloxane)	7	322.3	1.00	0.83

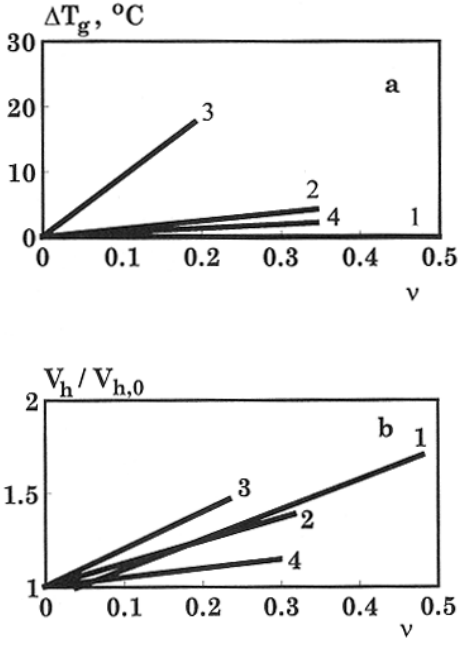

Figure 3.12. Dependence of ΔT_g (a) and $V_h/V_{h,0}$ (b) on ν for PS (1), PU (2), PMMA (3), and PDMS (4).

and

$$\nu_h / \nu_{h,o} = A + B\nu \qquad [3.23]$$

The results show that the main influence on the properties of filled polymers is not an absolute content of solid particles in the system but the fraction of the polymer in the surface layer.

It is of interest to explain the physical meaning of these coefficients. As follows from Eq 3.22, the magnitude of ΔT is controlled by the maximum increase in T_g, corresponding to the limiting case when the polymer phase is subjected to the influence of the solid surface ($\nu = 1$). It was found that the absolute value of ΔT correlates well with the hole density of the cohesion energy of the polymer, ε_h/ν_h. Table 3.2 shows that the maximum of ΔT occurs in PMMA, which has the highest cohesion energy, whereas for PS, for which this value is the lowest, ΔT does not depend on ν. Thus, in the general form, we may write:

$$\nu = f(S, \sigma, \gamma_s / W_c) \quad [3.24]$$

In fact, the transition of macromolecules into the surface layers becomes easier when the intensity of molecular interaction and increase in the polymer filler interaction energy are reduced, i.e., with an increase in the ratio of γ_s / W_c, where γ_s is the surface tension of a filler. As mentioned earlier, an important factor here is the chain stiffness, σ. The increase in ν with an increase in σ may be explained by the fact that with an increase in the stiffness of the polymer chain, there is a deterioration of the conditions of their packing in the surface layer, as a consequence of which the distance, at which the difference between the boundary regions and the bulk phase of the polymer disappears, likewise must increase. These concepts confirm the opinion that T_g of filled polymers depends, in a complex fashion, on the ratio of the entropy and energy factors of the interaction with the solid surface. As may be seen, the presence of boundary layers of polymers with low values of cohesion energy, transfer of molecules into the surface layer is a necessary but not sufficient condition for the rise in T_g.

For polymers with low values of cohesion energy, transfer of molecules into the boundary layer apparently has only a slight effect on their properties, i.e., the magnitude of ΔT in Eq 3.22 is relatively low, and corresponding T_g is practically independent on the filler concentration. But for polymers with strong molecular interaction, the presence of even a small fraction of macromolecules in the surface layer leads to a perceptible increase in T_g as a result of ΔT increase. Thus, the character of the changes in T_g of polymer containing filler cannot be regarded as an unambiguous criterion of the presence or absence of the surface layer in the system. Evidently, there must be a particular optimum combination of values from Eq 3.24 at which the rise in T_g of the polymer containing filler becomes most perceptible.

New data, obtained using the technique of neutron reflectivity, have been recently reported.[41] A remarkable difference in the time-scale for center of mass diffusion was found between adsorbed polymer chains (PMMA) and those existing entirely in a melt. Because the adsorbed chains are mixed intimately with chains from the bulk melt, it is plausible that surface exchange on the segmental scale would be quite rapid but that the requisite simultaneous loss of every segmental contact point, to activate a large-scale center of mass motion, is improbable. It was assumed that the topology of the adsorbed layer may contribute, because a dense mesh of adsorbed loops plays a role of a network with an extremely large entanglement density. This would also greatly impede the mobility of chains seeking to escape the boundary layer.

3.6 PHYSICO-CHEMICAL CRITERION OF POLYMERS HIGHLY LOADED WITH FILLERS

It is well known that the amount of a filler which can be introduced into the polymer depends on many factors (filler-polymer affinity, viscosity of melt or solution, etc.). It is important to give a definition of what should be considered to be high loaded polymer, because, up to now, there is not a distinct understanding of this question. The situation is somewhat similar to that existing some years ago in the field of polymer solution: “what is the meaning of the terms ‘dilute’ and ‘concentrated’ solution?” In the case of solutions, the problem was solved by introduction of the concept of coil overlap and critical concentration (cross-over region).[42] We propose to introduce the definition of a critical loading which corresponds to the filler concentration, φ_{crit}, at which filler particles have maximum packing density (for a given shape of particles), i.e., they begin to touch each other. Above this critical loading, the filled system loses its thermodynamic and mechanical stability.[43-45]

In the framework of the classical colloid-chemical concept, filled polymer can be considered as a suspension of solid particles, 1, separated by the interlayers of continuous polymeric phase, 2 (thickness, δ). The energy of interaction between any two particles of a solid phase is expressed as

$$U(\delta) \approx -A_{121} / \delta^2 \qquad [3.25]$$

where A_{121} is the parameter of intermolecular interaction. From this equation, it follows that the system, consisting of a structureless continuous phase and uniformly-distributed uncharged colloid particles, is, from the thermodynamic point of view, unstable, due to the action of the attraction forces between particles which cause coagulation. The system may still be mechanically stable due to a high viscosity of the dispersion media. However, such a hypotetic structureless system does not meet the present experimental data, which support the pres-

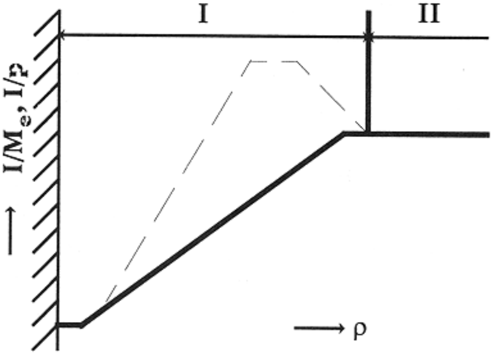

Figure 3.13. Scheme of the dependence of the entanglement network density and packing density on the distance from the surface: I-border layer, II-the bulk.

ence of surface layers in filled polymers, having structure and properties different than bulk.

Taking into account that the only structural feature of polymers in amorphous state is the existence of the network of intermolecular entanglements, one can suppose that the formation of the surface layers, on filler introduction, can only be caused by the changes in the initial network of entanglements. Consequently, the density of this network, in the surface layers, should differ from the same value for the bulk phase. The average molecular mass, M_e, between two adjacent junction points of the network can be used as a measure of network density. It is thus evident that the effect of a solid surface should extend by the distance from the surface of at least equal $\Delta\delta$ in relation to M_e. Using the empirical relationship $2M_e \approx M_c$ (where M_c is critical molecular mass for the entanglements) and available data on M_c for some flexible chains, it may be shown that the expected values of $\Delta\delta$ should be in the limits of 40-100 Å.[10] This prediction coincides with experimentally-found thicknesses of the surface layers in filled amorphous polymers. The values of $\Delta\delta$ are thus a measure of effective thickness of the surface layers formed as a result of the contact between the filler particle and polymer melt. It is evident that the formation of a thin polymer film, casted from solution, on a solid surface, gives much higher values of $\Delta\delta$, because the network density in solution is proportional to $1/M_e$ and diminishes with solution an increase in concentration. In this case, during solvent evaporation, the gradient of concentration is established (and correspondingly the gradient of entanglements) in a direction normal to the surface. Figure 3.13 shows the change of the density of entanglements as a function of the distance from the surface. The entanglement density should either monotonously increase with δ, from some minimum value near the interface, corresponding to the concentration of initial solution, up to "bulk" value (solid line), or pass through the maximum (dotted line). The first case is typical of a system having low energy of interaction between the solid and polymer, whereas the second case is typical of a strong interaction favoring formation of a defective intermediate layer which separates the surface layers and polymer bulk into different structures.

Independent of the formation of filled composition, the increase in the filler content is accompanied by the monotonous increase in the fraction of the surface layers, φ_1, up to their overlapping and formation of a continuous surface "phase". The amount of filler denoted by φ'_1 should be considered as corresponding to the transition of all polymer in the filled system into the state of a surface layer. φ'_1 may be considered as the limiting value of a highly loaded system. In the region $\varphi_1 > \varphi'_1$, the system preserves its mechanical stability due to adhesive interaction between filler and polymer and due to cohesive strength of the continuous phase. The thermodynamic stability of this system can be a result of compensation of some decrease in entropy of mixing of polymer coils (due to diminishing density of entanglement network in the surface layer) by decrease of enthalpy due to the thermal movement restrictions in the surface layer. At the same time, with the increasing amount of filler, the decrease in the thickness of the surface layer, up to values lower than the radius of inertion of the molecular coil $2\langle R_g\rangle$, leads to such a drastic decrease in conformational entropy of macromolecules that the thermodynamic stability also sharply diminishes. It means that the region of highly loaded polymer is restricted by some volume fraction of a filler, φ''_1, at which the effective thickness of the surface layer becomes comparable to the size of a macromolecular coil.

The analysis given above allows for the following definition: highly loaded polymer is a system where all polymeric component was transformed to the state of a surface layer having a thickness exceeding the size of macromolecular coil in the melt. Thus, the critical filler content, φ'_1, is a fundamental characteristic of the system and criterion for highly loaded polymer.

According to the experimental data[44] for some crystallizable polymers, the effective thickness of the interlayer, L, between filler particles

$$L = D[(0.80/\varphi_1'')^{1/3} - 1] \qquad [3.26]$$

is determined by the size of macromolecular coil in melt, $2R_g$ (D is the diameter of a filler particle). Because of the scaling dependence $R_g \approx M^{1/3}$, one may expect a similar relationship between L and M, which was confirmed elsewhere.[46] It was found that, at some concentrations and molecular mass, M, the saturation is reached at the interface PS-fumed silica. At $\varphi > \varphi_1''$, the number of contact points between macromolecules and the surface remains unchanged. The constant value of ν, for highly loaded polymers, independent of φ_1, is valid only if with growth in φ, in the region $\varphi > \varphi_1''$, the diminishing fraction of filler will interact with polymer (meaning the voids will be formed). Thus, the value φ_1'' is the upper limit of the existence of highly loaded polymer, above which the system, as mentioned above, losses its mechanical stability. It was discovered that value L (nm) depends on the molecular mass of polymer, according to the empirical relation:[47]

$$L = 5.25 \times 10^{-3} M_w^{0.62} \qquad [3.27]$$

Calculated values of L, for various systems, correspond to values R_g and in agreement with the results of theoretical analysis of polymer adsorption, according to which the thickness of an adsorption layer, δ, and polymerization degree, N, are connected by the scaling relationship $\delta \approx N^{1/2}$ at $\delta > R_g$ (see reference 22 in Chapter 1).

It is also evident that the limiting amount of a filler depends on the size and shape of its particles. To increase the amount of filler, the polydisperse filler can be used.[48] For such fillers, the geometric criterion of filling can be calculated, which is defined as the difference between the volume fraction of filler at its limiting packing density, φ_m, in the unitary volume, and its volume fraction in real composition, φ, is

$$\varphi_f = \varphi_m - \varphi \qquad [3.28]$$

where φ_f is an unoccupied volume available for polymer in unitary volume. This characteristic is more conveniently compared with the amount of filler.[49] For composites filled with randomly oriented fibers, theoretically, the limiting volume fraction $\varphi_m = kd/L$, where k is a constant and d and L are diameter and length of fiber. This relationship is valid for $L/d > 5.3$.[50]

3.7 MICROHETEROGENEITY OF SURFACE LAYERS

The action of a solid surface leads, as we have seen, to many structural rearrangements in the surface layers and to formation of a non-uniform or microheterogeneous structure.[51] In the filled polymer system, two types of heterogeneity are present: macroheterogeneity, due to the incorporation of solid particles, and microheterogeneity, which is determined by the formation of surface layers of a complicated structure. The surface layer, or the interphase region between solid and polymer in bulk, is the region of microheterogeneity. For polymer systems containing fillers, various levels of microheterogeneity may be distinguished. The first level is determined by the dependence of the surface layer thickness on the property which is investigated. The systems may differ in relation to one property but be similar in relation to another. The second level is determined by the differences in the conformational state of macromolecules in the surface layer and in the bulk, which, in turn, is responsible for differences in the packing density of macromolecules.

Non-monotonous change of molecular properties of the surface layers in direction normal to the solid surface indicates the microheterogeneity on the molecular level. The character of this microheterogeneity depends on the properties of both solid and polymer. The transfer of the influence from macromolecules bound to the surface to more remote macromolecules contributes to the microheterogeneity on the molecular level. The solid also affects the conditions of the formation of submolecular structures in the surface layers, and, in particular, the conditions of crystallization and crystallinity degree (see Chapter 4). This factor determines the structure of the polymer in the surface layers and the microheterogeneity on the submolecular level. By analysis of the chemical reactions proceeding at the interface with solid (see Chapter 4), it was established that chemical structure of a polymer (molecular-mass distribution and distribution of the polymer functionality) depended on the distance from the surface. This circumstance leads to another type of microheterogeneity - a chemical one, which, in turn, is connected with the appearance of additional molecular and submolecular microheterogeneity.

An important reason for the appearance of the microheterogeneity in the surface layers is the difference in the surface tension of polymer fractions of various molecular mass. Under the influence of a solid surface, the redistribution, according to the molecular mass and surface activity between surface layer and polymer bulk (colloid-chemical level of microheterogeneity), occurs. In polymer-polymer systems (see Chapter 6), an additional level of microheterogeneity also takes place due to the thermodynamic immiscibility of components and loosening of the interfacial region because of formation of an excess free volume. In such systems, redistribution of free volume and the emergence of non-homogeneous distribution take place, which is a direct cause of microheterogeneity at the level of molecular properties, determined by the free volume.

The analysis of the reasons for microheterogeneity in filled polymer systems allows us to give their following classification:[51]

- Molecular heterogeneity exhibited by changes in physical characteristics in the interfacial layer, determined by the macromolecular structure of polymer chains (thermodynamic properties, molecular mobility, density of packing, free volume, level of intermolecular interactions, etc.)
- Structural microheterogeneity due to the changes in the mutual disposition of macromolecules in relation to each other in the surface and transition layers at different distances from the phase boundary and characterizing the short-range order in amorphous polymers and degree of crystallinity in crystalline polymers
- Microheterogeneity at the supermolecular level, depending on the type and conditions of the formation and packing of supermolecular structures in the surface layer and the bulk;
- Chemical microheterogeneity caused by the influence of the interface on the reaction of the formation of polymer molecules. This type may be an additional cause of the above three types of microheterogeneity;
- Colloid-chemical microheterogeneity, determined by the difference in the surface energy and surface activity of polymer fractions having different molecular mass.

These types of microheterogeneity are inherent in all polymer systems, filled with particulate and fibrous fillers, in two-phase and multi-phase polymer systems (mixtures of polymers with discrete and continuous distribution of components), as well as in polymer glues, coatings, fiber-reinforced plastics, i.e., in all polymer composites. However, in polymers with mineral reinforcement, microheterogeneity appears as a result of interfacial phenomena only in the polymer matrix, whereas for polymeric reinforcement it is typical of polymer filler, polymer matrix, and the transition layer between two polymer components (Chapter 6). In filled polymer alloys, dissipative structures exist as a result of non-equilibrium process of the formation of the alloy structure. The formation of modulated structures, due to spinodal decomposition and the coexistence of structures having various wavelength of spinodal decomposition, contributes to the microheterogeneity.[51]

The preceding discussion allows one to address the problem of the phase state of surface and interfacial layers of polymers in composites. Despite the non-uniformity, they can be characterized by their intrinsic dimensions, thermodynamic functions (entropy, enthalpy, specific volume), and the distinctions of mean local properties from the properties of the polymer in the bulk. In a number of instances these distinctions may be similar to the difference in the properties between amorphous and crystalline regions in semicrystalline polymers. The redistribution of fractions of different molecular mass in a surface layer, taking account of limited thermodynamic immiscibility of polymer homologues,[52] provides a basis to consider the transition layer as an independent phase. However, whether the surface and interfacial layers can be considered as an independent phase in the thermodynamical meaning or not is a very important question.

Let us take into account that the difference in properties, between surface layers and bulk is not indicative of random fluctuations and not described by a statistical distribution. For polymer systems consisting of two phases, the condition of the existence of a sharp phase border is not applicable. The problem of whether the surface layers are an independent phase has been discussed for low-molecular-mass systems by Akhmatov.[53] He gave two indications of a phase as a volume-extended state: chemical and physical homogeneity, and the availability of a thin transition layer forming at the interface. It is evident that there is no single answer to the problem in view of a great variety of types and states of boundary polymer layers. According to Akhmatov, one cannot speak about the boundary or surface layer as a strictly thermodynamic phase of any size without relating to its characteristics. In some cases, these layers may be considered either as three-dimensional or two-dimensional. The problem of whether the surface layers are independent phases with their own thermodynamic properties and structure is similar to the endless discussion of whether semicrystalline polymers are one or two-phase systems. These systems, provided that the interface between amorphous and crystalline regions (the required condition of a phase by definition) is absent, are described as a two-phase system from the thermodynamic point of view. Surface and interphase layers would, by analogy, be considered as a phase if they were in equilibrium with the bulk phase. However, from the above it follows that surface layers are not systems that have attained thermodynamic equilibrium, although, should it be attained, the properties of the transition or surface layer would still be different from the properties of the bulk. Therefore, we think that surface layers should be considered not as a thermodynamic phase but as a non-equilibrium dissipative system which arises under the influence of the surface force field, causing the deviation of the system from the equilibrium state.

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THERMODYNAMIC AND KINETIC ASPECTS OF REINFORCEMENT

4.1 THERMODYNAMIC INTERACTION BETWEEN POLYMER AND FILLER

Reinforcement of polymers is accompanied by the formation of the region of interfacial interaction between the polymer matrix and solid, which leads to the general change in thermodynamic properties of the system. Let us now consider a model which gives a thermodynamic description of the interaction between polymer and filler. The first attempts to estimate this interaction have been made using thermodynamic analysis of the sorption processes and applying thermodynamic cycles. To estimate the change in Gibbs free energy, ΔG, or enthalpy, ΔH, of transition of a polymer from unfilled to filled state, Kwei[1] used the cycle which enables values ΔG and ΔH to be found from vapor sorption and its temperature dependence. This approach is possible only above a critical vapor concentration when the sorption is the same for filled and unfilled polymers. It was found that unfilled polymer has higher free energy and enthalpy than filled polymer, and the transformation from unfilled to filled polymer state is accompanied by decrease in both enthalpy and entropy. It is interesting to note that the values of ΔH and ΔS found[1] are considerably below the values observed in the phase transitions (e.g., during polymer melting), and are similar in order of magnitude to the values found from the heats of sorption of loosely or densely packed polymers.

Let us now consider a model which offers a thermodynamic description of the interaction between polymer and filler. It was used to evaluate the sorption of molecules of solvent by a free polymer offering the conclusion that the solvent sorption was greater than that of filled polymer. This model is applicable when the increase in packing density in the boundary layer is a consequence of powerful interaction of polymer and filler, leading to a reduction in the chemical potential of the polymer. It is assumed that this interaction becomes negligibly small at infinite distance from the surface, decaying rapidly with the distance. At a distance greater than r* (from the center of the filler particle), the polymer may be regarded as free of interaction with solid. On the other hand, the polymer within the sphere of radius, r*, is regarded as bound. It is also assumed that the chemical potential of the polymer in the boundary layer increases with an increase in distance from the center of the particle. In this case:

$$\mu_H(R^*) \approx \mu_p \qquad [4.1]$$

where μ_p is the chemical potential of the free polymer and $\mu_f(r^*)$ the chemical potential of the bound polymer at the distance r* from the center of the filler particle. The mixing of the free polymer with the molecules of solvent, the activity of which is a, reduces the chemical potential of the polymer to $\mu_{p(a)}$, whereas the chemical potential of the bound polymer at distance r* is higher than $\mu_{p(a)}$. Consequently, a certain proportion of the bound polymer must dissolve and become free, until at a new boundary, r, there is established an equilibrium of $\mu_f(r)$ and $\mu_{p(a)}$. Thus, in the presence of a filler, the boundary is shifted and the bound layer compressed. At a critical content of solvent, all bound polymer dissolves, and then $\mu_f(r) = \mu_p$. From Henry's law, for a small amount of sorbed solvent, n_1, it follows that:

$$\mu_p = \mu_p^o - RT(n_1 / n_2) \qquad [4.2]$$

where n_2 is the number of moles of chain segments. Then

$$\Delta\mu = \mu_p - \mu_f = RT(n_1 / n_2) \qquad [4.3]$$

In this equation, the following boundary conditions exist: $\mu_f(r) = \mu_f(r^*) = \mu_p$ and $r = r_f$ at $n_1 >> n_{1,crit}$; $\Delta\mu = 0$ with $n_1 = 0$ (r_f is the radius of the filler particle). Since it is assumed that the sorption takes place only in the free polymer, its proportion v_p in the total volume of the polymer at a given vapor pressure is determined by the relationship:

$$v_p = [(x/m)_f]/[\ (x/m)_p \qquad [4.4]$$

where (x/m) is the gain in weight during vapor adsorption.

The fraction of bound polymer $(1 - v_p)$ may be found from

$$(r/r_f)^3 - 1 = (1 - v_p)(v_{p,f}/v_p) \qquad [4.5]$$

where $v_{p,f}$ and v_p are the volumes of polymer in filled and unfilled specimen, respectively. Eqs 4.2 and 4.5 allow us to find $\Delta\mu$ and r/r_f from the values determined experimentally. Under the boundary conditions, $\Delta\delta = 0$. In this case, $r = r^*$ and $r^*/r_f = 2.36$. When $n_1 = n_{1,crit}$, the value of $r/r_f = 1$ and $\Delta\delta = \Delta\delta_{f(r)}$. The thickness of an unswollen boundary layer, equal to $r^* - r_f$, is approximately 1430 Å, the proportion of bound polymer $(1 - v_p)$ as calculated from Eq 4.5 is approximately 56%. Having determined the values of $\Delta\mu_{f(r)}$ at various temperatures, we can also calculate:

$$\Delta S_{f(r)} = -\delta(\Delta\mu_{f(r)})/\delta T \qquad [4.6]$$

$$\Delta H_{f(r)} = \Delta\mu_{f(r)} + T\Delta S_{f(r)} \qquad [4.7]$$

Thus, investigation of the processes occurring in the filled polymer systems from the thermodynamics standpoint makes it possible to draw conclusions as to the structure of the polymer in the boundary layer close to the interface. The influence of the filler is not restricted solely to the layers lying in the immediate proximity of the interface. It is substantiated by the data on thickness of adsorption layers, obtained by various methods. The influence of the filler on the structure formation is explained by the so-called “relay-race” mechanism. The use of thermodynamic methods for the investigation of sorption allows us to assess

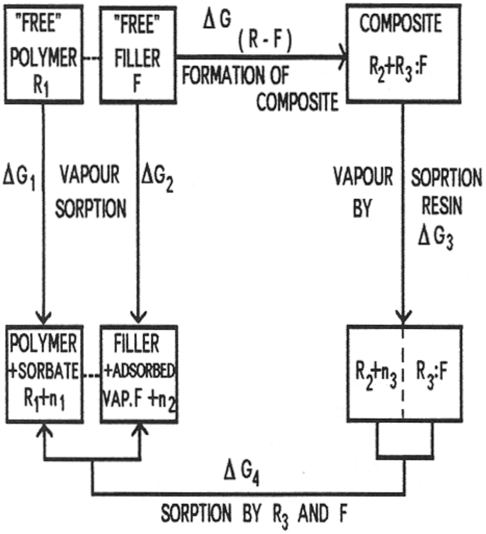

Figure 4.1. Thermodynamic cycle of sorption by a filled polymer. [Adapted by permission from B. Clark-Monks and B. Ellis, *J. Polym. Sci.- Polym. Phys.*, **11**, 2089 (1979)]

other characteristics of filled systems. If the sorption of vapors by filled polymer is higher, compared with sorption of pure polymer, it is possible to assess the adhesion between polymer and filler (Figure 4.1).[2]

Let n_1 be the number of moles of polymer before the incorporation of filler, n_3 the number of moles of polymer which are adsorbed on the filler surface, and n_2 the number of moles of polymer which are not perturbed by the filler, i.e., $n_3 = n_1 - n_2$ (please note that Kwei[1] considered a different case, where $n_2 = 0$ and $n_3 = n_1$). If in the compounding of filled polymer there is no change in the Gibbs free energy, then $n_2 = n_1$ and $n_3 = 0$. For calculations of thermodynamic function the cycle was proposed in Figure 4.1.[2] This cycle refers to the changes in free energy in the range of vapor pressure from $(p_1/p_o) = 0$ to $(p_1/p_o)_{crit}$. In this cycle, ΔG_1 and ΔG_2 are the changes in free energy of independent sorption of solvent by free polymer and filler up to a given value of $(p_1/p_0) > (p_1/p_0)_{crit}$. ΔG is the change in a free energy of formation of filled polymer, ΔG_3 the change in free energy of sorption by unbound polymer, n_2, ΔG_4 is the change of free energy associated with reduction of adhesion or break-up of the bonds and with independent sorption by unbound polymer, n_3, and filler. It may be seen that ΔG_3 and ΔG_4 determine the sorption and cannot be separated from each other. For the proposed cycle:

$$\Delta G = \Delta G_1 + \Delta G_2 - \Delta G_3 - \Delta G_4 \qquad [4.8]$$

Moreover,

$$\Delta G_1 = N_1 \Delta \overline{G}_{1,s} + n_1 \Delta \overline{G}_{1,\,pol} \qquad [4.9]$$

$$\Delta G_2 = N_2 \Delta \overline{G}_{2,s} + F \Delta \overline{G}_{2,fil} \qquad [4.10]$$

where subscripts s, pol, and fil refer to the sorbate, polymer and filler, N_1 and N_2 are the number of moles of sorbate, F is the number of moles of filler and n_1 is the number of moles of polymer. For sorption of vapor by unbound polymer, i.e., $(p_1/p_o)(p_1/p_o)_{crit.}$:

$$\Delta G_3 = N_3 \Delta \overline{G}_{1,s} + n_2 \Delta \overline{G}_{1,fil} \qquad [4.11]$$

In the final stage, when the relative pressure $(p/p_o) > (p/p_o)_{crit}$, the sorption obeys the equation

$$\Delta G_4 = \Delta G_{4,n_3} + \Delta G_2 \qquad [4.12]$$

where G_2 is determined from Eq 4.10 and characterizes the free energy of sorption by filler, while

$$\Delta G_{4,n_3} = N_4 \Delta \overline{G}_{4,s} + n_3 \Delta \overline{G}_{4,n_3} \qquad [4.13]$$

Substituting Eqs 4.13 and 4.10 into Eq 4.12, we obtain:

$$\Delta G_4 = N_4 \Delta \overline{G}_{4,s} + n_3 \Delta \overline{G}_{4,n_3} + N_2 \Delta \overline{G}_{2,s} + F \Delta \overline{G}_{2,fil} \qquad [4.14]$$

Then from Eqs 4.8-4.14, taking into account that $n_3 = n_1 - n_2$, we obtain:

$$\Delta G_{(\text{pol-fil})} = [(N_1\Delta\overline{G}_{1,s} + N_2\Delta\overline{G}_{2,s}) - (N_3\Delta\overline{G}_{1,s} + N_4\Delta\overline{G}_{4,s} + n_2\Delta\overline{G}_{2,s})] + [n_1\Delta\overline{G}_{1,\text{pol}} - n_2\Delta\overline{G}_{1,\text{pol}} - (n_1 - n_2)\Delta\overline{G}_{4,n_3}] \qquad [4.15]$$

or

$$\Delta G_{(\text{pol-fil})} = \Delta G^*_{(\text{pol-fil})} + (n_1 - n_2)(\Delta\overline{G}_{1,\text{pol}} - \Delta\overline{G}_{4,n_3}) \qquad [4.16]$$

The term G^* in Eq 4.16 can be determined from isotherms of sorption of free polymer, filler, and filled polymer. Based on the data on the sorption by free polymer, it is possible to find the magnitude of $N_1\Delta G_{1,s} + N_2\Delta G_{2,s}$, and from the data on the sorption by filled polymer, $N_3\Delta G_{1,s} + N_4\Delta G_{4,s} + N_2\Delta G_s$ can be found, which allows one to calculate $\Delta G^*_{(\text{pol,fill})}$, because from the conditions of the cycle, it follows that $N_1 = N_3 + N_4$. This quantity can be a relative characteristic of adhesion, although it is equal to the change in free energy of adhesion $\Delta G^*_{(\text{pol,fill})}$ only in limited cases, namely, when $(n_1 - n_2)(\Delta G_{1,p} - \Delta G_{4,n_3}) = 0$, i.e., with $n_1 = n_2$ (absence of an adsorbed layer). In actual systems this case never occurs. Experimental determination of $\Delta G_{\text{pol,fill}}$ is practically impossible, since the values of n_1 and n_3 are unknown. It is worth noting that in equations presented above the number of filler moles is used. In order to obtain expected data, the number of (moles) active centers should be used instead, because it depends on the dispersity degree of the filler.

The changes in free energy and enthalpy due to the interaction between polymer and filler have been estimated[3] from the sorption and calorimetric data for filled plasticized poly(vinyl chloride). Free energies ΔG and enthalpies ΔH of interaction between polymer and filler were calculated from the corresponding data on ΔG and ΔH of interactions of filled and unfilled polymers with a solvent in equilibrium conditions. Thermodynamic cycles have been used for this purpose. The experimental data[3] show various influences of the filler nature on the thermodynamic functions (Figure 4.2). The differences are explained by the effect of active and inactive fillers on the formation of the matrix structure. Using sorption method,[4] it was established that with increasing amount of the filler, partial specific entropy of polymer increases, which indicates structural and conformational rearrangements in filled system. Using thermodynamic cycles, one should have in mind that they are applicable only for the equilibrium systems and processes. Because in polymeric systems the establishing of thermodynamic equilibrium often takes a very long time, thermodynamic cycles may give an incorrect result for the systems, if data do not regard the equilibrium state. Thermodynamically, the interaction between filler and polymer can be estimated from the heats of dissolution of filled and unfilled polymers.[5] The heat of dissolution consists of two values:

$$\Delta H_{\boldsymbol{s}} = \Delta H_g + \Delta H_l \qquad [4.17]$$

where ΔH_g is the heat of polymer transition from the metastable state having higher enthalpy to the equilibrium state of lower energy in solution, ΔH_l is the heat of interaction equilibrium of melt with solvent. For filled polymer, the value of ΔH_g, calculated per g of polymer, is not the same as for unfilled polymer because of difference in packing density, and it depends on the filler concentration. If this value, however, does not depend on filler amount, then the value of ΔH_l for filled polymer can easily be calculated by subtracting $\Delta H_g \approx$ const from the heat of dissolution ΔH_s, using Eq 3.1. It was established that with increasing filler concentration, φ, calculated values of isothermal heat effects of filled polymers $\Delta H'_l < 0$ monotonously decrease up to a definite value of φ, after which it remains the same. It means that the heat of interaction in the polymer-filler system reaches its limiting value, corresponding to the saturation of interaction at the interface with solid. The critical concentration, $\varphi_{crit,}$ depends on the molecular mass and conditions of production of filled polymer.

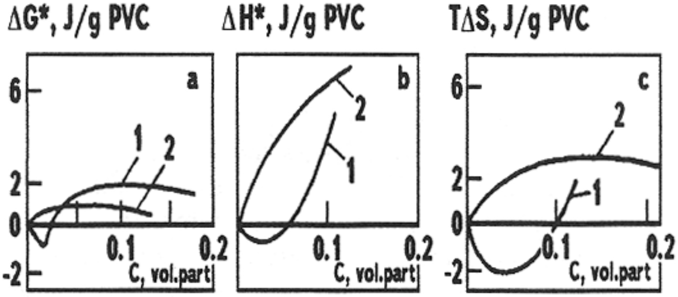

Figure 4.2. Dependence of free energy ΔG (a), enthalpy ΔH (b), and entropy TΔS on the filler content for poly(vinyl chloride) filled with fumed silica (1) and chalk (2).

Thermodynamic properties of filled melts can be found from the measurements of specific volumes of filled and unfilled specimens. Such investigation has been done for PS and PMMA melts containing fillers of various surface energy.[6-8] The calculation of thermodynamic functions can be performed based on the Hirai-Eiring theory modified by Smith.[9] According to the model, the melt at equilibrium may be considered as the saturated mixture of N_o molecules (segments) of volume, v_o, with N_h holes at volume, v_h, and energy, ε_h. The volume of the system is:

$$V = N_o v_o + N_h v_h \tag{4.18}$$

The change of outer conditions (temperature, T, and pressure, p) leads to an exponential decrease in the number of holes:

$$\frac{N_h v_h}{(N_o v_o)} = \frac{N_h}{(n v_o)} = \sigma^{-1}\exp\left[-\frac{(\varepsilon_h + p v_h)}{kT}\right] \tag{4.19}$$

where $n = v_o/v_h$, $\sigma = \exp(1 - n^{-1} - S_h/k)$, S_h is the change in entropy relative to hole formation. Taking $V_o = N_o v_o$, we obtain:

$$V = V_o\left\{1 + \sigma^{-1}\exp[-(\varepsilon_h + p v_h)/kT]\right\} \tag{4.20}$$

or after some transformations:

$$-\ln[(V - V_o)/V_o] = \ln\sigma + (\varepsilon_h + p v_h)/kT \tag{4.21}$$

This equation shows the linear dependence of the left side on 1/T and p can be found from the intercept and slope of the experimental curve of temperature dependence of the system volume, V, the parameters ε/K and $\ln\sigma$ of Eq 4.20 and values v_h/kT and $\ln\sigma + \varepsilon_h/kT$ of Eq 4.21. The parameters of Eq 4.20, found in this way, may be used to estimate the changes in enthalpy, H, entropy, S, and free energy, G, during the transition of polymer into a filled state. According to Smith,[9] ΔH is determined as:

$$\Delta H = N_h(\varepsilon_h + pv_h) \qquad [4.22]$$

which in conjunction with Eq 4.19 may be presented in the following form:

$$\Delta H = (v_o kT/v_h\sigma)\ x\ \exp(-x) \qquad [4.23]$$

where $x = (\varepsilon_h + pv_h)/kT$.

The absolute values of ΔH are changed with ε_h. The entropy changes are expressed as:

$$\Delta S = (v_o k/v_h\ \sigma)(1 + x)\ \exp(-x) \qquad [4.24]$$

and free energy changes as:

$$\Delta G = -v_o kT/v_h\sigma \qquad [4.25]$$

Substituting numerical data for various specimens into Eq 4.25, one can estimate the excess free energy during transition of polymer into filled state (or surface layer).

The difference between the values of the free energy of filled and unfilled polymer allows one to make some conclusions regarding the thermodynamic stability of the polymer in the presence of the filler. The formation of the surface polymer layer on a solid surface leading to its loosening has a significant influence also on the thermodynamics of polymer-solvent interaction (its dependence on the thickness of a film applied to a solid surface). Such estimation was done for filled poly (ethylene glycol adipate) and PS,[10] using inverse gas chromatography. Due to the peculiarities of the method, only a

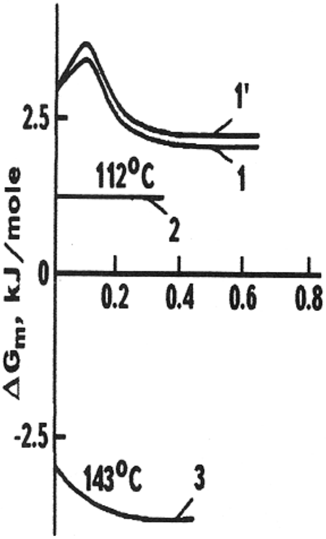

Figure 4.3. Dependence of ΔG on the filler content for annealed (1) and non-annealed (1') films of poly-(ethyleneglycol adipate), poly(ethylene-glycol) (2) and PS (3) (1 and 2 for heptane, 3-for toluene).

small amount of filler was used. Filled films were applied on the solid substrate.[11] Figure 4.3 shows the results of determination of the free energy of mixing of solvent with the polymer, ΔG. ΔG decreases with increase in filler content. The incorporation of filler leads to a loosening of the polymer, which eases the mixing of the polymer with the solvent. It must be noted that the value of ΔG is considerably influenced by annealing. For filled PS, annealed at 443K (above the temperature of transition to the viscous-flow state), there is some increase in its density, as follows from the value of the retention volume. However, the value of ΔG, for the annealed filled film, is lower, compared with non-annealed material. This observation indicates that annealing leads to compacting of the surface layer of the filled film at the interface: polymer-air. In fact, since, at T_g, the diffusion of the molecules of sorbate proceeds only to an insignificant depth of the film, the reduction in ΔG, at this temperature, is evidence of a compacting of the top layer at the interface with air. Simultaneously, the density of lower boundary layers remains lower than for the free filled films, as shown by the values of ΔG determined in the region of equilibrium adsorption, i.e., under conditions where the molecules of sorbate penetrate through the entire polymer film and consequently enter the boundary layer. Such marked compacting of the filled annealed film apparently indicates that the influence of the filler (or interface) extends to a considerable depth.

The same method was used[12] to establish the influence of thickness of the polymer stationary phase on the interaction parameters between polymer and solvent. It was found that the adsorption layers at the interface with a solid affect the thermodynamic quantities such as excess free energy, enthalpy, and entropy of mixing, calculated from the general expressions of gas-liquid chromatography. Also, the polymer-solvent interaction parameter, χ, has been determined as a function of the film thickness. It was shown that all thermodynamic functions depend on the thickness of the polymer film at the solid surface. Free energy of mixing is negative and it diminishes as film thickness decreases. According to these data, the solubility of polymer increases with a decrease in film thickness. This can be connected with the formation of an adsorption layer and its influence on more distant layers. As a result of adsorption interaction with the surface and restriction of molecular mobility, the density of packing near the surface diminishes more rapidly when the film thickness is smaller.

This leads to the increased solubility. The same conclusions have been obtained from the calculated values of the interaction parameter, χ, measured for PS films in the region of thicknesses of 200-600 nm, which diminishes with a decrease in the film thickness.

The analysis of the thermodynamics of the polymer reinforcement allows for a general conclusion. The formation of filled polymer, e.g., the transition of polymer, in the state of thin polymer layers at the interface with a solid, leads to a less stable state. During production of filled polymers, the system deviates from the state of thermodynamic equilibrium, and therefore filled polymers, as a rule, should be considered as non-equilibrium systems, due to the action of the surface on the equilibrium properties of macromolecules.

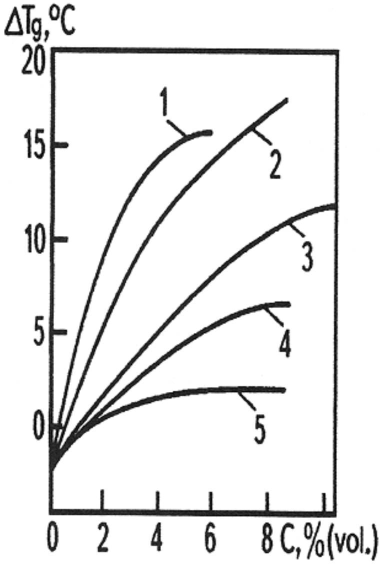

Figure 4.4. Dependence of the changes in T_g for PMMA vs. the fumed silica content, in measurements of T_g by various methods: 1-calorimetry, 2-dilatometry, 3-dynamic, 4-dielectric, 5-NMR.

4.2 GLASS TRANSITIONS IN FILLED POLYMERS

4.2.1 INFLUENCE OF FILLER ON THE GLASS TRANSITION OF FILLED POLYMERS

It is known that the glass transition temperature, T_g, corresponds to the temperature at which mobility of segments of the polymer begins to occur. Consequently, the adsorption and adhesion are to be reflected in T_g.

There is now a large amount of experimental data on the change in T_g of polymer under the influence of the solid surface. The comprehensive reviews were given earlier.[13,14] Therefore, there is no need to analyze all data and we confine ourselves only to describing the general picture. The data on the change in T_g of filled polymers have been obtained by various methods, including dilatometry, measurement of heat capacities, from dielectric and mechanical relaxation, NMR, RTL, etc. Each method has its own limitations and therefore the results of various methods do not always coincide. However, the general picture remains unchanged, namely, under the solid surface influence, the glass transition of a polymer shifts to the higher temperatures. For example, Figure 4.4 demonstrates the shift in T_g for PMMA filled with fumed silica, measured by various methods. While the general tendency is the same, the degree of the surface influence on glass transition depends on the method used. This effect is connected with varying frequency of action on the polymer by different methods. The effect is greatest when methods of low frequency are used (calorimetry, dilatometry). A great discrepancy was observed between the values of T_g for elastomers.[15] However, in the majority of cases with increasing filler content, T_g grows. The effect depends, at the same filler content, on specific properties of surface and conditions of production. Increase in T_g is determined by the nature of the filler surface and surface energy of a polymer (see Chapter 3). It is important that experimental data show that changes in glass transition temperature have a macroscopic character, i.e., are typical for the whole volume of filled polymer. Indeed, if the effects were to involve only the restrictions in molecular mobility in the surface layers, it would be impossible to detect any change in glass temperature.

It is known that processes taking place during glass transition are cooperative. Therefore, changes in T_g reflect the restrictions of mobility, not only those macromolecules which have direct contact with the surface, but molecules remote from the surface due to the relay-race mechanism and formation of various supermolecular structures near the surface. Aggregates are one example. At the same time, the increase in T_g with filler amount has, as a rule, some limits, which seem to correspond to the transition of all polymer molecules into the surface layer (see Chapter 3). Here the question may arise why we cannot distinguish between glass transitions in the surface layer and in polymer bulk not subjected to the action of the surface. The resolution of two possible maxima is a very rare case (as an example, see Figure 3.9). The reasons for a lack of resolution in most cases are discussed in Chapter 5.

The dependence of T_g on filler content may be expressed on the same basis of the changes in the properties of the polymer phase in the boundary layer in yet a different way.[16] Let the volume of polymer, which has been under the influence of the surface, be $v_p = V\varphi S\delta$, where V is the total volume of the system, φ is volume fraction of filler, S is specific surface, and δ is the thickness of the boundary layer. The whole polymer phase is under the influence of the filler when conditions are: $v_p = (1 - \varphi)V$ or $\varphi = 1/(1 + \delta)$. In spite of simplifications, the experimental data are satisfactorily expressed by the relationship:

$$T_g - T_{g,o} = \Delta T_{g,\infty}[1 - \exp(-B\varphi)] \qquad [4.26]$$

where $\Delta T_{g\infty}$ is the maximum shift in T_g and B is a constant. A simplified computation of the thickness, δ, leads to a value of 35-100Å.

4.2.2 THEORETICAL APPROACH TO GLASS TRANSITION PHENOMENA IN FILLED POLYMERS

The main difficulty in developing the theory of glass transition in filled polymer consists of insufficient understanding of the physical reasons that determine the long-range effect of surface on the properties of polymer. There are two glass transitions of surface layers and polymer in bulk, especially when the amount of the filler is low. The glass transitions in filled polymers are thus not only determined by the existence of an interphase but also by other factors. The traditional approach to the glass transition phenomenon consists of application of the concept of the iso-free volume.[17,18] This concept postulates that the fraction of free volume at T_g is constant for all polymers.

According to definition:

$$f_g = v_f/v_g = 1 - v_o/v_g \qquad [4.27]$$

where $v_f = v_g - v_o$ is a free volume, v_o and v_g are the values of occupied and real volume of liquid at T_g. Value v_o cannot be found experimentally. There are some methods of determination of f_g. In accordance with the model proposed by Simha and Boyer,[19] the following equations can be used as criteria for constancy of f_g:

$$f_{g,1} = \alpha_l T_g = 0.160 \qquad [4.28]$$

$$f_{g,2} = \Delta\alpha T_g = 0.113 \qquad [4.29]$$

where $\Delta\alpha = \alpha_l - \alpha_g$, α_l and α_g are the coefficients of thermal expansion above and below T_g. According to the "hole" model developed by Hirai-Eiring-Frenkel[20] the equilibrium value of a specific volume of liquid v_l is given by:

$$v_l = v_\infty[1 + \sigma^{-1}\exp(-x)] \qquad [4.30]$$

(see Eq 4.23). Here v_∞ is the value of v corresponding to the most dense packing, ε_h is the energy of hole formation, v_h is molar hole volume, σ is model parameter, and P is pressure. Substituting $v_\infty = v_o$ in Eq 4.27, we obtain value $f_{g,3}$.

It was shown[18] that, for filled and unfilled PMMA, the straight lines describing the dependence of v_g on T_g and v_β on T_β (where v_β and T_β are specific volume and temperature of the secondary transition) have an intercept at the point with coordinates v_∞ and T_∞. The last values are limiting values of the specific volume of a melt and temperature, at which, due to the high hydrostatic pressure, the segmental mobility is fully suppressed and free volume becomes zero. Using $v_\infty = v_o$ for Eq 4.27, one can find $f_{g,4}$.

In agreement with the Williams-Landell-Ferry (WLF) theory,[20] the translational mobility of macromolecular segments fully disappears, due to diminishing free volume which reaches zero at temperature $T_o < T_g$. For this theory, the following expression is valid:

$$f_{g,5} = (T_g - T_o)/B \qquad [4.31]$$

where B is a parameter of the Vogel-Tamman equation accounting for the temperature dependence of the Newtonian viscosity

$$\eta = A\exp([B/(T_g - T_o)] \qquad [4.32]$$

In Table 4.1, the values of f_g are given for various filled systems.[18]

The data presented in Table 4.1 demonstrate not only a sharp difference in values of f_g, depending on the method of calculation, but also varying magnitude for the same system having different filler concentrations. This fact may be related to changes in v_g and v_o during filler introduction.[21-23] Another reason may

Table 4.1: Calculated values of f_g for various amounts of filler

System	f_g	Filler amount, wt%					
		0	1	5	10	20	50
	$f_{g,1}$	0.237	0.211	0.194	-	0.239	0.959
PS+glass	$f_{g,2}$	0.115	0.093	0.091	-	0.152	0.151
	$f_{g,3}$	0.085	0.041	0.099	-	0.127	0.255
PMMA+glass	$f_{g,3}$	0.102	0.125	0.120	-	0.110	0.138
PMMA+Aerosil	$f_{g,4}$	0.124	-	0.138	0.158	0.192	-

be the appearance of structural defects, on the molecular or submolecular level, during filling.[7]

These results confirm the idea put forward previously[13,17] that the concept of the iso-free volume cannot be applied to filled polymers. Therefore, the empirical equations cannot be used as a basis to describe properties of filled polymers. The limitations of the iso-free volume concept may also be related to the fact that value f_g cannot be universal value, even for unfilled polymers, because it depends on molecular parameters of chains — specifically, on their flexibility.[24-26]

Another approach can still be taken to describe the glass transitions in filled polymers on the basis of a criterion of the constancy of excess entropy at T_g. In accordance with thermodynamic theory of glass transitions,[27] it is supposed that in polymers with flexible chains, the excess (in crystalline state) entropy of polymer liquid during its cooling monotonously diminishes to zero. The effect is due to the decrease in the relative amount of rotational isomers, having high energy, up to some critical minimum value at a hypothetical temperature of transition of the second order T_2. The temperature dependence of the excess entropy is described as:[28,29]

$$\Delta S_1 = \Delta S_m - \int_T^{T_m} \Delta C_p d\ln T = \int_{T_2}^{T} \Delta C_p d\ln T \qquad [4.33]$$

where ΔS_m is entropy of melting, $\Delta C_p = C_l - C_g$ heat capacities in the melt and glass, and T_m is a melting point. It is supposed[30] that the value of excess entropy, ΔS (calculated for single bond), which is frozen at T_g, should have a universal value for all polymers capable of vitrification. Neglecting the temperature dependence of ΔC_p, in the interval from T_g to T_2, and accepting that $T_2/T_g \le 1$, from Eq 4.33, one may obtain:

$$\Delta S_g = \Delta C_p \ln\left(\frac{T_g}{T_2}\right) = \text{const} \qquad [4.34]$$

The changes in molecular packing due to filling may influence the value of ΔC_p only through the value of C_l because the mobility in glassy state does not depend on packing.

In the majority of cases of filled polymer systems (especially filled with fine disperse active fillers such as fumed silica), the values of C_l and ΔC_p diminish with an increase in filler concentration.[18] Because the decrease in ΔC_p is accompanied, as a rule, by increasing T_g, from Eq 4.34 it follows that values of ΔS_g, for filled specimens are comparable to ΔS_g of pure polymer only when parameter T_2 remains constant or slightly decreases. Unfortunately, one cannot use the standard method of evaluating T_2 because of a lack of direct calorimetric measurements. This value, however, may be found from indirect data.

It was assumed[31-33] that the free volume and excess entropy of a liquid becomes zero at the same temperature, i.e., T_2 coincides with T_o from Eq 4.32. The measurements of the temperature dependence of Newtonian viscosity of melts in the system ethylene glycol-adipate-fumed silica have shown that introduction of 10 wt% of fumed silica leads to decreasing T_o from 175 to 155 K. Increasing the ratio of T_g/T_o, due to decrease of T_o, at constant T_g, is compensated by the decrease in ΔC_p. As a result, the calculated values of ΔS_g remain practically the same.[34]

It was also shown by Miller[35] that the value T_2 may be determined by extrapolation of a linear part of temperature dependence of $(\Delta S_l)^2$ to $\Delta S_l = 0$. Values of T_2 for PS-glass beads system, found from the temperature dependence of the calculated values of the excess entropy, decrease from 285 K for pure PS to 130 K at filler concentration of 50 wt%. Taking into account that for this system, T_g and

ΔC_p are constant, then, from Eq 4.34, the conclusion can be drawn that value of ΔS_g increases due to transition from unfilled to filled material. At the same time, for the system PMMA-glass beads,[24] constant values of T_2 were obtained which, together with $\Delta C_p \approx$ const, indicates approximate constancy of ΔS_g for all samples. From this discussion, it follows that the application of the iso-entropy concept to describe the glass transitions in filled polymers needs additional development.

Let us analyze another criterion of glass transition, namely, criterion of the viscosity constancy. It is known that with decreasing temperature, the shear viscosity of Newtonian liquid, η, monotonously increases, reaching values of the order of 10^{-10} Pas in the region of the glassy state. According to the empirical criterion proposed by Tamman,[36] the transition of a liquid into solid glassy state proceeds at the temperature T_g, at which the viscosity reaches its universal magnitude of $\eta = 10^{12}$ Pas. For unfilled polymers, this criterion meets experimental data. However, there is no data till now on viscosity of filled polymers near glass transition temperature, and therefore to investigate the applicability of the Tamman criterion to filled systems one has to use indirect data. In some works, the systematic increase of the viscosity of melts of filled polymers at temperatures $T >> T_g$ was found.[37-39] The analysis of such data allows for the following conclusion to be drawn: If the condition $\eta = \text{const} = 10^{12}$ Pas is valid for filled polymers, then introduction of fillers should lead to the sharp increase in T_g. The experimental data confirm this statement. However, increasing amount of filler also leads to the change of flow from Newtonian behavior, due to elimination of structures formed by the filler particles in viscous media (see Chapter 5). Therefore, the application of the Tamman criterion needs the following conditions to be met:

- measurements should be done in the stress range which corresponds to the Newtonian behavior of a filled melt
- temperature range of viscosity should be rather broad to find reliable data from Eq 4.32.

Experimental data collected[18] qualitatively meet the concept of the viscosity constancy at T_g for filled polymers.

4.2.3 STRUCTURAL RELAXATION IN FILLED POLYMERS NEAR T_g

For theoretical description of the behavior of filled polymer it is important to analyze the processes of structural relaxations near T_g. Some experimental[13] data concerning the volume relaxation in filled polymers were presented. These data show that the average relaxation time increases with increasing amount of filler at constant temperature. This is very significant for selecting conditions of processing of filled polymers, since optimum properties of material depend on the schedule of its processing (temperature, time, pressure), bound to differ from that for unfilled polymer. However, in order to understand the mechanism of the processes taking place at the polymer-filler interface it is desirable to compare the relaxation times, not at identical temperatures, but at temperatures at equal distance from the glass transition temperature (considering that it increases with filling). In such comparison, the relaxation times for filled systems are shorter.

Two effects should be taken into account to explain these results. The rise in T_g as a result of restriction of molecular mobility leads to the increase in the relaxation time, whereas diminishing packing density, accompanied by an increase in free volume, causes the shortening of the relaxation times. The volume relaxation is described by the relationship:

$$V = (v - v_\infty)/(v_o - v_\infty) = \exp[-(t - t_o)\tau] \qquad [4.35]$$

where v is specific volume at time t, v_∞ is equilibrium volume, t is current time, τ is average relaxation time. For filled polymers, experimental dependence of lnV on t is usually nonlinear. It is connected with the existence of the relaxation spectrum. The latter may be formally taken into account using the empirical relation:[40]

$$V = \exp[-(t - t_o)/\tau]^\beta \qquad [4.36]$$

where $0 < \beta < 1$ is a parameter characterizing the width of the relaxation spectrum (at $\beta = 1$ we arrive at Eq 4.35).The relaxation spectra of filled polymers are discussed in Chapter 5.

The influence of the fillers on the relaxation, during transition from glassy to liquid (rubber-like) state, may be estimated from analysis of the relaxation enthalpy.[41-43] Theoretical basis for the analysis is as follows: It is supposed that during cooling of melt at equilibrium from $T_1 >> T_g$ at the constant rate ($g = dT/dt$), there is a certain point at which the rate of structural rearrangements in the melt, determined by the heat mobility of the chain segments, is lower than g and further cooling leads to larger deviations of the "instant" melt structure from the equilibrium state. In other words, at rather low temperature, $T_2 < T_g$, the structure or a set of structures is frozen in a specimen which would have had equilibrium properties corresponding to some conditional temperature $T_2 < T_f \approx T_g$.[44] Temperature dependence of the structural parameter, T_f, is determined from the equation:[45,46]

$$T_f(T) = T_1 + \int_{T_1}^{T} \left\{ 1 - \exp\left[-\left(\frac{\int_{T'}^{T} dt''}{g\tau} \right)^{\beta} \right] \right\} dT' \qquad [4.37]$$

where

$$\tau = \tau_o \exp\{(X\Delta E)/RT + [(1 - X)\Delta E/(RT_2)]\} \qquad [4.38]$$

τ is the relaxation time, ΔE is activation energy, $0 < X < 1$ is the parameter of non-linearity of the relaxation processes, $0 < \beta < 1$ is phenomenological measure of the width of the spectrum of relaxation time, τ_o is coefficient, and dT' and dT'' are the magnitudes of increments determined by the necessary correctness of the numerical solution. Parameters of Eq 4.35 are determined by any structure-sensitive property of amorphous polymer during its cooling, heating or transition through the glass transition temperature point. If we choose as a phenomenological characteristic of the structural state the value of the relative enthalpy, ΔH, the value T_f at T_2 can be found from the expression:

$$\Delta H(T_2) = \Delta H(T_f) - \int_{T_2}^{T_f} \left(\frac{d\Delta H}{dT} \right) g dT \qquad [4.39]$$

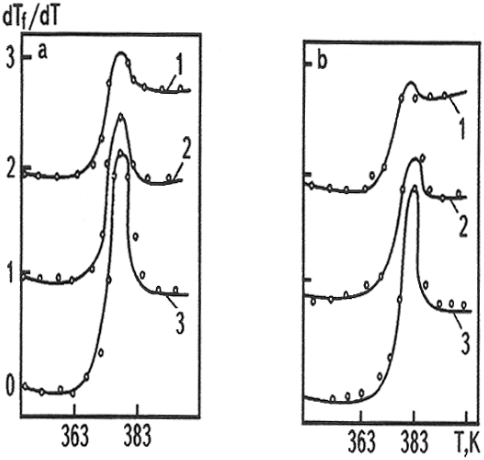

Figure 4.5. Calculated (solid lines) and experimental (points) temperature dependencies of the reduced heat capacity dT_f/dT for PS at heating rate 16 grad/min after preliminary cooling with various rates (grad/min) 1-16, 2-4, 3-0.5.

which, taking into account the standard definition of the heat capacity, $C = d\Delta H / dT$, may be transformed to:

$$\int_{T_1}^{T_f} (C_1 - C_g) dT' = \int_{T_1}^{T_2} (C - C_g) dT \qquad [4.40]$$

The differentiation of the last equation gives the temperature coefficient, T_f:

$$(dT_f/dT)_T = (C - C_g)_T/(C_1 - C_g)_{T_f} \qquad [4.41]$$

where C is the relaxation part of the heat capacity in the glass transition interval. The experimental study of the relaxation enthalpy[41-43] for PS having high content of filler allowed us to establish the kinetic parameters of the relaxation enthalpy for PS filled with fumed silica (0-35 wt%). Figure 4.5 shows experimental, and calculated according to Eq 4.37, temperature dependence of dT_f/dT (so-called reduced heat capacity; Eq 4.41). Good agreement between theory and experiment is pertinent. The numerical values of the parameter

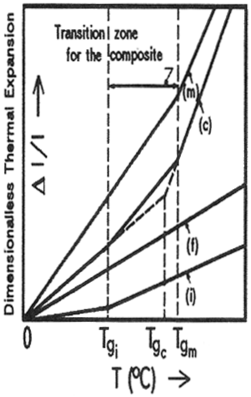

Figure 4.6. Scheme of volume changes for composite (c), filler (f), transition interphase layer (i) and matrix (m). [Adapted by permission from P. S. Theocaris, *Adv. Polym. Sci.*, **66**, 156 (1985)]

$\ln\tau_o$ proportionally changes $\Delta E/R$, and inversely proportionally to parameter β. Incorporation of fumed silica is accompanied by a regular growth of both $\Delta E/R$ and $\ln\tau_o$ and decrease of X and β. Diminishing b may be explained by a broadening of the relaxation spectrum of filled PS, due to increasing microheterogeneity as a result of the formation of the surface layers. At the same time, the increase in E/R and decrease of X show the retardation of the structural relaxation in boundary layers. This is confirmed by the correlation between parameters X and β, on one hand, and parameters found from independent experiments on the other. It is interesting that the transition of all polymer into the surface layers does not suppress segmental mobility and manifests itself only in the change of the kinetic parameters of vitrification. It is possible that this effect is related to enlargement of the border layer (the order of inertia radius of the coils, which is larger as compared with the size of segment). Theocaris[47,48] proposed another approach for determination of the glass transition temperature in filled polymers. Its advantage is in the introduction to calculations of the characteristics of the transition layer between filler and matrix. This method is based on determination of three thermal expansion coefficients, which correspond to matrix, transition layer, and filler. Correspondingly, the changes in these coefficients are analyzed (Figure 4.6).

Let the volume fraction of filler be φ_f, transition layer - φ_i and matrix - φ_m which have the corresponding expansion coefficients: α_f, α_i, and α_m. The transition region has its own glass transition temperature, T_{gi}. In accordance with Figure 4.6, the expansion coefficient of the filled polymer at $T < T_g$ is given by:

$$\alpha_{c1} = \varphi_f\alpha_f + \varphi_m\alpha_{m1} + \varphi_i\alpha_{i1} \qquad [4.42]$$

For $T_{gi} < T < T_{gm}$

$$\alpha_{c2} = \varphi_f \alpha_f + \varphi_m \alpha_{m1} + \varphi_i \alpha_{i2} \quad [4.43]$$

and for $T > T_m$

$$\alpha_{c3} = \varphi_f \alpha_f + \varphi_m \alpha_{m2} + \varphi_i \alpha_{i2} \quad [4.44]$$

The glass transition temperature of filled polymers corresponds to the intersection of the first and the last part of the curve (Figure 4.6), and can be calculated from:

$$T_{gc} = \frac{\varphi_i (\alpha_{i2} - \alpha_{i1}) T_{gi} + \varphi_m (\alpha_{m2} - \alpha_{m1}) T_{gm}}{\varphi_i (\alpha_{i2} - \alpha_{i1}) + \varphi_m (\alpha_{m2} - \alpha_{m1})} \quad [4.45]$$

This equation correlates T_{gc} with the thermal properties of matrix and transition layer.

4.3 REINFORCEMENT OF CRYSTALLINE POLYMERS

Crystalline polymers have some advantages, compared with amorphous polymers, because of their two-phase structure. This structure can be represented as a low-modulus continuous phase in which high-modulus crystallites are uniformly distributed.[49] Macroscopic properties of crystalline polymers are determined by the relative content of the crystalline phase (degree of crystallinity, X).[49] Similar to the degree of crystallinity, the conformational state of segments in tie chains, connecting amorphous and crystalline regions, plays a very important role. It is evident that any change in properties of crystalline polymers is connected with either the degree of crystallinity or the conformational state of tie segments. Introduction of fillers into crystalline polymers influences both the structure and physical and mechanical properties of crystalline polymers. These processes were discussed in detail by Solomko.[50] At the same time, the general physico-chemical principles of reinforcement of crystalline polymers are the same as for amorphous polymers, and based on the same approaches.

The interaction of polymer chains with a filler surface, which leads to reduction in chain mobility, must alter the kinetics of crystallization. Fillers may also influence the processes of nucleation in crystallization. The effectiveness of the nucleation is determined by the nature of both polymer and filler. Investigations of the influence of small additions of salts of organic acids, used as artificial nucleating agents, on crystallization shows[51-53] that they lead to changes in the supermolecular structure of polymer because changes of concentration of nucleating agents change conditions of crystallization and the process takes place at a higher rate. The mechanism of action of additives is as follows: on the surface of the solid particles of the nucleating agent there are formed ordered regions of polymer as a result of adsorption, acting as centers of crystallization. These ordered regions are maintained on the surface, even at above melting temperatures, when homogeneous centers of crystallization within its bulk are completely broken up. With sufficiently high concentration of additives, the number of heterogeneous centers on their surface considerably exceeds the number of homogeneous centers which are formed in the bulk in the course of crystallization. An increase in the number of centers of crystallization leads to an increase in the overall rate of crystallization and a reduction in size of the spherulites. Artificial nucleating agents, even at concentration of 0.2 wt%, alter the rheological properties of polymer melts, which is linked with their structure-forming action even in the melt.

By choosing substances of different nature as artificial nucleating agents and varying their concentration and particle size, it is possible to create polymer melts having high viscosity and resistance to temperature. Consequently, in the case of crystallizing polymers, the particles of filler are likewise centers of crystallization and structure-formation, just as in amorphous polymers, thus having a significant influence on the type of structure formed.

4.3.1 KINETICS OF CRYSTALLIZATION IN THE FILLER PRESENCE

The dependence of the equilibrium conversion degree, α, during crystallization from melt is described by the Avrami-Erofeev equation:

$$\alpha(t) = 1 - \exp(-K_p t^n) \qquad [4.46]$$

where K_p is the rate, and n is a geometric constant characterizing the nature of the nuclei and the type of structures formed. Values of K_p and n are determined from the crystallization isotherms of filled and unfilled polymer in coordinates $\log[-\log(1 - \alpha)]$ vs log t, whereas the half-periods of crystallization, t, may be found from semi-logarithmic dependence of α on log t. As a rule, the final stages of crystallization are characterized by the deviation from Eq 4.46. This deviation begins earlier for filled systems. For filled systems, the constant n is not an integer, being between 2.24 and 2.72. Deviations from the Avrami-Erofeev equation had been already observed even for unfilled polymers, and are due to various causes, namely: the possibility of occurrence of simultaneous or consecutive crystallization according to different mechanisms. It may be simultaneous growth of crystalline structures on the nuclei of various type or secondary crystallization, during which the structures, formed by primary crystallization, become more perfect and the total crystallinity degree increases. Since the value n is usually determined from the initial linear sections of crystallization isotherms, when the secondary crystallization is absent, it is most probable that a fractional value of n is brought about mainly by simultaneous growth of crystalline structures on nuclei of different type. They may be polymeric aggregates of fluctuating character, filler surface or micro-ordered regions, formed close to the polymer-filler interface. Deviations from straight-line dependence of the isotherms of crystallization of filled polymers are more evident than for unfilled polymers,[54-58] and they begin at lower degrees of crystallization. This may be brought about by the fact that the contact of the growing crystalline structures with each other, up to which stage the process is described by the Avrami-Erofeev equation, takes place at a lower degree of conversion because of the presence of filler. Filler is responsible for formation of a larger number of nuclei of crystallization, which brings about the formation of a larger number of crystallites, which rapidly fill the entire volume of the crystallizing polymer. Naturally, further increase in crystallinity is due to the perfecting of the primary structures. This process is no longer described by the Eq 4.46.

The above remarks are also confirmed by the fact that these deviations become more evident with a lowering of the temperature of crystallization. The lowering is accompanied, in turn, by an increase in the number of nuclei of crystallization.

The crystallization of polymer in the presence of fillers is influenced by two main factors:

- the interaction of polymer with filler, changing configuration of adsorbed segments of chains, contributing to the onset of crystallization
- the actual presence of filler in the polymer melt, which raises the viscosity and hinders crystallization.

These factors are predetermined by the nature of the filler surface and filler concentration. With low filler content, the rate of crystallization rises because filler particles act as nuclei of crystallization. With the rise of filler concentration, this process is hindered, and the rise in the viscosity of the system becomes the predominant factor. Thus, the kinetics of crystallization of filled polymers may only be described by Eq 4.46 in initial stages, with a fractional value of n. The rate of crystallization passes through a maximum at a low degree of filling, and then gradually becomes lower than the rate of crystallization of unfilled polymer as the amount of filler increases. In contrast to crystallization from melt, there is no considerable difference in the values of α, at which deviation from the Avrami-Erofeev equations begins (0.55-0.8), in crystallization from the rubber-like state in the presence of filler. This is explained by the fact that in crystallization from a filled melt, the formation of boundary regions of polymer with reduced mobility is equivalent to crystallization of unfilled polymer from the rubber-like state. In this case, the changes in n take place as a result of growth of crystalline structures on nuclei of a different type. It must be noted that the rate of crystallization, whether of unfilled or filled polymer, is higher in crystallization from the melt. Thus, the filler has a specific effect on the process of crystallization. Comparison of the constants n in crystallization from melt or from the rubber-like state indicates that the addition of even a small amount of filler to polymer leads to an action equivalent to transformation of the system from a melt of a rubber-like state, and this affects the mechanism of crystallization and its kinetic parameters. In accordance with the theory of phase conversion,[49] the overall rate of crystallization, G_{cryst}, at temperature, T, is expressed by the following equation:

$$G_{cryst} = G_o \exp\left(\frac{-\Delta G}{kT}\right)\exp\left(\frac{-\Delta E}{kT}\right) \qquad [4.47]$$

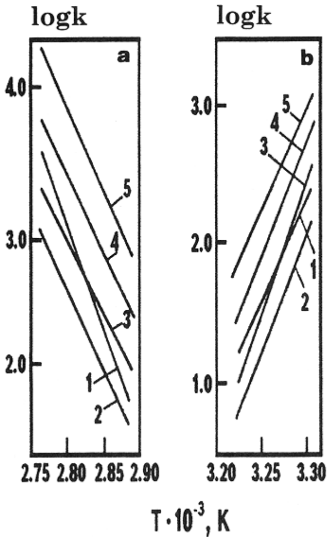

Figure 4.7. Dependence of logk on temperature of crystallization from the melt (a) or from the rubber-like state (b) Fumed silica content: 1-0%, 2-0.5%, 3-1.0%, 4-5%, 5-10% (by mass).

where G_o is for exponential member, exp(-ΔG/kT) and exp(-ΔE/kT) are the probabilities of the formation of a stable nuclei of crystallization and molecular transfer through the liquid-crystal interface, respectively, ΔG is the change in free energy during the formation of a nuclei of a critical size, and ΔE is activation energy of transfer.

From this equation, it is seen that the overall rate of crystallization from the melt may be regulated by introducing even a small amount of filler, if any parameters of Eqs 4.46 and 4.47 will be changed by this incorporation. The nucleating role of filler manifests itself either in increasing concentration of nuclei or in decreasing energetic barrier of nucleation due to the decrease in the interfacial energy at the polymer-filler interface. If the mechanism of crystallization is not changed with changing temperature, then the dependence of $\log G_{cryst}$ on log1/T will be a straight line from which the sum (ΔG + ΔE) may be calculated.

Figure 4.7 shows the dependence of the rate constant of crystallization of polyurethane on the temperature of crystallization from melt and rubber-like state. This dependence takes the form of straight lines, but the slope at low or high degrees of supercooling differs in sign. This is explained by the fact that the mechanism of crystallization from melt in the neighborhood of the melting point is determined mainly by the term ΔG/kT, and accordingly, the temperature coefficient of the overall rate of crystallization is negative. On crystallization from the rubber-like state, the processes of diffusion through the interface becomes predominant, i.e., a positive value of temperature coefficient is determined by the term ΔE/kT. Figure 4.8 shows plots of the dependence of (ΔG + ΔE) on the filler content (fumed silica) on crystallization from melt and from rubber-like

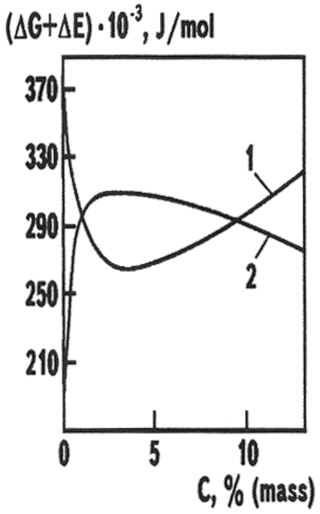

Figure 4.8. Dependence of ($\Delta G + \Delta E$) on fumed silica content in crystallization from the melt (1) or from the rubber-like state (2).

state. Bearing in mind that in the region of low ΔT, the crystallization is controlled by nucleation, it may be considered that the result given in Figure 4.8 indicates a reduction in the value of ΔG, necessary for the formation of a nucleus of a critical size. According to the existing theories of crystallization,[49,59] ΔG is determined by the equation:

$$\Delta G = \frac{4b_o \sigma \sigma_e T_m^o}{k\Delta H_m \Delta T T_{crit}} \qquad [4.48]$$

where σ and σ_e are, respectively, the free energy of the side and end faces of the crystallite, T_m^o is equilibrium melting point, $\Delta T = T_m^o - T_{crit}$, ΔH is the enthalpy of melting, b_o is the height of the surface nucleus. It may be reckoned that σ_e, T_m^o, ΔH and b_o do not depend on the presence of a solid phase in the system. Consequently, the reduction in ΔG with the addition of a filler to melt must be attributed to reduction in σ (for identical values of ΔT). The experimental results meet theoretical predictions. As Figure 4.8 shows, on crystallization from the rubber-like state in the neighborhood of T_g (in contrast with the case described above) the values of $(\Delta G + \Delta E)$ initially increase and then remain practically unchanged. In our opinion, this is explained by an increase in the activation energy of diffusion of chain segments in the melt, ΔE, as a consequence of raising the viscosity of the system. It is known that the value of ΔE may be expressed, with sufficient accuracy, by the expression:[60]

$$\Delta E = \frac{4120}{k(51.6 + T - T_g)} \qquad [4.49]$$

Thus the increase in $(\Delta G + \Delta E)$ with the addition of filler may be explained by raising the glass transition temperature of polymer. This conclusion is in line with the ideas about the influence of filler on the glass transitions of amorphous polymers. The constant value observed for ($\Delta G + \Delta E$) when changing the content of filler correlates well with the absence of change in the activation energy of viscous flow of melts of filled polymers with a rise in filler content. It must be noted that the values of ($\Delta G + \Delta E$) on crystallization from melt and from rubber-like state differ considerably for unfilled polymer, whereas in filled systems they are approximately identical (Figure 4.8).

Investigation on the influence of the nature of the surface of unmodified (fumed silica with free OH-groups on the surface) and modified (with dimethyl dichlorosilane with no OH groups on the surface) fillers shows that the degree of crystallization is higher in the case of unmodified fumed silica because of heterogeneous nucleation. The energy of interaction of polymer with a polar surface of filler is higher than with a non-polar, which facilitates the transfer of macromolecules into surface layers and formation of micro-ordered regions capable of acting as heterogeneous nuclei of crystallization. Introducing small amounts of filler into polymer with flexible chains may decrease the rate of the formation of the crystalline phase because of the increase in activation energy of transfer through the liquid-crystal interface. This effect is determined by the change in melt microstructure near the interface. The effect depends on the amount of the filler, i.e., on the fraction of the surface layers in the system. The influence of fillers on the crystallization of oligomers was also studied.[61,62]

4.3.2 CRYSTALLIZATION IN THIN LAYERS ON THE SURFACE

One of the most characteristic features of structural changes in the surface layers of crystallizing polymers is the transcrystalline morphology of the thin layers on the surface - distinct from the spherulitic morphology in the bulk.[63] For transcrystalline morphology, the appearance of column-like structures, oriented along the normal to the interface and extending into the bulk up to the distances $(10\text{-}20)\times10^{-6}$ m, is typical. The formation of transcrystalline layer is determined by higher concentration and higher activity of heterogeneous nuclei at the surface as compared with bulk.[49] When the melt is supercooled to the crystallization temperature, a great number of the centers of crystallization are formed, initiating the growth of half-spherulites, as the front of crystallization propagates from the surface to the depth of melt. Transcrystalline growth ends on the front of column-like crystals moving from the surface with the front of spherulite growth in the bulk. The thickness of the transcrystalline layer is determined by the ratio of the number of heterogeneous centers of crystallization at the surface and in the bulk.

The transcrystalline morphology is a result of the epitaxial growth and depends on the surface structure. It was established,[64-66] for transcrystalline structures in polyurethanes, that the action of the surface extends to tens of microns. The effect of transcrystallization is very important for reinforcement, as shown for transcrystallization of polypropylene in the presence of many synthetic fibres.[67] The formation of a transcrystalline interphase in fiber-reinforced polypropylene depends on the type of fiber, the isothermal crystallization temperature, and polymer molecular mass. The restriction of the front of spherulite growth by other interfaces (e.g., other filler particles) is of a great importance for reinforcement of crystallizing polymers. The diminishing of effective thickness of the interlayer between two particles, <L>, up to the values lower than the spherulite size ($\sim 5.10^{-6}$ m), leads to the regular decrease of the rate of the bulk crystallization, G_{cryst}, at the same supercooling ΔT.[68] For spherulitic crystallization, the rate of bulk crystallization, G_{cryst}, is determined from the equation:

$$G_{cryst} = \text{const}\, S_R v_R N_R \qquad [4.50]$$

where S_R is the surface of spherulite, v_R is the rate of the radial growth of spherulite, and N_R is the number of spherulites in a volume unit. In the presence of fillers, the decrease in the rate of bulk crystallization is connected either with N_R or with S_R. The most probable is the change of S_R with a decrease in the thickness of the polymer interlayer. A transition should be observed from three-dimensional to two-dimensional crystallization, according to the spherulitic mechanism. This effect manifests itself in a decrease of contribution of the value S_R from $S_R = 4\pi R^2$ to $S_R = 2\pi RD$, where R is radius of a disk of a growing crystal and D is its thickness. At condition $D \sim \langle L \rangle$, the linear decrease in G_{cryst}, proportional to <L> should be observed. It was proven for crystallization of polycaproamide in the presence of 83 % bm of glass spheres. However, with decrease in the interlayer thickness, not only does the rate of bulk crystallization diminish but also the spherulitic crystallization, G_R.[69-71] These effects have been observed for many polymers of different chemical nature on supports varying in the phase state and surface energy. It was established that the phase state of the support has no influence on the spherulitic growth rate, whereas diminishing

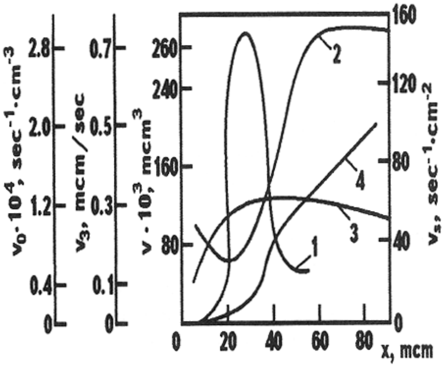

Figure 4.9. Influence of the thickness of interlayer of polypropylene between two glass surfaces on the volume of the spherulites v (1), the rate of nucleation v_o (2), the rate of linear growth v_3 per unit of bulk (3) or per unit of surface, v_s (4).

the interlayer thickness below a critical value (~10^{-6} m) leads to the decrease of G_R.[61] At the thickness of the interlayer <L> < 1×10^{-6} m, the full suppression of crystallization was observed for some polymers.[69]

The long-range influence of the surface on crystallization, which determines the thickness of the surface layers of crystalline polymers, is comparable with the spherulite sizes (5-10)$\times10^{-6}$ m. At a rather high amount of filler, when the distance between filler particles is lower than the spherulite size, the polymer is subjected to surface effects. In this case, the structure and properties of polymer in the surface layer must depend on the distance from the surface. In this respect, one more level of microheterogeneity of the surface layers arises, due to the influence of the surface on crystalline structure.

Let us analyze the influence of the surface on the inhibition of crystallization in the surface layers.[69-72] The study was conducted on the influence of the thickness of a polymer interlayer between two glass surfaces on crystallization for gutta percha, isotactic polypropylene, and cellulose tribenzoate. Figure 4.9 shows the data for PP. The character of the curve, indicating the influence of the thickness of layer on the rate of nucleation, is explained by the fact that the figure gives the sum of rates of nuclei formation at the interface and in the bulk. At a low thickness range, the nucleation on the surface is predominant; increasing the thickness of the interlayer leads to a more rapid increase in volume of spherulites than in the number of nuclei, and thus the curve turns downwards.

The minimum on curve 2 corresponds to the thickness at which the contribution of nucleation in the bulk to the overall rate of nucleation on the surface and in the bulk begins to increase. At sufficiently great thicknesses of the film, the nucleation in bulk begins to play a more important role than the nucleation on the surface, and the number of nuclei in the film increases proportional to the thickness of the film in the same way as the volume of the crystalline phase. This means that the rate of spherulite growth reckoned per surface unit, G_R, becomes independent of thickness. This explanation is confirmed by the shape of curve 4, which shows dependence of the nucleation rate, reckoned per unit of surface, on film thickness. The nucleation rate is practically independent of thickness up to a certain thickness which corresponds to the minimum on curve 2, and then the slope of curve 4 increases sharply. Accordingly, the dependence of the volume of spherulites on film thickness is of extreme character in the range of thicknesses at which the main part is played by crystallization in the surface layer. Reduction in the interlayer thickness of polypropylene, due to increasing amount of filler, has the same influence on the crystallization kinetics as does reduction in thickness of film between two glass surfaces.[72] At a particular concentration of filler, corresponding to a very thin interlayer of polymer, it is possible to arrive at conditions under which structure formation in a filled system is no longer observable under the optical microscope. This limiting interlayer has a thickness of the order of $0.3\text{-}2\times10^{-6}$ m.

The diameter of polypropylene spherulites (at low thickness, they are in the shape of discs) shows an extreme dependence on the thickness of polymer interlayer. With increase in thickness, the diameter of the spherulites increases to a maximum, then decreases and finally ceases to depend on thickness. This dependence is governed by the influence of a solid surface (glass) which holds back the growth of nuclei of crystallization in the adjacent layer of polymer. In isothermal crystallization of polypropylene and other polymers in layers of thickness 1 to 70×10^{-6} m, on substrates differing in surface energy and phase state, it was found that the surface energy has the main influence on the inhibition of spherulites growth.[71,72] Polymeric substrates do not influence the rate of linear growth of spherulites, but glass inhibits the process. Metal alloys in crystalline or liquid state slow down the growth in films of thinner than 20×10^{-6} m. It is interesting that at low film thickness, the dependence of spherulite growth

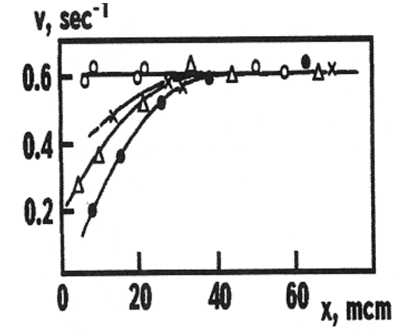

Figure 4.10. Dependence of the rate of linear growth of spherulites in polypropylene on the thickness of film on a surface of NaCl: o-(100) plane, x-(110) plane, ●-(111) plane, Δ-(100) plane of CaF_2.

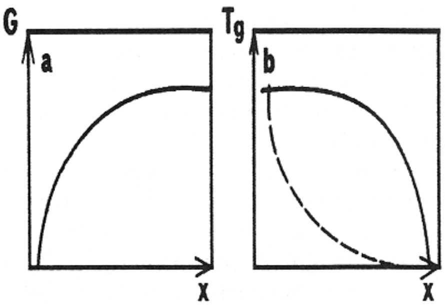

Figure 4.11. Schematic representation of the dependence of the crystallization rate, G, (a), glass temperature, T_g, (b), and on the interlayer thickness, x.

rate varies for different crystallographic planes (Figure 4.10). The rate of growth only decreases for substrates with a high surface free energy. The higher the free energy, the more marked this dependence becomes. The inhibition of polymer crystallization in the presence of filler may be explained by distortion in the ordering of surface layers.

All observations described above can be explained on the basis of the concept of reduction in molecular mobility and packing density in the surface layers. Strong adsorption interaction between polymer and solid surface slows down crystallization, whereas weak interaction has no influence on crystallization; then moderate interaction leads to the surface acting as a center of nuclei formation. These effects can be explained using Eq 4.47.[73] Studying the rate of spherulitic crystallization, G_R, of a linear polymer in a thin interlayer between two solid surfaces allowed us to establish that the surfaces with low surface energy have no influence on G_R in the range of thicknesses of $d(1\text{-}70)^{-6}\times 10$ m, whereas for high surface energy, at $d < (25\text{-}30)\times 10^{-6}$, G_R begins regularly decrease with decreasing thickness, as presented in Figure 4.11.

Based on Eq 4.47, the decrease of crystallization rate, G_R, with film thickness, d, decreasing cannot be compensated by an increase in contribution of the term (-$\Delta E/kT$), due to the increase in the glass transition temperature, T_g. It would require a larger increase of T_g with diminishing d (dotted line, Figure 4.11b). Usually, values of T_g increase sharply at high d and then stay almost constant (solid curve, Figure 4.11b).

It is evident that the change in G_R along with the change in the film thickness, d, is determined by the dependence of free energy of nucleation, ΔF, and the interlayer thickness, which is $\Delta G = Z_m/(\Delta g)^m$. Here Z_m is an energetic term, $\Delta g = \Delta S_m \Delta T$, $\Delta T = T_m - T$, T_m and S_m are melting point and enthalpy of melting, m is a constant. The increase in ΔG, required to diminish G_R at $\Delta T = \text{const}$ cannot be explained from the traditional point of view according to which Z_m can either decrease for good wetting of the solid by nuclei, or be unchanged when there is no wetting.[49] It is evident that the quantitative description of the decrease in G_R at small thicknesses of interlayers needs another approach.

The kinetics of the isothermal crystallization of polyamide-6 was investigated[68] in the presence of fumed silica. The experimental data allowed us to formulate the hypothesis about the similarity of phase transitions proceeding with decrease in volume in filled melts, on one hand, and solid aggregate state in some metal systems, on the other. The competition between moving force of crystallization and hindering phase transition by capillary forces, arising between solid surfaces due to the their wetting by polymer melt, leads to the dramatic growth of inner stresses in polymer interlayers.[74] Under their action, the nuclei of crystallization acquire the shape of thin discs. In this case, the energetic barrier of nucleation may be expressed as:[63]

$$\Delta F = Z_4/(\Delta g)^4 \qquad [4.51]$$

where $Z_4 = C_4 A^2(\sigma)$, $C_4 = 32\pi/3$ is a geometric constant, A is the density of the deformation energy of the lattice at the interface, and σ is the interfacial energy. Assuming $A \approx \Delta P$ (where $\Delta P = 2\gamma_m/r$ is capillary pressure, γ_m is the surface tension of the melt at the interface with air, and r is the radius of curvature of meniscus), and $r \approx d$, for the case under consideration we have:

$$Z_4 = C_4(2\gamma_m/d)^3(\sigma)^3 \qquad [4.52]$$

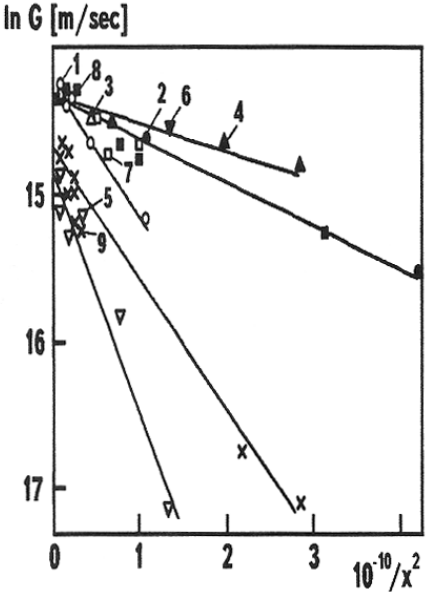

Figure 4.12. Dependence of lgG on $10^{-10}/x^2$ for polypropylene on various supports: 1-NaCl, plane (111), 2-solid alloy 1, 3-solid alloy 2, 4-NaCl, plane (110), 5-Cu, 6-CaF_2, 7- liquid alloy 1, 8-liquid alloy 2, 9-glass.

Thus, if our consideration is valid and dependence of G_R and d are determined only by the proposed mechanism, at constant values of G_R and ΔE, then the dependence of $\ln G_R$ on 1/d should be a straight line from which values of $\ln G_R$, corresponding to $d \therefore \chi 4D$ (intercept on ordinate axis) and $N = C_4(2\gamma_m)^2(\sigma)/(\Delta g)^3 kT$ may be found. Indeed, the dependence of the rate of spherulitic crystallization for gutta-percha and isotactic polypropylene on the interlayer thickness is linear.[75]

The same approach may be applied to the case of crystallization of a thin film in contact with the surface of high energy only from one side (Figure 4.12). The polymer volume in direct proximity to the surface (surface layers), does not change markedly with decreasing temperature (ΔT), due to a great difference between coefficients of thermal expansion of polymer and solid. At the same time, stretching stresses appear ("negative" hydrostatic pressure) which prevent a change of volume of surface layers during crystallization (analogous to the influence of the negative capillary pressure on crystallization between two surfaces). This effect increases with film thickness decrease, due to the increasing contribution of the surface layers, accounted for in Eq 4.52. Figure 4.12 presents the dependence of $\ln G_R$ on 1/d for isotactic polypropylene on the supports of varying chemical nature.[70,71] The slopes of relationships depend on the surface energy of the support. The same results have been obtained for polyoxypropylene and polyoxymethylene.

Still another course is observed for crystallization which proceeds with the folding of chains.[63] The investigation of kinetics of isothermal and non-isothermal crystallization of polycaproamide in the presence of fumed silica[76] has shown that the decreasing thickness of the polymer interlayer, $\langle L \rangle$, up to the values comparable with diameter of unperturbed coil, $2\langle R_g \rangle$, leads to a sharp shortening of the initial stage of crystallization and higher values of n in Eq 4.46. The process of crystallization proceeds to the end, with values $1 < n < 3$, typical of two-dimensional growth. Simultaneously, there is a dramatic change of energetic parameters of nucleation. It is connected with the change of chain conformation because of their interaction with the surface, which modifies melt structure and hinders nucleation. Slowing down nucleation causes a sharp increase of induction period of crystallization. Although highly loaded polymers are capable of crystallization, even at condition $\langle L \rangle < 2\langle R_g \rangle$, the degree of crystallization drops very markedly. At $\langle L \rangle = 30\times10^{-10}$ m, polycaproamide melt on cooling does not display any crystallization at all.[77] However, a prolonged isothermal heat treatment, at high degree of supercooling, gives an increase in crystallization degree. These data and linear dependence of $\log\tau_i$ (induction period) on T indicate slowdown in the molecular mobility in melt and increasing contribution of diffusion mechanism in crystallization. The ability of highly loaded polymers to crystallize in thin layers can be explained by participation of macromolecular segments in direct interaction with the surface (see Chapter 1).

The effect of the surface on crystallization depends strongly on the molecular mass of the crystallizing polymer. For low-molecular mass polymers (oligomers) in thin layers, the crystallization may be fully suppressed because of difference in conformation between high- and low-molecular mass polymers. The rate of crystallization in melt of filled polymer can also be regulated in a wide range by selection of filler able to inhibit or accelerate crystallization. The same filler at different conditions may have different action. However, in all cases the predominant role in crystallization belongs to the ratio between the molecular size of the polymer chain and the thickness of polymer interlayer. It thus follows that the degree of crystallinity depends on both crystallization conditions and filler content.

The degree of crystallinity, X, is a measure of the relative content of crystalline phase in semi-crystalline polymers. The value (1-X) is a measure of the fraction of defect regions which, for some thermodynamic or kinetic reasons, do not form a crystalline lattice.[63] For unfilled polymers, these regions may consist of folds of macromolecular chains, tie segments, and free ends of chains in the intercrystallite space. For filled polymers, such defects may be due to some segments of macromolecules in surface layers which, because of conformational or kinetic restrictions, have lost their ability to crystallize. The relative degree of crystallization in filled system can be expressed as $\alpha = X/X_o$, where X and X_o are the crystallinity degrees in presence and absence of a filler. They help in measurement of the amount of non-crystalline surface layers $\nu = 1 - \alpha$. Value ν may be expressed as:

$$\nu = \frac{S\rho_f \delta W}{(1 - W)} \qquad [4.53]$$

where S is the specific surface, ρ_f is the density of filler and δ is the thickness of the surface layer. From this equation, it follows that

$$\alpha = \frac{1 - KW}{(1 - W)} \qquad [4.54]$$

where $K = S\rho_f\delta$. The dependence of α on W/(1 - W) ratio is linear.

Figures 4.13 and 4.14 show that these dependencies are linear (with an exception of low density polyethylene). The slopes of lines are proportional to the thickness of the surface layer, δ, i.e., they increase together with the energy of interfacial interaction. Also, the experimental data[63] for a polyamide-6-fumed silica system, show correlation between the value of K and the heat of wetting of the filler by polar liquids. In some cases, the extrapolation of the dependence to W/(1 - W) = 0 leads to values of $\alpha > 1$ (Figure 4.14). It means that the same filler may, at low content, act as an initiator of crystallization, increasing the crystallinity degree, or prevent crystallization at higher concentrations because of the transformation of a majority of polymer chains in surface layers and increase of energetic barrier of nucleation. However, for some systems there is no dependence of α on W; values α equal 1 up to the high values of W. Formally, this case corresponds to $\delta = 0$ in Eq 5.10 as a result of weak interfacial interactions.

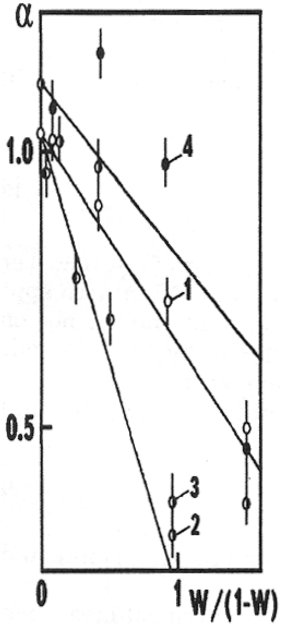

Figure 4.13. Dependence of α on the ratio W/(1-W): 1-poly(butylene terephthalate), 2-polycaproamide, 3-isotactic polypro-pylene, 4-polyethylene of low density.

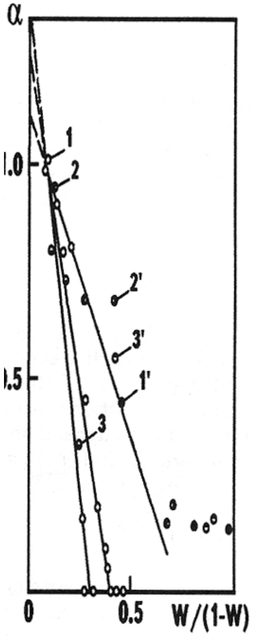

Figure 4.14. Dependence of polyoxyethylene ($M=6.10^3$) filled with fumed silica (1-3), carbon black (1'-3') (filled films obtained from dilute solution in benzene (1,1'), methanol (2,2'), and water (1,1').

The above discussion shows that filler also affects the structure of the amorphous region by changing the degree of crystallinity and the ratio between the amorphous and crystalline parts. The study of crystallization of oligoester in the presence of glass powder[78] shows that from the values of energetic parameters of nucleation at various thicknesses of the interlayer, the ratio of specific volumes of amorphous and crystalline phases, v_a/v_c, may be calculated. This value is related to the free energy of nuclei surface, σ_i, by the empirical ratio:[63]

$$\sigma_i = 0.15\left(\frac{v_a}{v_c}\right)^4 \qquad [4.55]$$

Changes in σ_i by filling control the density of the amorphous phase. The experimental data show that in the melts of oligoesters, for the whole range of interlayer thicknesses there are loosely packed regions. The dependence of the reduced specific volume, v_a, on <L> is nonlinear and characterized by the alternation of more dense and less dense regions typical for dissipative structures, formed as a result of non-reversible processes under non-equilibrium conditions.[79]

4.3.3 MELTING OF FILLED CRYSTALLINE POLYMERS

Melting point is the main characteristic of the equilibrium crystalline structure and quantitative measure of the thermodynamic stability. In accordance with the Gibbs-Thomson equation,[63] it is defined as:

$$T_{m(d)} = T_{m(\infty)}\left[\frac{1-2\gamma_{sl} v_{cryst}}{(\Delta H_{m(d)})}\right] \qquad [4.56]$$

where $T_{m(\infty)}$ and $T_{m(d)}$ are melting points of macrocrystal and crystal of the size d, v_{cryst} is a specific volume of crystalline phase, γ_{sl} is the interfacial energy at the solid-liquid interface, and ΔH is an enthalpy of melting. For polymers value d is the height of the folded crystal (folding period). The enthalpy of melting of macrocrystal may be calculated as follows:

$$\Delta H_m(l) = \frac{\Delta H_{m(\infty)} - 2H_e v_{cryst}}{l} \qquad [4.57]$$

where $h_e = (\gamma_{sl} - S_e T_m)$ is enthalpy term and S_e entropy term of interfacial energy. In accordance with earlier conclusions,[63] Eqs 4.56 and 4.57 may be applied to highly loaded polymers if the crystallite sizes are determined not only by thermodynamic conditions of crystallization but also by the <L> value.[80,81] Parameters γ_{sl} and h_e depend on the interaction energy at the interface.

Parameters T^{o}_{m} and ψ (parameter of structural rearrangements) were determined from equation:[74,82]

$$T_m = T^{o}_{m}(1-\psi) + \psi T_{cr} \qquad [4.58]$$

where T_m and T^{o}_{m} are experimental and equilibrium melting points and T_{cr} is crystallization temperature.

Parameters T^{o}_{m} and ψ dramatically change at a critical mass amount of filler, W_{crit}. A sharp drop of ψ at increasing W close to W_{crit} for polar polymers is related to an increase of energetic barrier of nucleation, whereas for non-polar polymers, it relates to the effect of the thickening of crystallites. A critical amount of filler, W_{crit}, correlates with molecular mass of polymer and diminishes with its growth. This allows us to postulate that there is a correlation between the effective thickness of the polymer interlayer between two particles at W_{crit}, $\langle L_c \rangle$, and the size of macromolecular coil (Figure 4.15). It is seen that $\langle L_c \rangle$ corresponds with the diameter of the unperturbed coil $2\langle R_g \rangle$. Here $\langle R_g \rangle^2 = \langle h^2 \rangle/6$ is the mean inertia radius, and $\langle h^2 \rangle$ the mean end-to-end distance. Thus, parameter T^{o}_{m}, for polymers of high molecular mass, is the temperature of melting of crystallites whose heights are determined by the thickness of the polymer interlayer, not by the length of the extended chain, as for unfilled polymers.

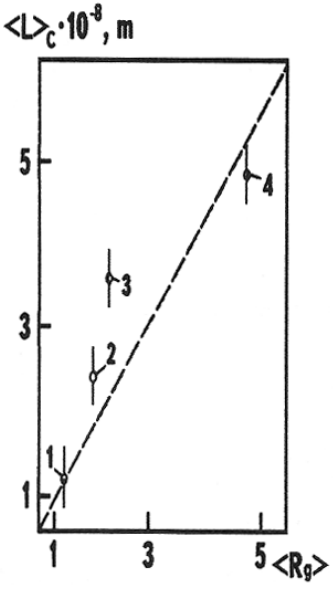

Figure 4.15. Dependence of the effective thickness of polymer interlayer between two particles <L> on the diameter of macromolecular coil $2\langle R_g \rangle$: 1 - PE, 2 - PBT, 3 - PA, 4 - iPP.

Data[50] show that the changes in the melting points are determined by the influence of filler on crystallization mechanism and the type of crystalline structure formed. These effects depend on the nature and amount of filler and on the nature of polymer. The formation of surface layers, which prevent crystallization, has also a definite effect on the heats of melting of filled polymers. It was established[83] that the heat of melting of filled by fumed silica polyethylene, determined by DSC, decreases linearly with an increase in the amount of the filler.

The decrease is accompanied by diminishing the crystallinity degree. These effects are explained by formation of the surface layers if there is no crystallization.

4.3.4 INFLUENCE OF FILLERS ON THE MORPHOLOGY AND STRUCTURE OF FILLED CRYSTALLIZING POLYMERS

Optical or electron microscopy studies of crystalline polymers filled with mineral fillers show that fillers have a great influence on the size and morphology of the spherulites.[50] There is an optimum filler concentration above which the influence of filler on the size of the spherulites becomes insignificant. This influence of filler depends not only on its nature but also on the size and shape of its particles. The influence of filler particles on the formation of supermolecular structures is affected by modification of the filler surface to increase the affinity for the polymer.

Fillers differ in their dispersion in polymer and in their influence on its structure. For instance, a particle of a fine filler may be a center of spherulite, or also be displaced, during crystallization, into inter-spherulitic non-ordered regions to be located mainly at the interface between spherulites in the defect region. Coarse fillers, having larger particles than the diameter of the spherulite core, cannot become centers of spherulites. It is the actual surface of the particles which influences nucleation. If the filler particles are anisodiametric in form, then depending on the length ratio and the size of the spherulites, there may be formed a variety of morphological types of spherulitic structures, from twined spherulites to extended spherulite chains. Polymers containing high filler concentration crystallize to a loose spherulite structure and contain aggregates of filler particles.

The filler also influences the size distribution of the spherulites. Small additions of filler lead to a spherulite distribution which depends on the shape and size of the filler particles. With the presence of anisodiametric particles, the distribution is non-uniform and exhibits two maxima. For any particular average size of spherulites, the character of the size distribution may vary. At the same time, high and low concentrations of fillers influence the supermolecular structure in different ways.

The addition of small amounts of filler brings about the formation of more perfect structures. The increase in concentration reduces the degree of perfection of the supermolecular structures. Also, the mechanism of failure of the polymer (crack development, adhesion or cohesion failure, determined by the filler concentration, etc.) is linked with the character of the supermolecular structure formation in crystalline polymers in the presence of fillers. Thus, the presence the filler influences the structure and morphology of crystalline polymers, differing in levels of their organization, and leads to the changes in size, form, and size distribution of the supermolecular structures. The qualitative understanding of the structural activity of fillers, meaning their capacity for exerting influence on the structure of the polymer, can be attained by studying these processes.[84]

In the influence of filler on the properties of crystallizing polymers, the effect on the non-ordered (amorphous) regions of polymer and the ratio between the ordered and non-ordered regions must also be considered. Accordingly, changes in the properties of crystalline polymers on the addition of fillers are determined by the changes taking place in the amorphous phase. Filler has a tendency to accumulate specifically in the less ordered regions.[85] Accordingly, crystalline polymers are modified largely due to the filler influence on the amorphous region, and by far, lower concentrations of filler are needed than when the filler is added to an amorphous polymer. This may be one of the reasons for the improvement of the mechanical properties of filled crystalline polymers by low filler concentrations.

The experimental data allow the definition of inter-structural reinforcement to be introduced.[50,85] As a basis, it was taken into account that the length of the tie chains, connecting various supermolecular structures, varies from hundreds of Å to micrometers.[50,85] It means that filler particles having particles smaller than 1 μm may be fully situated in the inter-structural (disordered) regions. It was found that particulate fillers are concentrated in disordered regions, preferably in the interspherulitic regions along the spherulite borders. Concentration of filler particles in these regions leads to the change in the molecular mobility of tie chains and change of their conformation. This, in its turn, has an effect on mechanical and other properties of reinforced crystalline polymers.

4. 4 INFLUENCE OF THE INTERFACE ON THE REACTIONS OF SYNTHESIS AND MECHANISM OF FORMATION OF LINEAR AND NETWORK POLYMERS

Up to this point, we have discussed the reinforced systems formed by introduction of fillers into the melts of linear polymers. One of the most frequently used methods of production of reinforced plastics consists in polymerization or polycondensation in the presence of fibrous or particulate fillers with highly developed surface. The formation of three-dimensional polymer networks in the presence of filler has its peculiarities differentiating this process from the synthesis of network polymers without filler. As a result, the transfer of regularities of reaction of the polymer formation or curing (reaction rate, molecular mass distribution, chain microstructure, network density) on filled system may be done only approximately. In practice, we should have in mind the influence of the interface on the reaction of the synthesis of linear polymers and the curing of network polymers.

Although these problems are not sufficiently investigated, there are some data indicating some general principles governing these applications.[86-90] The principal features of polymerization or polycondensation in the presence of fillers consist of essential influence at the interfacial phenomena of the reaction mixture-solid interface on the progress of reactions and properties of cured systems. The main role belongs to adsorption of reacting components (monomers, oligomers, etc.) on the filler surface which affects the reaction kinetics and the final properties of cured system. The usual goal of these studies is to select better conditions of binder curing during formation of filled and fiber-reinforced polymers.[91,92] Let us consider some features of the processes on synthesis of linear and cross-linked polymers in the presence of fillers.

4.4.1 LINEAR POLYMERS

During radical polymerization, the initiation rate depends on the way the initiator bonds with the surface. Chemisorption of initiator on the solid surface decreases the initiator decomposition rate, probably due to diminishing of the degree of freedom of initiator molecules which hinders diffusion separation of the radical pair. The restriction of mobility and recombination of radicals bound to the surface lowers the rate and effectiveness of polymerization. The rate of thermal decomposition of initiators and their efficiency of initiation also depend on the adsorption interaction with the surface, which depend on the chemical nature of initiator and surface.[87,90]

Opposite to chemisorption, physical adsorption has no influence on the rate of initiator decomposition. On the contrary, depending on the surface nature of filler, polymerization of vinyl monomers, in the presence of peroxides and azocompounds, is accelerated by fine, dispersed silica. The activation of monomeric molecules occurs, due to the complex formation of functional groups of monomers with OH-groups frequently present on filler surface.[93,94] Also, the orientation of monomer molecules on the surface and stabilization of macroradicals may take place,[86,92] hindering the termination reactions by decreasing molecular mobility in the adsorption layer.

These effects depend on the degree of dispersity of fillers (on their total area). The ability to bind peroxide initiator on the surface is of importance for polymerization of monomers in a filler presence. The treatment of the glass surface by hydrogen peroxide[95] shifts initiation to surface layers and favors adsorption of growing chains on the filler surface. Densely packed macromolecules are formed in the surface layers, as compared with the polymerization in the presence of untreated filler. The strength of adhesion bonding of polymer with the surface can be regulated in in situ polymerization. Initiator grafting on filler surface was postulated.[96] The methods of filler treatment for its use in polymerization were reviewed in earlier papers.[88,97]

The radiation-induced polymerization of monomers and the polymerization under UV was conducted in the presence of fillers.[88,90] The limiting value of the reduced reaction rate (ratio of the reaction rate to monomer adsorption at the surface) is reached at the full coverage of the surface by monomer molecules. The polymerization proceeds according to the radical mechanism, and the chain termination is due to the interaction of growing chains with the functional groups at the filler surface. When radical reactions occur in the surface layer, there is an increased possibility of grafting of growing chains onto the surface as a result of chain termination and transfer. During copolymerization of vinyl monomers in the presence of fumed silica, monomers are strongly adsorbed at the surface, and a strong temperature dependence of the copolymerization constants is observed. Increasing the adsorption energy of monomer molecules and growing chains determines the pronounced increase in the activation energy of chain growth and in the magnitude of the pre-exponential factor.[98]

Formation of linear polymers in the presence of fillers is also possible in the course of catalytic polymerization, if, as a result of the preliminary treatment of the filler surface by catalyst, catalyst is bound to surface.[99,100] In polymerization of styrene in the presence of $TiCl_4$, the growth of the chain proceeds according to the cationic mechanism for ionic pairs. Modification of filler surface by metal chlorides and metaloorganic compounds is presently used to obtain filled thermoplasts directly in the course of their synthesis. This method has some advantages compared with the radiation polymerization; however, its application is very complicated, due to complicated preparation of the fillers for modification. Fillers must be dried, the adsorbed oxygen removed, and metal-complex catalyst applied to the surface. The catalyst cannot be removed from the surface after polymerization.[101-103]

Introduction of disperse fillers (metals and their oxides) has an influence on anionic polymerization. The effect is connected with the presence of reactive surface centers such as OH-groups of various degree of acidity or basicity, metal cations, oxygen anions, admixtured atoms of metals, etc. Anionic polymerization at the surface of disperse carbons is determined by the possibility of the formation of the clathrate compounds of alkaline metals and graphite.[104]

The processes of polymer grafting to the surface are not considered here, since these problems traditionally refer to the modification of the filler surface (see Chapter 2).

The presence of fillers also has a strong influence on processes of polymer formation by polycondensation or polyaddition mechanism.[94] Polyurethane formation was studied[105,106] in the presence of fumed silica and chlorides of magnium and ammonium. It was found that oligoesters and oligoeters may either be strongly adsorbed at the surface or not adsorbed at all, depending on their chemical constitution. The difference in adsorption is determined by the presence of end-hydroxyl groups and oxygen of ether or ester groups in the main chain. The acceleration of the reaction of oligoester with diisocyanates was directly connected with adsorption and energy of interaction between oligomer and surface. Studying the reaction kinetics in the presence and absence of fillers allowed us to propose the mechanism of accelerating action of the surface. This mechanism consists in the redistribution between intra- and intermolecular hydrogen bonds of oligoester diols in the surface layer, accompanied by the formation of more reactionable states. In some cases, the acceleration is of catalytic character. The molecular mobility of components of polyaddition and polycondensation reactions are hindered, due to their interaction with a surface of filler. At the same time, the reaction rate in the presence of filler is higher, which may be explained by orientation of molecules on the surface and their ordering in the surface layer, which promotes reaction.[107]

There is a definite correlation between accelerating action of the solid surface and adsorption of oligomeric molecules from the reaction mixture. The adsorption increases a fraction of molecules activated by the surface. The acceleration increases with increasing interaction between reaction components and the surface.[107]

In summary, adsorption of monomers or oligomers on the filler surface affects the polymerization rate, which non-linearly depends on time as the process proceeds simultaneously in the surface layers and in the bulk. Introduction of filler leads to change in molecular-mass distribution because of change in the ratio of elementary reaction constants (hindering the growth and termination reactions). Adsorption also leads to a pronounced change in the reaction rate, due to the changes in concentration of reacting components in the surface layer and bulk as a result of the selective adsorption of components, diminishing molecular mobility, and formation of intermediate compounds with different reaction ability. The physical bonds between the surface and reaction components also change the structure of the reaction medium.

4.4.2 CROSSLINKED POLYMERS

The factors influencing formation of linear polymer in the presence of a solid surface play a similar role in the case of crosslinked polymers. The changes in reaction kinetics in the filler presence lead to increasing defectiveness of the network observed from lower cross-linking density.[86] The conversion degree during gelation depends on filler presence and its concentration.[91] The filler action is especially pronounced in the region of the gelation onset. At a high filler loading, the conversion decreases by 10% compared with unfilled systems, depending on filler concentration and its nature. This effect may be explained by the formation of an additional structural network, due to the interaction between filler particles and growing macromolecules. The filler presence not only affects kinetics of reaction but also the onset of gelation.[108] The effect of filler is determined by the elementary reactions typical of a given mechanism.[109]

The difference in the kinetics of the formation of linear and crosslinked polymers may be explained in the following way. It was shown in Chapter 3, that even the surface, which does not strongly interact with polymeric molecules, has an effect on the properties of the filled polymer, due to the restrictions imposed on chain conformation in the surface layer. It is probable that during formation of crosslinked polymer, the highly-branched molecules are formed even at the initial stages of the process. These branched molecules have restricted mobility, due to the reasons already mentioned, and as a result, they have diminished reaction ability, leading to the decrease in the reaction rate. During formation of linear macromolecules in filler presence, this effect appears only at high conversion degree. In the case of weak interaction between surface and reaction component, the filler effect manifests itself only for molecules of rather high molecular mass, where conformational effects are essential to have an influence on the properties of filled polymer.

Introduction of fillers into the reaction system may have an accelerating action during formation of both linear and crosslinked polymers because of redistribution of intra- and intermolecular interactions. This means that filler affects the very structure of the reaction mixture (solution or melt) in the same way as the formation of some aggregates or the development of entanglements affect the adsorption from solutions. These effects may be responsible for change in the reaction kinetics and changing the properties of the filled polymers.

It was also established[110-112] that the filler surface-treated with coupling agents influences both the reaction rate and the conversion degree of cured epoxy resins in glass-reinforced plastics. The development of stresses around the fiber and thus the mechanical properties are affected.

The curing of epoxy resin was studied in the presence of a glass surface-treated with dimethyl dichlorosilane.[113] It was established that, at the polymer-solid interface, the epoxy polymer has a heterogeneous structure as a result of the decreasing degree of conversion in surface layers due to the adsorption effects. Near the surface, the rate of curing is much lower than in bulk. As a result of the difference in cure rate around the fiber and bulk, inner stresses are developed which worsen the mechanical properties of the glass-reinforced plastic. The inhibition of cure near the interface also leads to diminishing cohesion strength in this region. The treatment of the surface by some surfactants diminishes this negative influence of the surface on the mechanical properties. Thus, the formation of the "undercured" zone near the fiber surface may be an important factor needed to be considered when selecting cure conditions. The mechanism of curing of epoxy resin at the surface of glass fibers was studied in detail for various reaction stages.[112] It was found that the kinetic conditions of reaction continuously change with conversion degree increasing because of restriction of molecular mobility. The latter depends on the conversion degree, which complicates dependence of the curing rate in filler presence.

It was also established[114] that filler incorporation into the reaction system hinders the processes leading to establishing the equilibrium state of the system. In the course of curing, various structural states appear, depending on the ratio between reaction rate and rate of the establishment of an equilibrium state. Non-equilibrity manifests itself in decreasing the density of the system, as compared with its equilibrium value. In the course of the curing, the non-equilibrium structure may be preserved. It has higher free volume and lower crosslinking degree because of formation of the surface layers. It is important to note that a lower degree of crosslinking at the surface facilitates the packing of macromolecules in the surface layer, which thus has higher density, compared with more crosslinked and loose-packed molecules in the bulk. These effects explain the dependence of properties of cured resin, having the same degree of curing, on the type and amount of filler and curing conditions.

When the reaction system consists of many components (e.g., epoxy resin-polyamine, methylolphenols-phenols, etc.) an important role is played by the selectiveness of adsorption of filler surface.[115] In the epoxy resin-polyethylene polyamine-glass fiber system, the epoxy resin is adsorbed preferentially. The molecules in the adsorption layer do not participate in reaction and the bulk contains more hardener. Due to this fact, the stoichiometric ratio of components is disturbed and resin cured in bulk becomes softer because of excessive amount of unreacted hardener playing the role of plasticizer.

When discussing the chemical reaction near the interface, it is necessary to take into account that the changes in the ratio of components in the surface layer and in the bulk may lead to substantial changes in the reaction conditions in various parts of the reaction system and at different distances from the surface. A gradient of chemical and physical structures arises.[113,116,117] The bilayer structure formed as a result of changing conversion degree in the surface layers and in the bulk is of great importance for understanding of adhesion. The interface contributes essentially to formation of a weak boundary layers playing an important role in adhesion (Chapter 2).

The factors discussed above determine the chemical and physical heterogeneity of the surface layers in composite materials and play an important role in their viscoelastic properties.

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5

VISCOELASTIC PROPERTIES OF REINFORCED POLYMERS

The drastic changes in the physical properties of polymers, due to reinforcement, also lead to pronounced changes in their viscoelastic behavior. Viscoelastic properties and relaxation behavior of composites change as a result of the formation of surface layers at the polymer-solid interface. The molecular mobility of polymeric chains is restricted in these layers, which affects mechanical properties.

5.1 DEPENDENCE OF THE ELASTICITY MODULUS OF PARTICULATE-FILLED POLYMERS ON THE AMOUNT OF FILLER

Dependence of the elasticity modulus of particulate-filled polymer is a tpical result of experimental studies. Understanding of the physical essence of reinforcement can be gained by performing a controlled experiment. To establish the dependence of modulus on filler concentration, various models have been proposed which allow us to calculate the elasticity moduli from corresponding values of the constituent components.[1] There is a large number of equations allowing us to calculate the moduli of heterogeneous polymeric compositions. The influence of fillers weakly interacting with polymer on the viscoelastic properties is determined by simple filling of the polymer volume by rigid inclusions. The filler particles are comparably large and the distance between them, even at high loading, is also large compared with the usual end-to-end length of a polymer chain. Filler particles are separated from one another and they cannot be bridged by the macromolecular chain. For such systems, the contribution of interphase layers can be neglected.

The dynamic mechanical properties of a filled system, in the absence of interaction between components, can be described on the basis of a mechanical model proposed by Takayanagi[2] for non-interacting polymer mixtures. This model is very useful for describing properties of filled systems with interfacial layers. Based on hydrodynamic considerations, an equation was proposed (analogous to the Einstein equation for viscosity of suspension) to calculate the modulus of composite, E_c:[3]

$$E_c = E_p (1+ 2.5\varphi) \tag{5.1}$$

where E_p is the modulus of unfilled polymer and φ the volume fraction of filler. This equation is only valid at low filler concentrations. A more precise model was proposed later:[4]

$$E_c = E_p(1 + 2.5\varphi + 1.4\varphi^2) \tag{5.2}$$

For non-spherical particles, the form-factor, f, was introduced, which is a ratio of particle length to its diameter. In this case, the following equation is used:

$$E_c = E_p(1 + 0.67f\varphi + 1.62f^2\varphi^2) \tag{5.3}$$

Various models have been proposed to calculate the moduli of composites. All models are based on assumed morphological structures of composites. A comprehensive review was published,[5] and we consider this problem only briefly. Kerner,[6] in his calculations, used the following model: The filler particle is surrounded by the shell of matrix. This shell is in contact with media having elastic properties of heterogeneous composition. The media and the shell are separated by an intermediate zone. The spherical structure formed is subjected to a uniform hydrostatic pressure. The average bulk deformation and average stress are equal to the corresponding values for a homogeneous body with the same elastic constant as a heterogeneous one. The equation proposed by Kerner includes the Poisson ratio of polymeric matrix, μ, and the real part of the complex shear modulus of filler, G'_f, and matrix, G'_p:

$$\frac{E_f}{E_p} = \frac{G'_f \varphi / [(7-5\mu)G'_p + (8-10\mu)G'_f] + (1-\varphi)/[15(1-\mu)]}{G'_p \varphi / [(7-5\mu)G'_p + (8-10\mu)G'_f] + (1-\varphi)/[15(1-\mu)]} \qquad [5.4]$$

This equation was transformed[7] into a more convenient form:

$$E_c/E_p = 1 - (AB\varphi)/(1 - B\varphi) \qquad [5.5]$$

where $A = (7 - 5\mu)/(8 - 10\mu)$; $B = [(E_f/E_p) - 1]/[(E_f/E_p) + A]$.

This equation may be transformed[8] to:

$$E_c/E_p = (1 + AB\varphi)/(1 - B\Psi\varphi) \qquad [5.6]$$

where Ψ is a function of limiting loading, φ_m:

$$\Psi\varphi = 1 - \exp[-\varphi/(1 - \varphi/\varphi_m)] \qquad [5.7]$$

However, in using the Kerner equation, it is necessary to take into account that interaction occurs at the phase border and a part of polymer is bound by filler, as a result of which, the effective proportion of filler has to be increased to $\varphi_e (\varphi_e > \varphi)$:[9]

$$\varphi_e = \varphi(1 + \delta/r) \qquad [5.8]$$

where δ/r is the relative increase in particle diameter as a result of interaction (the thickness of the surface layer) which may be found from the rheological data or from comparison of loss modulus of filled and unfilled specimens:

$$E_c''/E_p'' = 1 - \varphi(1 + \delta/r)^3 \qquad [5.9]$$

Taking this into account, the Kerner equation may be transformed by incorporating the value $\varphi_e = \varphi B$, where parameter B describes the interaction at the interface. With $\mu = 0.5$ and $E_c >> E_p$, the equation assumes the form:

$$E_c/E_p = (1 + 1.5\varphi B)(1 - \varphi B) \qquad [5.10a]$$

and mechanical loss tangent is:

$$\tan\delta = \tan\delta_o/(1 + 1.5\varphi B) \qquad [5.10b]$$

The mechanical losses diminish when filler is introduced. The equation presented above takes into account the real structure of a filled system and the existence of an intermediate layer between the particle and matrix, despite the fact that their contribution to the change of properties of polymer matrix has not been estimated. Introduction of parameter B (Eq 5.10) has a very formal character. This parameter may be estimated from the experimental dependence of E_c/E_p on φ (Eq 5.10). Experimental data show that B diminishes with increase of φ. The thickness of the bound layer decreases with decreasing thickness of the intermediate layer between two filler particles which has no meaning. Dependence of B on φ means that we cannot use the modified Kerner equation (5.10), which does not take such a dependence into account. The values of B are changed in the range of 6-1, i.e., in the limit of the case when the surface layer is absent. Therefore, this approach is only interesting because it takes into account the existence of the bound surface layer, but the dependence of B on φ makes its justification doubtful, especially because the thickness of the bound layer, as determined from mechanical measurements, depends on the frequency.[9]

Theoretical calculations of elastic constants of polymer systems with a particulate filler enable us to find the analytical expressions for effective values of Lame coefficients μ^* and λ^*m at varying filler loading:[10]

$$\mu^* = 2(C_1 + C_2)\Psi(\varphi) \qquad [5.11]$$

$$\lambda^* = 2.15(C_1 + C_2)\Psi(\varphi) \qquad [5.12]$$

$$\Psi(\varphi) = 0.435\{[(\varphi_m/\varphi)^{1/3} - 1] + 1.15[(\varphi_m/\varphi)^{1/3} - 1]^2\}^{-1} \qquad [5.13]$$

where φ_m is the limiting loading and C_1 and C_2 are the Mooney constants. The modulus of composition is expressed as follows:

$$E_c = 5(C_1 + C_2)\Psi(\varphi) \qquad [5.14]$$

Due to some simplifications in calculations, the experimental data differ from the theoretical by one order.

Nielsen[11] proposed a generalized equation for calculation of the elasticity moduli of a two-phase system in the form:

$$E_c/E_p = [1 + (K - 1)B\Psi]/(1 - B\chi\varphi) \qquad [5.15]$$

where B is the constant determined by the ratio of the moduli of two phases, K is the generalized Einstein coefficient (equal to 2.5 for dispersion of spherical particles in an incompressible medium), and χ is a parameter depending on the particle shape and determined by the coefficient of filling the volume by particles at maximum dense packing.

The influence of the volume filler concentration on the dynamic modulus was considered[12] on the basis of analysis of propagation of waves in the two-phase medium. For this case, the following expression was derived:

$$E_c = \frac{E_p(7-5\mu) + (8-10\mu)E_f + (7-5\mu)(E_p - E_f)\varphi}{E_f(7-5\mu) + (8-10\mu)E_f - (8-10\mu)(E_p - E_f)\varphi} \qquad [5.16]$$

The deviations of experimental values of moduli from those calculated theoretically are connected with the fact that the change in moduli cannot be explained only by pure hydrodynamic factors related to particle presence. For filled rubber in a glassy state, the influence of carbon black on the shear modulus, G_c, may be described using an equation taking into account the adhesion at the interface:[13]

$$G_c = G_m(1-\varphi) + AG_f\varphi \tag{5.17}$$

where A is the factor of adhesion.

The interlayer model represents an extension of van der Poel's theory[14] derived from works by Fröhlich and Sack[15] devoted to viscosity of suspension by a shell-model. Van der Poel obtained expressions for G and K (bulk modulus). In his model, the filler sphere of a radius, a, is supposed to be surrounded by the sphere of the matrix material with radius 1. The sphere in sphere obtained in this way is surrounded by the great sphere of radius, R, consisting of material with macroscopic properties of heterogeneous composition. The results of calculations according to the equations proposed by van der Poel are very close to those obtained using the Kerner equation. Detailed description of this approach can be found elsewhere.[1]

Budiansky[16,17] derived the equation for shear modulus which includes the values of mean deformations, γ_i, in each phase, ϕ_i volume fraction of component i, and shear stress, τ:

$$\frac{1}{G_c} = \frac{1}{G_1} + \sum_{i=2}^{n} \phi_i\left(1-\frac{G_i}{G_1}\right)\left(\frac{\gamma_i}{\tau}\right) \tag{5.18}$$

This equation may be used for a system consisting of many phases. The bulk modulus, K, of composition may be found from the equation:

$$\sum_{i=1}^{n} \phi_i \frac{(K_i - K_c)}{(K_c - \beta_c K_i)} = 0 \tag{5.19}$$

where $\beta_c = 2(1 + \mu_c)/(1 - 2\mu_c)$, μ_c is the Poisson ratio for isotropic heterogeneous composition. The values G_c and K_c are connected in the equation:

$$\mu_c = (3K_c - 2G_c)/(6K_c + 2G_c) \tag{5.20}$$

The common shortcoming of all approaches considered before consists of neglecting the adhesion interaction at the phase border, which plays a very important role in mechanical properties of PCM.

In some theoretical works by Theocaris,[18-25] adhesion was taken into account. The interlayer between the filler particle and matrix, called "mesophase" by Theocaris, is considered as a homogeneous independent phase. It is convenient for calculation but not correct from the thermodynamic point of view. Theocaris used the model of the particle separated by the mesophase (interlayer) from the matrix. The analysis of the mechanical behavior of the system is done for a three or N-layer model. In the latter case, the mesophase is considered to be formed by N layers with various properties.

The modulus of composite is expressed as:

$$E_c = E_f v_f + E_i v_i + E_m v_m \qquad [5.21]$$

where E_i and v_i are the modulus and volume fraction of the interlayer, E_m and v_m are the same for the matrix, and E_f and v_f are the same for the filler. Considering the mechanical model as consisting of three concentric spheres[25] (Figure 4.1), one can see that the following correlation is valid:

$$v_f = \frac{r_f^3}{r_m^3}; \quad v_i = \frac{(r_i^3 - r_f^3)}{r_m^3}; \quad v_m = \frac{(r_m^3 - r_i^3)}{r_m^3} \qquad [5.22]$$

Taking the continuity of distribution of stresses in this model, we have:

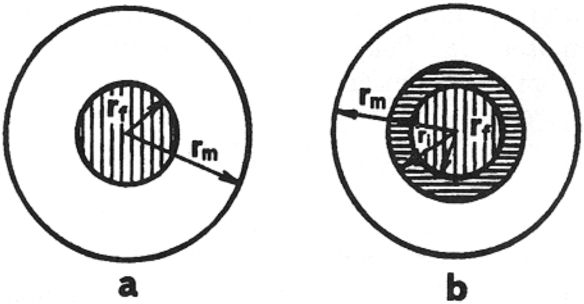

Figure 5.1. Principal section of two-phase (a) and three-layer (b) model for a typical particulate composite. [Adapted by permission from P. S. Theocaris, *Adv. Polym. Sci.*, **66**, 156 (1985)]

$$E_c = \frac{E_f r_f^3}{r_m^3} + E_i\left[\frac{(r_i^3 - r_f^3)}{r_m^3}\right] + E_m\left[\frac{(r_m^3 - r_i^3)}{r_m^3}\right] \qquad [5.23]$$

If we consider the element of filled polymer with cylindrical inclusions (reinforcing fibers), the expression for the modulus has the following form:

$$E_c = E_f\left(\frac{r_f^2}{r_m^2}\right) + E_i\left(\frac{r_i^2 - r_f^2}{r_m^2}\right) + E_m\left(\frac{r_m^2 - r_i^2}{r_m^2}\right) \qquad [5.24]$$

If the hydrostatic pressure, P_m, is applied to the particulate-filled polymer along the outer border of the matrix, the main theoretical equation acquires the following form:

$$\frac{3(1-2\mu_c)}{E_c} = \frac{3(1-2\mu_f)v_f}{E_f}\left[\frac{\lambda_{fi}}{\lambda_{im}}\right]^2 + \frac{3(1+\mu_i)v_f^2}{2BE_i v_i}\left[\frac{(1-\lambda_{fi})}{\lambda_{im}}\right]^2 +$$

$$\frac{3v_f^2(1-2\mu_i)}{E_i v_i}\left[\frac{\lambda_{fi}}{\lambda_{im}} - \frac{1}{B\lambda_{im}}\right]^2 + \frac{3v_f(1+\mu_m)}{2BE_m v_m}\left[1 - \frac{1}{\lambda_{mi}}\right] + \frac{3(1-2\mu_m)}{E_m v_m}\left[\frac{v_f}{B\lambda_{im}} - 1\right] \qquad [5.25]$$

with values λ_{fi} and λ_{im}, which are hydrostatic pressures at the filler-interlayer and interlayer-matrix interface, determined as follows:

$$\lambda_{fi} = \frac{3(1-\mu_i)(v_f + v_i)E_f}{2v_i E_i(1-2\mu_f) + [3v_f(1-\mu_f) + v_i(1+\mu_i)]E_f}$$

$$[5.26]$$

$$\lambda_{im} = 1 - \frac{2v_m(1-2\mu_m)}{3(1-v_m)} - \frac{E_m v_m(1+\mu_i)}{3E_i(1-\mu_m)}$$

Here B = vf/(v_f + v_i).

These correlations allow one to determine the modulus of the composites using the moduli and Poisson ratios of the elements of the model. If values E_c and μ_c, E_f and μ_f, and E_m and μ_m are known, the properties of the mesophase may be easily estimated. The Poisson ratio of the interlayer may be found for particulate fillers from the equation

$$\frac{1}{\mu_c} = \frac{v_f}{\mu_f} + \frac{v_i}{\mu_i} + \frac{v_m}{\mu_m} \qquad [5.27]$$

To calculate these values, one has to know the volume fraction of the interphase layer, v_i. It may be shown that

$$B = (1 - v_f)/[1 - v_f(1 - \nu)] \qquad [5.28]$$

which allows one to estimate value v_i from B. In this equation, ν is the fraction of mesophase calculated according to Eq 3.17. For fiber composites a simple law of mixtures is valid, expressed by:

$$E_c = E_f v_f + E_i v_i + E_m v_m \qquad [5.29]$$

The theoretical calculations show that for glass-reinforced epoxy resin, at 70% loading, the thicknesses of the mesophase r_i is of the order of 6 μm and volume fraction ~6%. The modulus of the interlayer depends also on the amount of the filler or on the radius of the fiber:

$$E_i(r) = E_m + E_f\left(\frac{r_f}{r}\right)^{\eta_1} - E_m\left(\frac{r_f}{r}\right)^{\eta_2} \qquad [5.30]$$

For $r = r_f$ and $r = r_i$ the corresponding boundary conditions are:

$$E_i(r) = E_f \text{ and } E_i(r_i) = E_m + E_f\left(\frac{r_f}{r_i}\right)^{\eta_1} - E_m\left(\frac{r_f}{r_i}\right)^{\eta_2} \qquad [5.31]$$

In these correlations, the exponents η_1 and η_2 are parameters of adhesion, determining the transfer of stresses from the matrix to the particle. From the equation presented above, it follows that:

$$(\eta_1 - \eta_2) = \log\left(\frac{E_f}{E_m}\right) : \log\left(\frac{r_i}{r_f}\right) = A \qquad [5\ 32]$$

where A is the coefficient of adhesion. At high A, the adhesion is high and the difference between r_i and r_f becomes smaller. Theocaris based this conclusion on the belief that in the case of perfect adhesion, the interphase layer (mesophase) is absent, which does not seem valid, because adhesion changes the properties of the interphase layer, as was shown in Chapter 2. At the same time, parameters η_1 and η_2 are very convenient for characterizing adhesion.[22-24]

The model representations developed by Theocaris were extended by him to the systems where the interphase layer should be considered as a multilayer. Taking into account the gradient of properties in such a system, this concept gives the optimum approach to the experimental data. However, the modelling of the interphase layer, characterized by some gradient, has shown[26,27] that at the number of layers exceeding 10, viscoelastic properties cease to change as compared with the model with a lesser number of layers, i.e., for modelling the properties, it is sufficient to use discrete distribution of the layers according to their properties.

The interlayer model was developed by Maurer et al.[28-32] The model of the particulate-filled system is taken in which a representative volume element is assumed which contains a single particle with the interlayer surrounded by a shell of matrix material, which is itself surrounded by material with composite properties (almost the same as Kerner's model). The radii of the shell are chosen in accordance with the volume fraction of the filler, interlayer, and matrix. Depending on the external field applied to the representative volume element, the physical properties can be calculated on the basis of different boundary conditions. The equations for displacements and stresses in the system are derived for filler, interlayer, matrix, and composite, assuming the specific elastic constants for every phase. This theory enables one to calculate the elastic modulus of composite, depending on the properties of the matrix, interlayer, and filler. In the approach developed, it was assumed that the matrix, interlayer, and filler, characterized by linear viscoelastic behavior, are homogeneous and have no defects or inner stresses.

To calculate the bulk modulus of particulate filled systems, which incorporate the effect of filler-matrix interaction, the same authors[30,31] proposed a molecular theory. This theory treats the composite as a molecular mixture, specifically as a binary polymer blend of super-macromolecules (filler) in a polymer matrix. The model in this theory is a lattice with sites either occupied by the segments of the two components or vacant. It is exactly the presence of these vacant sites that introduces an excess free volume into the system. A melt and a glassy matrix are then distinguished by the fact that in the melt at thermodynamic equilibrium, the free volume fraction is uniquely determined by minimization of the free energy. The molecular parameters of such a system are the ratios of attraction and repulsion potentials between the filler and polymer. This approach has enabled us to evaluate the bulk modulus of composite and to compare it with that obtained by using the interlayer model. These two very different approaches are in good agreement and meet the experimental data.

Using the theories considered above, one should have in mind that they do not take into account the distribution of particles by their size and shape. In many cases, there is a need to modify these equations.[33] The mechanical models are also very useful for calculation of viscoelastic moduli and mechanical loss in particulate-filled polymers. The most well-known model was proposed by Takayanagi[33] and is described in many books. The application of this model to the calculation of dynamic mechanical properties is described in detail.[34] The mechanical models allow us to calculate the viscoelastic properties of PCM with various morphology. The dynamic modulus depends on both the filler concentration and morphology. The comparison of theoretical results with experimental data has shown that calculations give agreement between the dynamic properties and composition of a system. At the same time, the phase morphology of the system and the structure of particles of the disperse phase should also be taken into account.[1]

When calculating the viscoelastic properties of compositions with high concentration of reinforcement, the theoretical dependencies of the modulus on concentration usually do not coincide with experiment. It is therefore necessary to introduce into the theoretical equations the empirical correcting coefficient accounting for the "effective" fraction of the filler (i.e., filler particle covered by the surface layer). For a two-component heterogeneous composition, the following equation has been derived to calculate the effective volume fraction:[1]

$$\varphi_2^* = \frac{(G_m - G_c)(G_m + \alpha_m G_f)}{(G_m - G_f)(G_m + \alpha_m G_c)} \qquad [5.33]$$

where G_m, G_f and G_c are experimental values of the dynamic moduli of matrix, disperse phase, and composite, respectively, $\alpha_m = 2(4 - 5\mu_m)/(7 - 5\mu_m)$. The expression for φ_2^* may be presented as:

$$\varphi_2^* = \varphi_2 \left(\frac{1 + 3\delta}{r_o} \right) \qquad [5.34]$$

where δ is the thickness of the surface layer and r_o is the radius of the filler particle. For example, analysis of the dynamic properties of chlorinated PE filled with TiO_2 gives the thickness of the surface layer equal to 200 Å.[35] This value depends on the surface treatment of the filler. The ratio of the tangents of mechanical losses, $\tan\delta_c/\tan\delta_m$, may serve as characteristics of reinforcement. The experimentally found changes in the dynamic and equilibrium moduli for polyvinylchloride filled with fumed silica of various surface nature show that the stronger the interfacial interaction, the higher the rigidity of the material. The increasing interaction leads to the increase in thickness of the interphase layer and diminishes the rates of stress relaxation.[36] The interphase layer also plays an important role in changing mechanical properties, including tensile strength.[1]

In cases when the packing of filler particles exerts an additional influence on the concentration dependence of the modulus of composition, the following ratio can be used:

$$\frac{\varphi_m^*}{\varphi_m} = \frac{1+\varphi_m(1-\varphi_m)}{\varphi_{m(max)}^2} \qquad [5.35]$$

where φ_m is the maximum volume fraction of filler particles. A comprehensive review of application of mechanical models for the analysis of the elastic and dynamic properties of heterogeneous compositions can be found elsewhere.[1,34]

5.2 CONTRIBUTION OF INTERPHASE LAYERS TO VISCOELASTIC PROPERTIES

5.2.1 THEORETICAL APPROACH

One of the reasons for deviation of theoretical equations, connecting elasticity modulus with filler amount from the experimental data, is the formation of surface layers at the polymer-filler interface (interphase layers). The properties of these layers are different than in bulk. It is very important to estimate the contribution of the interphase to the viscoelastic properties of composites.

To estimate theoretically the contribution of the interphase, the phenomenological model of Takayanagi may be used.[37,38] Particulate-filled polymer is presented as a cube of matrix (Figure 5.2) with edge length, b. In the center of this cube, another smaller cube is inserted made of the filler material (the edge length, a). The smaller cube is covered by the uniform layer of polymeric

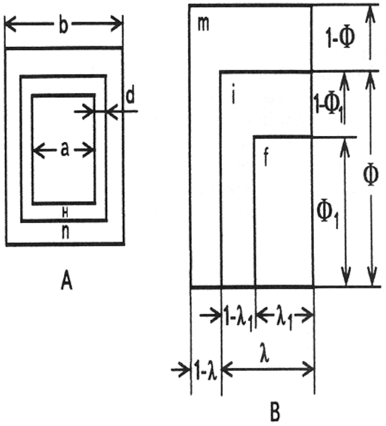

Figure 5.2. Model of elementary cell of filled polymer (A) and its equivalent (B).

material whose properties represent the properties of the interphase. The equivalent presentation of the model is given in Figure 5.1. This model may be considered as consisting of a two-component model (filler with the interphase layer) and a three-component model where one of the components is the first two-component model. For calculations, it was accepted that the thickness, d, of the interphase layer does not depend on the filler content f = a/b.

The parameters of the first model λ_1 and Φ_1 and of the second model and λ and Φ may be calculated from Figure 5.2:

$$\Phi_1 = a/(a + 2d); \quad \lambda_1 = a^2/(a + 2d)^2 = \Phi_1^2 \qquad [5.36]$$

$$\Phi = (a + 2d)/b = [(a + 2d)/a]\varphi_f^{1/3}; \quad \lambda = (a + 2d)^2/b^2 = \Phi^2 \qquad [5.37]$$

In accordance with the data,[39] the real G′ and imaginary G″ parts of the shear modulus in the Takayanagi model may be expressed using parameters λ_1 and Φ_1 and mechanical characteristics of components G′ and G″:

$$G' = (1-\lambda_i)G'_i + \frac{\lambda_i x}{x^2 + y^2} \qquad [5.38a]$$

$$G'' = (1-\lambda_i)G''_i + \frac{\lambda y}{x^2 + y^2} \qquad [5.38b]$$

where

$$x = \frac{(1-\Phi_1)G'_i}{(G'_i)^2 + (G''_i)^2} + \frac{\Phi_1 G'_f}{(G'_f)^2 + (G''_f)^2} \qquad [5.39a]$$

$$y = \frac{(1-\Phi_1)G''_i}{(G'_i)^2 + (G''_i)^2} + \frac{\Phi_1 G''_f}{(G'_f)^2 + (G''_f)^2} \qquad [5.39b]$$

In the same way, the values G′ and G″ of the three-component model may be calculated using values G′ and G″ as characteristics of both components. The equations for calculation of G′ and G″ are similar to Eqs 5.38 and 5.39.

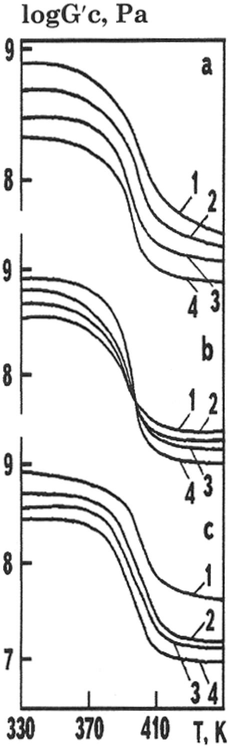

Figure 5.3. Calculated temperature dependencies of real part of complex modulus of particulate composite: a-no interphase, b-interphase with $\Delta T=T-T_g=-15^0$, c-with $\Delta T=+25^0$; ϕ_f: 0.6(1); 0.4(2);0.2(3); 0(4).

To calculate temperature dependencies of G′ and G″, the experimental dependencies of real and imaginary parts of the modulus were taken for cured epoxy resin.[40] The properties of the interphase layer have been chosen assuming that the curves of the temperature dependence of moduli have the same shape but are shifted along the temperature axis to a lower temperature (“soft” interphase) or higher temperature (“rigid” interphase).

Value d was accepted as d = 0.1a. Figure 5.3. shows calculated dependencies G′=f(T) at various φ. If the interphase is absent, the increase in filler concentration shifts the G′(T) curves along the ordinate axis to a higher G′ in such a way that the curves are separated equidistantly (Figure 5.3a). The presence of the interphase with lower glass transition temperature leads to the approaching of the curves G′(T) at the transition temperature region, whereas in the glassy and rubber-like state, the curves are separated equidistantly.

If the glass temperature of the interphase is higher, compared with the matrix, the equidistancy of the curves G′(T) is preserved from the side of low temperatures and is distorted at high temperatures (Figure 5.3b), if the concentration of the interphase is sufficiently high. If this concentration is small and glass transition temperature of the interphase is close to that of the matrix, the influence of the interphase on the G′(T) curves is not very strong. In a more generalized form, the influence of the interphase layers on the viscoelastic properties may be seen from the concentration dependencies at various temperatures (Figure 5.4). If the interphase is present the character of the curve G″ = f(φ) depends on the temperature and properties of the interphase.

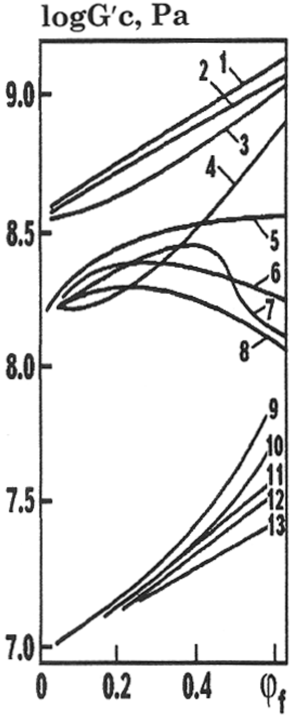

Figure 5.4. Concentration dependence log G_c‘ at 330 (1-3), 380 (408), 410(9-13), and T_m 390, 400, 410, 420 (1), 360 (2), 370, 380 (3), 390, 400, 410, 420 (4), 380 (5), 370 (6), 350 (7), 360 (8), 420 (9), 410 (10), 400 (11), 390 (12), 380, 360, 350 K (13). Temperature of maximum tanδ of the binder is 400K.

At temperatures below glass transition temperature of the interphase and matrix, dependence logG′ = f(φ) is close to linear, because in the glassy state the properties of the interphase are almost the same as for the matrix. At the same time, at transition temperatures the same dependences are non-linear. The character of deviation from linearity depends on the difference between glass transition temperatures of the interphase T_{gi} and matrix T_{gm}, ΔT. If , ΔT > 0 increasing φ leads to a more rapid growth of logG′ as compared with linear growth, and vice versa. At high concentration of low-modulus interphase, there may be observed a negative slope of the concentration dependence, i.e., increase in φ leads to diminishing G′. Further increase in filler concentration leads again to increasing G′. In such a way the existence of the interphase determines the appearance of the non-monotonous dependence of G′ on φ which has extrema. Their position at the concentration, a, is determined by the properties and the thickness of the interphase.

The temperature dependencies of the mechanical loss, tanδ, are also changed when interphase is present, especially in the case when $T_{gi} << T_{gm}$. With increasing filler concentration (and together with it, the concentration of the interphase), the height of the maximum on the curves tanδ-T diminishes and the position is changed. At a great difference between the properties of the interphase and matrix, maximum of tanδ may not only be shifted along the temperature axis, but a second additional maximum may appear, whose height and position strongly depend on the properties of the interphase.

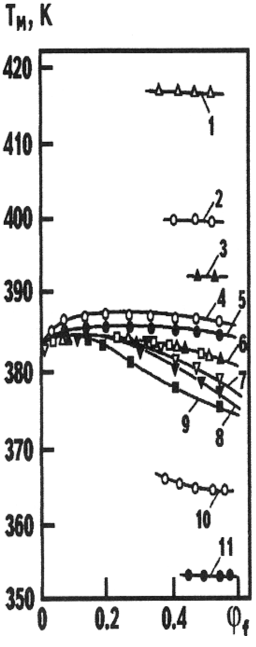

Figure 5.5. Influence of the filler concentration on the temperature of maximum tanδ at various T_m (K): 1-420, 2-410, 3-400, 4-360, 5-350, 6-390-420, 7-380, 8-375, 9-370, 10-360, 11-350.

Figure 5.5 shows the temperature of the maximum of mechanical loss as a function of filler amount at various T. It is seen that if the interphase has higher T_g as compared with matrix and ΔT does not exceed 10K, increasing φ shifts T_g of the composite to higher temperatures. If this temperature difference is more than 15K, increase in filler concentration does not change the glass transition temperature but leads to the appearance of the second maximum at temperatures corresponding to the glass transition temperature of the interphase. For the soft interphase layers, increase in φ diminishes T_g of composites, if ΔT exceeds 15K.

At high filler content, as follows from the theoretical calculations, again the second maximum of the mechanical loss appears. The growth in φ, leading to the transition of the matrix in the interphase layer, leads to disappearance of the maximum corresponding to the glass transition temperature of matrix and only one maximum is preserved, corresponding to the interphase layer. The range of filler concentrations at which both maxima are observed depends on the thickness of the interphase layer and on ΔT.

5.2.2 RESOLUTION OF RELAXATION MAXIMA IN TWO-PHASE POLYMERIC SYSTEM

In Chapter 4, it was shown that increasing filler amount in almost all cases leads to a shift in the glass transition temperature to a higher region. At the same time, there are a few experimental cases when both maxima, corresponding to the interphase layer and to the matrix with unchanged properties, are observed. However, it is not clear why the splitting of the maxima on experimental curves of temperature dependence of mechanical or dielectric losses is not observed. This question was studied theoretically using mechanical models.[40-43] In real filled polymers, the surface layers and unchanged polymer matrix are arranged randomly with regard to the direction of deformation. This makes it difficult to describe the behavior of the system theoretically. However, the study of some simple models may be sufficient to determine the viscoelastic behavior of the system if we exclude the deformation of the filler. To elucidate the conditions of maxima resolution, we have applied simple models with a polymer consisting of two regions or domains, each with different properties. These domains are thought to be coupled in parallel or in series with respect to the direction of deformation. The model of Takayanagi[2] was also investigated.

A simple equation enables us to estimate the main peculiarities in viscoelastic properties of the specimen made of two constituent parts. All calculations were done by computer simulation. Typical curves of temperature dependence of the real part of shear modulus G' and $\tan\delta$ were taken as initial data for calculations. For such curves, the experimental data on the temperature dependence of G' and $\tan\delta$ for an epoxy polymer in the region of transition from glassy to rubber-like state were chosen.[44] These experimental dependencies may be approximated as follows:

$$\log G' = A \operatorname{arc\,tan} B(T - T_g); \quad \tan\delta = C\exp[-D(T - T_g)] \qquad [5.40]$$

The properties of the second component (surface layer) were specified by shifting the experimental curves along the temperature axis in either direction, which simulated the decrease or increase of the glass transition temperature of the polymer in the surface layer. The temperature dependence of G' and $\tan\delta$ for two-component systems were distinguished from those for the first component by value of T_g in Eq 5.40.

The calculations of G' and $\tan\delta$ for the two-component system with parallel deformation were performed according to Eq 5.41:

$$G' = \varphi_1 G'_1 + \varphi_2 G'_2; \quad \tan\delta = \frac{\varphi_1 G'_1 \tan\delta_1 + 2G'_2 \tan\delta_2}{\varphi_1 G'_1 + \varphi_2 G'_2} \qquad [5.41]$$

where φ_1 and φ_2 are volume fractions of the components, and G'_1, G'_2, $\tan\delta_1$, and $\tan\delta_2$ are the values of viscoelastic characteristics at any arbitrary temperature. For the case of series model, Eq 5.42 was used:

$$G' = \frac{G'_1 G'_2}{\varphi_1 G'_1 + \varphi_2 G'_2} \quad \tan\delta = \left(\frac{\varphi_1}{G'_1} + \frac{\varphi_2}{G'_1}\right) + \left(\frac{\varphi_1}{G'_1 \tan\delta_1} + \frac{\varphi_2}{G'_2 \tan\delta_2}\right) \qquad [5.42]$$

Substituting the function of temperature dependence of each component, values for the temperature dependence of G′ and tanδ of the two-component specimen are obtained. To determine T_g of a two-component system, an analytical expression is needed for the first derivative of tanδ, which is then equated with zero at various ratios of the components. Numerical integration was used to calculate the values G′ and tanδ of the system for different temperatures using Eq 5.42, varying volume fractions, and glass transition temperatures of components.

Figure 5.6. Transformation of curve tanδ=f(T) with variation of the ratio polymer/interphase 1-0.6, 2-0.7, 3-0.8, 4-0.9, 5-0.95, 6-0.99 for T_g=398K and T_m=373K.

Figure 5.6 shows theoretical temperature dependence of tanδ for a two-component system at various ratios of polymer-surface layer and for arbitrary chosen difference in their T_g. One of the components has a constant T_g = 398K, whereas for the second component, T_g was varied in the range of 363-523K. Hence, the model includes both an increase and a decrease of T_g in the surface layer under the influence of the filler surface. With increasing fraction of the surface layer, regular shifts occur, broadening and then splitting the mechanical losses into two maxima. Analogous calculations were performed for other values of ΔT. As generalized characteristics of the curves of the type presented in Figure 5.6, temperatures of the maximum of T_g and tanδ were taken. The concentration dependence of T_g was considered for two cases:

- the surface layer has a higher glass transition temperature as compared to that of the polymer in bulk, i.e., the layer is more “rigid”
- the layer has lower T_g.

The analysis of various cases allowed us to establish that the shift in T_g of the whole polymer depends on the ratio of the constituents and their glass transition

Table 5.1: Effect of composition on the properties of epoxy resins

	ED-20 parts	PEPA phr	Glass beads vol%	T_g (ED-20) K	PBMA	T_g (PBMA) K	T_g (interphase layer) K	PMBA vol fraction
1	100	10	-	385	-		-	-
2	100	10	8	392	-		-	-
3	100	10	16	398	-		-	-
4	100	10	40	399	-		-	-
5	100	10	8	396	0.015	313	-	-
6	100	10	16	392	0.015	306	355	0.36
7	100	10	40	385	0.015	313	363	0.30
8	100	10	8	377	0.08	306	335	0.60
9	100	10	16	377	0.08	315	332	0.64
10	100	10	40	388	0.8	313	-	-
11			-		100	302	-	-
12			8		100	302	-	-
13			16		100	302	-	-
14			40		100	304	-	-

temperatures. On the basis of calculations, which were done for different models, it was shown that with the appearance of the two maxima, corresponding to the unchanged polymer matrix and surface layer, it is possible to make predictions if there exists an essential difference in their glass transition temperatures of the order of 20-40K. This also depends on the surface layer concentration (dependent on filler content) and conditions of deformation.

In general, the theoretical calculations meet the experimental data. One can also suppose that in real systems, the appearance of the maximum of the losses corresponding to the polymer in the surface layer is determined by the chain flexibility, cohesion energy of the polymer, and surface energy of filler.

5.2.3 EXPERIMENTAL EVIDENCE

Let us now consider some experimental data on the influence of the interphase on the viscoelastic properties. One of the most convenient ways to study the problem is to use some model composites, consisting of the reinforcement covered by polymer, modelling the interphase layer, and polymer matrix. The system epoxy resin-glass beads covered with poly(butyl methacrylate) was prepared[45] and the temperature dependence of viscoelastic characteristics were studied (see Table 5.1). Figure 5.7 shows temperature dependence of the mechanical loss maximum for both epoxy resin and PBMA filled with glass beads. As was expected, introducing filler into epoxy resin shifts the transition temperature to higher values (curves 1-4). This shift is accompanied by a decrease in the absolute value of the maximum. For PBMA, there is no change in the temperature position of the main maximum, but considerable decrease in its value and some broadening are observed (curves 11-14).

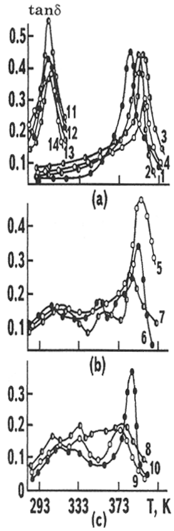

Figure 5.7. Temperature dependences of mechanical loss, tanδ, in the system: epoxy resin-glass beads covered by PBMA. Compositions corresponding to the curves are given in Table 1. Curve numbers: (a) Left curves: 11, ● 12, 13, o 14. Right curves: ●-1, -2, -3, o-4; (b) o-5, ●-6, -7, (c) -8, o-9, ●-10. [Adapted by permission from Y. S. Lipatov, V. F. Rosovitsky, and V. V. Shifrin, *J. Appl. Polym. Sci.*, **27**, 455 (1982)]

In the model system chosen, the difference between temperature positions of the main maxima is $\Delta T = 80$, which excludes the overlapping maxima for both polymers. Figure 5.7b shows the results for epoxy resin filled with PBMA-covered particles (layer thickness 0.015 mm). Increasing filler concentration from 8 up to 40 vol. parts leads to a shift in tanδ maximum to lower temperatures. On curve 5 there may be detected a weak maximum corresponding to glass transition of PBMA. With increasing filler content, this maximum manifests itself more markedly with some shift to higher temperature (curves 6,7). At the same time, the maximum for epoxy resin shifts to lower temperatures. Such effect of mutual influence of two components on their transition temperatures was described earlier.[46] Two intermediate maxima of tanδ at 355 and 363K (curves 6,7) are of interest. Their appearance shows the existence of an interphase layer at the interface between epoxy resin and PBMA. The formation of composite took place initially at room temperature close to T_g of PBMA. The high mobility of PBMA segments at this temperature region promotes the diffusion of reaction mixture (epoxy resin and curing agent) into PBMA phase. This may lead to the formation of an interphase region having its own tanδ maximum (curves 6-9). This interphase is supposed to be a kind of semi-interpenetrating network consisting of network epoxy resin and linear PBMA. The maximum positions for the interphase region on the temperature scale are dependent on the number of crosslinks in epoxy resin which are in entanglement with linear PBMA molecules. It is clear that increasing content of PBMA should shift glass temperature of interphase region to lower temperatures (82°- curve 6, 62° - curve 8, 59°- curve 9).

A considerable change was observed in the shape and position of maximum tanδ for layer with thickness 0.8 mm. Curves 8 and 9 allow us to suppose that the absolute values of losses for PBMA and epoxy resin (curves 8,9) are approximately equal, which is a sign of continuity of both phases. It is remarkable that there are intermediate maxima on curves 8 and 9 at 335 and 432K. The temperature difference observed in the position of tanδ maxima for layers of different thickness may be explained by enrichment of the interphase region with epoxy resin (at thickness 0.015 mm) and with PBMA (thickness 0.8 mm).

Having used the Gordon-Taylor equation[47] for compatible mixtures, the volume fraction of PBMA and epoxy resin in the interphase region, φ_1 and φ_2 may be calculated:

$$T_{g12} = T_{g1} + K\left[\frac{\varphi_2(T_{g2} - T_{g12})}{\varphi_1}\right] \qquad [5.43]$$

where T_{g1} is the glass temperature for PBMA, T_{g2} the same for epoxy resin, T_{g12} is the glass transition temperature of the interphase region, and K is constant. The calculations according to the experimental data have shown that in the interphase region, redistribution of components takes place, depending on the system composition. As is seen from Figure 5.7, curve 10, there are two sharp maxima for PBMA and epoxy resin, the intermediate maximum is less pronounced. The comparison of peaks in maxima tanδ allows us to suppose that epoxy resin forms a continuous phase.

The greatest fraction of interphase region is present in curves 8 and 9, as follows from the peak height of tanδ corresponding to the glass transition. Curves 2 and 5 show the influence of thin PBMA layer (0.015 mm) (glass beads concentration 8 vol%) on glass transition temperature. In such a composition, a very small fraction of component with lower T_g increases glass transition temperature of epoxy resin; the maximum tanδ becomes broader. Increasing glass transition temperature in the system with PBMA shows that surface influence manifests itself through such a soft layer and leads to the increasing rigidity of epoxy resin. In such a way, the intermediate layer exerts complicated influence on the viscoelastic properties, depending on its thickness.

The model composites were prepared[48] from glass beads covered with a varying thickness of elastomers. These composites were studied in terms of viscoelastic behavior and the influence of the interlayer thickness on this behavior was established. It was found that the presence of untreated glass beads in the epoxy matrix reduces the mobility of chains in the main relaxation region. With increasing thickness of the rubbery interlayer, the glass transition is slightly lowered and the mobility of the epoxy network increases in comparison with untreated or silane-treated glass composites.

The mechanical properties of interfacial regions between fiber and matrix were also determined.[49] The three-phase model was proposed, composed of fiber, interphase and matrix. If the properties of fiber, matrix and interphase layer are known, the mathematic procedure can be used to compute the elastic properties of the interphase. The mathematical model allows also to determine both the properties and the volume fraction of the interphase.

Experimental data for epoxy resin composite show that the change in the composite moduli with respect to the interphase thickness is the greatest for high fiber volume fraction and the lowest for low fiber volume. This trend is typical, regardless of the ratio of matrix modulus to interphase modulus. The authors believe that the properties of the interfacial region often arise from chemical interaction between the constituents. The resulting interphase mechanical properties are *in situ* properties which can only be determined through mathematical analysis of composite bulk properties measurements.

The dynamic mechanical properties (shear modulus and loss tangent) of polymer composites prepared from carbon fiber and thermosetting and thermoplastic resins were studied in the frequency range 0.01-5.0 Hz.[50] The surface of the fiber was covered by the interlayer from styrene-co-maleic anhydride polymer. It was established that different interphase composition causes a difference of dynamic mechanical behavior and that the interphase contributes both to glass transition and to energy dissipation.

A very interesting attempt was made[51] to establish the thickness of the intermediate layer from parameters characterizing the interaction at the filler-matrix interface. To study the system polypropylene-fillers differing in particle size and specific surface, the authors have used the equation:

$$E_c = E_m \left[\frac{1-\varphi_f}{1-2.5\varphi_f} \right] \exp B\varphi_f \qquad [5.44]$$

where B is the constant characterizing the interaction at the interface (specific surface - A_f). Parameter B is expressed as:

$$B = (1 + A_f \rho_f \delta) \ln \frac{x_i}{x_o} \qquad [5.45]$$

where δ is the interlayer thickness, x_i and x_o are given properties of composite and matrix. Value of B was found from the composition dependence of modulus. Rearrangement of Eq 5.45 gives:

$$B = C_1 + C_2 A_f \qquad [5.46]$$

where $C_1 = \ln(E_c/E_m)$, $C_2 = \rho_f \ln(E_c/E_m)$ (ρ_f is filler density). According to this equation, B is a linear function of A. The thickness may be determined as $\delta = C_2/C_1\rho_f$. If, instead of the modulus in Eq 5.44, other properties are used (tensile strength, yield stress, etc.), the same equation is valid. However, the value B and thickness of the interlayer are dependent on the properties studied, and are in limits

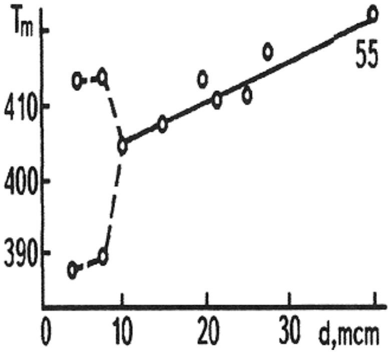

Figure 5.8. Dependence of the temperature of maximum tanδ on the initial thickness of the layer (frequency 700 Hz).

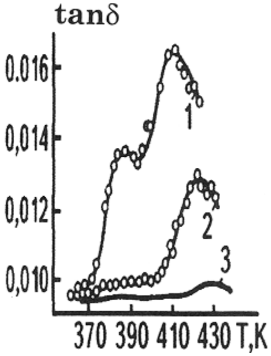

Figure 5.9. Temperature dependencies of tanδ at successive removing of the upper layer: 1-thickness 4, 2-2, 3-1x10^{-6}m.

of 0.005-0.16 μm. Interphase thickness calculated from the modulus is small, while that calculated from the yield or tensile strength is an order of magnitude larger. The difference is explained by varying conditions of deformation in measurement of these properties.

A very interesting approach to the estimation of the interphase thickness is based on the method of reduced variables.[52,53] Calculations are based on the hypothesis that the interphase layer in the transition region remains in glassy state when the main part of matrix has already passed into the rubber-like state. In this case, the dependences of the modulus on the filler content may be investigated both for glassy and rubber-like states. By extrapolation of the experimental curves up to the point of their intersection, so-called critical concentration of filler, φ_{crit}, may be found at which all matrix should pass to the state of interphase, i.e., preserve its glassy state at the temperature which is higher than the glass temperature of initial matrix. Knowing the value of φ_{crit}, one can calculate the thickness of the interphase by dividing the volume of a binder at φ_{crit} by the area of the interface. The experimental results of many authors give the thickness of the interlayers, which varies in the range from tenths to hundreds of nanometers. This parameter is important because it allows for qualitative estimation of interaction intensity at the phase interface.

Earlier, it was noted that the interphase should be considered to have a multilayered structure. It means that at different distances from the surface the mechanical properties of the interphase should also differ. This question was

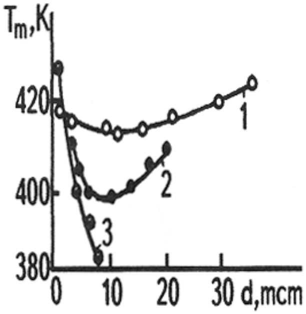

Figure 5.10. Dependence of temperature of tanδ maximum on the thickness of the remaining layer. Initial thicknesses: 1-37, 2-20, 3-8x10^{-6} m.

studied by analyzing the gradient of segmental mobility of thin epoxy films on a copper surface.[54] The experimental method consisted of layer-by-layer removal of the upper layers of the film and determining temperature of mechanical loss maximum for the remaining film. It was found (Figure 5.8) that with decreasing film thickness, T_g diminishes, and at thicknesses smaller than 10 μm, one maximum is split into two. The difference in properties of layers is seen from Figure 5.9. Curve 1 characterizes temperature dependence of tanδ for initial film and curve 2 after removing the upper layer. The heights of maxima change, and the low-temperature maximum on curve 1 disappears, whereas at high temperature the maximum shifts to higher temperatures. It means that the layer in proximity to a solid surface has lower molecular mobility, compared with the bulk of film. Figure 5.9 shows that with decreasing thickness of the residual film layer, T_g changes. The dependence is connected with the initial thickness of film. Some methods were proposed to calculate T_g values at different distances from the surface. The results of calculations are presented in Figure 5.10. T_g and the segmental mobility in the surface layer depend on the distance from the interface. The latter indicates that surface layers have a complicated structure, as a result of which the properties of the layer change non-monotonously with change in the distance. This fact is of great importance to understand the mechanism of failure of adhesion joints, because at various distances from the surface, different levels of cohesion strength are expected.

5.3 BASIC PRINCIPLE OF TEMPERATURE-FREQUENCY-CONCENTRATION SUPERPOSITION IN REINFORCED POLYMERS

Limited molecular mobility in the boundary or interphase layer is equivalent to increasing chain stiffness or formation of additional bonds in the structural network of polymer. The addition of filler has the same effect on the polymer as temperature decrease or increase of frequency of deformation. It follows from this that a principle of temperature-frequency-concentration superposition must ap-

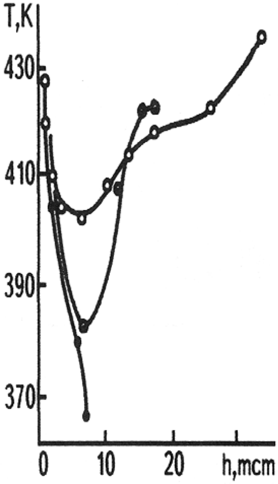

Figure 5.11. Dependence of the temperature of tanδ maximum on the distance from the surface at various initial thicknesses: ● - 10, ⊖ -15, o-20x10^{-6} m.

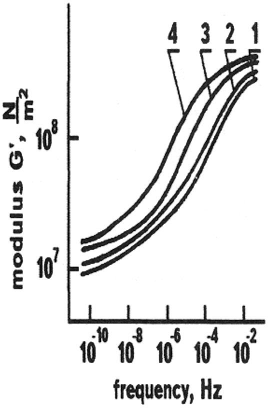

Figure 5.12. Generalized curve of dependence of log G' on logωa$_T$ for epoxy compositions with quartz filler at 353K. Volume fraction of filler: 1-0.045, 2-0.11, 3-0.32, 4-0.44. [Adapted by permission from Y. S. Lipatov, V. F. Babich, and V. F. Rosovitsky, *J. Appl. Polym. Sci.*, **18**, 213 (1974)]

ply to filled polymers as well as the well-known principle of temperature-frequency superposition.[55]

In temperature-frequency analogy, the curves of frequency dependencies of moduli and losses, at various temperatures, in the range of transition temperatures, have similar character and may be displaced by parallel shift along the frequency axis. The value of the shift depends on the temperature and is described by the well-known equation of Williams-Landell-Ferry (WLF):[55]

$$\log a_T = \frac{C_1^g (T - T_g)}{C_2^g + T - T_g} \qquad [5.47]$$

where a_T is the coefficient of frequency shift, representing the ratio of relaxation times at temperature T and T_g (or any arbitrarily taken reduction temperature), and C_1^g and C_2^g are constants. Using this analogy, one can calculate the same dependencies in a broad range of frequencies at any given temperature from the

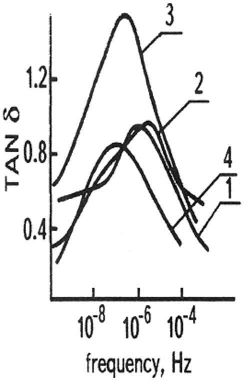

Figure 5.13. Dependence of tanδ on frequency for various volume fractions of filler: 1-0.045, 2-0.11, 3-0.32, 4-0.44. [Adapted by permission from Y. S. Lipatov, V. F. Babich, and V. F. Rosovitsky, *J. Appl. Polym. Sci.*, **18**, 213 (1974)]

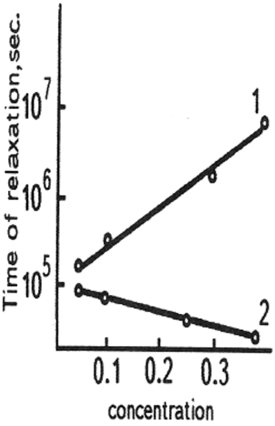

Figure 5.14. Dependence of relaxation time on filler concentration. [Adapted by permission from Y. S. Lipatov, V. F. Babich, and V. F. Rosovitsky, *J. Appl. Polym. Sci.*, **18**, 213 (1974)]

data on the frequency dependence of viscoelastic properties in a rather narrow frequency range. Until now, only one paper has been published on this subject.[58]

The principle of temperature-frequency-concentration superposition may be stated as follows. Increase in the filler concentration leads to the same increase in the real part of the complex elasticity modulus as a rise in frequency of deformation or reduction in temperature. The most general result includes the dependence of stress on deformation standardized with respect to temperature and filler concentration. However, it is not possible to present all the parameters in a concentration-invariant form by using one method of standardization in the full range of filler concentration. In particular, the influence of the filler in the initial section of the stress/strain curve is greater than the prediction by the general method of reduction. The magnitude of the elongation at break may in turn be presented in a concentration-invariant form by horizontal or vertical shift of experimental curve. Generalized plot of $\log G'$ vs $\log \omega a_T$ relationship for specimens for varying filler content, φ, is presented in Figure 5.12.[56,57] A proof of the applicability of the WLF method was found in the form of the $\log a_T$ vs $T-T_g$ relationship.

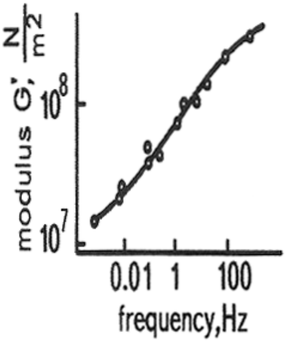

Figure 5.15. Generalized logG' vs. logωa$_T$ curve for filler content 0.045 at 387K. [Adapted by permission from Y. S. Lipatov, V. F. Ba-bich, and V. F. Rosovitsky, *J. Appl. Polym. Sci.*, **18**, 213 (1974)]

It was also important to investigate the influence of filler concentration on the average relaxation time of the polymer matrix in a filled material. The generalized dependence of tanδ on frequency is given in Figure 5.13. With filler concentration increasing, the mechanical loss maximum shifts towards lower frequencies. Since the relaxation time, $\tau = 1/\omega_m$, where ω_m is the frequency corresponding to the loss maximum, the relationship logτ vs filler concentration, φ, can also be calculated. This dependence is nearly linear, which points to exponential dependence of the relaxation time on filler concentration and leads to the conclusion that filler concentration-time superposition can be applied for filled polymers. The characteristic form and position of the log G′ vs log ω curves is known for various concentrations of filler. Figure 5.14 indicates that the WLF method is applicable to these systems. Introducing the concentration coefficient of reduction, a_φ, it becomes possible to plot the generalized curve log G′ vs. $\log\omega a_T$ (Figure 5.15). Figure 5.16 shows the relationship of $\log a_\varphi$ vs filler concentration. The coefficient of reduction is the ratio of average relaxation times in specimens with different filler content:

$$A_\varphi = \frac{\tau_{av,\varphi_1}}{\tau_{av,\varphi_2}} \qquad [5.48]$$

and characterizes the shift of the log G′ vs ω curves on the frequency scale.

Thus, the concentration-time superposition may be expressed as follows: increase in filler concentration leads to the same rise in elastic modulus as raising the frequency of deformation. The application of superposition allows us to investigate the effect of filler on the dynamic mechanical properties and to extend the range of experimental data by predicting properties of the materials. With filler concentration increasing, the average relaxation time increases. Fig-

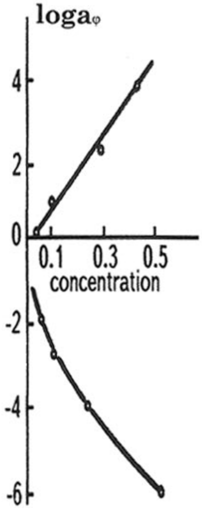

Figure 5.16. Concentration dependence of a_φ at 387K. [Adapted by permission from Y. S. Lipatov, V. F. Babich, and V. F. Rosovitsky, *J. Appl. Polym. Sci.*, **18**, 213 (1974)]

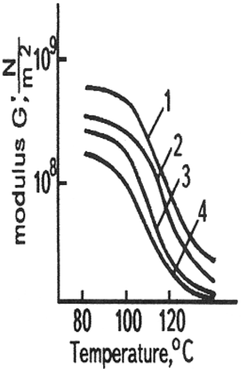

Figure 5.17. Temperature dependence of G′ on volume fraction of filler: 1-0.045, 2-0.11, 3-0.32, 4-0.44. [Adapted by permission from Y. S. Lipatov, V. F. Babich, and V. F. Rosovitsky, *J. Appl. Polym. Sci.*, **18**, 213 (1974)]

ure 5.17 shows the temperature dependence of G′ at various filler concentrations. From these data we can find the concentration dependence of the modulus at various temperatures (Figure 5.18). The logG′ vs φ curves have a very characteristic shape and equidistant spacing, which allows us to apply the WLF method.

The generalized curve is plotted in Figure 5.19. The relationship loga$_{T,\varphi}$ vs T is almost linear. Increasing the filler concentration leads to the same increase in G′ as lowering of temperature, which may be interpreted as fulfillment of the condition for concentration-temperature superposition. The frequency (or temperature-concentration superposition) is a consequence of the exponential dependence of the viscoelastic properties on filler concentration. The physical meaning of these observations is related to the fact that mineral filler practically does not deform, which changes the conditions of deformation of the polymer matrix. In filled specimens, the amplitude of deformation increases significantly with increase in filler content with constant total deformation, and this again may be a reason for increased stress and modulus.[59] The modulus also increases because of transition of part of polymer into the state of the surface or

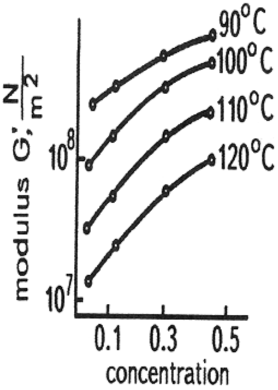

Figure 5.18. Concentration dependence of G' in T_g region. [Adapted by permission from Y. S. Lipatov, V. F. Babich, and V. F. Rosovitsky, *J. Appl. Polym. Sci.*, **18**, 213 (1974)]

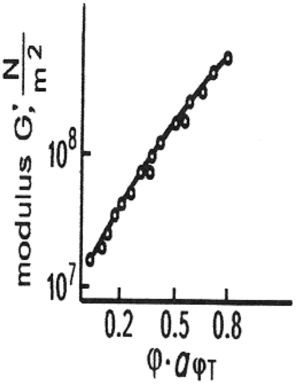

Figure 5.19. Generalized curve for the composition as plotted in accordance with Figure 5.18 at 393K. [Adapted by permission from Y. S. Lipatov, V. F. Babich, and V. F. Rosovitsky, *J. Appl. Polym. Sci.*, **18**, 213 (1974)]

interphase layers which have different mechanical characteristics and reduced molecular mobility. The existence of such a rigid or undeformed layer is in fact equivalent to increasing the apparent particle size or volume concentration of filler.

5.4 INFLUENCE OF THE INTERPHASE LAYERS ON VISCOELASTIC PROPERTIES

Let us consider the relative modulus, i.e., the ratio of the moduli, G'_1 of filled and G'_o of unfilled specimens at various temperatures (Figure 5.20). The dependence of $\log(G'_1/G'_o)$ on filler concentration is linear but the slope of the curves is different for various temperatures. Consequently, the values of relative moduli vary with filler concentration and temperature. It is explained by difference in contribution of the surface layer to the overall properties at different temperatures. In this case, we can assess the change in thickness of the surface layer with temperature. With constant number of filler particles, their volume fraction in polymer, φ, is proportional to their volume, V, at which a surface layer has been formed. For spherical particles:

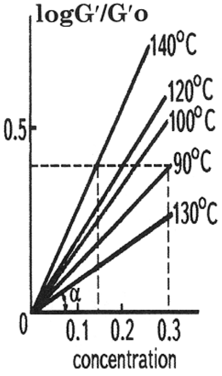

Figure 5.20. Concentration dependence of the relative modulus. [Adapted by permission from Y. S. Lipatov, V. F. Babich, and V. F. Rosovitsky, *J. Appl. Polym. Sci.*, **18**, 213 (1974)]

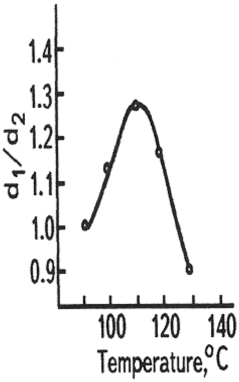

Figure 5.21. Influence of temperature on the relative thickness of the surface layer. [Adapted by permission from Y. S. Lipatov, V. F. Babich, and V. F. Rosovitsky, *J. Appl. Polym. Sci.*, **18**, 213 (1974)]

$$\frac{\varphi_1}{\varphi_2} = \frac{V_1}{V_2} = \frac{(r + \Delta r_1)^3}{(r + \Delta r_2)^3} = \frac{D_1^3}{D_2^3} \qquad [5.49]$$

where subscripts 1 and 2 refer to two temperatures. If we designate the slope of the log (G'_1/G'_o) vs φ curve as A, then:

$$\tan A = \log (G'_1/G'_o)/\varphi \qquad [5.50]$$

and hence

$$D_1^3 = D_2^3 = \varphi_1/\varphi_2 = \tan A_2/\tan A_1 \qquad [5.51]$$

Consequently

$$\frac{D_1}{D_2} = \left(\frac{\tan A_2}{\tan A_1}\right)^{1/3} \qquad [5.52]$$

Figure 5.21 shows the modulus ratio at various temperatures. This dependence has a maximum in the region in which the maximum of mechanical loss occurs. The coincidence is due to the fact that at this temperature the time taken to carry the experiment is comparable with the average relaxation time of the polymer matrix. At a temperature corresponding to the mechanical loss maximum, the relaxation times in the surface layer are longer than the characteristic time of the experimental scale, and accordingly, the layer cannot deform significantly. Simultaneously, at great distances from the interface, the relaxation times of the polymer are comparable with the time of action, and accordingly the overall deformation of the material is determined by the deformation time of the layers which are distant from the interface. The data allow us to anticipate that there should be also a dependence of mechanical properties of composites on the frequency, determined by the presence of interphase.

The temperature and frequency dependencies of the modulus and mechanical losses were calculated[37] on the basis of a simplified Takayanagi model for two cases: in the absence and presence of the interphase layers. It was established that the deformations of a filled specimen, ε_c, interphase layer, ε_i, and filler concentration, φ, are connected by the relationship:

$$\varepsilon_c / \varepsilon_i \approx (1 - \varphi^{1/3})^{-1} \qquad [5.53]$$

At high loading, the real rate of deformation of interphase layers is much higher, compared with the deformation rate of the specimen. If we accept that increase in the deformation rate is equivalent to increasing deformation frequency, we can conclude that the real rate of deformation of the interphase will differ from the rate (frequency) of specimen deformation similar to their deformations. To calculate the frequency dependence of $E_c(\omega)$ and $\tan\delta(\omega)$ for composites with different φ, for each φ curve, $E(\omega)$, for the interphase, must be shifted by the value $\Delta\log\omega = \log(1-\varphi^{1/3})^{-1}$. It means that the average relaxation time in composite material increases exponentially with filler content, even when interphase layers are absent.

The presence of an interphase layer requires us to consider the polymer matrix as consisting of two parts: interphase and free matrix, i.e., the model for a two-component system must be used. The viscoelastic properties of such a system depend on the ratio between these two parts and frequency. On the other hand, the frequency dependence of a composite containing interphase depends on the amount of the interphase layers and their properties, determined by factors discussed above.

The principles of modelling of viscoelastic properties which account for the interphase participation were developed.[60,61] Also, the dependence of viscoelastic properties on thickness of the interphase was theoretically studied using a mechanical model.[62]

The model is a cube of high-modulus filler covered by an uniform polymeric layer, the thickness and properties of which are arbitrarily changed during calculations made for the glass transition temperature range. Maximum values of mechanical loss tangent, tanδ, loss modulus, E'', temperatures at which maxima take place, and values of complex modulus, E*', have been chosen as generalized characteristics of viscoelastic properties. Results of theoretical calculations have shown that varying the interphase thickness and its viscoelastic properties, it is possible to change in a wide range the viscoelastic properties of filled polymers and their temperature dependencies. The interval in which properties of filled polymer can be regulated depends on the difference between properties of interphase and matrix. The larger these differences, the higher the possibility to regulate composite properties.

Figures 5.22 and 5.23 show some results of calculations for "soft" interphase (ΔT is -40°C). The changes in properties depend on the filler amount and ΔT value (soft or rigid interphase).

Still another approach to the estimation of interphase contribution to dynamic properties was proposed by Theokaris.[63] Interphase (or mesophase, in the terminology of Theocaris) is viewed as having its own glass transition temperature and the properties of composite may be derived from analyzing a mechanical model based on the well-known mechanical models of Maxwell and Voigt.

For the loss factor the following relationship was derived:

$$\eta(\omega) = \frac{E'_m(\omega)\eta_m(\omega)v_m + E'_i(\omega)\eta_i(\omega)v_i}{E'(\omega)v_m + E_f v_f + E'_i(\omega)v_i} \qquad [5.54]$$

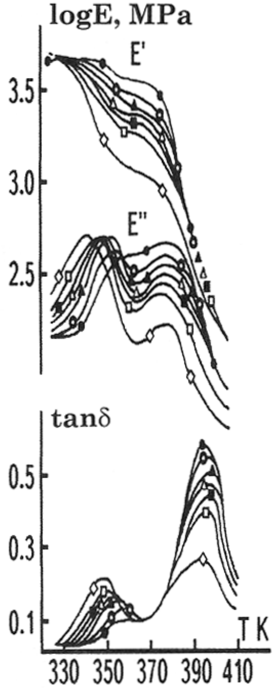

Figure 5.22. Calculated E', E" and tanδ values in terms of temperature with d=0.01-●, 0.02-○, 0.04-s, 0.06-Δ, 0.08-■, 0.1-□, 0.2-◇; ΔT=-40, ϕ=0.2. [Adapted by permission from L. N. Perepelitsyna, Y. S. Lipatov, and V. F. Babich, *Mech. Compos. Mater.*, No. 4, 610 (1991)]

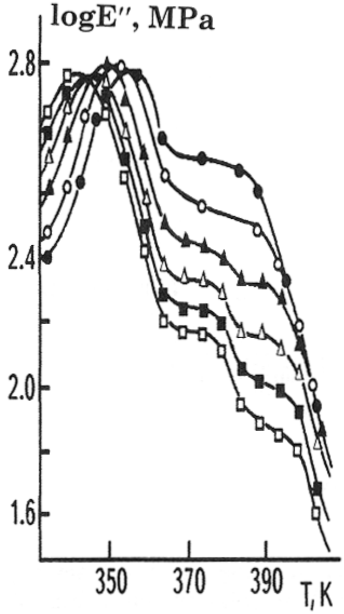

Figure 5.23. The calculated E" values in terms of temperatures for various thicknesses of interphase layer. ΔT=-40, ϕ=0.4. The notations are the same as in Figure 5.22.

where v_m, v_i, and v_f are volume fractions of matrix, interphase and filler, respectively, K is coefficient, and ω frequency. If we assume that ω_g and ω_{gm} are the frequencies corresponding to transition temperatures of composite and matrix, then at $\omega_g > \omega_{gm}$, $T_g > T_{gm}$, and at $\omega_g < \omega_{gm}$, $T_g < T_{gm}$. At the transition frequency ω_g, the loss factor, assumes its maximum value; hence it is valid that:

$$\left|\frac{\delta\eta(\omega)}{\delta\omega}\right|_{\omega=\omega_g} = 0 \qquad [5.55]$$

Further, Eq 5.56 may be found :

$$\left|\frac{\delta\eta(\omega)}{\delta\omega}\right|_{\omega=\omega_{gm}} = \left[\left(-\frac{\delta E'_m}{\delta\omega}\right)\eta_m v_m E_f v_v K + \left(\frac{\delta\eta_i}{\delta\omega}\right)E' E'_i v_i + \left(\frac{\delta E'_i}{\delta\omega}\right)\eta_i E_f v_i v_f K - \Delta E\right][(E')^2]^{-1}$$

where:

$$E' = E'_m(\omega)v_m + E'_i(\omega)v_i + E_f v_f K \qquad [5.57]$$

$$\Delta E = \left(\frac{\delta E'_m}{\delta\omega}E_i - \frac{\delta E'_i}{\delta\omega}E'_m\right)(\eta_i - \eta_m)v_m v_i \qquad [5.58]$$

and

$$\left|\frac{\delta\eta_m(\omega)}{\delta\omega}\right|_{\omega=\omega_{gm}} = 0 \qquad [5.59]$$

Expressing the frequency dependences of E'_m and E'_i, using equations of Maxwell or Voigt, which include the average relaxation times, and taking that these times are almost equal for matrix and interphase, the contribution of interphase to the position of maximum of losses of composite may be analyzed. The sign of Eq 5.56 depends mainly on terms $(\delta E'_m/\delta\omega)_{\omega=\omega_g}$ and $(\delta\eta/\delta\omega)_{\omega=\omega_g}$. The first term is always positive, whereas the value of the second term depends on the relative position of the glass transition of the interphase. If $T_{gi} > T_{gm}$, then $\omega_{gi} > \omega_{gm}$. This means that the loss factor of interphase has reached its peak at a frequency smaller than ω_{gm} and it has already started decreasing with $(\delta\eta_i/\delta\omega)$ at $\omega = \omega_{gm}$ (Figure 5.24 a). If $T_{gi} < T_{gm}$, the opposite behavior takes place, and this is indicated in Figure 5.24b.

The conclusion can be drawn that if the strong intermolecular bonds are present, between filler and matrix (strong adhesion), interphase has a higher glass transition temperature and T_g of composite will also be higher. For a weak adhesion, the opposite is true. From this consideration, a great contribution of the interphase and its volume fraction to the viscoelastic properties is evident. Theocaris states that the presence of interphase leads to well-separated regions

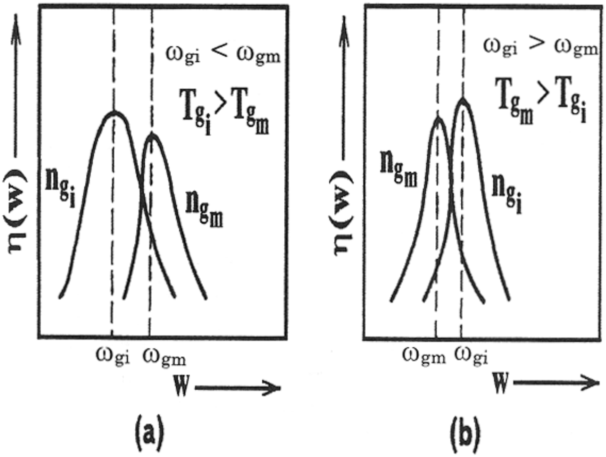

Figure 5.24. Typical curves for the loss factor of the matrix and the interphase in their transition region: (a) Case $\omega_{gi} < \omega_{gm}$, (b) $\omega_{gm} < \omega_{gi}$. [Adapted by permission from P. S. Theocaris and G. D. Spathis, *J. Appl. Polymer. Sci.,* **27**, 3019 (1982)]

of composite with two different glass transitions. The combination of these two transitions determines the total glass transition of the composite material.

5.5 RELAXATION SPECTRA OF FILLED POLYMERS

Experimental data on viscoelastic properties give the possibility to construct the fundamental function of viscoelasticity-relaxation spectra.[12] There is an abundance of data indicating an increase in the average relaxation time in polymers which are on the surface of solid particles.[64,65] This is linked to changes in the structure of surface or interphase layers and adsorption interaction, which limits the molecular mobility, and also with their influence on the packing of macromolecules. From this point of view, we may expect that with an increase in the surface area or filler concentration (equivalent to increasing the fraction of polymer in the surface layer) and reducing the thickness of the interlayer between the particles, there will be a systematic reduction in the molecular mobility and an increase in the average relaxation times until strong binding of macromolecules by the surface excludes from the participation in the relaxation process these relaxors, which are characterized by long times of relaxation.

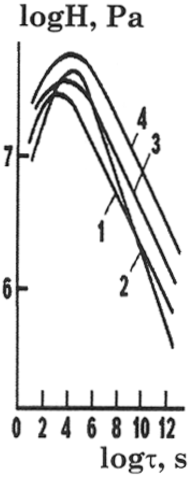

Figure 5.25. Spectra of relaxation times of specimens containing epoxy resin with quartz filler at concentrations 1-0, 2-0.04, 3-0.31, 4-0.44.

Accordingly, it might be supposed that with a change in filler concentration, there will be a predictable change in the spectrum of mechanical relaxation times. In fact, there are some data in literature which confirm these suppositions.[34]

Viscoelastic properties of filled polymers under dynamic loading conditions were investigated to verify the ideas put forward above.[66,67] The frequency and temperature dependence of the elastic modulus in shear, G′, and of the mechanical loss tangent, tanδ, for epoxy compositions with differing concentration of quartz filler were studied. From the dependencies of G′ on the frequency of deformation, the spectra of relaxation times were calculated using the method of Ninomiya-Ferry.[68] Figure 5.25 shows the plot of the spectrum function, H, for various relaxation times, τ, with a different volume fraction of filler. At low filler concentration (0.04 wt%), the relaxation time spectrum undergoes perceptible changes in the region of short times, shifting somewhat towards short relaxation times. Increasing the concentration of filler, in addition to broadening the spectrum in the region of short times, leads also to a broadening of, and shift of, the spectrum towards long relaxation times (curves 2 and 3). In addition, the values of the spectrum function, H, increase with increasing concentration of filler, and the slope of the linear part of the spectrum in the filled specimen is smaller than in the unfilled polymer.

Taking into account that the spectrum of relaxation times of quartz does not overlap with the spectrum of matrix, these changes should evidently be linked only with the changes in properties of the matrix and with change in the conditions of deformation as a consequence of the influence of the volume of high-modulus filler.

Let us turn to analyze the change in conditions of deformation of polymer in the presence of filler. A high-modulus filler practically does not deform under stress, since its modulus is thousands of times higher than that of epoxy matrix.

Accordingly, the deformation of a filled specimen occurs solely on account of matrix deformation. The presence of a large number of particles of undeformed filler means that the relative deformation of polymer interlayers between the filler particles may be many times in excess of the overall deformation of a filled specimen. Consequently, very high amplitudes of stress are set up in the polymer interlayers. According to experimental data,[69] the increase of stress leads to reduction in relaxation times, which may explain the initial shift of the spectrum towards short times.

The comparison of the spectra of relaxation at the different amplitudes shows that increase in amplitude of deformation shifts the spectrum significantly towards shorter times.[66] The presence of quartz filler should shift the spectrum curves to the left, and the extent of shift should increase with filler concentration. Figure 5.25 shows, however, that no such shift takes place. With increase in filler concentration, the spectra shift to the right and broaden, and the slope of linear section of the spectrum changes. This indicates that the increase of filler concentration or total filler surface reduces the segmental mobility of polymer and shifts the spectra towards longer times. It not only compensate for the shift of the curves to the left, which would be expected because of the incompressibility of the filler, but even shifts spectrum curves to the right. The shifts are noticeable in the region of long relaxation times, meaning that the limited mobility regards longer structural elements, which control an increase in the average relaxation times. Some broadening of the spectrum in the direction of short relaxation times may be interpreted as a consequence of increase in the defectiveness of the polymer network in the presence of the filler, and loosening of the molecular packing in the boundary layer of polymer.

The experiments with the quartz filler show that shift of the curves of the spectrum function, H, in polymers filled with a high-modulus filler, is a result of interaction of at least two factors: a change in conditions of deformation in the presence of filler particles (as a result of which the spectrum shifts to the left) and the influence of filler surface on the properties and structure of the polymer matrix (the spectrum shift to the right).

It was thought desirable to carry out further investigations excluding the influence of one of the factors. It was found convenient to exclude changes in the conditions of deformation of the polymer matrix by using filler similar in mechanical properties to the matrix. A powder of the same cured epoxy resin was used as filler. Figure 5.26 shows the spectra of relaxation times for specimens with varying content of polymeric filler. For comparison, the spectrum curve of the matrix is presented (epoxy resin cured in the absence of filler). There is a significant shift of the spectrum curve towards longer relaxation times as compared with the spectrum of pure cured resin. The addition of filler changes the slope of spectrum. It is characteristic that the shift and broadening of spectra, are in this case, greater than for the specimens containing quartz filler. This is due to the elimination of non-deformability of filler.

Also, Figure 5.26 shows that with increase in filler concentration, the right part of the spectrum shifts towards longer times. This is evidence that the spectra of the surface layers of the matrix, cured in the presence of filler, are significantly dissimilar from those of a polymeric filler of the same nature.

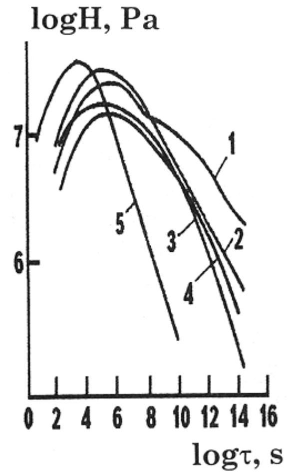

Figure 5.26. Spectra of relaxation times of epoxy resin filled with epoxy resin powder at 353K at concentrations: 1-0.05, 2-0.10, 3-0.40, 4-0.25, 5-with no filler. [Adapted by permission from Y. S. Lipatov, V. F. Ba-bich, and V. Rosovitsky, *J. Appl. Polym. Sci.*, **20**, 1787 (1976)]

A very interesting picture is revealed when analyzing the concentration dependence of the average relaxation time. A non-monotonic relationship, with a broad minimum after initial increase, is obtained. Such character of dependence may be connected with increase in filler concentration, contributing to decrease in the average relaxation time of the whole system, since the average relaxation time of filler is lower than that of binder cured in its presence. With concentration of interphase increasing (long relaxation times), its effect on the relaxation times becomes prevalent. The resultant contribution of these two factors is that the average relaxation time of the polymer, filled with polymeric filler of the same nature, is a non-monotonous function of the filler concentration.

The non-monotonic changes of the relaxation time may be also connected with non-uniformity of the interphase structure, which depends both on its volume fraction and the thickness. Similar results were presented for relaxation spectra of epoxy resin filled with fine particles of iron.[70]

The changes in the relaxation behavior, due to decreasing molecular mobility, may be followed by measurement of dielectric relaxation and NMR. For example, experimental data[71,72] on the dielectric properties of the styrene-methyl methacrylate copolymer filled with fumed silica were used to calculate the circular diagrams of Cole-Cole and parameter of distribution of the relaxation times, α. It was established that increasing filler concentration, i.e., the fraction of interphase, led to essential changes of α in the region of low and high temperature relaxation. The reduction of α in the region of dipole relaxation is brought about by the less dense packing of the polymer in the surface layer. It is evidence of the formation of a large number of relaxors and increase in the mobility of functional groups and all kinetic units which are not bound to the surface. In the region of segmental mobility, increase in the distribution parameter, α, points to hindering of segmental movement at the interface, leading to a narrowing of the spectra of relaxation times.

It is of importance to compare experimental data with results of theoretical calculations.[38] Using the simplified mechanical model, the relaxation spectra were calculated for composites with “soft” and “rigid” interphase (Figure 5.27). Increased concentration of high-modulus filler in the absence of interphase spectral curves should shift to higher logH without changing shape and position of the maximum on the time axis. When interphase is present, increasing φ leads to the essential shift of the spectral curves to the shortest times, if the interphase has $T_{gi} < T_g$ (soft layers, curves 8-10). For rigid layers, the shift to higher relaxation times was not observed. The position of the spectrum depends on the difference between glass temperatures of the interphase and matrix. Lowering T_{gi} (at constant filler concentration and layer thickness) causes a shift of the main maximum to lower times and some decrease of its height. The slope of the curve in the region of high relaxation times is also changed. It is typical for rigid interphase that the spectral curves do not change as much as for soft interphase and the maximum shifts to higher relaxation times only slightly.

The analysis of the relaxation spectra of filled elastomers,[73-75] in the region of very high relaxation times, gave a possibility to observe splitting of the main maximum of the segmental losses into two maxima. An additional high-temper-

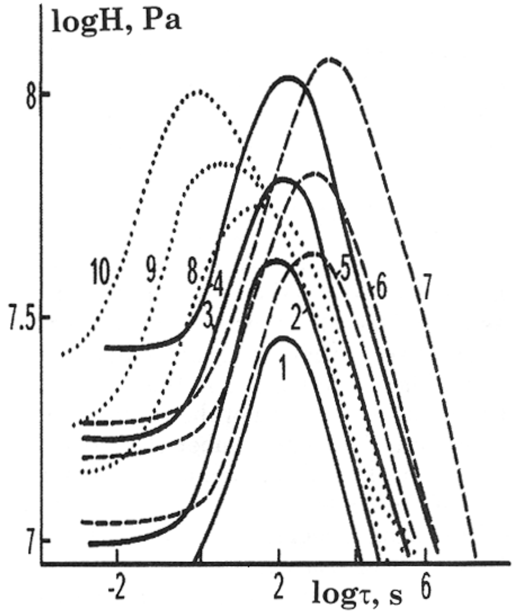

Figure 5.27. Calculated relaxation spectra for various filler amounts and various T_{gi}. 1-4 no interphase, 5-7 ΔT=+35K, 8-10 ΔT=-25K, ϕ=0 (1); 0.2 (2,5,8); 0.4 (3,6,9); 0.6 (4,7,10).

ature maximum was assigned to the interphase.[76] The difference in position of the maxima reaches 333K, which corresponds to the conditions discussed above. With increasing filler content, the height of the main maximum decreases and that of the interphase increases. However, it was discovered that rubber transition temperatures do not depend strongly on the type and content of filler. On this basis, the conclusion was drawn that the relaxation processes in the interphase, which does not depend on the filler amount, are determined preferentially by the conformational and not the energetic contribution to segmental mobility. This statement agrees with the concepts presented in Chapter 3. Thus, the conclusion may be drawn that all factors determining the change in the properties of the interphase, under influence of filler surface, contribute to the relaxation behavior and relaxation spectra. Presently, however, it is very difficult to distinguish between various factors contributing to the change in molecular mobility and spectra of the relaxation times.

5.6 RHEOLOGICAL PROPERTIES OF FILLED POLYMERS

Rheological properties of filled liquid oligomers and polymer melts have a great importance for the production of reinforced polymers.[77,78] Viscosity of melts and flow temperature are strongly dependent on filler concentration, its interaction with dispersion media, and the shape of particles. The structure formed, due to the presence of filler particles, gives an additional contribution to the rheological properties of a filled system. The simplest relationship connecting the viscosity of a filled disperse system is based on the Einstein equation for suspensions:

$$\eta = \eta_o (1 + 2.5\varphi) \qquad [5.60]$$

where φ is the volume fraction of filler and η is the viscosity of the matrix changed under the influence of filler, and η_o is the initial viscosity. Another simple equation was developed by Guth:

$$\eta = \eta_o (1 + \alpha\varphi + \beta\varphi^2) \qquad [5.61]$$

where α and β are constants. If between polymer and filler, there act only dispersion forces, then $\alpha = 2.5$ and $\beta = 14.1$. These equations were derived for the case when there is no interaction between filler and media, and when the media behaves as a Newtonian liquid. At strong adsorption or chemical interaction between the components of the system, parameters α and β are variable. These equations are valid only for a small amount of dispersed phase. In some cases, on the basis of the experimental data on deviation of the system behavior described by the above-mentioned equations, the conclusions are drawn in the same way as for the peculiarities of the structure of polymeric dispersion media. However, such conclusions cannot be valid if the conditions used to derive the equations are not fulfilled. At higher filler concentration, the Mooney equation is the most frequently applied:

$$\log \frac{\eta}{\eta_o} = \frac{K\varphi}{1 - \varphi/\varphi_m} \qquad [5.62]$$

where φ_m is the limiting filler concentration at dense packing of particles, and K is Einstein's coefficient (equal 2.5 for spheres). For non-spherical particles the following equation may be used:

$$\eta = \eta_o \exp\left(\frac{\alpha\varphi}{1/f - K\varphi}\right) \qquad [5.63]$$

where α and K are coefficients of the particle shape (α = 10.5-24.8, K = 1.35-1.90), f is the value determined by the ratio of thickness of the surface layer and the particle size.

There are many empirical equations describing the rheological properties of filled polymers but their practical applicability to an actual system is very restricted. However, there are certain general principles determining the rheological behavior of filled systems[78] which link concentration and geometry of particles with the viscosity. On the basis of theoretical concepts of correlation between the parameters of viscous flow and the elasticity of solid, it was suggested that the viscosity of liquid containing filler and the shear modulus of a solid containing filler are related by:

$$\eta / \eta_o = G / G_o \qquad [5.64]$$

If this equation correctly describes the viscosity of filled systems, it is possible to use the equations of Kerner type which give the ratio of shear moduli in filled and unfilled systems and thus allow us to find the corresponding equation for η / η_o. Experimental investigations carried out for filler particles of varying shapes in thermoplastics established conditions under which Eq 5.64 may be used. Eq 5.64 is applicable if the following conditions are observed: The viscosity has to be measured in the absence of anisotropy in polymer melt, i.e., under conditions of steady flow with shear stresses below 10 Pa, when the flow is Newtonian. For non-spherical particles, the viscosity must be measured in the region of concentration where structures formed by filler particles do not occur. Finally, the particle size has to exceed 1 mm because the surface area of particles should not to be so large that a considerable amount of polymer is affected by adsorption forces.

The rheological behavior of filled systems is influenced by a change in the properties of a polymer medium as a result of adsorption interaction of the particles with the polymer and restriction of the molecular mobility of chain in the adsorption layer. Thus, the viscosity is determined not only by hydrodynamic effects but also by mechanical reinforcement of the matrix as a result of interaction with the filler. It has accordingly been suggested[79] that the relative change in viscosity of the medium, due to interaction, is linked with the shift of T_g towards higher temperatures with increasing filler content. The temperature dependence of the viscosity above T_g may be expressed by the WLF equation in terms of the shift of T_g:

$$\log \frac{\eta_{T_g}}{\eta_T} = \frac{40(T - T_g)}{(52 + T + T_g)} \qquad [5.65]$$

If T_{gf} is a characteristic temperature of filled polymer, then:

$$\log \frac{\eta}{\eta_o} = \frac{2080(T_{gf} - T_g)}{(52 + T - T_{gf})(52 + T - T_g)} \qquad [5.66]$$

From this equation, the relative viscosity of a suspension with interacting components may be found:

$$\eta_{rel} = \frac{\eta_f}{\eta} \exp \frac{2080(T_{gf} - T_g)}{(52 + T - T_{gf})(52 + T - T_g)} \qquad [5.67]$$

It must be noted that, although the flow of polymers containing fillers does not, in a number of cases, obey the equation derived for spherical particles in the disperse phase, this does not mean that there is no interaction between the filler particles and the polymer. In many cases, flow takes place in a system where filler particles are covered with an adsorption layer of polymer, as a result of which there is an effective increase in the volume of dispersed phase.[80,81] The existence of this layer, which moves as a single entity along with the filler particle, is governed by the presence of powerful interactions between filler particles and macromolecules. It is interesting to note that sharp increase in viscosity does not bring about any changes in the temperature coefficient of the viscosity. Accordingly, it may be suggested that the mechanism of flow of filled and unfilled polymers is the same, i.e., there is no rupture of the bonds between polymer and filler during the flow.

As it was noted in Chapter 3, the relative increase in the apparent volume fraction of filler particles may be used to determine the thickness of the adsorption layer. Temperature dependence of viscosity of filled polymers is generally non-linear and may be described by the Fogel-Tamman equation:

$$\log\eta = A + \frac{B}{T - T_o} \qquad [5.69]$$

Parameters T_o and B depend linearly on the fraction of polymer not bound to filler. The apparent energy of activation of viscous flow is determined by these parameters:

$$E_a = RB\left(\frac{T}{T - T_o}\right) \qquad [5.70]$$

and depends on the fraction of unbound polymer. With decreasing temperature, one can expect essential diminishing in E in the filler presence, due to an increase in the difference of T-T_o. Diminishing T_o with increase in filler content is connected with increasing fraction of the free volume in the system, which in turn increases with an increase in the fraction of polymer in the surface layers.

Temperature dependence of viscosity is determined by one more factor - the thickness of an adsorption layer, which also depends on temperature. The thickness diminishes with rising temperature and with shear stress. This fact is explained by the differences in chain mobilities at various distances from the surface: more remote layers begin to take part in flow, whereas macromolecules bound to the surface do not participate in this flow. At higher shear stresses, macromolecules with lower mobility begin to take part in flow, which is confirmed by the dependence of the apparent activation energy on the filler content. Thus, current hydrodynamic theories and experimental data show that the viscosity of a filled polymer system increases with filler concentration. At the same time, the change in viscosity when small amounts of filler are introduced may have another character, especially when the dispersion medium possesses its own structure.

Introduction of small amounts of filler of different chemical nature (0.5-1.0%) into the polymer melts leads to a marked drop in viscosity and only after some critical concentration does the viscosity begin to increase again.[82-85] The effect of the decreasing viscosity may reach 10-40% of the viscosity of unfilled melt. The nature and the size of filler particles is of great importance. Increase in the size or asymmetry of particles diminishes this effect. The decrease in viscosity is not sensitive to the nature of the filler if the comparison is made at a constant shear rate. However, the viscosity changes if we compare the results of measurements at constant shear stress. The latter effect is connected with the influence of shear stress on the thickness of an adsorption layer. The appearance of the minimum viscosity was explained by formation of additional free volume in surface layers of filler particles.[34]

The influence of free volume and explanation of sharp increase in viscosity, after reaching critical concentration, is based on the model presentation of the structure of surface layer. In Chapter 3, it was shown that this layer may be considered as consisting of two parts, one more dense and the other more loose. The ratio between these two layers may change, depending on the nature of the matrix and filler. Taking into account such a model, it was supposed[84] that, under the action of shear stresses, the flow in the system proceeds preferentially along the loose layers which have the greatest free volume. This effect leads to diminishing viscosity of the filled melt. However, after reaching a certain concentration, all polymer may be involved in the state of surface layers. In this case, the loose sublayers begin to touch and overlap. After this point, viscosity begins to increase again.

The rheological properties of a filled system are also strongly dependent on the formation, in the dispersion media, of independent structures due to interaction between filler particles.[34] According to Vinogradov and Malkin,[34,77] the properties of filled systems at low shear stress are determined by the mechanical properties of the structure frame formed by filler particles. The viscosity of a filled system, in this range of shear stresses, does not depend on the molecular mass and viscosity of polymer and is about 10^9-10^{10} Pas. At high shear stresses, when the structure frame is fully destroyed, the viscosity of filled melt depends both on polymer viscosity and amount of filler. It should be noted that this effect may be observed only at a rather high content of filler, when the structure frame may be formed. In the course of flow, the structure frame changes, depending on the conditions of deformation.

The influence of filler concentration is more visible at low shear stresses at which the yield stress may exist. It usually appears at filler concentration above 10 vol% (depending on the nature of filler and its particle size). The shear stress corresponding to the yield stress depends exponentially on filler concentration. At the same volume concentration, the strength of the structure frame is higher for smaller particles. Therefore, the relationship between the strength of the structure frame and filler concentration is also exponential.[90] In connection with this, it is important to keep in mind that the particles of small dimensions are capable of agglomeration and the structure frame is formed not by single particles but by their agglomerates.

At high shear stress, the filler structure is destroyed and filler begins to behave like inactive component. The activation energy in this case corresponds to the value typical of an unfilled system. Therefore, one may suppose that the apparent activation energy should not be dependent on the filler type, its concentration and particle size. However, if the structure is not fully destroyed, activation energy is determined by interaction between filler particles and existence of structure.[90] Increasing temperature leads to a more pronounced influence of the structure frame on viscosity. The flow curve of filled melts may be presented as consisting of three regions:

- the region where the flow is realized in the system with undestroyed structure
- the region of transition through the yield stress with sharp decrease of an effective viscosity (by some orders of magnitude)
- the region of flow in the system with destroyed structure when the shear stresses essentially exceed the yield stress and the viscosity is determined by the viscosity of dispersion media with filler particles.

It was also shown[91] that rheological properties of filled melts may be changed when some modification of the filler surface takes place. This effect is connected with change in interaction between particles, formation of surface layers of various thickness, and varying ability of particles to form structural frame. Adding surfactants to the system is an effective way to regulate the rheological properties of the filled system.[92,93]

The investigations of model compositions, based on linear elastomers and various fillers, have shown[94] that the yield stress also may be characterized by the value of the complex shear modulus measured at various frequencies. The dependence of the dynamic modulus on the filler concentration characterizes critical concentrations of the filler, above which the viscoelastic behavior of composition drastically changes. Dynamic modulus corresponding to the yield stress does not depend on the matrix viscosity or its nature. This fact indicates a predominant role of the structural frame for rheological properties of filled polymers.

The modification of theological properties also may be achieved by addition of a small amount of another polymer which is not miscible with matrix polymer.[41] Thus, the general conclusion may be drawn that the peculiarities of the rheological properties of filled polymers are determined by the combined action of various factors, namely, by hydrodynamic effects, the interaction between the filler particle and a matrix, leading to the formation of the surface layers and the formation of the structural frame by the filler particles.

Rheological properties of polymers reinforced with fibrous fillers have their specific features. Fibrous filler is capable of formation of a mechanically entangled system.[95] In this case, the rheological properties are determined by the length of the particle and its flexibility, which is especially important at low shear stresses. For such systems, the activation energy at low shear stress is much lower, compared with unfilled polymer. This effect has its explanation in that the elementary act of flow in a filled system at low shear stress is probably affected by slipping particles in contact with each other, while the resistance to slipping is weakly dependent on temperature.

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6

POLYMER ALLOYS AS COMPOSITES

6.1 POLYMER BLENDS AND ALLOYS

Polymer blends and alloys of linear and crosslinked polymers may be considered as an independent class of PCM. They represent one of the most rapidly growing areas in polymeric materials science. Alloying and blending provides a straightforward and relatively inexpensive method to develop polymeric materials with desirable properties. Polymer blends and alloys have many features inherent to particulate filled polymers. They are, as a rule, heterogeneous systems with developed phase boundaries between constituent components. At the polymer-polymer interface, there are formed interphase layers whose structure and properties depend on the thermodynamic interaction between components. However, up to now, there is no strict definition of polymer blends and alloys. We propose the following definitions based on the thermodynamic consideration and taking as a basis the analysis of phase diagrams of binary mixtures.

It is known that the most common and convenient method of mixing two polymers is by melt blending, which is typical for metallic alloys. Alloys are macroscopically uniform substances obtained by fusion of two or more metals, non-metals, and organic compounds. In general, alloys are not obtained by simple mechanical mixing of the components. By fusing, the components may form mixtures of various phases. The phase state of alloys in equilibrium may be determined from the phase diagrams. It also is known that for linear polymers, the

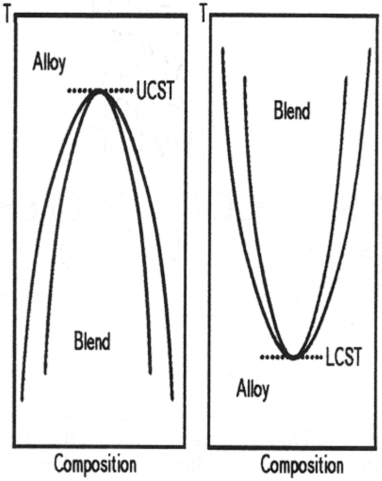

Figure 6.1. Phase diagrams of two-component systems. Left: system with UCST. Right: system with LCST. Interior curves: spinodal. Exterior curves: binodal.

phase diagrams are of two types, with upper and lower critical solution temperatures (UCST and LCST). Taking the phase diagrams as a basis, we give the following definitions (Figure 6.1):[1]

1. Alloys of linear polymers are binary or multicomponent systems that when mixed in the molten state are situated in the region of the phase diagram corresponding to mutual miscibility of the components and to the formation of single-phase solution. This means that the system is thermodynamically stable (at equilibrium) in a molten state. By cooling the melt, a structure develops which depends on the thermodynamic state at a given temperature. If, by cooling, the system with UCST enters the region of unstable states in the phase diagrams (immiscibility or thermodynamic incompatibility arises), it results in the two-phase structure, determined by the conditions of phase separation.

The structure depends on the degree of phase separation occurring and its mechanism (nucleation or spinodal decomposition). The ratio and composition of two phases will be determined by the kinetics and mechanism of phase separation. For binary systems with UCST, the mixing alloy components should be conducted in the region above the spinodal and for the systems with LCST, below the spinodal, i.e., in the range of one-phase solution. For systems with LCST, one-phase structure is preserved by cooling, i.e., a compatible system is maintained.

There is a restricted amount of polymer pairs that are miscible in the whole composition range and in a broad temperature interval. These pairs always remain a single-phase system and represent a group of polymer alloys having the structure of a solid solution.

2. Blends of linear polymers are binary systems that, by mixing in the molten state, are not miscible and do not form a one-phase system (they are not thermodynamically miscible). The components forming a blend may also have UCST or LCST. For systems with UCST, the formation of blend proceeds at temperatures below the binodal and for systems with LCST above the binodal. The transition from two-phase to one-phase state for systems with LCST is practically impossible by lowering temperature because of high viscosity of a melt and the lower rate of the mutual dissolution process. Thus, the structure of blend is determined by the degree of dispersion of one or both components achieved during mixing in the melt.

In such a way, depending on the temperature range of mixing relative to the position of the binodal or spinodal, the same polymer pair may form both alloys and blends. The realization of both possibilities depends on the relationship between the temperature of phase separation for a given composition of a mixture and the glass transition temperature or melting points of both components. As the formation of blends or alloys by fusing the components (mixing in the molten state) is always followed by temperature decrease, the definitions given above allow us to distinguish between the structural features of polymer alloys and blends. The analysis made above allows the conclusion to be drawn that two-phase or multi-phase blends are typical of systems with UCST, whereas one-phase alloys are typical for systems with LCST.

The principle feature of polymer alloys consists of an incomplete phase separation in the system. By cooling a melt of two polymers, the thermodynamic incompatibility or immiscibility of two components arises, which causes the incomplete phase separation of the system. The incompleteness of the phase separation causes the development either of the microphase separation regions of various composition and transition or an interphase zone between coexisting microregions. The system with incomplete microphase separation is not in the state of thermodynamic equilibrium. A segregated structure develops in the bulk because of these processes with complex specific properties: appearance of the regions with different density, composition and mechanical properties, appearance of the internal interphase boundaries, etc.[2]

Polymer alloys may be considered as hybrid matrices[2] or binders of the second generation because they themselves are composite materials. The processes proceeding during their formation lead to the development of the complicated structure because of incomplete phase separation. Therefore, these systems may be considered as self-reinforced (filled) or disperse-reinforced systems, wherein the size, properties, and distribution of the regions of microphase separation - quasiparticles of filler - are determined by a phase diagram of a multicomponent system, conditions of system transition through the binodal and spinodal, and by the mechanism of phase separation (nucleation or spinodal decomposition).[3]

The definitions of polymer alloys, given above, may be applied to the mixtures of network polymers, namely, to the interpenetrating polymer networks, IPNs. However, if the analysis of the behavior of the mixture of linear polymers may be done based on the phase diagrams, for IPNs it is impossible. During the chemical reaction of their formation, the system transits from the low molecular weight components to high molecular ones, connected with crosslinks. However, for these systems, the value of the principle of thermodynamic stability preserves its meaning. The original reaction system for producing IPNs is always a single-phase solution of monomers or oligomers. During the reaction and an increase in the molecular masses of the network fragments, components become immiscible. The non-equilibrium phase separation of the reacting system leads to the formation of two phases of variable composition. Phase separation depends on the kinetic conditions of reaction (see below). Due to chemical crosslinking, the phase separation is hindered and the system never reaches an equilibrium state. The structure of IPNs depends on the conditions of a transfer from a single- to a two-phase system. It is a feature of IPNs that allows one to relate them to polymer alloys in accordance with the definitions given above. Again, there are some cases when during the formation of IPN, the phase separation does not proceed and the system stays miscible, being in the state of thermodynamic equilibrium. Such IPNs may also be considered as polymer alloys (solid solutions).

In the present chapter, we consider the peculiarities of the structure and properties of polymer alloys as hybrid matrices, which allows us to refer them to self-reinforced polymer composites.

6.2 THERMODYNAMICS OF THE MIXING OF POLYMERS

The bibliography of works dedicated to the thermodynamics of polymer mixtures and blends is large,[4-9] and we only briefly review the current approaches and their limitations. The main characteristics of polymer blends is thermodynamic compatibility or incompatibility of the components, which is determined by the phase diagram of the system. It should be emphasized that such consideration in principle is incorrect. because compatibility depends on many factors, among which are temperature and composition. Polymer pairs are neither fully compatible nor incompatible, but various conditions exist at which the polymer pair is miscible or immiscible. However, depending on the chemical constitution of mixed components, the window of miscibility may be very broad, or, on the contrary, very narrow.

The term “ compatibility ” is widely used in literature (see, for example, ref.[7]). This term is also used to describe good adhesion between the constituents, average mechanical properties, and other factors. It is more correct to use the term “miscibility” for description of thermodynamic behavior of polymer mixtures.[5] The term ”miscibility" was chosen to describe polymer-polymer mixtures having behavior similar to that expected of a single-phase system.[5] However, it does not imply ideal molecular mixing but suggests that the level of molecular mixing is adequate to yield macroscopic properties expected of a single-phase material.[5] A miscible polymer-polymer pair is a solution of one polymer in another. Mutual miscibility does not imply that solubility of segments is necessarily related to the statistical arrangements of segments: interactions between similar and dissimilar macromolecules can result in formation of molecular aggregates or associates (clusters), or in other non-statistical arrangements of segments.[4]

The diminishing Gibbs free energy of mixing, ΔG, is frequently used as a criterion of miscibility:

$$\Delta G = \Delta H - T\Delta S \qquad [6.1]$$

where ΔH and ΔS are changes in enthalpy and entropy of mixing. The thermodynamically stable system is formed when $\Delta G < O$. This condition is realized if $\Delta H < 0$ and $T\Delta S > 0$, or if $\Delta H > 0$ but $|T\Delta S| > |\Delta H|$. The experimental data show that both cases, $\Delta H > 0$, $\Delta H < 0$ and $\Delta S < 0$, may be observed on mixing of two polymers.

In most cases, in order to estimate the miscibility of two polymers, the approximations of the theories of regular solutions are used. New statistical theories developed by Prigogine,[10] Patterson,[11] Sanchez,[12-14] and Flory[15,16] are also widely used.

The change in Gibbs free energy of mixing of two polymers at the total volume of the mixture, V, may be calculated according to the equation:

$$\Delta G_{mix} = (RTV / v_r)[(\varphi_A / r_A)\ln\varphi_A + (\varphi_B / r_B)\varphi_B + \chi_{AB}\varphi_A\varphi_B] \qquad [6.2]$$

where v_r is the volume of segment taken as equal to the volume of repeating unit of the chain, r_A and r_B are numbers of segments in molecules of type A, and B, C_A, and C_B are volume fractions of the mixture components; χ_{AB} is the thermodynamic interaction parameter of segments in volume v_r. Parameter χ_{AB}, in accordance with the Flory theory,[15] can be calculated as

$$\chi_{AB} = Z\Delta W_{AB}/kT \qquad [6.3]$$

where $\Delta W_{AB} = 1/2(W_{AA} + W_{BB} - W_{AB})$; W_{AA}, W_{BB} are the energies of interaction of segments of respective molecules and Z is the coordination number of the lattice in the lattice model of liquid (solution) taken for calculations.

Eq 6.3 makes it possible to determine the conditions for the system at the critical point, critical values of the concentration, and the interaction parameter. For polymers of a high molecular mass, the $(\chi_{AB})_{cr}$ value is very small (close to zero) and such polymers may be immiscible at any, even very low, positive heat of mixing.

The equation describing the dependence of ΔG on temperature, concentration, and molecular mass for a binary mixture of polydispersed polymers is as follows:[17]

$$\Delta G_{mix} = RT[\sum_i \varphi_{1i} m_{1i}^{-1} \ln\varphi_{1i} + \sum_i \varphi_{2i} m_{2i}^{-1} \ln\varphi_{2i} + \Gamma(T,\varphi_2)] \qquad [6.4]$$

where φ_i and m_i are the volume fractions and the relative length of the i-type chain and $\sum \varphi_i$ is the total volume of fractions P_i. The last term of Eq 6.4 is equivalent to the van Laar interaction parameter

$$\Gamma(T,\varphi_2) = g(T)\varphi_1\varphi_2; \quad \varphi_1 = \sum \varphi_i = 1 - \varphi_2 \qquad [6.5]$$

The equations given above are usually referred to in books dedicated to polymer mixtures. However, the validity of these approaches is questionable, because the theory for regular solutions is used as a base for the theoretical consideration of polymer mixture and the solutions of one polymer in another.

The equations allow for calculation of the parameter of thermodynamic interaction, χ_{AB}. Theoretically, its value only depends on temperature, not on the mixture composition. On the other hand, according to Eq 6.3, the sign of a change in free energy of mixing depends on the sign of χ_{AB}. The system is thermodynamically stable if $\chi_{AB} < 0$ or if $\Delta G_{AB} < 0$. However, at any temperature, the miscibility is a function of a composition, and a system that is miscible at one composition may become immiscible at another. Thus, the parameter χ_{AB} depends on the composition, which is not accounted for in Eqs 6.2 and 6.3. For this reason, one cannot calculate this parameter from the solubility parameters of the mixture components, δ_A and δ_B, from Eq 6.6:

$$\chi_{AB} = \frac{V_c}{RT}(\delta_A - \delta_B)^2 \qquad [6.6]$$

where V_c is the mean volume of a monomeric unit. The calculated parameter is positive and does not depend on concentration, which contradicts the above.

According to Flory,[15] polymers are primarily miscible at a negative χ_{AB}, i.e., when A-B type interactions are predominant over A-A and B-B interactions (which can usually be observed when some specific interactions are taking place). On the other hand, a positive parameter should correspond to all immiscible system. If one proceeds from the above-mentioned equations, the value χ_{AB} loses its physical meaning, because it applies to a heterogeneous system separated into two phases, rather than to a molecular solution. However, positive values of the interaction parameter may characterize the interaction at the interface between two phases and, as such, have a quite definite physical meaning.

The limitation of the use of parameter χ_{AB} is due to the fact that it has been introduced based on the theory of solutions, and its application to polymer mixtures, especially in the solid state, has not been theoretically proven so far. The extension of the concept of interaction parameter to such a system is to a certain extent very formal and contains many arbitrary assumptions. This consideration should be born in mind when experimentally determining this value and interpreting the results. The ΔG_{mix} and χ_{AB} values can be found using various experimental techniques reviewed elsewhere,[6] and can be used for calculations of the binodal and spinodal regions from the concentration and temperature dependence of one of the values.

The concentration dependence of the interaction parameter was derived by Koningsveld,[18,19] based on the concept of the Huggins theory, in the following form:

$$g = g_o(T) + g_1\varphi_1 + g_2\varphi_2 + \cdots \tag{6.7}$$

where φ is a volume fraction of component; $g_1 < 0$, $g_2 > 0$, $|g_2| > |g_1|$. The use of such a relationship allows one to obtain a bimodal shape of the phase diagram, experimentally observed for many systems.[20] The bimodality of the phase equilibrium curves may stem from the effect of the environment of a given polymer segment on the flexibility of the latter. The theory suggests that either compression or expansion of a coil of polymer A in polymer B may be expected. This indicates the restriction of the molecular mobility of a more flexible chain in the mixture with more rigid chains.[21] The same assumption was made earlier,[22] based on the data on molecular mobilities in polymer mixtures.

It is therefore evident that the experimental values of parameter χ_{AB} are closely related to the microstructure of a mixture. It has been demonstrated for the immiscible mixture of atactic PS and PMMA, for which the parameter χ_{AB} was determined by inverse gas chromatography and its microstructure from IR spectrum.[23] It was found that in the composition range of 20-40% PBMA, where χ_{AB} decreases, compared with other compositions, there is observed a redistribution of the rotational isomers of PS on addition of PBMA. The statistical weight of trans-isomers increases, which evidences a change in the flexibility of macromolecules. Because the system is immiscible, one may suppose that the effect of PBMA on the flexibility of PS molecules occurs at the phase interface or in the interphase region, whose fraction varies with composition. PS macromolecules assume, in the interphase layer, a conformation ensuring a maximum interaction with PBMA, resulting in a decrease of χ_{AB} and an increase in the thermodynamic stability of the system.

Parameter χ_{AB} as a function of the system composition can also be calculated on the basis of the equations of state, using an approach of the hole theory.[24] The procedure for determining ΔG_{mix} and χ_{AB} was analyzed earlier,[6] and limitations of the methods were discussed.[25] If the values of the free energy of mixing or parameter χ_{AB} have been determined over a broad range of temperature and composition, then points on the spinodal, in accordance with Eq 6.2, can be found by a double graphic differentiation of the curves $\Delta G = f(\varphi)$ or $\chi_{AB} = f(\varphi)$ at different temperatures and by extrapolation of the dependence of $\delta^2\Delta G/\delta\varphi_2^2$ at a given concentration to its zero value.

Even the availability of experimental phase diagrams of binary polymer mixtures cannot provide the required indication of the phase state of a polymer alloy. A phase diagram for low-molecular liquids or oligomers makes it possible to calculate, for any temperature and composition, the ratio of phases in a separated system and their composition. For polymer alloys, however, this is not the case, since the phase separation in them proceeds incompletely for many reasons, and the system remains in a thermodynamically non-equilibrium state of incomplete phase separation (often called microphase separation). This state is kinetically stable during any given time (especially when, on temperature change, a system has passed through the melting point or vitrification points of its components).[4,26] It is the state of incomplete microphase separation, which, as will be discussed below, gives rise to interphase layers and governs the principal features of the microphase structure and physico-mechanical properties of alloys.

This situation creates many difficulties in estimating the composition and ratio of separated phases. At equilibrium conditions, it is sufficient to know the phase diagram to obtain these values. In real conditions of producing polymeric alloys, it can not be done, due to the non-equilibrium conditions of a phase separation. As a consequence, the final state of the alloy may be far removed from the equilibrium state that is determined by the phase diagram.

As a rule, in real polymer-polymer systems, after transition through binodal or spinodal regions, the non-equilibrium transitional states appear. The degree of non-equilibrity depends on the conditions of that transition (the rate of cooling, temperature gradient in the system, the relationship between the glass temperatures and melting points of the components, etc.). It should be noted that the type of the phase diagram depends on the structure typical for each component in the solid state. Polymer pairs formed by two amorphous polymers, by amorphous and crystalline, and by two crystalline polymers have different types of phase diagrams. The presence of one crystallizing component generally results in the phase diagram which has both the liquidus line, typical of the liquid-crystal transition, and the binodal, typical of liquid-liquid transition, the concentration regions of one or more transitions determined by the nature of pairs.[27-30] In such a way, various non-equilibrium structures may be frozen in the region inside the spinodal. Thus, the knowledge of the shape of the phase diagram is not yet sufficient to characterize the state of the systems arising when the figurative points are situated inside the binodal or spinodal regions. Being thermodynamically unstable, these systems may stay kinetically stable for a prolonged time.

It is known that the rules of equilibrium thermodynamics may be applied to such metastable states,[31] which gives the possibility to estimate the state of thermodynamic miscibility in the region of thermodynamic instability using values of the free energy of mixing or the interaction parameter.

One more effect should be taken into account. Because the miscibility of two species depends on the ratio of their molecular mass, the situation arises where, on the change of the outer conditions, the system remains in a thermodynamically stable state for some fractions of definite molecular mass, while already undergoing the phase separation for other fractions. Although this point has practically not been dealt with in the literature, its role in the formation of a non-equilibrium frozen structure should be essential. It means that the state of a system turns out to be dependent on its history. Thus, again, the phase diagram by itself yields a poor indication of the system state within the region of immiscibility bound by the spinodal or binodal curve.

Thus, the phase separation in polymer alloys, especially the ones proceeding according to the spinodal mechanism, does not reach the stage of a complete separation into two corresponding phases. It follows that the arising structures can be described most adequately with the use of the approach of non-linear thermodynamics and the concept of dissipative structures. Prigogine[32,33] has demonstrated the so-called dissipative structures, which are stable because of interaction with the environment, and arise far from the equilibrium.

Lindenmeyer[34-36] discovered an analogy between the alternation of high- and low-energy regions, typical for dissipative structures, and origination of modulated structures at a spinodal decomposition. If a system has a sufficient number of defects, then spatially-dependent fluctuations increase their concentration in one region and decrease it in the other. The fraction of the latent heat of transition, released in the low-defect concentration region, is dissipated through concentration of the defects in another place. The dissipative structure shows up in the course of solidification, when the kinetic energy of molecules can be dissipated efficiently through the formation of inhomogeneous structures in solid matter, in which the energy released in some regions is dissipated through concentration in the high-energy structures in adjacent regions. From the standpoint of the approaches developed by Lindenmeyer, the formation of the transitional states between the initial single-phase and final two-phase system, resulting from the phase separation, can be regarded as a result of disturbing the stability of the phase separation process below the spinodal. In this case, the thermodynamic forces tend to be at a minimum, while kinetic fluxes can increase in one part of the system and decline in the other, giving rise to dissipative structures. Hence, the concept of dissipative structures explains from other side the principle of emergence of microregions of incomplete phase separation and a diffuse boundary (a “boundary” between high- and low-energy regions, which may be represented by phases of different compositions). The approach to, and analysis of, the nature of microheterogeneity in alloys, from the point of view of formation of dissipative structures, was first presented by this author in 1981.[26]

For practical purposes, a simplified approach may be used. It is known that equilibrium thermodynamics may be applied to metastable states of polymers.[31] These metastable states can be kinetically and chemically stable. To apply thermodynamic relations to such systems, it is important to know the correlation between the relaxation time of the system, τ_r, and the duration of the measurement, τ_m. At $\tau_r >> \tau_m$, the metastable system behaves like a system at equilibrium, which gives the possibility to estimate the state of thermodynamic compatibility in the region of thermodynamic instability, using values of the free energy of mixing or interaction parameter. There exist a number of experimental techniques for estimation of ΔG_{mix} and χ_{AB}, but many of them cannot be applied to polymer mixtures because of either theoretical or experimental limitations. The most reliable methods are based on the small angle scattering of X-ray spectroscopy, thermal neutrons spectroscopy,[37-42] and inverse gas chromatography,[43,44] despite many limitations of the latter.[45,46] Simultaneously, taking into account the disagreement between χ_{AB} values given by various techniques, it has been suggested that a correct estimation calls for the use of a set of methods.[46]

Let us consider now the physical meaning of the ΔG_{mix} and χ_{AB} values determined experimentally.[6] For convenience, we consider a system with UCST, although the type of critical solution temperature is insignificant for the analysis. If the figurative point of the system is situated inside the binodal or spinodal region, than theoretically the system should be separated into two phases, with compositions determined by the phase diagram. One phase should be the solution of component A in B, and the other, the solution of B in A. Each phase should be an equilibrium molecular solution, i.e., a fully miscible system. It is obvious that at complete separation into two phases, the contribution of interaction between these phases at their interphase to the free energy of the separated system (which is mixture of two equilibrium phases) is negligible.

Should we, however, wish to determine experimentally the parameter χ_{AB} (or ΔG_{mix}), we can use the following relation:

$$(\chi_{AB})_{exp} = (\chi_{AB})_{I}\varphi_{I} + (\chi_{AB})_{II}\varphi_{II} \qquad [6.8]$$

where subscript I and II denote the separated phases and φ their volume fractions. Since each phase is at equilibrium and miscible, values $(\chi_{AB})_I$ and $(\chi_{AB})_{II}$ are negative.

At a phase separation of a real system, the level of mixing of the components in the separating phases, corresponding to a higher temperature (if the phase separation has been caused by the lowering of temperature) or to other initial conditions of the separation, causes molecules to get frozen at some stage of the latter. Such a system is in a state of “forced compatibility“.[3] In this case, the expression for $(\chi_{AB})_{exp}$ may be written as:[47]

$$(\chi_{AB})_{exp} = (\chi_{AB})_{I}\varphi_{I} + (\chi_{AB})_{II}\varphi_{II} + (\chi_{AB})_{i}\varphi_{i} \qquad [6.9]$$

where subscript i denotes an interphase layer, originating in a non-equilibrium system at the interface between two separating phases. In general, the two microphase separation regions I and II should be at a non-equilibrium and immiscible, but not separating, and the system as a whole is in non-equilibrium state as well. Parameters $(\chi_{AB})_I$ and $(\chi_{AB})_{II}$ may have both a negative and a positive sign for every microregion, while $(\chi_{AB})_i$ is positive (otherwise the interphase would be a region of miscibility). This follows, in particular, from Helfand’s theory,[48] where $(\chi_{AB})_i$ for immiscible pairs is determined just by the interaction in the interphase zone at the interface between two immiscible phases.

Eq 6.9 differs from Eq 6.8 because it allows for the contribution of an interphase region and because $(\chi_{AB})_I$ and $(\chi_{AB})_{II}$ can be either negative, or positive. The latter means that the separated phases are at non-equilibrium state and are in the state of forced compatibility. As seen from Eq 6.9, the experimental value of the interaction parameter (the same relates to the free energy) consists of three terms, the value of each is determined by conditions of the microphase separation and the degree of the deviation from the equilibrium which was attained. Thus, a system which is in a non-equilibrium state may be characterized by a set of values of the three components of the experimentally-found parameter χ_{AB}.

It follows that this value is defined not only by the system composition and the position of the corresponding point on the phase diagram, but also by the system history, i.e., by the set of states preceding the non-equilibrium state attained at this point. Due to this, when estimating the state of the system from the value of the thermodynamic interaction parameter, we cannot help by dealing with different values of (χ_{AB}). The latter circumstance leads to an important conclusion: the χ_{AB} values, determined experimentally in the region of immiscibility, have the physical meaning of characteristics of the system non-equilibrium degree and allows us by its magnitude to compare systems under identical conditions, but having reached these conditions by different ways. The same holds valid for the value of ΔG_{mix}, which also is a quantity depending on the way passed by the system until it reached the state in question. The latter means, in particular, that as distinct from using thermodynamic cycles for estimation of ΔG_{mix} for equilibrium processes, for polymer systems with incomplete phase separation, we shall have different values, due to dependence of the state of a real system on the manner of its attainment. From this point of view, the estimation of the free energy of mixing from the thermodynamic cycles may be incorrect as the prehistory of the system is not taken into account (in the real non-equilibrium system, its state does depend on the manner of the process).

6.3 THE MECHANISMS OF THE INTERPHASE FORMATION

6.3.1 THERMODYNAMIC GROUNDS

Polymer alloys may be considered as independent composite materials because they have many common features similar to filled systems such as two-phase structure and interphase layer. Considering the reinforcement of polymer alloys, one should have in mind a very complicated structure of the matrix, consisting conventionally of three phases. The distribution of particulate filler in such a system will be dependent both on the structure of various regions and on their composition, determining the affinity of the matrix to the filler surface. In its turn, as shown below, the filler may influence the formation of the alloy structure, which is especially important when reinforcing with fibrous fillers.

Two mechanisms of the phase separation of binary mixtures of any substances (including polymeric) are known: nucleation and spinodal decomposition.[5,49] Our task does not involve detailed examination of the phase separation mechanisms. When interphase phenomena in polymeric composites are considered, however, these mechanisms are essential from two standpoints: they govern the microphase structure of a polymer-polymer composite and the filler influence on the microphase structure and they also determine the mechanism of the formation of the interphase.

In accordance with Gibbs thermodynamics, condition $\delta^2 G_{mix} / \delta\varphi^2 > 0$ is observed for a system beyond, and $\delta^2 G_{mix} / \delta\varphi^2 < 0$ for a system within, the spinodal region. In the former case, the system is unstable only to great fluctuations of concentration. The system starts decomposing with formation of nuclei enriched with one of the components. This mechanism is called a nucleation mechanism, since phase transformations occur through nucleation and growth of the daughter (i.e., newly formed) phase in the parent (i.e., initial) phase. The composition of daughter phase regions does not change with time and the interface between them remains clearly defined. The free energy gradient between two phases is very high. If the daughter phase was formed, it grows through diffusion of the substance towards the surface. From the thermodynamical point of view the formation of nuclei may be conceived as origination of great fluctuations of the composition, occurring in small volumes. Phase separation, according to the nucleation mechanism, proceeds in the phase diagram regime near the binodal. For polymer alloys this condition corresponds to systems with a low concentration of one of the components. Nuclei of the new phase have the form of microdroplets. Their coalescence proceeds, according to Livshitz,[50] according to a mechanism of capturing ("eating up") fine droplets by larger ones. When a sufficient mobility is retained in the system, a further coalescence of droplets occurs and various structures are formed from the droplets.

Such a picture is possible only when the system, during the entire phase separation time, is maintained in a metastable region near the binodal region. The stability of the nucleation and growth process for the entire system is provided, due to retention of a positive sign of the diffusion coefficient. A progressive transition of the system to a glassy state results in freezing of non-equilibrium states and formation of diffuse regions. In such a way the interphase regions are formed between microregions of phase separation.[51]

With condition $\delta^2 G_{mix} / \delta\varphi^2 < 0$ (within the spinodal region), the system is unstable to small fluctuations of concentration. The supersaturated solution starts decomposing through the entire volume simultaneously, without generation of nuclei. The spinodal separation is a kinetic process of a spontaneous formation and continuous growth of another phase in an unstable parent phase,[5,52,53] caused by the origination of low-amplitude fluctuations of the composition. As a result, the rapid growth of the second phase proceeds with charac-

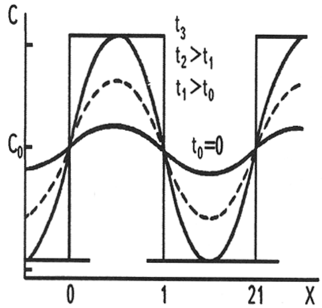

Figure 6.2. Fluctuation amplitude as a function of time for decomposition inside spinodal. [Adapted by permission from C. N. Rao and K. J. Rao in **Phase Transitions in Solids**, *McGraw Hill*, New York, 1978]

teristic sinusoidal variations of the composition. The decomposing system has, at a certain level, a high degree of interpenetrating of the forming phases and morphologically represents two interconnected networks whose mesh size changes little with time, while the difference in their composition increases. A periodic change in concentration indicates origination of a periodic modulated structure. The separation proceeds through the stage of emergence of two phases differing in the composition during separation. If, by nucleation, the diffusion flow of components is directed towards decreasing the composition fluctuations, then at a spinodal decomposition the diffusion flow directions are inverse and directed opposite to the concentration gradient. The intensity of composition fluctuations in the system rises, which increases its instability.

The transition from a single- to two-phase system involves enhancing of composition fluctuation and development of microregions of the new phase in a metastable or unstable region of the phase diagram. If the transition proceeds continuously, then the decision on when the system ceases to be a single-phase system is, to a certain extent, arbitrary.

Figure 6.2 shows the time variation of the amplitude of sinusoidal fluctuations of the composition.[5] The amplitude increases with time and, when the system decomposes into two final phases, the amplitude value becomes formally infinite. From Figure 6.2, in particular, a very important consequence ensues concerning the mechanism of formation of transition layers in systems decomposing through the spinodal mechanism. If C_0 is the starting concentration of one of the components in the system, then the developing phases are characterized by compositions determined by the composition fluctuation amplitudes.

According to de Gennes,[54,55] the development of the phase decomposition is based on appearance of composition fluctuations with a wavelength of the order of 2δ, where δ is the interphase layer thickness in the Helfand-Tagami theory.[56] The optimum spinodal decomposition wavelength is

$$\lambda_{opt} = \sqrt{3\pi}\delta \qquad [6.10]$$

(this expression relates to a mixture of two flexible-chain polymers).The spinodal decomposition wavelength governs the periodicity of modulated structures at decomposition and may be regarded as the spacing of centers of two forming microregions of phase separation. Since, as follows from Figure 6.2, the concentration is varying continuously, a region whose composition is close to starting concentration, C_0, can always be separated out in space. The length of the region may be defined arbitrarily, and it may be treated as an interphase region between the regions of microphase separation. Expression 6.10, which includes the layer thickness, refers to the case when a spinodal decomposition proceeds to completion, i.e., is not retarded at any stage. From the point of view of structure formation during spinodal decomposition, the kinetics of this process is very important.[57-61] Theoretically, the processes of demixing, caused by the instant change of thermodynamic parameters of the system, were previously described.[62-67]

At the final stage of decomposition, the size and composition of separated phases should be the same as with the nucleation mechanism, i.e., two separated phases should coexist. Due to this situation, the distinguishing features of the spinodal decomposition process manifest themselves just in their kinetics and in the structural changes which accompany decomposition.

Studying kinetics of the fluctuation changes gives one a possibility to evaluate the conditions of the formation and thickness of the interphase region. Theoretically, it was established[68] that the time of the establishing of the equilibrium state during the spinodal decomposition may be long. At the late stages of the spinodal decomposition, amplitudes of fluctuation reach equilibrium magnitude, with the structure of the phase particles continuously changing. It was found that at various stages, the diminishing excess free energy, concentrated in the interphase, is replaced by its increase. The duration of the increasing free energy is higher, and the depth of the local minimum is lower, when the system approaches the equilibrium state. As a result of this process, the density profile becomes sharper, as compared with the preceding metastable state. The appearance of density distribution, at which the surface phases have an excess of energy, compared with the bulk, serves as a defense mechanism which prevents system from an inevitable destruction of kinetically stable distribution.

The transition to the state of thermodynamic equilibrium was found to be accompanied by the rearrangement of metastable structures.[68] The destruction of the space-uniform state may be described as the sequence of rearrangements with continuous decrease of free energy. As a result, the growth of forming structures takes place, which is connected with the energetic changes in the interphase between two microphases. Each metastable state during spinodal decomposition has its own life-time. During this life-time, the transfer of energy proceeds from the interphase into microphases and the free energy of the interphase diminishes.

To understand the nature of the interphase regions, the concept of the formation of various structures, depending on temperature and composition, is very important.[69] For many binary systems with various types of the phase equilibria, it was established that the structure of the interphase region is determined by the remoteness of the state of the system from the equilibrium.

A general examination leads to determining the following principal differences between a phase decomposition through nucleation and the spinodal mechanism:[49]

For the mechanisms of nucleation and growth:

- the composition of the second phase remains unaltered and unchanged with time (equilibrium phase)
- the interface between the nucleating phase and a matrix is sharp
- a distinct tendency exists for random distribution of both sizes and positions of the equilibrium phases
- particles of separated phases tend to be spherical with low connectivity.

For the spinodal mechanism:

- the composition varies continuously until equilibrium is attained
- the interface is initially very diffuse (i.e., a transition mesophase region exists) but eventually sharpens
- a regularity exists, both in size and distribution of the phases

- the separated phases are generally non-spherical and possess a high degree of interconnectivity.

The formation of microphase structure is conditioned by crystallization or its absence of polymer alloy components. Variations of microphase structures are more substantial when mixture components are capable of crystallization. The complexity of the phase structure stems from the coexistence of amorphous and crystalline phases in each phase separation region.[52,69-72] The formation of a common amorphous phase by the components is also possible.[73,74]

Possible structures which may arise during the phase separation of binary mixtures have been discussed elsewhere.[75] It is important that the microphase particles evolved in this process, which have different composition and size be considered as quasi-particles of polymeric filler and the system as a whole- as a self-reinforced composite material. Thus polymer-polymer systems with incomplete phase separation may be described as systems consisting of polymeric matrix and polymeric filler. The common feature for both such systems and polymers obtained by the introduction of polymeric filler consists of formation of an interphase zone between two separated coexisting phases.

From brief analysis of various phase separation mechanisms, it is clear that one of the causes of origination of an interphase regions in polymer alloys lies in the separation process itself. Besides, it is substantially dependent on whether or not the separation is at equilibrium and completed. As has been noted, a separation in polymer-polymer mixtures remains, as a rule, incomplete and hence results in formation of interphase layers. Accordingly, these will be more pronounced at a spinodal mechanism of the phase separation. Cases are possible where, at the temperature change, the system first gets into a metastable region, where the separation commences through the nucleation mechanism, and at a further temperature change, gets into a region inside spinodal. In this case, as a result of an incomplete separation which has initially begun by the nucleation mechanism and then continued by the spinodal one, interphase regions can acquire a very complex structure. Such transitions have not been studied experimentally, but their role is obvious.

6.3.2 THEORIES OF POLYMER-POLYMER INTERFACE

Many theories have been developed describing the interface between two polymers. According to Gibbs, if the phase interface, representing a conventional geometric dividing surface, is two-dimensional, then the mean Gibbs free energy of mixing per 1 g of mixture is given by the expression:

$$\Delta G_{mix} = \Delta G_A + \Delta G_B + \sigma S \qquad [6.11]$$

where ΔG_A and ΔG_B are free energies of mixing in each two-component phase, σ is the interfacial tension, and S is specific dividing surface. For polymeric interfaces, σ is very small, and therefore the last term makes no significant contribution to ΔG_{mix}.[76]

For a real two-phase system with an interphase region of definite thickness and volume, it is more correct to use the Gugenheim method,[77-80] which results the in equation:

$$dG_{mix} = dG_0 + [\sigma + (\mu_1 dC_1 + \mu_2 dC_2)\delta] \qquad [6.12]$$

where μ_1, μ_2, and C_1, C_2 are, respectively, the chemical potentials and concentrations of components in a δ-thick interphase layer, and dG_0 is the energy of mixing, independent of the degree of dispersity and determined by the thermodynamic affinity alone. When the affinity is fully absent, $dG_0=0$. However, the impossibility of experimental determination of the values μ and C, appearing in Eq 6.12 prevents the practical use of the equation.

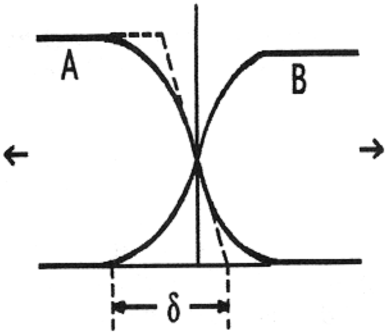

Figure 6.3. Symmetric concentration profile at the interface between A and B (the thickness of the interphase region δ). [Adapted by permission from E. Heltand in **Polymer Compatibility and Incompatibility**, Ed. K. Soll, *Harwood Academic Publishers*, London, 1982, p. 143]

For polymer-polymer interfaces, the first substantiated theory was developed in a number of works by Helfand and Tagami.[81-85] It describes the state of the interphase region between two immiscible phases, polymers A and B, and relies on the existence of repulsive forces acting between dissimilar molecules and related to the thermodynamic interaction parameter, χ_{AB}. The theory assumes limited mixing of components of two phases in the interphase region. For low values of parameter χ_{AB}, typical for most polymer pairs, the transition region thickness should be much greater than that of a typical interface between low-molecular substances. Based on the lattice model of the interface (interphase zone, where Gaussian chains of components are located), Helfand derived the expression for the density profile between two phases (Figure 6.3):

$$\rho_A(x) = \rho_B(-x) = \rho_o[(1/2) - (1/2)\tanh[(6\chi_{AB})^{1/2}x/b]] \qquad [6.13]$$

where $\rho_A(x)$ is the density of phase A at a distance x from the interface, χ_{AB} is the interaction parameter, and b is the effective length of segment. Here a symmetric case is considered, i.e., the densities of pure phases are assumed to be $\rho_{0,A} = \rho_{0,B} = \rho_0$. Parameter χ_{AB} is determined in accordance with the well-known Flory-Huggins theory: $\chi_{AB}kT$ is the change in the free contact energy per monomeric link of polymer A at a transfer of chain A, surrounded only by molecules of A, into medium B. The theory relates the interphase layer thickness, δ, to the interaction parameter by an expression:

$$\delta = (2/6)^{1/2}\frac{b}{\chi_{AB}^{1/2}} \qquad [6.14]$$

According to Helfand, the δ value may be high enough (thus, for a polystyrene-polyisoprene mixture at 90^0, δ = 1.8 nm). Hence, the interphase region makes a certain contribution to the properties of an inhomogeneous material. The interphase energy may be calculated as

$$\sigma_{AB} = 6^{1/2}\rho_o bkT\chi_{AB}^{1/2} \qquad [6.15]$$

From Helfand's theory, it follows that the free energy of a system will be less with a diffuse interface. As a measure of the interphase thickness, the theory assumes the segment between the points of intersection of the inflectional tangent to the density gradient curve with density levels ρ_1 and ρ_2:

$$\delta = (\rho_A + \rho_B)\left[\frac{d\rho(x)}{dx}\right]^{-1} = 2\left(\frac{\rho_A b_A^2 + \rho_B b_B^2}{6\chi_{AB}}\right)^{1/2} \qquad [6.16]$$

where b_A and b_B are statistical segment lengths of components A and B. Despite the simplifications made, Helfand's theory yields a well-founded picture of the equilibrium properties of the interphase region.

A conversion from describing the behavior of isolated macromolecules of A and B near the interface to discussing the behavior of bulk phases[48] requires that the flexibility of a polymer chain and its molecular mass should be accounted for. The Gaussian coil model is acceptable when the inhomogeneity scale (i.e., the interphase thickness) is large as compared with the link length b. From Helfand's theory it follows that, due to a very small (ca. 0.01) value of χ_{AB} at which a separation commences in mixtures, its increase, resulting in a rise of immiscibility, leads to transition region thickness comparable with the monomer link size.

For understanding of the properties of polymeric alloys, it is essential that a limited interdiffusion of chains in a very small region is possible at the interface between two immiscible components, A and B. It is in this region that the interactions of components A and B, characterized by parameter χ_{AB}, are accomplished.

The general theory of the interphase was developed by Kammer,[87-90] with allowance for a density gradient in the layer. Kammer's theory relies on Gibbs's conditions of an equilibrium between two phases with an interphase region existing between both phases. Kammer derived, within the framework of the Flory-Huggins theory, a theoretical expression for the interphase region thickness:

$$\rho = \frac{2b}{3^{3/2}}\left[\frac{b(T/T_o)}{\chi_{AB}(1-1.33T/T_o)}\right]^{1/2} \qquad [6.17]$$

where T_0 is a characteristic temperature. Calculations using of this equation yield values of the order of 7-10 nm for PS-PMMA mixture. Considering the thermodynamics of interaction for immiscible pairs of polymers, Kammer assumes preserving of phases of separated components, whereas the interaction between components is realized in a very small interphase region. As seen, Helfand's and Kammer's theories make use of interaction parameter χ_{AB}, which characterizes the degree of miscibility of components. It follows that the transition region thickness is related to the component's miscibility. This fact leads to an important conclusion that the value δ is a function of the temperature, composition, and critical solution temperature. The latter is essential in analyzing the temperature dependence of viscoelastic properties of polymer alloys if the effective characteristics and fraction of the interphase region are introduced into calculations.

The modern approach developed[91] takes into account the numbers of segments in the chains, r_A and r_B:

$$\delta = \frac{2b}{(6\chi_{AB})^{1/2}}\left[1 + \frac{\ln 2}{\chi_{AB}}(1/r_A + 1/r_B)\right] \qquad [6.18]$$

The temperature dependence of the interaction parameter for PS/PMMA and PS/styrene-acrylonitrile copolymer mixtures was measured by ellipsometry and evaluated from experimentally-found thickness of the interphase layer using Eq 6.18.[92] It was found that the interfacial thickness increases with temperature.

Another approach to the analysis of the interface, involving no Gibbs concepts of the dividing surface, has been accomplished by Cahn,[93] who considered two boundary surfaces defining the interphase region. The existence of two surfaces located in the bulk of two coexisting phases is closer to reality but fails to eliminate the uncertainty in selecting the interface region thickness. In the case of a spinodal decomposition, this value relates to the optimum spinodal decomposition wavelength (Eq 6.10). A detailed analysis of theories of the interphases in polymer mixtures is presented in a monograph.[6] It should be pointed out that most theories describing the interphase region assume it to be inhomogeneous and allow for the gradient of density of components.[94-98]

Nose's theory[96] introduces a local coefficient of volume expansion to account for a change in the size of macromolecules near the interface. This theory relates the interphase thickness to the system's position in the phase diagram and predicts a collapse of polymer chains in a direction perpendicular to the interface in the critical region. Sanchez[94,97,98] also takes into account the gradient approach and model of a compressible liquid lattice, which allows us to derive an expression for the interphase layer thickness.

In contrast to most calculations, where the interface is considered in a region far from the separation point, Joanny and Leibler[99] examined the properties of the interface near the phase separation point, based on the concept that the nature of the interphase region is substantially dependent on the degree of immiscibility and that the mean field theory of Flory-Huggins and Helfand's theory are not applicable to this region, due to importance of density fluctuations, resulting in a greater thickness of a transient region. On condition that $\rho_A = \rho$, $\rho_B = 1 - \rho$, the system's free energy is given by the expression:

$$G/kT = (1/2)b\delta\rho^2 + (1/4)c\Delta\rho^4 \qquad [6.19]$$

where $\Delta\rho$ is the difference between component concentration in the interphase and at a critical point (assumed to be a small value). Parameters B and C are given by the following expressions:

$$B = E[1/\rho_o N_A + 1/(1-\rho_c)N_B] \qquad [6.20]$$

$$C = 1/3[1/N_A\rho_c^3 + 1/N_B(1-\rho_c)^3] \qquad [6.21]$$

where N_A and N_B are degrees of polymerization of components, $E = (T_c - T)/T_c << 1$, and T_c is the critical temperature. Concentration of A in two phases is determined from the condition of minimum energy, G:

$$C\delta\rho^2 + B = 0 \qquad [6.22]$$

Free energy G can be approximated as

$$G = (1/2)\sum_N \frac{\chi^{-1}(q)}{[\Delta\rho(g)]^2} \qquad [6.23]$$

Here Δρ(q) denotes a Fourier transformation; χ(g) is a factor of osmotic compressibility of the system:

$$\chi^{-1}(q) = B(1 + g^2\xi^2) \qquad [6.24]$$

where the correlation length is

$$\xi = \left[(1/18)\left(\frac{1}{\rho_c} - \frac{1}{(1-\rho_c)}\right)\right]^2 |B|^{-\frac{1}{2}} \qquad [6.25]$$

From the minimization condition, the concentration profile, Δρ, may be found:

$$\Delta\rho = \Delta\rho_\infty \mathrm{th}(x/2^{\frac{1}{2}}) \qquad [6.26]$$

where the boundary condition is x→ ±∞.

The transition region thickness is related to the correlation length according to the expression $\delta = 2^{\frac{1}{2}}\xi$ and hence is of the same order of magnitude as the correlation length. Estimates of δ near the separation point yield values much larger than the values found far from the separation point.

So far, two cases have been discussed:

- two polymers are treated as completely immiscible
- the critical region where the volume fractions of components in coexisting phases become nearly identical.

Binder and Frisch[100] studied this problem at general volume fractions, which is intermediate between two limiting cases mentioned. The symmetrical mixture was considered with chain length of both components equal, and the interfacial profile between two coexisting phases was analyzed. The thickness of the interface was found to be equal to

$$L = \xi_{\mathrm{coex}}(\chi_{\mathrm{crit}}/\chi)^{\frac{1}{2}} = (\sigma/3)\chi^{-\frac{1}{2}} \qquad [6.27]$$

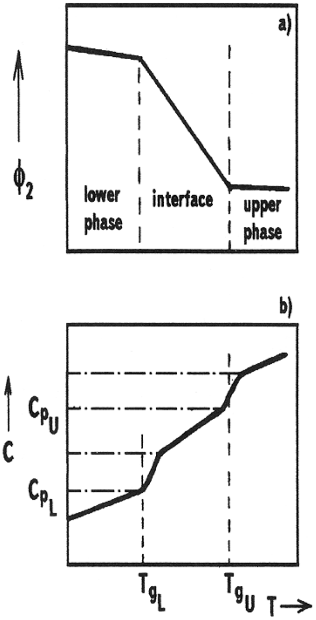

Figure 6.4. (a) Concentration profile of the interfacial region of a phase-separated mixture of two amorphous polymers, (b) DSC thermogram of a phase-separated mixture. [Adapted by permission from J. Beckman, F. G. Karasz, R. S. Porter, W. J. Mc Knight, J. van Hansel, and R. Koningsveld, *Macromolecules*, **21**, 1193 (1988)]

where ξ_{coex} is a correlation function, related to the characteristic lengths describing the concentration variation $\varphi(x)$ in a direction x perpendicular to a flat interface between coexisting phases. Eq 6.27 reproduces Helfand's result that the interface thickness $L \propto \chi^{-1/2}$ independently of the chain length. Simultaneously, it was noted that the results for L are only qualitatively correct, because the real mixtures are rather asymmetric and because the derivation of equations assumed that the Flory-Huggins theory parameter χ is independent of volume fraction. However, it is known that there is a rather distinct dependence of χ on φ, which will also affect the detailed form and width of the profile.

The density profile and the width of the interfacial region is a very important characteristic of the binary polymer-polymer systems and therefore many models have been proposed describing this profile.[101-104]

6.3.3 EXPERIMENTAL DATA ON THE THICKNESS AND FRACTION OF THE INTERPHASE REGIONS

The experimental methods to estimate the thickness and structure of the interphase region in polymer-polymer systems were reviewed.[105,106] Using various physical principles, it became possible to evaluate both the thickness and density profile of many systems. The most informative methods are based on the neutron reflection from the interface between two polymers.[107-110] Ellipsometry and secondary ion mass spectrometry, IR-spectroscopy, and inverse gas chromatography also can be used, among other methods.[111-113] For example, the segment density profile was estimated for PS-PMMA[108] in the presence of symmetric block copolymer of PS and PMMA. It was shown that the interface formed between PS and PMMA in the presence of copolymer is broader than that formed by the two homopolymers. Significant penetration of the two homopolymers into an interfacial region was found. From the reflectivity profile, the volume fractions of PS and PMMA in the copolymer at the interface were determined. The copolymer is segregated in the interfacial region, with the segments of each block penetrating significantly into the respective homopolymer phases.

Segregation of components within a polymer mixture in the surface or substrate interface was studied by secondary ion mass spectrometry.[112] It is interesting that the analogy between segregation in polymer mixtures and metal alloys was considered. In an annealed binary alloy A-B, the surface concentration of component A may be enhanced as a consequence of surface free energy minimization. A depletion or a monotonic decrease in the concentration of A may then be observed, and depending on the annealing temperature, a new surface phase may also appear. A similar behavior is observed in polymer alloys. The surface segregation profile has been studied[112] for the mixture of PS-deuterated PS at the interfaces with vacuum and Si substrate.

Using the time-resolved light scattering method, various stages of spinodal decomposition in polybutadiene-polyisoprene mixture, near critical composition, have been studied.[114-116] The average thickness of the interfacial region was estimated on the basis of the theory by Joanny and Leibler.[99] It was established that this thickness decreases towards an equilibrium value during the spinodal decomposition until reaching equilibrium. For the same system, the temperature dependence of the interfacial thickness was estimated experimentally[116] and compared with theoretical values. It was found that some discrepancies between experimental and theoretical values exist (experimental values of the thickness are 3-5 times higher), which, however, may be explained. Authors note the following observation on the structure formation: the composition difference between two phases first reaches an equilibrium value in the beginning of the late stage, followed by the equilibration of interfacial thickness, although the local and global structures are still changing with time toward equilibrium. In the late stage, the local structure relaxes faster towards equilibrium, then the global structure and then the two structures eventually relax at the same rate.

It should be noted, however, that estimating the thickness of the interphase region in real systems often yields contradictory results, because different procedures give quite different gradients of properties in the interphase.[61,70] Also, the dependence of the interphase thickness and structure on the conditions of producing polymer alloy (i.e., non-equilibrium structures being determined experimentally) should be taken into account.

An interesting approach to the evaluation of the fraction of the interphase region in partially miscible mixtures was also proposed.[117] The method is based on the thermodynamic considerations and experimental application of DSC. A qualitative picture of the actual interface and the resulting DSC thermogram are shown in Figure 6.4. The bulk regions A and B and the interface I are divided into layers of constant composition, Φ_2. The T_g of each layer is a function of its composition, whereas ΔC_p is dependent on the total mass in the layer. In regions far from the interface, the T_g is fairly constant from layer to layer, and therefore the ΔC_p of the layers in these regions is additive, resulting in two major jumps in heat capacities (Figure 6.4b). T_g of each phase can be found from an equation proposed for miscible polymer pair, for example, the Couchman equation:[118]

$$\ln T_{gl} = \frac{w_{1l} \Delta C_{p1} \ln T^o_{1g} + w_{2l} \Delta C^o_{p2} \ln T^o_{2g}}{w_{1l} \Delta^o_{p1} + w_{2l} \Delta c^o_{p2}} \qquad [6.28]$$

and

$$\ln T_{gu} = \frac{w_{1u} \Delta C_{p1} \ln T^o_{1g} + w_{2u} \Delta C^o_{p2} \ln T^o_{2g}}{w_{1u} \Delta^o_{p1} + w_{2u} \Delta c^o_{p2}} \qquad [6.29]$$

where $w_{1u} = m_{1u}/(m_{1u} + m_{2u})$. Assuming limited mutual solubility to be the sole reason for the T_g shifts, the heat capacity jumps may be expressed as

$$\Delta C_{pu} = \Delta C^o_{pl}(m_{1u}/m_T) + \Delta C^o_{p2}(m_{2u}/m_T) \qquad [6.30]$$

and

$$\Delta C_{pl} = \Delta C^{o}_{pl}(m_{1l} / m_T) + \Delta C^{o}_{p2}(m_{2l} / m_T) \qquad [6.31]$$

where m_{iu} and m_{il} are the masses of constituent i in the upper and lower phases and m_T is the total mass of the system.

In the interfacial zone I, the composition of the layer changes from the lower phase to the upper phase and T_g varies from T_{gl} to T_{gu}. The ΔC_p of this region is too small to be distinguished and the result is a smooth curve with positive slopes. The weight fraction of the blend constituents in the interface is given by

$$w_I = 1 - \frac{m_{1u} + m_{2u}}{m_T} - \frac{m_{1l} + m_{2l}}{m_T} \qquad [6.32]$$

From equations, the value of the weight fraction of the interphase zone mass, w_I, may be expressed in terms of ΔC_p and T_g only, as

$$w_I = 1 - \frac{\Delta C_{pu}(\Delta C^{o}_{p2}\ln(T^{o}_{2g} / T_{gu}) - \Delta C^{o}_{p1}\ln(T^{o}_{1g} / T_{gu})}{\Delta C^{o}_{p1}\Delta C^{o}_{p2}\ln(T^{o}_{2g} / T_{1g})}$$

$$- \frac{\Delta C_{pl}(\Delta C^{o}_{p2}\ln(T^{o}_{2g} / T_{gl}) - \Delta C^{o}_{p1}\ln(T^{o}_{1g} / T_{gl})}{\Delta C^{o}_{p1}\Delta C^{o}_{p2}\ln(T^{o}_{2g} / T_{1g})} \qquad [6.33]$$

Using the proposed equations, for the sulfonated polyphenyleneoxide and polystyrene, the weight fraction of interfacial material in 50/50 mixture was found to be 0.4-0.6, depending on composition. Despite some possible errors, such a treatment may have importance, not only for amorphous mixtures, but for filled mixtures and other systems where the interface plays an important role and the only data available are DSC thermograms.[117]

According to the data scattered in the literature, the thicknesses of the interphase layers in polymer-polymer mixtures are usually no more 5-10 nm.[6,51] Simultaneously, according to the electron microscopy data, these thicknesses may reach a few micrometers.[119] The latter may be determined by the non-equilibrium state of the systems with incomplete phase separation, or by the conditions of production. The latter have been discussed in detail elsewhere.[120-123] Strictly speaking, these interphase zones cannot be considered as real interphase regions because the reasons for their appearance are of no thermodynamic character. However, they contribute essentially to the properties of polymer alloys.

At the phase border between two polymers, in the course of the mixture preparation, there proceed some morphological changes, due to the mutual influence of contacting polymers on the formation of structure at the interface. If one of the components is crystallizable polymer, its crystallization may be suppressed (see Chapter 4). Mutual influence may lead to the appearance of the structure-less (amorphous) region between two phases. This mechanism is realized when mixing of two polymers in melt, independently of whether these polymers are miscible or not, because the formation of the interphase proceeds as a result of the changing system conditions (for example, lowering the temperature). By producing alloys from the melt the other mechanism, namely, the colloid-chemical mechanism, may be operative.

It is known that real polymer systems are characterized by a definite type of molecular-mass distribution. Due to this fact, in the melt, i.e., at the conditions of an alloy formation, the redistribution of fractions of various molecular mass is possible. The difference in the magnitude of the surface tension for various fraction may reach 10-20 mN/m. The change in the amount of low-molecular weight fractions in the interphase region, according to the principle of the free energy minimization, leads to the diminishing of the interfacial tension. As a result, the interface becomes unstable and the spontaneous formation of microemulsion is possible.

Thus, together with the existence of thermodynamically-caused equilibrium interphase region of small thickness, by mixing two polymers, the microvolumes of one polymer may penetrate into the bulk of another polymer, forming microemulsions. The latter results in the spreading of the interfacial border, and the very interphase zone is a microheterogeneous formation. By mixing in the melt of immiscible polymers, due to the redistribution of various fractions in the interphase zone, the region of miscibility may arise. By cooling, the phase separation may proceed in this region as well; however, at other conditions, as compared with the bulk. Thus, only after the evolution of large volumes of separated phases, the phase separation in the interphase region will begin. It is evident that this mechanism is connected with parameters of producing polymer alloy. We believe that these are the reasons why theoreticians do not pay any attention to such interphase zones, in spite of their important contribution to the properties of polymer alloys.

From all that was said above, it follows that the polymer alloy is a complicated multiphase system with properties which are determined by the properties of constituent phases. It is very important to note that if, on the macrolevel, the thickness of the interphase regions is low, as compared with the size of the polymer species, for small sizes of the microregions of phase separation such approximation is not valid. In comparison with the size of the microphase regions, the thickness of the interphase may be of the same order of magnitude. Therefore, they should be taken into account as an independent quasi-phase in calculation of properties of polymer alloys. We say “quasi-phase” because these region are not at equilibrium and are formed as a result of the non-equilibrium, incomplete phase separation. The interphase region may be considered as a dissipative structure, formed in the course of the phase separation. Although it is impossible to locate its position in the space (the result of arbitrary choice of the manner of its definition), its representation as an independent phase is convenient for model calculations (compare the situation with calculations of the properties of filled polymer systems, which takes into account the existence of the surface layer).

6.4 THE DEGREE OF SEGREGATION IN POLYMER ALLOYS WITH INCOMPLETE PHASE SEPARATION

It was already mentioned that the properties of the polymer alloys are determined by their microphase structure. The microphase state may be characterized by the degree of microphase separation (segregation degree) and by the size and distribution of microregions of phase separation. These characteristics are connected with the history of the system. The system with incomplete phase separation is characterized by the segregated structure with non-equilibrium regions of microphase separation. These regions may have different composition, density, and size.

The basic problem arising in the description of alloy formation is the determination of a relationship between the conditions of their formation and the

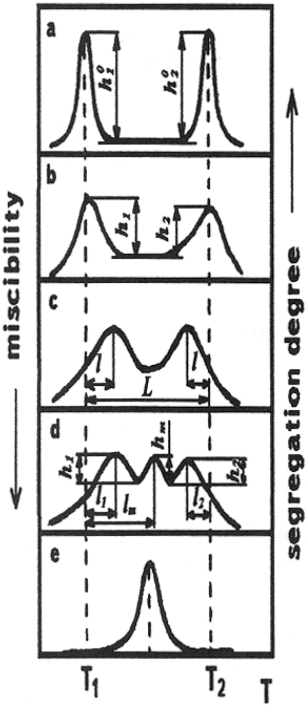

Figure 6.5. Schematic representation of the temperature dependencies of mechanical losses for system having different degree of component segregation and miscibility. [Adapted by permission from Y. S. Lipatov, *Pure Appl. Chem.*, **43**, 273 (1975)]

microphase structure. This structure may be characterized by one fundamental parameter, viz., the degree of segregation, which may be estimated experimentally. The concept of segregation degree was introduced by Bonart.[124] The following characteristics are important.[51]

1. The difference between the local density, $\rho'(x)$, and the mean density, ρ'. The value $\overline{\Delta}\rho^{2'}$ represents an overall measure of all density variations. For multicomponent systems, it is of a great interest to compare the value $\overline{\Delta}\rho^{2'}$ with theoretical values of the mean square of electron density fluctuation. $\Delta\rho_s^2$ may be calculated from the electron density of phases ρ_1 and ρ_2 and the phase volume fraction φ. In this case

$$\Delta\rho_c^2 = \varphi(1-\varphi)(\rho_1-\rho_2) \qquad [6.34]$$

The ratio

$$\alpha = \Delta\rho^{2'}/\Delta\rho_c^2 \qquad [6.35]$$

provides an overall measure of the degree of segregation.

2. The mean square of electron density fluctuation, $\overline{\Delta}\rho^{2''}$ may be obtained from small-angle X-ray scattering data. The ratio

$$\beta = 1-(\overline{\Delta}\rho^{2''}/\overline{\Delta}\rho^{2'})^{-1} \qquad [6.36]$$

is a measure of boundary diffusiveness.

For a heterogeneous structure, assuming some degree of component mixing, parameter ρ_M^2 may be introduced, which depends on the electron density of microregions and their volume fraction:

$$\Delta\rho_M^2 = \varphi(1-\varphi)(\rho_1 - \rho_2)^2 \qquad [6.37]$$

In this case, ρ_1 and ρ_2 are electron densities of various regions, and φ is the volume fraction of one of the regions. Comparison between $\overline{\Delta}\rho^{2''}$ and $\Delta\rho_M^2$ allows one to verify the assumed model of heterogeneous structure.

The results of corresponding measurements for many polymer-polymer systems are presented in the monograph.[51]

A more graphic scheme of the microphase separation process and determination of the degree of segregation may be presented as follows. It is based on the estimation of the tangent of mechanical losses. As known, its maximum is in the area of relaxation transition and changes at glass temperature by more than an order of magnitude. It is also known[4] that the polymer-polymer miscibility can be established from appearance of one or two or more maximums of mechanical (or dielectric) losses. Let us consider schematically the temperature dependence of mechanical losses in a two-phase polymer system with a different degree of component segregation (Figure 6.5).[2] Following a great deal of experimental data from many authors, the diagram is idealized and can be described as follows.

$$\alpha_1 = \frac{h_1 + h_2 - (l_1 h_1 + l_2 h_2 + l_m h_m)/L}{h_1^o + h_2^o} \qquad [6.38]$$

The case $\alpha = 1$ (a) corresponds to a complete phase separation, $\alpha = 0$ (e) to that of full mixing. Calculations using this correlation produce the data included in Figure 6.5: (b) $\alpha = 0.5$, (c) $\alpha = 0.23$, (d) $\alpha =0 .14$.

The comparatively low values of segregation degree show that a great amount of the system mass is preserved in the unseparated state and is distributed in two phases. Thus, segregation degree is a measure of incompleteness of the phase separation or deviation of the system from the state of true thermodynamic equilibrium.

6.5 INTERPENETRATING POLYMER NETWORKS

Interpenetrating polymer networks (IPNs) are the basis of a new generation of binders for polymer composites: hybrid matrices.[2] They may be considered as mixtures of two or more network polymers, or of network and linear polymer (semi-IPNs or pseudo-IPNs). The classification of IPNs was suggested by Sperling.[125] Based on the method of synthesis, the original definition given by Millar in 1966[126] considered a molecular level of mixing of chains between cross-links of constituent networks and formation of molecular entanglements between them.

The production of IPNs[125,127] may be considered as a method of blending polymers which cannot be mixed by conventional procedures because the network polymers cannot be melted or dissolved. The application for IPNs synthesis of oligomers, differing in their chemical structure (oligoglycols, oligobutadienes, oligoesters, oligoesteracrylates, epoxide, phenolic, etc.) and their combinations with traditional monomers makes it possible to change considerably the properties of network polymers by their combination and to obtain materials with a great diversity of properties on the basis of comparatively limited choice of the large-capacity initial components. Two methods exist for the production of IPNs:[125,127]

- a simultaneous formation of two different networks of oligomers or monomers reacting by different mechanisms (polymerization-polyaddition, polymerization-polycondensation, etc.)
- a sequential formation of a second network in the matrix of the swollen, primarily-formed first network.

At present, the former, which is a more technological method, is widely employed. However, theoretical problems arising when describing the mechanism and kinetics of the production of IPNs and their structure formation are common for both types of synthesis. Subsequent investigation, mainly conducted by Frisch and coworkers, Sperling and coworkers and by us,[128,129] has emphasized a more complicated structure of IPNs, due to peculiarities of self-organization during their synthesis and phase transformations, which allow IPNs to be considered as polymer alloys in accordance with definitions (see 6.1).

According to the definition,[130] a self-organization involves the appearance,development, and disappearance of macroscopic structures under non-equilibrium conditions. The self-organization means the appearance and development of the structure in the initially homogeneous environment. The microheterogeneity of the structure of IPNs and the appearance of periodic modulated structures, under definite conditions,[131-133] is the result of two different processes participating in the formation of IPNs. These processes are in non-equilibrium, and they proceed simultaneously. These are chemical reactions leading to the formation of a three-dimensional network and physical processes of microphase separation in the system. They occur at a definite stage of the reaction as a result of immiscibility arising between the chains of the constituent networks.

The kinetic conditions of the IPNs formation are different from conditions for individual networks,[134-139] and therefore transferring data on the kinetics of the the individual networks to the kinetics of IPNs is difficult for the following reasons. In the case of simultaneous or successive IPNs, the reaction proceeds almost from the very beginning in the matrix of one of the networks, since even for simultaneous IPNs, the kinetics of the constituent network formation is different, and so a certain network is formed earlier and serves as a matrix for the formation of the other.

The matrix network changes the reaction conditions in the kinetic region at the expense of variation in the ratio of the rates of elementary reactions of propagation, termination, and transfer of chains into matrix chain, as well as at he expense of the influence of the propagating chain intermolecular interactions with the matrix chain (analogous to the influence of the filler surface on the network formation - see Chapter 4). The matrix network changes the diffusion parameters of the reaction and influences the reaction proceeding in the diffusion region (the same analogy). In the course of the synthesis of simultaneous and successive IPNs, microphase separation of the system occurs as a result of the appearance of chains of high molecular mass and their immiscibility. These three principal factors should lead to differences in the kinetics of IPN formation, as compared to individual networks. A review of the kinetics of IPN formation was recently given.[136] Changing the kinetic conditions allows one to regulate the processes of microphase separation in the system. Their completeness depends on the rate of the network formation which prevents the separation. From these points of view, three cases are typical:[140]

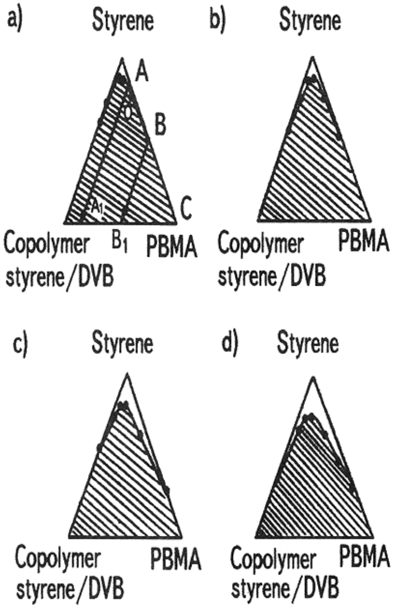

Figure 6.6. Phase diagrams of semi-IPN (styrene-divinylbenzene)/poly(butyl methacrylate) at temperatures: a-333K, b-343K, c-353K, d-363K. [Adapted by permission from Y. Lipatov, O. Grigor'eva, and G. Kovernik, *Makromol. Chem.*, **186**, 1401 (1985)]

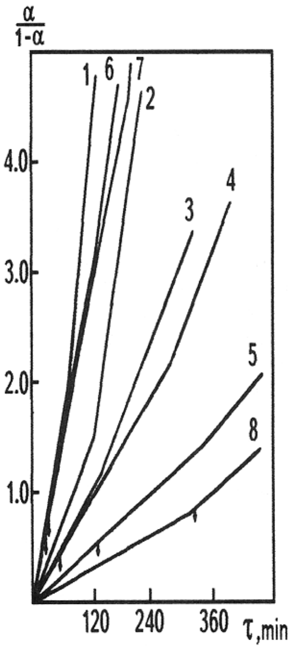

Figure 6.7. Anamorphoses of kinetic curves of polyurethane formation in presence of 15 wt% of poly(butyl methacrylate) (α - conversion degree).

- The formation of one network proceeds much faster than the other. In this case, the first network is formed in a liquid medium of components for the second network. Phase separation may begin rather early and will not be hindered. The evolution of the first swollen network is possible. Liquid medium begins to form the second network later. As a result, IPN with a high degree of component segregation may appear.
- Both networks are formed with high reaction rate. Here there is no time for phase separation, and the structures, corresponding to the liquid one-phase state, may be frozen (such a case should be typical of the reaction injection molding processes used for the production of IPNs). This case is a real chemical quenching.

- Both reactions proceed rather slowly. Phase separation begins at early stages of the reaction and proceeds up to the gel point of one of the networks. The phase separation stays incomplete and the degree of segregation strongly depends on the reaction rates of the formation of each network.

6.5.1 MICROPHASE SEPARATION IN THE COURSE OF IPN FORMATION

The thermodynamic immiscibility of constituent networks in IPN arises at low conversion degree for both full and semi-IPNs. For example,[141] Figure 6.6 shows the phase diagrams of IPN based on styrene-divinylbenzene copolymer and poly(butyl methacrylate). The regions corresponding to the two-phase state of semi-IPN (hatched) are much larger than the regions of the one-phase state. In the phase diagram, heterogeneous regions are separated from the homogeneous ones by a binodal curve. In the course of semi-IPN formation, the polymerizing system passes from point A to point A_1, which corresponds to the initial mixture of reaction components and to semi-IPN, respectively. After reaching the border of two-phase region (point 0), phase separation might occur. Increasing the reaction temperature does not change the shape of the diagram; however, the area of one-phase state slightly increases, which is typical for systems with UCST. If one analyzes the region of IPN composition, situated inside the triangle BB_1C, it may be seen that a one-phase system cannot be realized at all. The data shows that polymerization with the content of the second component above some definite value from the very beginning proceeds in the phase-separated system.[142] Figure 6.7 presents anamorphoses of kinetic curves of the reaction of IPN formation on the basis of cross-linked polyurethane and PBMA. The arrow indicates the onset time of the phase separation. It is seen that microphase separation begins very early and depends on the kinetic conditions.[139] There exists a definite correlation between the kinetic conditions of chemical reactions leading to IPN formation and the degree of microphase separation.

Both processes that accompany IPN formation - chemical reaction of cross-linking and physical process of microphase separation - proceed simultaneously in the definite time-interval between the onset of phase separation and gel-point of each network. Such superposition results in a complicated microphase structure of IPN. It means that these processes proceed in non-equilibrium conditions. After reaching a definite degree of chemical conversion and cross-linking, the microphase separation is impeded and the system gains the non-equilibrium structure which is determined by the incomplete phase separation. The non-equilibrium structure depends on the prehistory of the system and essentially affects the IPN properties. The completion of IPN formation then proceeds in two evolved phases. The separated system may be characterized by the segregation degree (see 6.4.).

In a number of works,[143-146] it was established that the process of microphase separation in IPN proceeds according to the spinodal mechanism. As a result, a periodic structure appears during curing. This periodicity is largely preserved to the end of microphase separation. Since the heterogeneity microregions are very different in their composition from pure components, it is possible that phase separation in such systems initiates and proceeds in the region of unstable states (inside a spinodal) and is subject to spinodal decomposition peculiarities.[147] A difficulty arising in the investigation of microphase separation processes by the formation of IPNs is that the composition of the system varies continuously during curing (the growth of conversion degree). This impedes the use of the available theories[148-150] to describe phase separation. In order to avoid complications caused by simultaneous reactions, the reaction conditions should be selected so that the reaction rates are minimal compared with the rate of microphase separation, in order to determine the latter under quasi-stationary conditions (the minimum change in conversion).

The experimental data shows that the formation of semi-IPN occurs according to a spinodal mechanism which is realized in spite of the preceding reaction and, consequently, the non-equilibrium conditions of the process. It was also shown that under these conditions the reaction kinetics determine the beginning of microphase separation, i.e., the thermodynamics of formation of the system and its thermodynamic state are determined by the reaction kinetics.[136]

The establishment of these principal peculiarities for the formation of an IPN structure gives a simple opportunity for a theoretical description of these processes and the establishment of a relation between the reaction conditions, the degree of microphase separation, and physical properties. It was Binder and Frisch[144] who made an attempt to create a strictly statistical theory of microphase separation during the synthesis of IPN (both simultaneous and successive). The phase separation taking place during the reaction is inhibited by the simultaneously proceeding crosslinking, which is considered to be “chemical quenching”. Cases of deep quenching, which occurs when the reaction rate is considerably higher than the relaxation rate of the system to the equilibrium state, have been analyzed. However, such relaxation is possible only for weakly crosslinked networks.

A mean field theory of the microphase separation was proposed by Shulz[152] for the same case of chemical quenching and weakly cross-linked IPNs. It was established that microphase separation is related to the competition that exists between elasticity and repulse of the two network components. As a result of the mean field, approximation follows a characteristic size of the microphase. The ordered phase is characterized by a macrolattice with lamellar-, hexagonal-, or body-centered cubic lattice symmetry, which is dependent on the composition and the interaction parameter, χ.

Obviously, the mechanism of spinodal decomposition, which determines the microphase structure of cured IPN, is not the only mechanism, i.e., separation may also take place by the nucleation mechanism under definite conditions.

Sperling[153] considered theoretically the conditions for the formation of domains in successive IPNs for the case when separation proceeds by the nucleation mechanism, since one of the networks has already been formed. Sperling[154-156] emphasized that “double” phase continuity, near the phase inversion region - which means that the phases may consist of both components - plays a key role in the properties of IPNs.[157] In the end, the phase separation mechanism of IPN depends on the position of a figurative point in the phase diagram. Unfortunately, to obtain the latter for multicomponent reacting systems is a matter of great difficulty. For simple systems, when semi-IPN, obtained from a linear polymer, and a bifunctional polymer form a three-dimensional network, it is possible to plot phase diagrams for a three-component system.[142,158]

The formation of the phase structure according to the nucleation mechanism was studied in detail by Rozenberg and coworkers.[159-161] It was found that phase structure of the composition based on epoxy resin and rubber oligomers depends on their miscibility and kinetic conditions of reaction. Phase separation in this system proceeds by nucleation mechanism as a result of the appearance of incompatibility. It was supposed that phase separation, connected with chemical reaction, may proceed as a fading autooscillation process. The existence of such a regime of reaction is possible only at a definite correlation between the rates of reaction and interdiffusion of components. Diffusion controls the growth of particles of heterophase and gives the possibility of phase separation, due to periodical appearance of new centers of growth. The nucleation process depends on the nearest growing centers and is localized in space, being discrete in time. As a result, the volume fraction of particles of dispersed phase depends on the reaction rate.[161] The thermodynamic and kinetic data[160] allow one to propose the following mechanism of the formation of the phase structure. Phase separation begins by nucleation and growth of the particles of a new phase. The rate of the formation of nuclei depends on the degree of supersaturation of the solution of rubber in curing epoxy oligomer. This supersaturation changes in line with the curing rate. The concentration gradient, dc/dx, appears in the system because the difference between the rubber concentration in solution and equilibrium solubility. The rate of nuclei growth is determined by the mass flow which is equal to the product of the interdiffusion coefficient, D, by gradient dc/dx. As these two values change in opposite directions, the nuclei growth rate, as a function of the conversion degree, has an extremum.

If the primary nucleation proceeds in the range or conversion, where the total rate of phase separation is limited by dc/dx, the increase in the supersaturation of the solution, in the course of reaction, is compensated by the diffusion flow to the growing center and formation of new centers is suppressed up to a negligible extent. Again, here the coalescence of small particles into large ones takes place. When D diminishes, the radius of the zone of diffusion flow to the growing center diminishes. As a result, the appearance and development of the regions of local supersaturation on the borders of this zone proceeds. In these regions, the proceeding chemical reaction leads to the formation of new centers of growth - the secondary nucleation, which prevents the growth of initially evolved particles. As a result, the two-stage process of the formation of phase structure takes place. This process also may be defined as self-organization.

It is important that the phase separation, in IPNs formed by the same components, depends on the condition of production.[137] It was shown that the introduction, into IPN based on polyurethane, of monomeric or polymeric butyl methacrylate leads to a great difference in the viscoelastic properties, due to different condition of phase separation. Changing the semi-IPN formation method results in changing the continuous medium of the system. When PBMA is introduced, the continuous medium (matrix) is the PBMA-enriched phase, while PU-enriched phase is the continuous medium when monomeric butyl methacrylate is used. Depending on the component ratio, in all the systems, the phase inversion proceeds, but the concentration range in which this is observed depends on the method of PBMA introduction into the system.

6.5.2 NON-EQUILIBRIUM STRUCTURES IN IPNs

It is known that self-organization in any system involves the appearance, development and disappearance of macroscopic structures under non-equilibrium conditions. The data presented above permit us to establish that the following two processes underlie the self-organization in the formation of IPN:[162]

- the crosslinking and formation of the three-dimensional network, i.e., gel formation or sol-gel transition for each network
- phase separation of the system caused by the appearance of immiscibility of constituent fragments of various networks at a precise degree of conversion.

We can determine qualitatively the general conditions of self-organization by the formation of IPN occurring under thermodynamic non-equilibrium conditions.

The initial reaction system for the synthesis of IPN represents a homogeneous mixture of components which are able to form two independent networks in the course of chemical reactions proceeding by different mechanisms. When a precise degree of conversion is achieved (as a rule, long before the sol-gel transition), thermodynamic immiscibility of the propagating fragments of the constituent networks arises in the system. Its conditions are determined by the critical value of the thermodynamic interaction parameter χ_{AB} predicted by theory. The initial conditions of phase separation are preset by conditions for the transition of the parameter χ_{AB} from the negative value (miscibility region) to the positive (immiscibility region) or by conditions at which χ_{AB}, at the given composition of the system and the given temperature, reaches the zero value. In most cases, this phenomenon occurs at the initial stages of the reaction in its kinetic region. However, phase separation takes place from the very beginning under non-equilibrium conditions, since it proceeds simultaneously with the developing reaction. In the course of reaction, the parameter χ_{AB} changes and attains the critical value for the phase separation. The rate of achievement of the critical value is determined by the rates of two independent reactions, and the phase separation process begins before gel formation in the constituent networks has been completed.

In the initial period of reaction (small degree of conversion), the beginning of phase separation is determined only by the reaction rate, i.e., by the rate of polymer formation and an increase of its molecular weight. However, cross-linking of the propagating chains into the continuous network and rapid growth have a hindering action on phase separation, which, in this way, becomes possible only within a definite range of conversion and time interval, Δt. The later value is a function of the reaction rates. In this case, since cross-linking continues within the time interval, the phase separation occurs under non-equilibrium conditions because the composition of the phases and their ratio change with time. Thus, the real situation, arising as a result of the formation of IPNs, essentially differs from the case of “chemical quenching”, which is considered to have substantially shorter the curing time than the relaxation time of the system in an equilibrium state.

Both processes - chemical reaction and phase separation - proceed simultaneously. This circumstance determines the development of structure in the system and its transformation at different stages of the reaction and separation. It was shown[147] that the modulated structures of IPNs are typical of the structures arising due to spinodal decomposition. At the initial stages, the kinetics of phase separation is described by the linear theory of Cahn-Hillard, in spite of the fact that continuous changes of conversion occur in this case. That means that the system drifts along the phase diagram with a continuous change of both parameter χ_{AB} and also the composition of the separated phases. Thus, one more principal peculiarity of IPN structure formation is established. It consists of the continuous sequence of structures which differ in composition not only at various stages of phase separation according to the theory, but also due to the reaction. Therefore, the microphase structure arising during the reaction is a result of non-equilibrium phase transition of the liquid-liquid type, and the final result of such a transition is determined by the composition of the system (the ratio of networks, the reaction rates, and the depth of non-equilibrium phase separation in the time interval, Δt).

In IPN formation, structures typical of spinodal decomposition may appear only within a definite time interval, which is always lower than the time of gelation and formation of final IPN structure. Subsequent crosslinking (after the Δt interval)occurs in the evolved microregions of phase separation up to the moment when the ultimate conversion is reached. This permits an important conclusion to be made. The final structure of IPNs is determined by a coexistence of three types of microregions of incomplete phase separation (dissipative structures).

- Two microregions arising due to spinodal decomposition. Their composition is determined only by the time interval, Δt, and temperature. Each of these microregions is an IPN, and they differ in composition from each other and from average composition of the system. Of importance is the fact that these two microregions may be considered as independent IPNs in which phase separation did not take place (the state of "forced compatibility"[163]) and in which molecular entanglement of various network chains occurs, i.e., mixing on the molecular level, since these phases are a result of incomplete separation. The presence of these two IPNs of different composition creates a microheterogeneity of their structures which was determined experimentally and served as the basis for conclusions on phase separation in IPN.[51]
- Non-equilibrium transition region. It is known that in the case of spinodal decomposition, there is no sharp interphase between coexisting regions of phase separation.

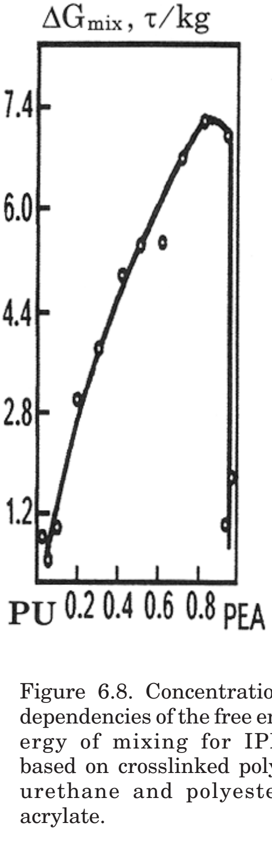

Figure 6.8. Concentration dependencies of the free energy of mixing for IPN based on crosslinked polyurethane and polyester acrylate.

We have already mentioned that the transition region between them may be chosen so that its composition corresponds to the average composition of the system. In this case, it is possible to consider that there is a molecular mixing of the constituent networks in the stoichiometric ratio taken for the reaction. This region also may be considered as independent non-equilibrium IPN with a molecular level of mixing.

Thus, the final structure is characterized by the presence of three regions which differ in composition, each region being an independent non-equilibrium IPN with preserved molecular level of mixing. In each of these regions, the phase separation did not take place, i.e., the structure responding to a lower degree of conversion is frozen. The final crosslinking is accompanied by the sol-gel transition, which occurs after the phase separation, possible for the system, is completed. The complication in the formation of the IPN structure is in the superposition of two sol-gel transitions in the constituent networks on phase separation. At high rates of gelation of one of the networks, the sol-gel transition may precede phase separation of the liquid-liquid type. Therefore, the sequence of phase transitions, characterized by a change in the binding nature, may vary, depending on the system composition and the kinetic parameters of the reaction. Sharp gelation of one of the networks may cause separation according to the nucleation mechanism.

Thus, the general conditions of self-organization, in the production of IPNs, may be formulated in a qualitative form. They are determined by

- the ratio of the rates of chemical reactions of two networks
- the sol-gel transition and the phase separation, which proceed differently, depending on their sequence.

From these, the peculiarities of the microheterogeneous structure of IPNs are evident, being the result of the self-organization.

We may conclude that, in general, the microphase structure of IPN may be described as a non-equilibrium structure. However, in such non-equilibrium IPN, we can distinguish various microregions which can be described as quasi-equilibrium stages, i.e., with a molecular level of mixing.[164] It is worth noting that we discuss here only the thermodynamic stability of IPN. Their non-equilibrium state and thermodynamic non-stability do not imply the non-stability of physical and mechanical properties, because the relaxation time required to attain true thermodynamic equilibrium is too large.

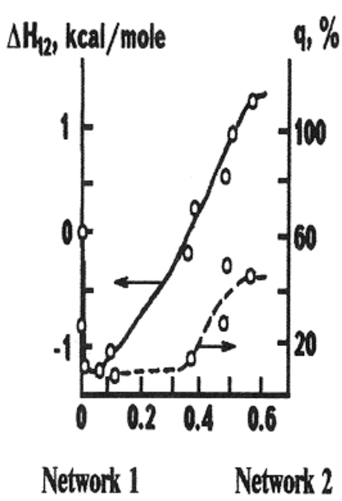

Figure 6.9. Dependence of the proportion of the interphase, q, and the enthalpy of mixing, ΔH_{12}, for IPN based on crosslinked PU and styrene-divinylbenzene copolymer on the amount of the second network.

All these ideas regarding non-equilibrium multiphase structure of IPNs are in good agreement with the comparatively low segregation degree in IPNs. In such a way, the whole structure of IPN may be presented as a mesophase matrix with embedded microphase regions which represent the evolved phases. We can distinguish two thermodynamic states in IPN as polymer alloys. IPN as a whole is a non-equilibrium system, due to incomplete phase separation and the lack of miscibility of constituent networks. For example, Figure 6.8 shows the free energy of mixing of two networks in IPN; the positive values indicate the lack of miscibility. However, the evolved phases may be considered as quasi-equilibrium, as they are the result of microphase separation, and each phase preserves the structure corresponding to one-phase state, i.e., to the molecular level of mixing. In general, the non-equilibrium microphase structure of IPN may be presented as a microheterogeneous two-phase system with lack of molecular miscibility of two constituent networks throughout the whole bulk and with molecular level of mixing in each of evolved phase and transition zone (mesophase).

From the discussion, it follows that to characterize the structure of IPNs with incomplete phase separation, it is very important to know the composition of each evolved phase and composition of the interphase. Up to now, such data have not been available because of experimental and theoretical difficulties. In principle, such an estimation may be done in the following way. If we know the position of glass transition for each phase (Figure 6.5, case b and c) and there is no distinct maximum for the interphase, the composition of each phase may be calculated. For this purpose, one of the equations connecting the glass temperatures of components and glass temperature of the miscible polymer-polymer system may be used.[165,166] Such estimation was performed for gradient IPNs using the Fox equation:[165,167]

$$1/T_g = \varphi_1/T_{g1} + \varphi_2/T_{g2} \tag{6.39}$$

Here, φ_1 and φ_2 are the volume fractions of components, T_{g1} and T_{g2} are their glass transition temperatures, and T_g is the glass transition temperature of miscible blend. Considering each phase, in accordance with the concept developed above, as independent quasi-equilibrium IPN, the composition and the ratio of phases may be found

$$\varphi_1 = \frac{T_{g1}T_{g2} - T_{g1}T_g^{I}}{T_g^{I}(T_{g2} - T_{g1})} \tag{6.40a}$$

and

$$\varphi_2 = \frac{T_{g1}T_{g2} - T_{g2}T_g^{II}}{T_g^{II}(T_{g1} - T_{g2})} \tag{6.40b}$$

where T_g^{I} and T_g^{II} are glass temperatures of evolved phases and φ_1 and φ_2 are volume fractions of each component in the phase enriched by this component.

From these data, it is easy to calculate the ratio of phases in IPN. This approach can only be used if the interphase glass transition temperature cannot be detected.

The existence of the interphase was shown using combined broad-line NMR spectroscopy and inverse gas chromatography[168,169] for a sequential IPN based on crosslinked polyurethane and polystyrene. The excess enthalpy of mixing of two networks (Figure 6.9) was also calculated. At low concentration of the second network, enthalpy of mixing is negative, indicating the formation of miscible system. However, the enthalpy of mixing increases as the concentration of the second network is increased and becomes positive. Figure 6.9 shows the proportion of material in the transition region, q, estimated from the gas chromatographic data. The increase in the enthalpy of mixing above zero is accompanied by an increase in q, that is, by an increase in the boundary region where miscibility of two components is observed. Thus the heat of mixing, a strictly thermodynamic quantity, indicates the emergence of phase boundary material.

It was postulated[169] that the intermediate region has a loosely-packed structure, leading to a shift to lower temperatures at the beginning of each transition. This result is particularly interesting in the light of the work by Helfand, which predicts a rarefication of mass at the interface of immiscible blends. This rarefication is caused, fundamentally, by the positive heat of mixing and loss of conformational entropy within the region of intermolecular contact.

For understanding the properties of IPNs, it is important to know the transition layer thickness. Using small-angle X-ray scattering technique, this value was estimated for some IPNs.[170] The thicknesses are within the limits of 20-50 Å.

6.5.3 MECHANICAL PROPERTIES OF IPNs

Mechanical properties of IPNs will differ, depending on the mechanism of the phase separation. For the case of nucleation, the traditional models may be used, which have been discussed in Chapter 4 for filled polymers. These models allow one to predict the properties of two-phased systems of the "matrix-inclusion" type. For IPNs which are decomposed according to the spinodal mechanism, the appearance of two interconnected phases and dual-phase continuity[171] should be taken as a basis for calculations.

An equation which satisfies the requirements of symmetry for two-phase systems containing two continuous phases may be written as follows in the general form:[172]

$$P = P_A^n \varphi_A + P_B^n \varphi_B \tag{6.41}$$

where P is some property of the system, for example, the modulus of elasticity, φ_A, φ_B are the volume fractions of the components, n is the exponent, characterizing the type of the system structure and the type of properties.

The calculations of the effective properties of a two-phase structure are given below for the case of an interconnected continuous structure developing as a result of spinodal decomposition. The equations proposed by Nielsen[172] for systems with two continuous phases are used in the calculations:

$$P = P_A \varphi_{A.} + P_B \varphi_{B.} + P_A P_B(\varphi_{A\perp} + \varphi_{B\perp})/(P_A \varphi_{B\perp} + P_B \varphi_{A\perp}) \qquad [6.42]$$

where $\varphi_{A.}$ and $\varphi_{B.}$ are the volume fractions of components A and B, which behave like a continuous media; $\varphi_{A\perp}$ and $\varphi_{B\perp}$ are volume fractions of components which behave as a dispersed phase when subjected to force. It is clear that

$$\varphi_{A.} + \varphi_{A\perp} = \varphi_A; \quad \varphi_{B.} + \varphi_{B\perp} = \varphi_B; \quad \varphi_A + \varphi_B = 1$$

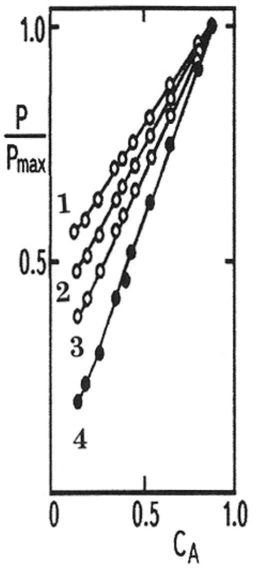

Figure 6.10. Dependence of P/P$_{max}$ on the phase connectivity coefficient, C$_A$: P$_A$/P$_B$: 1-2, 2-5, 3-10, 4-100. [Adapted by permission from Y. S. Lipatov, *Pure Appl. Chem.*, **43**, 273 (1975)]

According to Nielsen, the morphology of a system with two interconnected components is characterized by two parameters of phase connectivity:

$$C_A = \varphi_{A.}/\varphi_{A\perp}; \quad C_B = \varphi_{B.}/\varphi_{B\perp}$$

For calculations, a matrix was constructed[2,173] with dimensions of 100x100 elements, which by means of unities and zeroes depicts a two-phase structure in a plane close to interconnected structures formed by the spinodal mechanism of phase separation.

In the case chosen, $\varphi_A = 0.3856$ and $\varphi_B = 0.6144$. An algorithm has been developed with parameter λ_{crit}, which makes it possible to relate each of the 10,000 matrix elements to the continuous or dispersed phase. λ_{crit} is a value altering the response of the two-phase system under consideration to the action of force, F. The interconnectivity of the components decreases with increasing λ_{crit}, which is indicated by a decrease in the parameters C_A and C_B.

However, it is possible to find formal indication, whereby λ_{crit} may characterize different stages of phase separation. The effective values of the property, P, have been calculated for different values of λ_{crit} and for several ratios of the properties of components, $P_A:P_B = 100:1, 10:1, 5:1$. The ratio P_A/P_B overlaps the conceivable scatter of properties of the polymer phases in the actually existing IPNs.

An increase in λ_{crit} causes a decrease in $\varphi_{A.}$ and $\varphi_{B.}$ and in coefficient of connectivity of phases C_A and C_B. These changes considerably affect the effective values of the property, P. The property, P, of a two-phase system decreases for all $P_A:P_B$ values with increasing λ_{crit} (or decreasing phase connectivity). After having normalized P versus P_{max} at $\lambda_{crit} = 5$, the dependence of P/P_{max} on λ_{crit} may be plotted. It has been found that this dependence is of non-linear character and synonymously indicates that the effective property, P, of the composite decreases with increasing λ_{crit}. The influence of phase interconnectivity on P is more clearly displayed in Figure 6.10, plotted as P/P_{max} versus C_A. This dependence is linear, and the slope may characterize the influence of interconnectivity of the components on the general properties of the system P at various P_A/P_B ratios. The effect of interconnectivity is most essential at a larger difference between the properties of the components. Thus, the calculations make it possible to state that the interconnectivity of components, characteristic of the spinodal mechanism of phase separation, may considerably influence the final properties of the polymer-polymer composite.

In spite of a great number investigations in IPNs, the influence of phase interconnectivity on the final properties of these materials has not been studied experimentally. Meanwhile, the establishment of such regularities enables one to disclose the new ways of adjusting and improving many physical and mechanical properties of composites of this type. Despite the fact that the calculations, discussed above, were made without considering the actual dimensions of structural elements responsible for the interconnectivity of the components, it is clear that the formation of interconnected structures by the spinodal decomposition (with the dimensions of the structural elements being several nm) will ensure maximum advantages for the final properties of the composites, in particular, for mechanical properties. The practical aspect of this problem consists of a controlled management of the phase separation process and fixation of the structure in certain stages of decomposition.

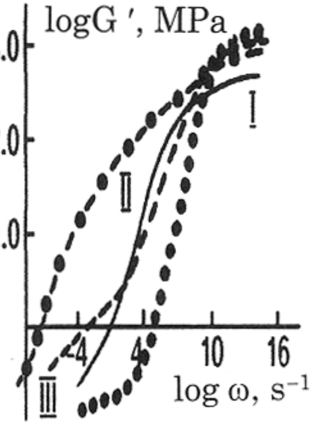

Figure 6.11. Generalized curves of dynamic shear modulus for OU (I), PBMA (II), and IPN's 65/35 (III) and 50/50 (IV) reduced to 273K. [Adapted by permission from Y. Lipatov, V. Rosovitsky, and

The development of microheterogeneity regions, as well as periodic or modulated structures, points to the role played by interphase interaction and interphase regions influencing the properties of these systems. According to theoretical and experimental estimates,[106] the volume fraction of interphase in the matrix may reach 30-50%. The increase in the segregation degree leads to the decrease in the thickness and fraction of the interphase. We have already mentioned that the effect of thickness of interphase regions is negligible on the macroscopic level when compared to the dimensions of the body; this is not the case with small regions connected through the interphase. The contribution of interphases increases with a growing thickness and with decreasing dimensions of phase separation microregions. A theoretical estimate of the influence of the interphase may be presented on the basis of simple phenomenological models of the Takayanagi type, within the framework of notions suggested by us for considering the role of the interphase layers in filled polymers.[174]

A theoretical analysis of the contribution of the interphase to the properties of a composite material[175,176] makes it possible to derive the following relationship:

$$E_C = (1-\lambda)E_P + \lambda[(1-\phi)/(E_P + \phi E_i)]^{-1} \qquad [6.43]$$

where E_C is the modulus of composite, λ and ϕ are parameters of the model taken for calculation, E_P is the modulus of polymer, E_i is the value of modulus associated via model parameters with the modulus of elasticity of the interphase. However, the application of this relationship to IPNs is uncertain because of the uncertainty the value of E_P which should be taken for calculations. The quantitative estimation of the contribution of the interphase to the IPNs properties is still a matter of future investigations, as well as many problems connected with their mechanical behavior.

It is evident that combination of two networks in IPN and the arising of the interphase should lead to essential changes in the relaxation behavior of IPNs. In principle, the general scheme of these changes was given in Figure 6.5. However, of great interest are the changes in the relaxation spectra of IPN, compared to spectra of constituent networks. The relaxation behavior of IPNs based on cross-linked polyurethane and weakly cross-linked poly(butyl methacrylate) have been studied in a wide frequency range.[177] Figure 6.11 represents a generalized curve constructed for individual networks and IPNs. The method of reduced variables was applied to thermorheologically complicated materials.[178] The generalized curve may be considered as consisting of three regions. The first is the region of glassy state (I) where chain mobility is frozen. The second region is the zone of transition from glassy state to rubber-like state (II). The viscoelastic properties in this zone are determined by the cooperative processes of segmental mobility. The third region (III) is a plateau of high elasticity where dynamic properties are connected with the existence of a network of molecular entanglements or chemical cross-links. The analysis of generalized curves shows that the PU network has the greatest value of the shear modulus G′ in the glassy state (3-4 frequency decades). For cross-linked PBMA, the glassy region is spread all over 7-8 decades along the frequency axis. IPN is characterized by intermediate values of G′ in the glassy state and is spread all over 5-6 decades. The most marked distinctions in generalized curves for IPN are observed in the transition region from glassy to rubber-like state (zone II). The analysis of position of transition zone on the frequency axis shows that both PU and PBMA have a rather narrow transition region and curves for both polymers are almost parallel. The transition zone for PU is shifted 4 decades to the higher frequencies, compared with PBMA. The distinctive feature of IPN is that they have a much wider transition region and therefore have a broader set of the relaxation times. For IPN 50/50, the transition zone is much broader as compared with IPN 65/35, and it is spread to the lower frequencies all over 6-8 decades. We can conclude that IPN 50/50 is characterized by relaxation processes with higher relaxation times. In such a way, the changing ratio of components in IPN leads to the change in relaxation behavior. Figure 6.11 shows that in the elasticity zone for all materials, the low values of logG′ are typical. The plateau region is typical only for PU network. The high elasticity zone for IPNs is situated at lower frequencies, as compared with pure PU and PMBA.

It is known that the most fundamental characteristic of relaxation behavior is the relaxation spectrum, which may be calculated from the following equation:

$$G(t) = G_e + \int_{-\infty}^{+\infty} He^{-t/\tau} d(\ln\tau) \qquad [6.44]$$

where G(t) is shear modulus at time t, G_e is the limit value of shear modulus independent of frequency, H is the distribution function of relaxation times, and τ is the mean relaxation time. Using generalized frequency dependencies of the real part of the complex shear modulus, the relaxation spectra have been calculated using the method proposed by Ninomia and Ferry.[179] The results are given in Figure 6.12. It is seen that both initial networks and IPNs are characterized by a broad maximum of the relaxation spectrum, which corresponds to the most realized relaxation times. The region of a sharp decrease of logH (logτ) is typical of the transition region from glassy to rubber-like state. The end zone for cross-linked PBMA is characterized by some drop of relaxation spectrum, whereas in the pseudo-equilibrium region, the plateau is observed (curve 2). For cross-linked PU (curve 1), the relaxation times are rather low and logH (logτ) maximum corresponds to $10^{-12} < \tau < 10^{-8}$ sec. That means that in the PU-network, the rapid conformational rearrangements take place. In the pseudo-equilibrium zone, there is some sign of a plateau connected with the existence of a chemical network. For weakly cross-linked PBMA (curve 2), the region of glassy state is situated at small relaxation times. The maximum of the main relaxation

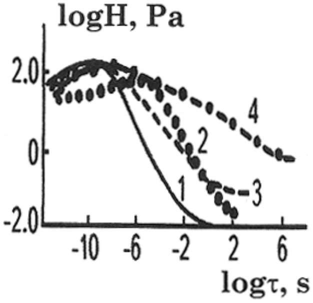

Figure 6.12. Relaxation spectra for PU (1), PBMA (2), and IPN's 65/35 (3) and 50/50 (4). [Adapted by permission from Y. Lipatov, V. Rosovitsky, and N. Babkina, *Polymer*, **34**, 4697 (1993)]

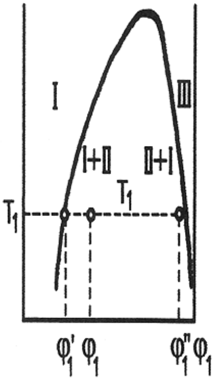

Figure 6.13. Conventional phase diagram of the polymer-polymer system and schemes of the structure organization (explanations see the text).

transitions is observed at $10^{-7} < \tau < 10^{-5}$ sec. The comparison of PU and PBMA spectra shows the slowness of relaxation processes in PBMA, compared with PU. Simultaneously, from the dependence of logH on logτ, it is seen that the spectrum slope for PU and PBMA is practically the same. According to the theory, this slope for homopolymers is equal to -1/2, which corresponds to the data for PU and PBMA. At the same time, for IPNs there is observed the sharp deviation of the slope from -1/2. This fact may be explained by the microheterogeneity of the system and by the greater set of relaxation times in IPNs as compared with homopolymers. For IPN 65/35, maximum logH (logτ) is observed at $10^{-12} < \tau < 10^{-7}$ and the transition from the glassy state is characterized by the relaxation times $10^{-12} < \tau < 1.0$ sec (curve 3). For 50/50 IPN, the broad maximum takes place at the same interval $10^{-12} < \tau < 10^{-7}$ sec, and for transition region $10^{-12} < \tau < 10^{5}$ (curve 4). Thus, 50/50 IPN has a much greater set of relaxation times, compared with 65/35.

These results show that in general, IPNs have much greater set of relaxation times, compared with pure constituent networks. The relaxation spectra of IPNs cannot be obtained by a simple superposition of spectra of components. The broadening spectra, compared with individual components, may be explained by the existence of a two-phase structure, where each phase is enriched in one of the components and the interphase between them. Simultaneously, the coexistence of two phases is reflected in the relaxation spectra, only indicated by their broadening and a shift along the time axis. It is evident that in spite of the immiscibility of two network components, there exists a strong interaction between macromolecular chains of various chemical nature. It is worth to noting that the problem of intermolecular interactions in IPNs has not been considered thoroughly up to the present time. These interactions are of a physical nature and may be described using both the entanglement concept and the concept of strong polar interactions between various chains. The latter may be the reason why 50/50 IPN has the relaxation spectrum shifted to higher relaxation times, compared with pure networks and IPN 65/35.[177]

We may also note that in order to explain the mechanical and relaxation properties of IPNs, it is necessary to take into account their morphology.

6.6 THE FORMATION OF THE PHASE STRUCTURE IN OLIGOMER-OLIGOMER AND OLIGOMER-POLYMER SYSTEMS

We have considered IPNs originating from the initially one-phase solution of the reaction components. However, in many cases, polymer-polymer composites may be produced from the oligomer-oligomer or polymer-oligomer systems which are not miscible. At the same time, after curing, their structure resembles the structure of IPNs, which is two- or multiphase structure. The structures formed in such conditions are also determined by the phase diagram of initial system.[180-182] Let us consider the following scheme of the phase diagram for oligomer-polymer blend (Figure 6.13).

Two cases are possible. At the volume fraction of oligomer $\varphi_1 > \varphi_1{}'$ at $T = T_1$, the one phase system is formed in an equilibrium state, i.e., solution I with high concentration of polymer. At $\varphi_1 > \varphi_1{}''$, the one-phase solution II is formed with high concentration of oligomer. In the interval $\varphi_1{}' \leq \varphi_1 \leq \varphi_1{}''$, the whole system consists of two solutions, which are two-phase systems. However, the phase separation does not proceed, due to high viscosity. Such a system may be considered as an emulsion, where the continuous phase is solution I and a dispersed phase is solution II. At a constant temperature, in the whole concentration range, corresponding to the two-phase state, the oligomer concentrations in each phase, $\varphi_1{}''$ and $\varphi_1{}'$ are constant. Increasing φ_1 does not change these concentrations but changes the ratio of volumes of two phases. At a definite concentration φ_1, the phase inversion proceeds and solution II becomes continuous phase and solution I becomes a dispersed phase. The morphology of the system depends on its prehistory. By curing an initially two-phase system, the oligomer polymerization proceeds in both solutions. Each phase formed may be considered as independent semi-IPNs. As distinct from true semi-IPNs, in the case under consideration, there should exist a sharp interface between two phases in the structure formed. The final structure depends on the phase organization of the initial system. Polymer-polymer compositions obtained by curing two-phase systems may be also considered as blends of two alloys.

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7

FILLED POLYMER ALLOYS

Many multicomponent polymer systems may be, and are, used as matrices for composite materials. The concept of hybrid matrices was put forward.[1] These matrices are polymer alloys of miscible and immiscible polymers (both linear and cross-linked). Because a structure of alloys of immiscible polymers is formed during the phase separation, it is very important to establish the influence of the interface with solid on these processes, on the thermodynamic state of filled polymer alloys, and, correspondingly, on their viscoelastic properties. The interface with solid in hybrid matrices affects both the structure formed during phase separation and the properties of composites based on filled hybrid matrices. Here the solid phase plays not only the traditional role of reinforcement but also the new role of a regulator of the phase structure, due to the phase border influence on the phase separation and thermodynamic stability or instability of the system.

7.1 THERMODYNAMIC BACKGROUND

The selectivity of interaction of the polymer alloy components with the solid plays an important role in the thermodynamic behavior of filled polymer alloys (see Chapter 1). Let us consider some simple thermodynamic relations.[2] The free energy of mixing of two different polymers, ΔG_{AB}, may be approximated as

$$\Delta G_{AB} = RT\chi_{AB}\varphi_A\varphi_B \qquad [7.1]$$

where φ_A and φ_B are volume fractions of polymers A and B. For a binary mixture in contact with a solid surface, we can express the change in the free energy of the system, due to interaction with solid, as

$$\Delta G_{mix} = \Delta G_{AS} + \Delta G_{BS} - \Delta G_{AB} \qquad [7.2]$$

where $\Delta G_{AS} = RT\chi_{AS}\varphi_A\varphi_{S(A)}$ and $\Delta G_{BS} = RT\chi_{BS}\varphi_B\varphi_{S(B)}$ are free energies of interaction of components with the surface, φ_A and φ_B are volume fractions of components, and $\varphi_{S(I)}$ is the volume fraction of active points occupied by the segments A and B at the interface. The thermodynamic stable system is formed when $\Delta G_{mix} < 0$. Two cases can be distinguished.

Case 1. The interaction of each component with the surface is symmetric, i.e., the energies of pair interactions are approximately equal. In this case, $\Delta G_{AS} \approx \Delta G_{BS}$. If both values are negative, and the components are immiscible ($\Delta G_{AB} > 0$), then ΔG_{mix} is negative.

For miscible polymers, free energy of their mixing is negative and adsorption will proceed only when $|(\Delta G_{AS} + \Delta G_{BS})| > |\Delta G_{AB}|$.

Thus, the interactions with the surface are preferential when polymers are immiscible. These relations are valid, independent of the fraction of polymers A and B interacting with the surface. For symmetric interactions, there is no selective adsorption and the composition of the mixture in the interphase is the same as in bulk.

Case 2. The interactions are non-symmetrical, ΔG_{AS} is greater or lower than ΔG_{BS}. In this case, if the sum $(\Delta G_{AS} + \Delta G_{BS})$ is negative and components are immiscible, there exists a selective adsorption of one of the components. The composition of the interphase differs from the bulk. Preferential adsorption is equal to increasing the motive force for phase separation of two immiscible polymers. The interphase is enriched in component A, if $-\Delta G_{AS} > -\Delta G_{BS}$, and vice versa. For miscible pairs with non-symmetrical interactions for adsorption, the following relation should be valid: $|\Delta G_{AS} + \Delta G_{BS}| > |\Delta G_{AB}|$.

These considerations are consistent with experimental data which show the enrichment or depletion of a surface layer in one of the components of the binary mixture (surface segregation). As a result of changing the composition of the system, a component's miscibility in the interphase may increase or decrease; the same is valid for the bulk. One of the important factors here is also the redistribution of polydispersed components according to their molecular mass between the surface and the bulk. The second reason for changing miscibility is the difference in conditions of interactions between two polymers, due to conformational restrictions in the interphase and the bulk.[3]

As compared with a great deal of theoretical and experimental works in the field of polymer alloys and blends, the study of the filler influence on the phase behavior of these systems is at its very early stage, and there are only a few data and attempts to describe the phenomena theoretically. The only review one can mention was written by Dolinny and Ogarev,[4] in which the results of theoretical and experimental investigations were analyzed for phase transitions in semi-infinite two-component systems (capable of mixing liquids and polymers). In the framework of the mean field theory, accounting for short range interactions between the solid surface and mixture components, the conditions of the formation of wetting layer of one of the equilibrium phases on the substrate surface have been discussed. Phase transitions in polymer solutions were explained on the basis of Cahn theory and the data on the concentration profile at the interface with solid. The jump in the thickness value of the layer in contact with substrate may be considered as phase transition of the first order (it should be remembered that adsorption phenomena also can be considered as a phase transition - see Chapter 1). It was shown[5,6] that the phase diagrams of thin layers of polymer solutions are essentially changed, compared with the phase diagrams of the bulk solution. However, the transitions at the interface between solid and solid mixture have not been considered.

The two-parameter model of polymer-polymer excluded volume, in conjunction with the renormalization group, was developed to include an interacting plane surface.[7,8] It was theoretically shown that such a system has two types of volume exclusion: the usual polymer-polymer excluded volume interactions and the "excluded volume" constraint of the boundary. In such systems, there is a competition between the gain of internal energy with the formation of attractive surface contacts and the loss of configurational entropy, due to the proximity of the surface.[9]

Reich and Cohen[10] were the first who proposed the thermodynamic description of the effect of interface on the phase separation in polymer mixtures. They considered the lattice-cell model, where the coordination number of lattice points is uniform throughout the lattice, but, in the surface layer, it should be lower than in bulk. The number of pair interactions in the total sample of N lattice sites is

$$N = Z/2 - (1/2)[(2H_b/H)N(Z - Z_b)] \qquad [7.3]$$

where N is the total number of lattice sites in the entire system, H is the sample thickness, H_b is the boundary layer thickness, Z and Z_b are coordination numbers of lattice points in the bulk and the surface layer. At $Z_b < Z$, the thermodynamic interaction parameter equals:

$$\chi_{AB}(T,H) = \chi^{o}_{AB}(T)F(H) \qquad [7.4]$$

where χ_{AB} is interaction parameter corrected for surface effects, and χ^{o}_{AB} is the interaction parameter neglecting surface effects, i.e., for $H_b/H = 0$. Function F(H) is obtained as

$$F(H) = 1 - 2(1 - Z_b/Z)(H_b/H) \qquad [7.5]$$

Since the value of χ_{AB} at the spinodal is invariant at fixed composition, it follows that

$$\frac{dT_{sp}}{dH} = -\frac{(\partial\chi_{AB}/\partial H)_T}{(\partial\chi_{AB}/\partial T)_H} = \frac{F(H)(\partial\chi^{o}_{AB}/\partial T)}{\chi^{o}_{AB}(T)(\partial F/\partial H)} \qquad [7.6]$$

It follows that for a system with LCST, $d\chi^{0}_{A}/T > 0$, dT_{sp}/dH is negative, i.e., the system stability should increase with decreasing thickness of the surface layer. An opposite effect should hold true for mixtures with UCST, where $d\chi_{AB}/dT < 0$ and dT_{sp}/dH is positive.

The effects of upgrading the stability of a binary system can also be observed for systems characterized by UCST. To predict the dependence of the spinodal temperature on the film thickness, parameter χ_{AB} at T_{sp} is expressed as

$$\chi_{AB}(T_{sp}) = (1/2)\left(\frac{1}{\varphi_A} - \frac{V_A}{V_B\varphi_A}\right) \qquad [7.7]$$

where φ_A is the volume fraction, and V is molecular volume. Substituting Eq 7.3 and 7.5 in Eq 7.7, we obtain:

$$\chi^o_{AB}(T_{sp}) = \left(1 - \frac{2(1 - Z_b/Z)H_b}{H}\right) \qquad [7.8]$$

Expressing $\chi^o_{AB} = \chi^o - \chi_1/T$, χ^o and $\chi_1 > 0$, and using this expression in Eq 7.8 for $H_b/H = 0$, and for finitely small H, we find:

$$1/T^o_{sp} - 1/T_{sp}(H) = \frac{1}{2\chi_{AB}}\left(\frac{1}{\varphi_A} + \frac{V_A}{V_B\varphi_B}\right)\left(\frac{1}{F(H)} - 1\right) \qquad [7.9]$$

where T_{sp} is the temperature on the spinodal at $H_b/H = 0$. If $T_{sp}(H)$ does not differ much from unity, $1/T_{sp}$ will be a linear function of 1/H:

$$\frac{1}{T_{sp}(H)} = \frac{1}{T^o_{sp}} - \frac{1}{\chi_{AB}}\left(\frac{1}{\varphi_A} + \frac{V_A}{\varphi_B}\right)\left(1 - \frac{Z_b}{Z}\right)\frac{H_b}{H} \qquad [7.10]$$

From this equation, the stabilizing effect of the decrease in film thickness, observed by authors in films of all compositions showing spinodal decomposition layer, can be estimated. Calculations have demonstrated the effect of the layer thickness on the spinodal decomposition in PS-poly(vinyl methyl ether) mixture to begin at a thickness of 0.1-0.8 mm.

7.2 PHASE STATE OF BINARY POLYMER MIXTURES IN PRESENCE OF FILLERS

From the thermodynamic point of view, the system can be characterized if the phase diagrams are known for filled and unfilled systems and if the free energy of mixing or interaction parameters in the presence of a filler are known. It was shown above that the temperature of the phase separation in the surface layer changes as compared with the bulk. Therefore, when analyzing the experimental phase diagrams of a filled binary polymer system, one should have in mind some uncertainties which may arise in the interpretation of the results. The experimental data, which will be discussed below, show that introduction of a filler changes the shape of phase diagrams. This effect may be explained by consideration of the changes in the matrix composition, due to formation of the border surface layer near the interface. This layer has another composition as compared with the bulk, due to the selectivity of interactions. The enrichment of the surface layer of the alloy, in one of the components, should shift a figurative point in the phase diagram along the composition axis. For example, let us consider a case when component A is adsorbed preferentially. Then, the phase separation will begin in the surface layer later (at lower temperature), compared with the bulk for the systems with UCST, and later (at higher temperatures) for the systems with LCST. The reason for this effect is the difference in temperatures of phase transition from a one- to a two-phase system of various composition. Thus, the reliability of experimentally-found diagrams depends on the volume ratio between the parts of alloy in the surface layer and in bulk. In real systems, these effects may be not so pronounced, due to the existence of the composition gradient between the surface layer and bulk, which is described by the concentration profile. Obviously, the shift of the phase transition temperature is larger, the higher the selectivity of interactions. In such a way, we meet some experimental difficulties in finding the phase diagrams of filled polymer alloys. For the systems with UCST, turbidity by cooling occurs, whereas for LCST, clearance by heating appears earlier in the bulk. Presently, it is unclear in what way the coexistence of these two regions reflects upon the experimentally-found cloud point curves.

7.2.1 PHASE DIAGRAMS OF THE SYSTEMS POLYMER-POLYMER-SOLID

Let us now consider some experimental data on phase diagrams of filled polymer alloys. The effect of a solid surface on the equilibrium in ternary systems of polymer-polymer-solvent has been studied.[11] This effect should be connected with the adsorption of one or both components of the polymer mixture at the interface with a solid. Figure 7.1 shows that introducing silica into ternary system PS-PBMA-benzene and PS-polycarbonate-chloroform results in the displacement of the binodal and change of its shape. For both polymer pairs investi-

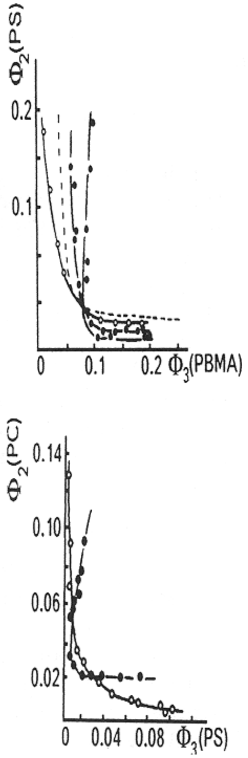

Figure 7.1. (a) Binodals for PS-PBMA-benzene system: 1-without silica, 2-with 0.5 g per 100 ml, 3-with 1.0 g per 100 ml of silica at 295 K; 4-spinodal; (b) binodals for PS-PC-chloroform system: 1-without silica, 2-with silica at 295.5 K. [Adapted by permission from Y. S. Lipatov, A. E. Nesterov, T. D. Ignatova, N. P. Gudima, and O. T. Gritsenko, *Eur. Polym. J.,* **22**, 83 (1986)]

gated, the region of miscibility broadens. Increase in the amount of silica introduced leads to broadening of the miscibility window. It is evident that the effect cannot be explained by a simple change in solution composition after adsorption. If it were so, the position and shape of binodal would not be changed. The points in the binodal region corresponding to the definite volume fractions of components in this case would only be displaced along the initial binodal. The simple explanation of the broadening of the region of mutual miscibility of two polymers is based on their polydispersity. It is known that high molecular weight fractions are primary adsorbed on a solid surface (see Chapter 1). As a result of such preferential adsorption, the solutions become enriched with the low molecular weight fractions of the polymer, which has been selectively adsorbed, and the mutual miscibility increases. It should be noted that effects depend on the ratio of components in solution. To understand the phenomenon, it is also necessary to take into account various thermodynamic qualities of solvent for each component, which in its turn determine adsorption from the mixture (see Chapter 1).

Figure 7.2 shows the phase diagram for polystyrene-polycarbonate alloy including various fillers. The diagrams have been constructed from the cloud point determinations.[12] It is seen that introduction of a filler changes the shape of the phase diagram. In the region of the mean compositions, the phase separation temperature becomes higher, i.e., the system has higher thermodynamic stability. However, in the composition range with excess of one of the components, the phase separation temperature decreases. Figure 7.3 represents the phase diagram for the PS-PBMA mixture, where introduction of 10% filler decreases thermodynamic stability. These effects may be connected with the changes in matrix composition, due to formation of a border layer near the filler surface which has another composition as compared with bulk.[13] However, in such a case we should distinguish between two regions coexisting in the system of given composition, each characterized by its own phase separation temperature. These regions are the bulk of a matrix and the matrix border layer. Their compositions are not the same as in the initial mixture. It is unclear, however, in what way the coexistence of these two regions reflects upon the experimentally-found cloud points.

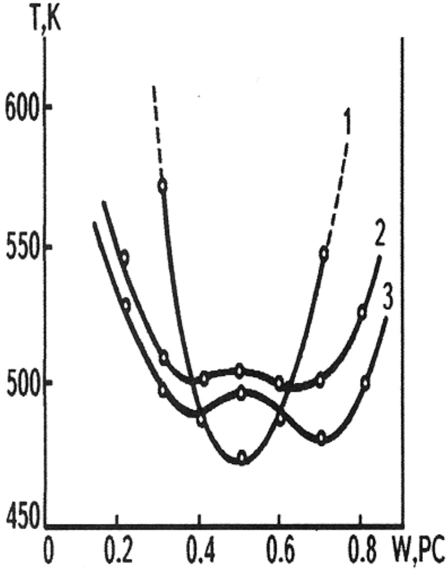

Figure 7.2. Phase diagram for PS-PC mixture: 1-in absence of a filler, 2-in presence of 10 wt% modified fumed silica by ethylene glycol, 3-with 10% fumed silica modified by butanol.

The cloud point curves for unfilled poly(vinyl acetate) - poly(me-thyl methacrylate) mixtures and those filled with 10% of non-modified and silanized fumed silica show that curves for filled mixtures are situated at much lower temperature than those for unfilled material.[14] It should be noted that the temperature of phase separation decreases sharply in the region where one alloy component has a predominant content. The addition of silane-treated fumed silica also results in a lower temperatures of phase separation. These effects were attributed to the difference in adsorption of both components at the interface with a solid[15] and are connected with the asymmetry of interaction in the system. The phase separation temperature in this alloy also depends on the filler content (Figure 7.4). At the same time, the phase separation temperature depends on the ratio of components. This fact may be interpreted as indirect confirmation of the role of asymmetry of interactions, because increasing the filler content should affect the asymmetry of the interactions and therefore have an

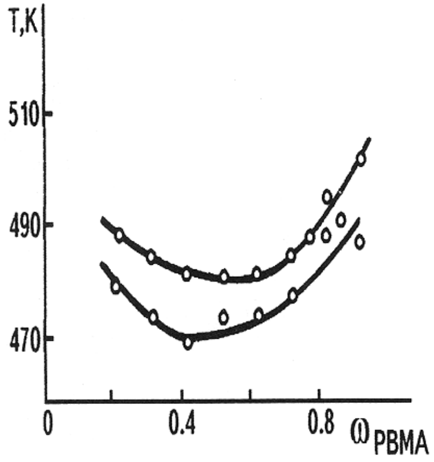

Figure 7.3. Phase diagrams of PS-PBMA mixtures without any filler (1) and with 10% fumed silica (2).

effect on the temperature of phase separation. It is seen that the selective adsorption leads to the composition change in the border layers and in the matrix bulk, which contribute to the change of miscibility of the components in the bulk, because miscibility is a function of composition.

The enrichment and depletion of the surface layers in filled alloys (surface segregation) was discovered in studies of the ternary system:[16] polybutadiene carboxylate rubber-epoxy resin-ammonium perchlorate. Using the method of total attenuated inner reflection in the IR region, it was found that in a chemically-formed system, the epoxy resin preferentially interacts with solid, displacing rubber. The enrichment of the surface layer by the epoxy resin is energetically favored, due to its higher surface tension (48 mN/m), compared with rubber (39 mN/m), which leads to the sharp decrease of the interfacial tension at the polymer-solid interface. It was established that, under the reaction conditions used, the distance from the surface at which the layer is enriched in epoxy resin, reaches 5 mcm. These data have shown that there is no sharp border between two polymers in the surface layer, but a stepwise change of their ratio. The results correlate with the data on the selective adsorption of the same polymers.

For an immiscible polyethylene-poly(butyl methacrylate) pair filled with fumed silica,[17] using NMR technique, the composition of the border layer was established (Table 7.1). As can be seen, with a growing filler content, the fraction of PBMA in the boundary layer increases and that of polyethylene decreases, i.e., the boundary layer is enriched by PBMA. Only 3% filler addition to the alloy, containing 75% polyethylene, results in small enrichment with this polymer, but above 10% filler the PBMA content increases. When considering the struc-

Table 7.1: Boundary layer composition of PE/PBMA alloys

Filler content, %	PE content, %			PBMA content, %		
	25	50	70	75	50	25
3	20.08	50.68	79.85	79.92	49.32	20.15
5	17.46	43.61	76.44	82.54	56.39	23.56
10	14.44	43.61	74.27	85.56	56.39	25.73
15	9.46	37.06	69.47	90.54	62.96	30.53

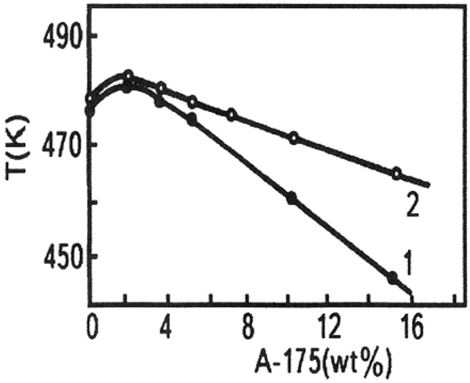

Figure 7.4. Phase separation temperature as a function of filler concentration for the mixture PVA-PMMA in ratio: 0.8:0.2 (1) and 0.6:0.4 (2). [Adapted by permission from A. E. Nesterov, Y. S. Lipatov, V. V. Gorichko, and O. T. Gritsenko, *Polymer*, **33**, 619 (1992)]

ture of the surface layers in filled polymer alloys, one also has to account for the conformational changes of both components in the surface layers, which depends on both the surface nature and component ratio.[18]

As we have already noted, there should be various contributions to the phase separation temperature, due to the existence of the border layer with its own composition and the bulk with another composition. Consequently, the effect of the film thickness, at the interface with a solid, on the phase separation temperature is important. Figure 7.5 shows this dependence for the PMMA-PVA system on various supports. For the glass surface, there were observed two phase separation temperatures after the thickness of the film reaches 10-12 μm.[19] Films casted on silanized glass, regardless of their thickness, exhibit only one phase separation temperature.

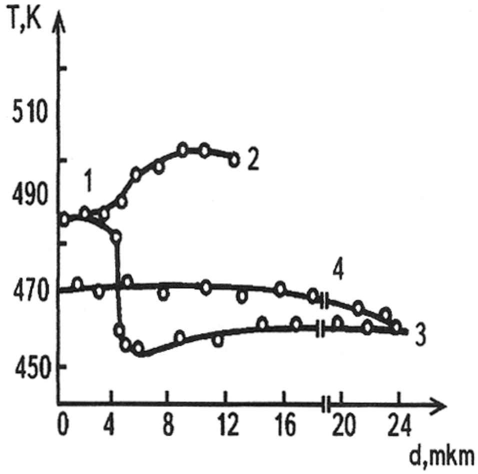

Figure 7.5. Temperature of phase separation of 0.7:0.3 PVA/PBMA mixture on non-silanized (1,2,3) and silanized glass (4) as a function of the film thickness. [Adapted by permission from Y. S. Lipatov, *J. Adhes.*, **37**, 180 (1992)]

The limited amount of experimental data on phase diagrams of filled polymer alloys and many factors involved in the processes of phase separation presently give no possibility to present any general concept regarding the solid surface effect on the position of phase diagrams. Only some general considerations may be presented. It is evident that in the region of metastable states between the binodal and the spinodal, the border layers with preferred amount of one alloy component may be formed. These layers may be considered as nuclei of a new phase formed by separation according to the nucleation and growth mechanism initiating the phase separation. If the system happens to be inside the spinodal, these layers are able to initiate the appearance of the selective fluctuations of the composition with the formation of periodic modulated structure of interconnected regions of spinodal decomposition. However, in the case when the distance between filler particle approaches the radius of the intermolecular interaction and all the matrix is transferred to the state of the surface layer, there is no composition redistribution. The filler influence manifests itself in the change of the conditions of interaction between different macromolecules, which may lead to a change in the phase diagram, and in the total retardation of the phase separation (see below).

These considerations show that filler introduced into a polymer alloy plays a role of an agent changing the conditions of the phase structure formation, not only a traditional role of reinforcement.

Thus, it is clear that changing the position and shape of phase diagrams of polymer alloys in the presence of filler should be taken into account when selecting condition of production of composite materials on their basis.

7.2.2 THERMODYNAMIC INTERACTION PARAMETERS IN FILLED POLYMER ALLOYS

Even if we have correctly drawn phase diagrams, they may only answer to the question at which range of compositions and temperatures the system is — one- or two-phase system. The phase diagrams cannot characterize the system in the region where the incomplete phase separation took already place. Such characteristics may be obtained only if we are able to calculate the changes in the free energy of mixing in the presence of a filler or determine the thermodynamic interaction parameter.

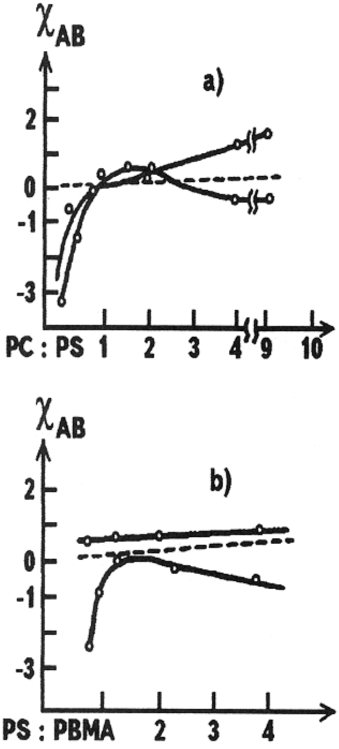

Figure 7.6. Concentration dependence of thermodynamic interaction parameter for PS-PC (a) at 476 K and (b) at 454 K. 1-without silica, 2-with silica (10% by weight). [Adapted by permission from Y. S. Lipatov, A. E. Nesterov, T. D. Ignatova, N. P. Gudima, and O. T. Gritsenko, *Eur. Polym. J.*, **22**, 83 (1986)]

In some of our work,[20-22] the values of the interaction parameter, χ_{AB}, have been determined for unfilled and filled polymer alloys in the melt state, using the inverse gas chromatography method,[23] in spite of many experimental difficulties and uncertainties. This parameter, as was shown in Chapter 6, may serve as a characteristic of the remoteness of the state of the system from its equilibrium state. Generally, it was shown that depending on the composition and amount of the filler introduced and its chemical nature, the parameter χ_{AB} may increase or decrease, i.e., the changing thermodynamic stability is of a very complex character. By introduction of fillers to binary mixtures of crystallizing polymers, due to the change in the thermodynamic stability, the crystallinity degree can be changed. For the system with lower thermodynamic stability in the melt, the crystallinity degree in a solid state is higher, whereas for more stable systems, crystallinity degree decreases with cooling.[24-26]

For PS-PBMA systems, the thermodynamic interaction parameters χ_{23} have been determined[11] using inverse gas chromatography. Figure 7.6 shows the increase in thermodynamic stability of PS-PBMA mixture by introducing silica (parameter χ_{23} diminishes). For PS-PC mixture, the dependence of χ_{23} on composition is rather complex. For low and high PC content in the mixture, where preferential adsorption of PC proceeds, χ_{23} diminishes. In the composition range, where preferential adsorption of PS takes place, χ_{23} becomes greater than for the mixture without adsorbent.

The experimental data can be treated on the basis of statistical theories of polymer solutions.[27-29] Parameter χ_{12} (polymer-solvent) may be presented in the form:

$$\chi_{23} = -\frac{U_1 V^2}{RT} + \frac{C_p \tau^2}{2R} \qquad [7.11]$$

where $\tau = 1 - T_1^*/T_2^*$. In Eq 7.11, the first term is due to the interchange of energy for forming contacts between a polymer segment and solvent. The second term gives the structural contribution arising from changes of free volume of mixing. The quantities T_i^* are the temperature reduction parameter of the solvent (component 1) and the polymer (component 2), τ is temperature dependent molecular parameter, U_1 and C_p are the configurational energy and its temperature derivative. The second term contributes unfavorably to the miscibility, due to the difference in a free volumes of components. It is evident that the unfavorable contribution to mixing is diminished when the difference between T_1^* and T_2^* becomes smaller, and vice versa (τ^2 is always positive).

What happens when we introduce the filler into a mixture of two polymers? It was shown (see Chapter 4) that in the polymer layer at the interface with a solid, there is a decrease of the thermodynamic interaction parameter χ_{12} (solvent-polymer). Such behavior was explained by diminishing molecular packing density in the surface layer and by increasing fractional free volume. These data indicate that the selective adsorption also leads to increase of the free volume of adsorbed polymer. Calculations[11] have shown that, for the case under investigation, the difference between T* for two pairs of polymers, in a definite range of composition, due to looser packing, reduces, and as a result, both τ^2 and χ_{23} diminish. Thus, there is an increase of thermodynamic stability of the systems.

This phenomenon is connected with the adsorptional interaction of components with the surface and with the selective adsorption of one of them. The transition of macromolecules in the interface into the surface layer changes the conditions of interaction between macromolecules in such a way that the interaction parameter χ_{23} decreases. The difference between free volumes of components in the surface layer and in the bulk contributes markedly to the increase of thermodynamic stability.

For the system PBMA-polyethylene filled with various amount of fumed silica, the interaction parameters have been determined.[30] Because of the method involved, all the data relate to the melted state of alloys. For all the compositions, the difference $\Delta\chi_{AB} = \chi_{AB} - \chi_{AB(filled)}$ has been estimated at various compositions of alloy. This difference is a measure of increasing stability of the system by filler introduction. The experimental results have shown that for a given system, the increasing amount of filler leads to an increase in interaction between different segments in the surface layer[3] (Table 7.2). The most general interpretation of these results may consist of the dependence of χ_{AB} on the lattice coordination number in the surface layer. It was supposed that the coordination number depends on the conformational state of macromolecules, which is different in the surface layer and in the bulk.

Table 7.2: Interaction parameters, χ_{AB} for the boundary layers of polyethylene/poly(butyl methacrylate)/fumed silica system (wt%)

PE/PBMA ratio	400 K		417 K	
	5%	15%	5%	15%
3:1	0.51	-0.83	-0.22	-1.45
1:1	0.20	-1.85	-1.60	-2.10
1:3	-2.00	-2.20	-2.60	-2.80

Figure 7.7 shows concentration dependencies of the enthalpy and entropy contributions to the total interaction parameter, χ_H and χ_S, which characterize the change of the interaction parameter in the surface layers of polymer alloy.

These contributions have been calculated from the temperature dependencies of χ_{AB}. It is seen that with an increase in the fraction of PBMA in the system, χ_H, essentially drops, whereas χ_S goes through a maximum. These results show the important role of non-combinatorial entropy contribution in the interaction in the interphase, which depends on the composition. Using a traditional model of filled polymers, it was supposed that the interaction parameter, found experimentally, is a sum of parameters, characterizing the surface layer and the bulk:

$$\chi_{AB(\text{filled})} = \chi_{AB}(1 - \varphi) + \chi_{AB(\text{surface layer})}\varphi \qquad [7.12]$$

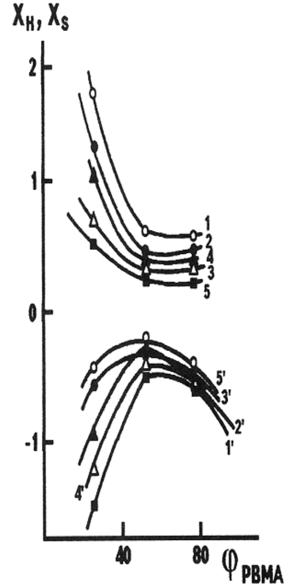

Figure 7.7. Concentration dependence of parameters χ_H and χ_S for PE-PBMA mixture without filler (1) and with 5 (2,4) and 15 weight parts (3,5) of fumed silica (2,3) and fumed silica modified with diethylene glycol (4,5).

where φ is a volume fraction of the mixture in the surface layer. The value χ_{AB}(surface layer) can be calculated from the experimental data on the volume fractions of the surface layers.[17] The results of calculation have shown that in the surface layer, the interaction parameter χ_{AB}(surface layer) is much lower, compared to the value in bulk. This result allows for the conclusion to be drawn that the phase interface with a solid increases the thermodynamic stability of immiscible polymer pair even in the melt; the effect is probably connected with the changing conditions for interaction of various chains. It means that increasing the total surface of the filler introduced, it is possible to transfer the system from a thermodynamically unstable state to a stable one (effect of increasing miscibility of components in the surface layer). The additive relation 7.12 may be transformed into

$$\chi_{AB}/\varphi = (\Delta\chi_{AB})_{(\text{surface layer})} \qquad [7.13]$$

where $(\Delta\chi_{AB})_{(\text{surface layer})} = \chi_{AB(\text{surface layer})} - \chi_{AB}$. The relation 7.13 shows the change of the interaction parameter for a hypothetical system where both components are fully in the state of the surface layer. Value $(\Delta\chi_{AB})_{(\text{surface layer})}$ may be considered as a measure of thermodynamic activity of a filler.

The value of the interaction parameter in the surface layers depends on the filler nature (on its activity) at comparable specific surface. Not all fillers increase thermodynamic stability of the filled alloy. It is also evident that the effect depends on the conditions of the alloy production.[31] Theoretically, the effect of the surface on the behavior of polymer mixtures was considered by Nooland.[32]

For binary alloys of crystallizing polymers (polyethylene-polypropylene-kaolin, polyethylene-polyoxymethylene-kaolin), the same effects of decreasing the interaction parameters in melt, due to the filler presence, have been observed.[24] However, it is interesting that the crystallinity degree in solid state (it should be remembered that all the measurements of χ_{AB} were performed in the state of a melt, due to the peculiarities of the method of inverse gas chromatography) correlates with χ_{AB}. The χ_{AB} maximum in the filled melt corresponds to the maximum crystallinity degree. Therefore, if, in the filled melt, the system is less stable, its crystallinity degree increases, and *vice versa*. These data testify that during crystallization from the melt, where both components are miscible, at the same cooling rate, the phase separation is hindered and crystallization degree is lower. If the system is not stable, the phase separation is more complete and crystallinity increases.

Another picture is observed when filling alloys of compatible polymers.[33] By introducing filler (kaolin) into the miscible alloy poly(vinyl acetate)-ethylene-vinyl acetate copolymer, the interaction parameters in the surface layers increase in the whole range of compositions. This indicates the diminishing thermodynamic stability of filled alloy. The effect is explained by the independent adsorption of both components at the interface diminishing the interaction between various macromolecules. Thus, for filled alloys of miscible components, the effect of filler introduction may be opposite to that observed for immiscible alloys.

The very method of determination interaction parameter, using inverse gas chromatography from the retention volume, leads to some uncertainties. According to the theoretical relationships, which we do not discuss here, to calculate this parameter, one has to use the value of the retention volumes of pure

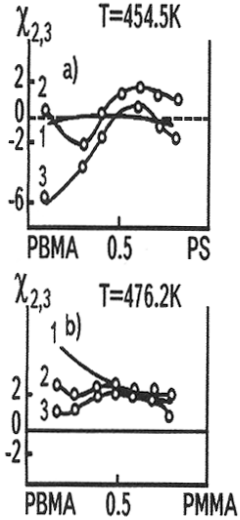

Figure 7.8. Concentration dependence of interaction parameter for PS-PBMA (a) and PMMA-PBMA (b) alloys 1-without filler, 2-with filler (calculation according to the first method), 3-calculation according to the second method. [Adapted by permission from Y. S. Lipatov in **Controlled Interphases in Composite Materials**, Ed. Ishida, *Elsevier*, Amsterdam, 1990, p. 594]

components. For filled polymer mixtures, however, it is not clear what volume to use for calculations, namely, the retention volume of each pure component, or the same volume of each component in the presence of a filler. The comparison of calculations, in which both values have been used, was done.[34] Two values of retention volumes have been used: an “unperturbed” one, for pure components, and “perturbed retention volume” for each component with a corresponding amount of filler. Such an approach is important because, as it was shown in Chapter 4, introduction of filler leads to the loosening of molecular packing, and in such a way as to result in change in the retention volume.[34] The calculations of χ_{AB} based on “perturbed” retention volume give, in the majority of cases, a lower value, compared with the unfilled mixture. This may be considered as a sign of the increasing compatibility in filler presence. (In discussing this problem, we prefer to use the term “compatibility”, as it is not clear how we can speak about increasing miscibility in filler presence). Correspondingly, the calculations of χ_{AB}, based on the “unperturbed” retention volumes, result in lower changes in parameter as compared with the first method. In some cases, the calculated values of χ_{AB}, for the filled systems, are higher, compared with unfilled systems. At the same time, as seen from Figure 7.8, the concentration dependence of χ_{AB}, determined by two methods, is the same. The result may be explained if we take into account that the transition into the state with lower packing density means the transition to the thermodynamically less stable state.[35] By decreasing polymer packing density of the filled system, its entropy diminishes and enthalpy increases.[36] In such a way, the polymer matrix, in the presence of a filler, is always less stable thermodynamically, independent of its formation from one polymer or from a polymer mixture. Therefore, by analysis of the stability of filled system, one can distinguish the contribution of decreasing stability of each component to the total stability. The calculations, according to the second method, accounting for perturbing surface action, show that interaction of perturbed chains of each component increases the stability of binary mixture; the filled mixture is more stable compared with a mixture without a filler. At the same time, if we compare it with the pure mixture, the filled mixture may happen to be less stable if its stability estimation is done without accounting for perturbing surface action. Thus, the comparison of two calculation approaches allows us to distinguish the effects connected with the instability appearance, due to surface action on each polymer component and the effect due to change of interaction between perturbed chains of both components. The difference in χ_{AB}, calculated by two methods, shows the contribution of perturbing action of the surface to the component interaction in the interphase region near the phase border.

The perturbing action of the surface cannot be accounted for by comparison with the phase diagrams for filled and unfilled alloys. For comparison of the phase diagrams and data on χ_{AB}, we have to use the unperturbed χ_{AB} values. The comparison of data calculated by two methods allows estimation of the contribution to the system stability both of the changes in the perturbed component interaction and in the decreasing stability of each component in the filled system. The calculation by the first method gives only changes in the interphase interaction between two polymers, whereas the second method represents the total effect of filler action on the thermodynamic stability of the system.

Thus, in all cases, the introduction of a filler changes the thermodynamic stability of the polymer alloy. The effect is determined by two opposite contributions to the stability, one determined by decreasing packing density and another by changing the system volume by mixing. Taking into account the relative character of χ_{AB} estimation, the analysis of the experimental data may be done in the framework of either method of calculation. It is important only to have in mind that perturbing action of the surface favors the component mixing in the border layer near filler surface. The role of both contributions to stability changes with mixture composition and filler content. This fact explains the sophisticated character of χ_{AB} changes with alloy composition.

7.2.3 ON KINETICS OF THE PHASE SEPARATION OF FILLED POLYMER ALLOYS

There are only a few data on the kinetics of the phase separation in filled polymer alloys. From the general point of view, the adsorption interaction near the interface restricts the molecular mobility of polymer chains and makes their movements slower. The retardation of relaxation processes in the boundary layers should also slow down the phase separation rate. For many systems, we have observed the linear time dependence of the log of the light scattering intensity at the initial stages of phase separation. This enables us to use the Cahn-Hilliard theory[37] to calculate the amplification factor 2R(β), where β is the wave number, which characterizes the rate of increases of concentration fluctuations. Figure 7.9 shows the dependence of 2R(β) on the temperature. It is seen that this value for unfilled alloys increases sharply with temperature, i.e., with the remoteness from the cloud point. For filled alloys, the growth rate 2R(β) with temperature is much lower, i.e., the growth rate of fluctuation amplitude decreases. This effect is the result of adsorption interaction at the interface retarding the diffusion processes and relaxation in the border layer. Figure 7.10 represents the dependence of 2R(β) on the filler content for various temperatures of phase separation. As expected, the value 2R(β) increases with temperature. This fact indicates the acceleration of the concentration fluctuation growth with temperature, which proceeds by spinodal mechanism. Introducing filler results in decreasing amplification factor 2R(β). Increasing filler concentration leads to the growth of the fraction of the interphase in the system. Due to restrictions of molecular mobility of polymer chains near the interface, a moderation of diffusion takes place, leading to the growth

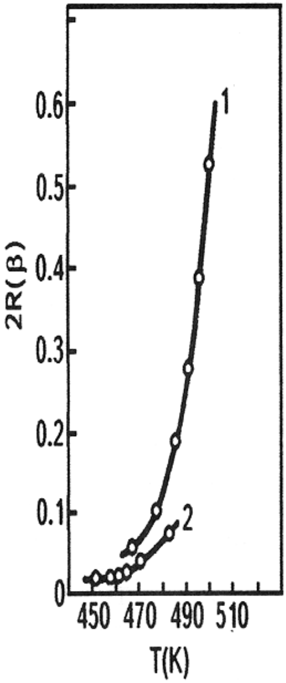

Figure 7.9. Amplification factor 2R(β) as a function of temperature for the mixture PVA-PMMA (0.6:0.4) without filler (1) and with 10% of fumed silica (2). [Adapted by permission from A. E. Nesterov, Y. S. Lipatov, V. V. Gorichko, and O. T. Gritsenko, *Polymer*, **33**, 619 (1992)]

of concentration fluctuations by phase separation. The greater is the fraction of the interphase, the lower should be the rate of the phase separation, and as a consequence, parameter 2R(β) diminishes with increasing filler amount.

The same picture is observed for the dependence of 2R(β) on the film thickness.[2] As can be seen from Figure 7.11, the value 2R(β) drops sharply when the film thickness decreases below 10-12 μm.

Some data on the surface-directed spinodal decomposition have been given,[38] for the phase separation of the mixtures of poly (ethylene propylene) with its predeuterated analog, which were spun cast from toluene on silicon wafers. It was found that the composition waves of the bulk mixture coarsen more rapidly with time as compared with the mixture at the surface (film thickness 9,000 Å). Authors have concluded that the preferential attraction of the surface for one of the components can lead to spinodal decomposition waves with a preferred wave vector normal to the surface. The composition of the mixture is enriched with the preferred component at the surface. Although, as it was noted, it is unclear how far these coherent waves extend into the bulk before they break up into an isotropic structure. The range of these waves is certainly large enough that they will affect many surface and near-surface properties.

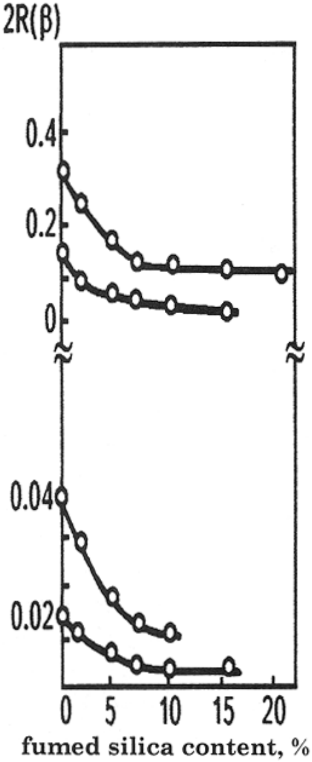

Figure 7.10. Dependence of 2R (β) on filler content for PVA-PMMA mixture (0.5:0.5) at 460 (1), 467 (2), 482(3) and 500 K (4).

We can conclude that in the retardation of the phase separation, two cases may be considered. If the interactions of both polymers with the surface are symmetric, the phase separation in the interphase is much slower, compared to bulk. Some heterogeneity of the structure should arise as a result of non-simultaneous phase separation in the system. If the interactions are asymmetric and preferential adsorption takes place, the phase separation is initiated by the filler surface, but the formation of that phase, which is in contact with the surface, is retarded. All these circumstances lead to formation of many non-equilibrium states in filled polymer alloys which influence their structural heterogeneity and mechanical properties.

7.2.4 ON EQUILIBRIUM AND NON-EQUILIBRIUM COMPATIBILIZATION OF POLYMER ALLOYS

The data presented in preceding paragraphs allow some conclusions to be drawn regarding the filler effect on the compatibility of two polymers. We can substantiate two different principal ways of polymer alloys compatibilization using particulate fillers.[39]

The first way may be called equilibrium compatibilization. Its essence consists of equilibrium increase of thermodynamic stability of a binary system, which is the result of symmetric pair interactions of each component with the filler surface. When the energy of polymer-filler pair interactions is approximately the same, near the interface, the interphase layers are formed with different properties but with the same composition as in the initial blend. This means the lack of essential selectivity of adsorption of one of the components. Simultaneously, due to conformational changes, the thermodynamic stability in the interphase increases. Depending on the surface nature and interaction energy, the effects under consideration may be manifested in various ways. It is known that, for ternary polymer systems, the increase in asymmetry of pair interactions decreases thermodynamic stability.[40-42] However, even if there is some asymmetry or selectivity of adsorption, the increase in thermody-

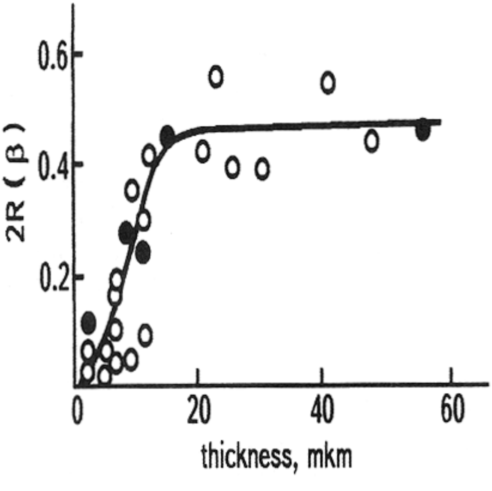

Figure 7.11. Amplification factor 2R(β) as a function of the film thickness for 0.7:0.3 PVA/PMBA alloy on non-silanized (○) and silanized (●) glass at 482K. [Adapted by permission from A. E. Nesterov, V. V. Gorichko, and Y. S. Lipatov, *Makromol. Chem. Rapid Commun.*, **12**, 571 (1991)]

namic stability may be reached, due to preferential adsorption of high molecular mass fractions from the bulk at the interface and due to enrichment of the bulk with low molecular fractions, which leads to better miscibility in accordance with general thermodynamic principles.

This effects depend on the alloy composition, choice of components, and their ratio. By an appropriate choice of components and knowing the polymer-solid interaction parameter, χ_S, the pairs may be selected for which introduction of particulate fillers will lead to increased compatibilization. There exists some analogy with improvement of miscibility of two polymers by introducing a third polymer miscible with each of the polymer components of the blend.[43-46] We should like to note that for miscible polymer pairs the filler decreases the compatibility. This effect is probably a result of interaction asymmetry.

The second method of compatibilization is not connected with a true increase in the miscibility of components and manifests itself in the case of strong interactions of each component with the surface, independent of the interaction symmetry. In this case, the phase separation,which should proceed through the change of temperature conditions in the course of alloy production, is hindered, due to pure kinetic reasons, resulting from a sharp decrease in molecular mobility of adsorbed macromolecules of both polymers. In this case, the polymer alloy, in the non-equilibrium state, preserved the structure corresponding to one closer to equilibrium. Such a system will have a high kinetic stability. For real systems, both suggested mechanisms of compatibilization are supposed to take place simultaneously.

Using the proposed approach, the compatibilization of immiscible mixture of polyamide-6 and polypropylene was realized by introducing glass beads covered with a coupling agent into the mixture.[47] The agent was chosen in such a way that it has functional groups compatible with one of the components. The compatibilizing effect was proved by the data on viscoelasticity and DSC measurement. It is interesting that introduction into the composition of the same coupling agent, not bound chemically with glass surface, has no compatibilizing effect.

7.3 MODEL REPRESENTATION OF A FILLED POLYMER ALLOY

The discussion presented above allows one to formulate a model representation of the structure of the border layer of polymer alloys near the interface and of the filled polymer alloy. We accept that the border layer consists simultaneously of both polymers, each interacting with the solid independently.[47] In the binary mixture near the interface, as in the matrix bulk, there exists an interphase region between the two immiscible polymers (Figure 7.12). The interaction between components in this interphase region is characterized by the parameter χ_{AB}, which serves as a measure of miscibility. The experimental data allows one to conclude that the conditions for various chain interactions are not the same as in the matrix bulk. As a result, the experimental values of χ_{AB} for the interphase and the matrix are different. Thus, we can distinguish two types of interphases in filled polymer alloys: the surface layer of both components, which is analogous to the surface layer in one-component filled polymers, and the interphase zone between two components in this layer (it should be remembered that such a zone exists in binary polymer alloys - see Chapter 6). The conformational changes in the surface layers lead to the changing conditions of interaction between macromolecules of both types, compared with the bulk. All this results in the change of thermodynamic interaction parameters in filled alloys which are dependent on the volume fraction of the surface layer and its composition. Surface segregation depends both on χ_{AS}, χ_{BS}, and χ_{AB}. The lack of miscibility enhances surface segregation.

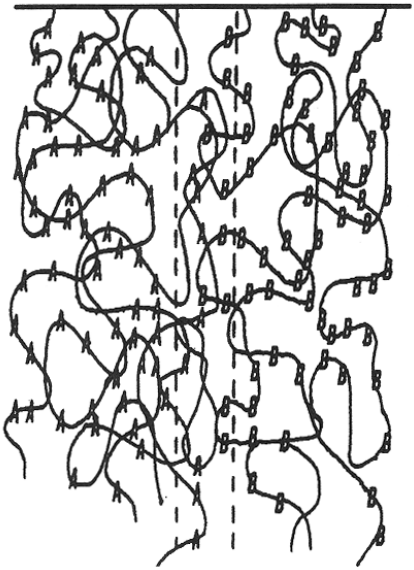

Figure 7.12. Scheme of the structure of the boundary region of two-component immiscible polymer alloy near the filler surface. [Adapted by permission from Y. S. Lipatov in **Controlled Interphases in Composite Materials**, Ed. Ishida, *Elsevier*, Amsterdam, 1990, p. 594]

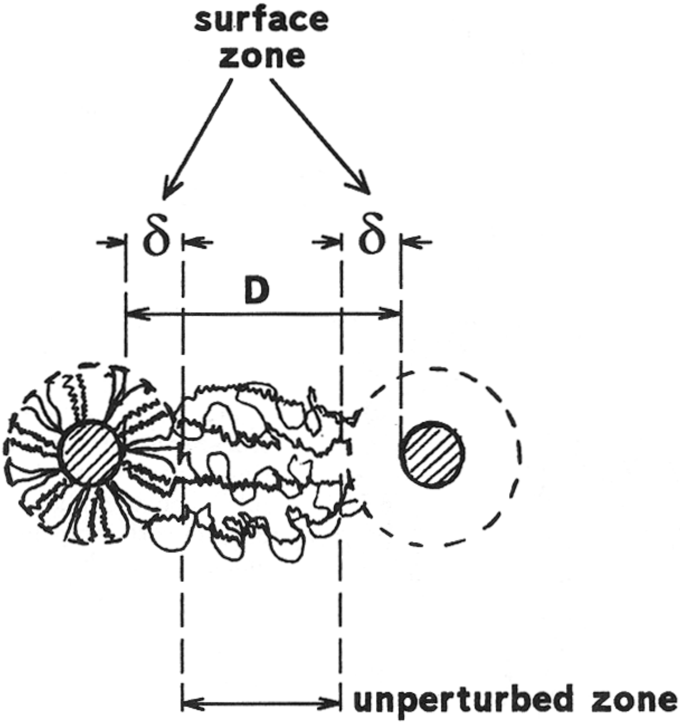

Figure 7.13. The scheme of two-component filled polymer alloy.

Now, we can apply the model of a filled polymer presented in Figure 3.1 to describe filled polymer alloy. As distinct from the model of filled polymer, the surface layers in polymer alloy differ in the ratio of alloy components, due to the selective interaction with the surface. However, all the factors determining properties of the surface layers in filled polymers are operative. Namely, the molecular conformations in the surface layer, packing densities, molecular mobility, etc., are different from the bulk. The simplified model of filled polymer alloy is presented in Figure 7.13. In this model, the layer of thickness has a composition that differs from that in the bulk. For such a model, various possible composition profiles may be constructed, because we do not yet know the distribution function of components in the surface layer.

Let $(\phi_A)_{av}$ to be the volume fraction of component A in the unfilled alloy, and $\phi_A(z)$ its fraction at the distance z from the wall. Three hypothetical profiles may be considered:[48]

- A two-layer profile (Figure 7.14a) for which:

  $\phi_A(z) > (\phi_A)_{av}$ if $z \le \delta$ and $\phi_A(z) = (\phi_A)_{bulk} < (\phi_A)_{av}$ if $z > \delta$

  It is important to note that in this and following possible profiles, there is no place for the alloy with initial value of ϕ_A because of a selective interaction and redistribution of components between the surface layer and the bulk. The higher the filler concentration, the lower the deviation of $(\phi_A)_{bulk}$ than $(\phi_A)_{av}$.
  At high filler concentration, where all the molecules are under an effect of the surface, the distinction between two regions erodes and $\phi(z) = (\phi_A)_{av}$.
  In such a way, the compositional non-uniformity of filled alloys depends on the filler amount.

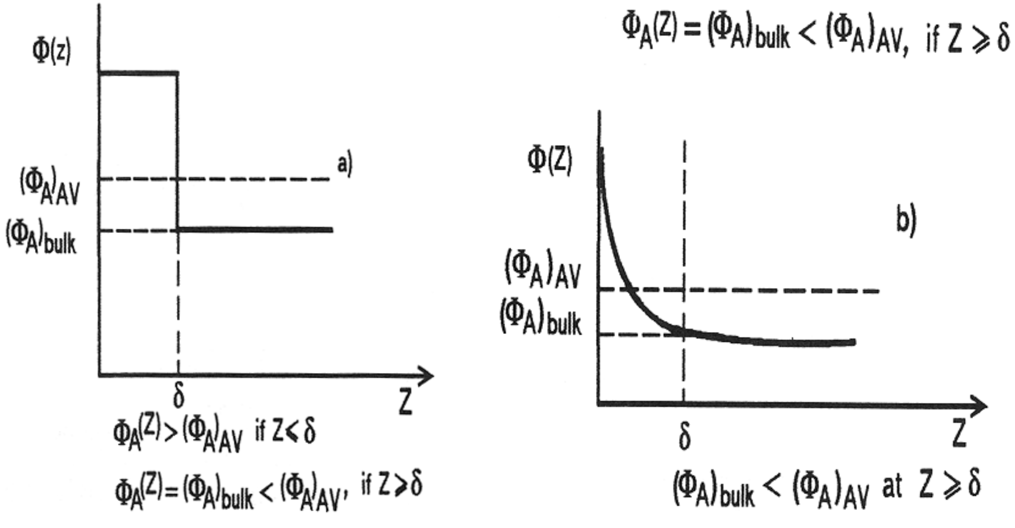

Figure 7.14. Possible concentration profiles of filled polymer alloy (continued on the next page).

- Exponential profile (Figure 7.14b). $\phi(z)$ decreases exponentially up to $(\phi_A)_{bulk}$. Here we have $(\phi_A) < (\phi_A)_{av}$ at $z > \delta$.
- Enrichment-depletion profile. There is a depletion zone at $\delta_1 < z < \delta$. For this case, $(\phi_A) > (\phi_A)_{bulk}$ at $z > \delta_1$ and $\phi_A < (\phi_A)_{bulk}$ at $\delta_1 < z < \delta$.

The position of the line $(\phi_A)_{av}$ remains indefinite. This situation corresponds to the case of enrichment of the surface layer in one component. The nearest layer is impoverished in this component. This profile may also be the result of spinodal decomposition.

In the same way, we can construct the profile of free energy of mixing as a function of composition or distance z. As a rule, which follows from the shape of the phase diagrams, the miscibility of two polymers is always higher at small fractions of one of the components.

We would like to emphasize that different conformations of chains in the surface zone, as compared with the bulk, seem to play an essential role in these processes (the experimental evidence was presented earlier).[49]

It is worth noting that all the processes of surface segregation may proceed only in a melt state of the system where the molecular mobility of the polymer chain is sufficiently high. This statement is valid both for blends of linear polymers and IPNs. However, in IPNs, surface segregation proceeds from the very beginning in an initially one-phase system, whereas in polymer blends, conditions are determined by the type of critical solution temperature. Because majority of linear blends have LCST, the surface segregation in such a system in melt should proceed from the two-phase state.

Surface segregation enhances phase separation in the system. Enrichment and depletion of the surface layer in alloy components should be considered as phase separation in microvolumes near the interface.

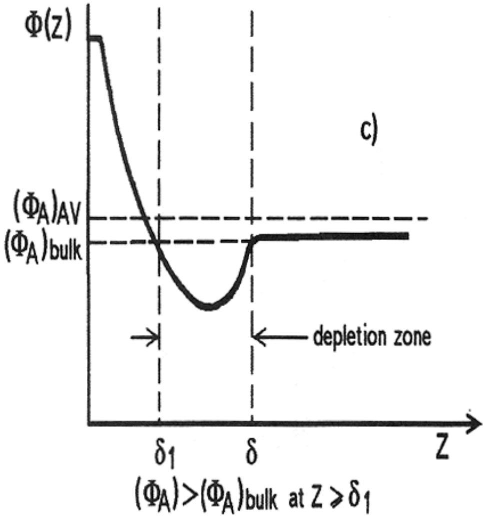

Figure 7.14. continuation

The effects of surface segregation take place only for systems with asymmetric interaction with the solid surface ($\chi_{AS} \neq \chi_{BS}$). During the course of alloy formation, in the presence of a solid, two processes proceed simultaneously: surface segregation and phase separation.

Binary filled (reinforced) polymer alloy should be considered as conventionally consisting of four phases: two separated phases near the interface and two phases in the bulk. Their compositions differ from the average composition of an alloy. It is pertinent that these are not the equilibrium states, and the phase structure may be considered as a result of forced compatibility.

The equilibrium process of the surface segregation is possible only at the constant temperature of the melt. At conditions of the formation of filled alloys by transition from liquid to solid states, the segregation proceeds until the necessary molecular mobility is preserved in the system, i.e., up to crystallization or vitrification temperature of one of the melt components. It means that surface segregation proceeds in non-equilibrium conditions in the definite temperature interval. If the phase separation temperature is above glass transition or crystallization temperature, the surface segregation may proceed from each evolved phase separately.

7.4 SOME PROPERTIES OF FILLED POLYMER ALLOYS

Some data, regarding mechanical and other properties of filled polymer alloys, are available from which changes in the thermodynamic state, resulting from the incorporation of fillers, can be estimated. It was established[50-52] that there is an interrelation between viscoelastic properties of polymer alloys and their thermodynamic state. This interrelation manifests itself in a positive or zero deviation of the viscosity-composition relationship from the logarithmic additivity rule - typical for a thermodynamically stable region of composition (a negative deviation corresponds to the region of instability). The rheological and mechanical properties of the alloys both in melts and in a solid state depend on their thermodynamic stability. As a rule, the minimum in the melt viscosity of alloy corresponds to the maximum of ultimate properties.[53]

7.4.1 MECHANICAL PROPERTIES

A specific type of the mechanical behavior of polymer alloys is determined from their structural heterogeneity. The existence of two separated phases of varying composition yields an appearance of two relaxation maxima, corresponding to these phases (see Figure 6.5). The position of these maxima depends not only on the phase composition but on the filler influence on molecular mobility in a given phase when filler is present. These effects have been discussed in detail in Chapter 5. Let us consider some experimental data for filled alloys.

Figure 7.15 shows the influence of a filler on the position of maxima in the system polyvinylchloride-copolymer styrene-methylmethacrylate-acrylonitrile.[54] These two polymers differ in chain flexibility and polarity. It is seen that because of the mutual influence of components on their molecular mobility, the latter is restricted for both polymers, which is typical for the data for other binary mixtures. In the presence of a filler, the change in molecular mobility corresponds to the selective interaction of one component (polyvinylchloride) with the surface. It may be supposed that preferential interaction of one component with the surface severely restricts its mobility, whereas the second component, being displaced from the surface, acquires a higher molecular mobility as compared with unfilled mixture. In the filler presence there is observed a marked decrease of the temperature of maximum tanδ for copolymer and an increase for polyvinylchloride.

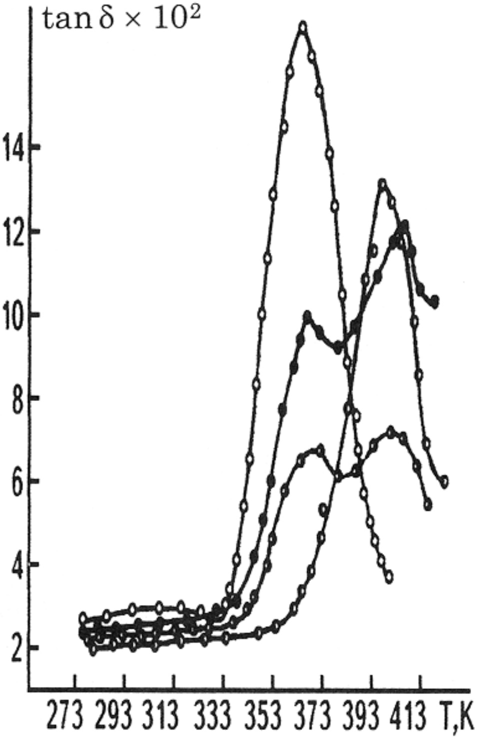

Figure 7.15. Temperature dependence of the dielectric loss tangent for PVC (1), copolymer (2), mixture of both polymers (3), and the same mixture with 20% of fumed silica (4).

Analogous results have been obtained for other filled alloys.[55] Figure 7.16 shows the temperature dependence of tanδ for polyvinylacetate (PVA) and ethylene-vinyl acetate copolymer (EVC), their alloy (1:1) and filled alloy.

The alloys are characterized by two maxima of mechanical losses, close to the glass transition temperatures of components. Two maxima of tanδ are close each to other, and the glassy region is extended, compared with pure components. Simultaneous extension of the glass temperature range (increase of the lower T_g and decrease of the higher T_g) indicates that the system is in a state close to the compatibility of components and may be described as partially compatible. The latter is also substantiated by the glass temperature dependence on the mixture composition. The presence of particulate filler in alloy in an amount sufficient for the formation of its structural network (≈ 5%) shifts the region of the main relaxation transition of the PVA-component towards lower temperatures, the shift, as compared with an individual component, amounting to 20°C (Figure 7.16). This correlates well with the variations of the parameter χ_{AB} for filled compositions found in this paper; i.e., under such conditions the interaction parameter shifts towards miscibility of PVA and EVC.

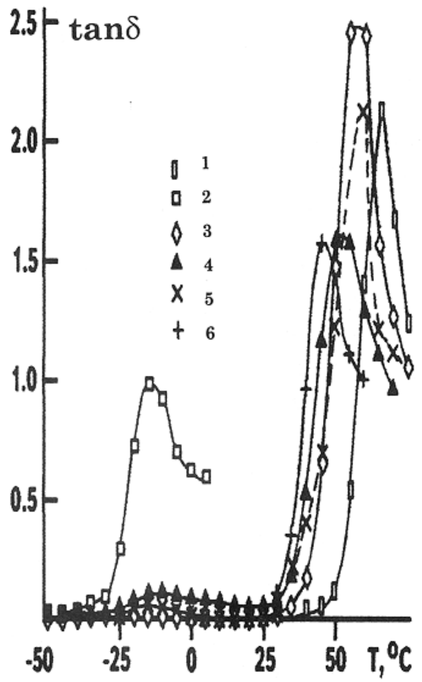

Figure 7.16. Temperature dependence of tanδ for PVA-EVC and PVA-EVC alloys of various compositions as well as for PVA/EVC=1:1 alloy at various fumed silica mass fractions 1-PVA, 2-EVC, 3-PVA/EVC=9:1, 4-PVA/EVC=5:5, 5-PVA-EVC=5:5+1% fumed silica, 6-PVA/EVC=5:5+5% fumed silica. [Adapted by permission from Y. S. Lipatov, V. F. Shumsky, V. F. Rosovitsky, I. P. Getmanchuk, and N. A. Kvitka, *J. Appl. Polym. Sci.,* **47**, 841 (1993)]

Similar results were obtained[56] for mixtures of polyurethane and PVC and poly(ε-caprolactone) with styrene-acrylonitrile copolymer. It was found that fillers (silica, carbon black, and talc) broaden the rubbery PU transition, shifting it to higher temperatures. This effect was found to be less pronounced for the high temperature PVC relaxation. The positions of the relaxation maxima are shifted

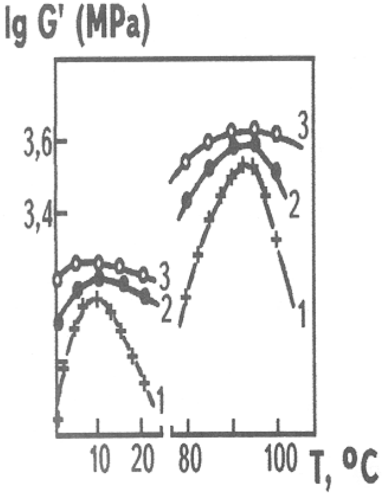

Figure 7.17. Concentration dependence of the real part of complex shear modulus logG' for PE-POM alloy: 1-pure alloy, 2-with 15% chalk, 3-with 15% kaolin.

under the influence of a filler. Both damping and loss moduli spectra indicate that, at similar loading, increasing the filler specific area affects the viscoelastic region associated with physical entanglements. Apparent activation energies at 10% filler were also determined for both main relaxation. The results indicated that silica filler interferes with the low temperature relaxation to a greater extent than the coarser talc filler. This was explained by a more effective filler-matrix interaction of the fine filler particles. However, examination of the loss moduli spectra indicated that mixtures under investigation remained incompatible.

In the same work,[56] it was shown that the mechanical properties of filled polymer mixtures may be described by various equations connecting the moduli with the filler amount (see Chapter 5). It is of interest also to attempt calculation of a thickness of the boundary layer, using data on heat capacities (see Chapter 3). It was established that the boundary layer associated with PVC component has a smaller thickness. Since most of the matrix consisted of PVC, it was suggested that silica, because of its acid character, immobilizes to a greater extent the proton-accepting PU component; hence, the thickness of the boundary layer for PU is higher.

This author investigated the binary system in compositions near their miscibility, and in this region, no compatibilizing effect of the filler was found.

The correlation between the thermodynamic state of the filled alloy melt and mechanical properties in a solid state was detected.[57] In the region of the alloy composition and filler concentrations,where the thermodynamic stability of the melt increases, increase in the thermodynamic stability leads to growth of the modulus, together with broadening of its maximum (Figure 7.17). The inter-

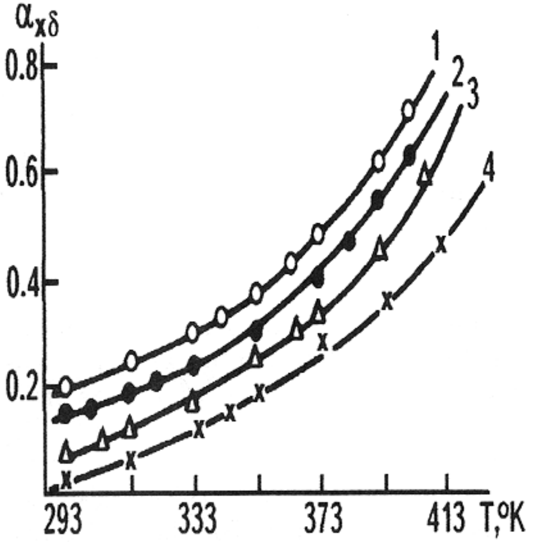

Figure 7.18. Temperature dependence of the parameter of the relaxation time distribution for pure PVC-copolymer mixture, (1) and with 3 (2), 24 (3) and 48% (4) fumed silica.

relation between the thermodynamic stability of polymer mixtures and their rheological and mechanical properties have been discussed in detail.[53]

The relaxation behavior of the PVC-copolymer (styrene-methylmethacrylate-acrylonitryle) was studied by the dielectric method.[58] The Cole-Cole parameters, characterizing the distribution of relaxation time (relaxation spectra) and its temperature dependence have been calculated (Figure 7.18). It is seen that with an increase of filler amount, the parameter of relaxation time distribution decreases, i.e., the broadening of the spectra occurs. These effects, similar to analogous effects described in Chapter 5 for filled polymers, are explained by the restriction of molecular mobility of alloy components in the surface layers and by their contribution to the total relaxation spectrum.

Chemical modification of the filler surface (transition from pure fumed silica to modified with dimethyl dichlorosilane) gives the same picture of the broadening of the relaxation spectra.[59] These data allow for the conclusion that the conformational restrictions imposed by the solid surface, not the energetic interaction between alloy components and solid, play a major role in the change of relaxation spectra.

However, in order to postulate a compatibilizing action, one must observe a remarkable broadening of the maxima of relaxation or two relaxation maxima eroding into one maximum. Such effects are much more pronounced for filled interpenetrating polymer networks (see 7.5).

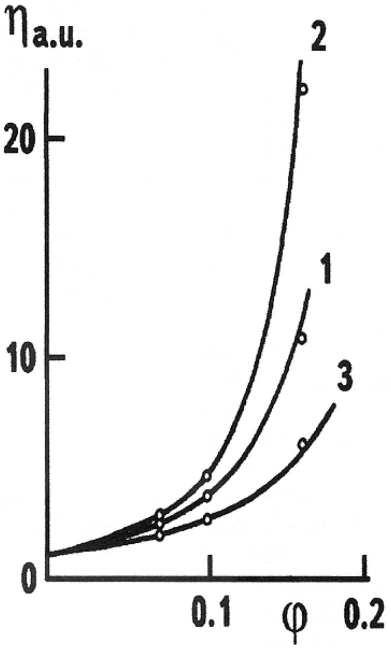

Figure 7.19. Dependence of relative viscosity on the volume fraction of carbon black for PE at 453 (1) and PE-POM alloy (5% POM) at 413 (2) and 453 K (3).

7.4.2 RHEOLOGICAL PROPERTIES

There are few data on rheological properties of melts of filled alloys. It was shown[55] that the main features of the rheological behavior of filled alloy PVA-EVC can be related to the formation of the structural network formed by filler particles. For the production of filled polymer alloy, it is important to use the effect of substantial decrease of melt viscosity by addition of a small amount of one component to another.[53] Due to a sharp decrease of viscosity in a definite concentration region, it becomes possible to introduce larger amounts of filler, compared with pure components.

It was shown[60] that introduction of carbon black into a melt of polyethylene-polyoxymethylene alloy leads to viscosity increase (as should be expected). However, addition of polyoxymethylene to filled polyethylene melt decreases the viscosity. Figure 7.19 shows the dependence of the relative viscosity $\eta_{rel} = \eta/\eta_0$ (η is the viscosity of filled polyethylene, and η_0 is its initial viscosity) of alloy melt on the filler amount. The results are described by the equation:

$$\eta_{rel} = \left(1 + \frac{1.25\varphi}{\varphi_{max} - \varphi}\right) \qquad [7.14]$$

where φ is the filler volume fraction and φ_{max} is maximum fraction at which the most dense packing of particles occurs. Experimental points fit this equation with the value of φ_{max} =0.24. Introduction of polyoxymethylene into the filled melt of polyethylene leads to diminishing φ_{max} at temperatures below the polyoxymethylene melting point, and to its increase above this temperature.

Therefore, in filled alloys the viscosity is lower, compared with filled pure component, and filler particle packing becomes more dense. This effect is important for production of filled alloys, which allows one to introduce a greater amount of the filler at the same viscosity of melt or to improve its distribution in the melt.

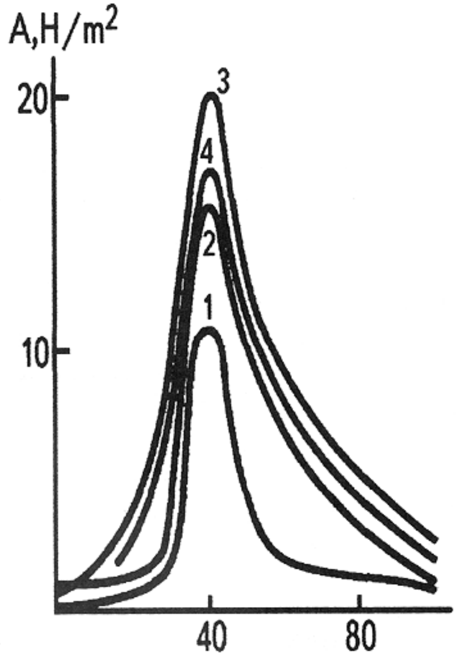

Figure 7.20. Concentration dependence of the adhesion joint strength (PU:PE): steel (1) and the same with 10(2), 20 (3), and 40% (4) of filler.

7.4.3 ADHESION

The properties of composite materials, based on filled polymer alloys, should depend on the adhesion at the interface polymer alloy-solid and on the formation of weak boundary layers. Unfortunately, there are no available data dedicated to this problem. Only a general description may be given, in the following form. From the analysis given in paragraph 7.1, it follows that adhesion should be promoted when components are not miscible. Using simple thermodynamic relations discussed in Chapter 2, and according to the model of filled polymer alloy, we should have the following expression for the thermodynamic work of adhesion for a symmetric case:[2]

$$W_A = \varphi_A W_{CA} + \varphi_B W_{CB} \qquad [7.15]$$

where W_{CA} and W_{CB} are the cohesion energies of two phases, and φ_A and φ_B are their volume fractions in the interphase. The ratio of separated phases in the interphase may not coincide with that for the bulk, due to the surface influence on the phase separation. Thus, thermodynamic work of adhesion of polymer alloys depends not only on the ratio of components in the system, but on the composition and ratio of two phases evolved near the interface. Thus, we can conclude that adhesion strength may be changed, depending on the conditions of the adhesion joint formation.

The interrelation between the thermodynamic stability of filled polymer alloy in the melt and thermodynamic work of adhesion and adhesion joint strength was proven[34] in polymer mixture of polyethylene and polyurethane filled with kaolin (Figure 7.20). The influence of component miscibility on the critical surface tension, γ_c, and the adhesive properties was studied.[61]

In considering adhesion of polymer blends to solid, the wetting of the surface is of importance. No data are available. However, the strong interplay between phase separation in polymer mixtures and wetting was discovered.[62] It was found that the wetting plays a drastic role when the minority phase is more wettable to the glass surface.

7.5 FILLED INTERPENETRATING POLYMER NETWORKS

The first work dedicated to filled interpenetrating polymer networks was published in 1974.[63] The possibility to change many physical and mechanical properties by introducing filler initiated the development of studying such systems as a potential hybrid binders for polymer composites.

7.5.1 THERMODYNAMIC STATE OF FILLED IPNs

Earlier (Section 6.5.2), the equilibrium and non-equilibrium states of IPNs were considered. To understand the properties of filled IPNs, it is necessary to known their thermodynamic state in the presence of fillers. For IPNs based on cross-linked polyurethanes (PU) and polyesteracrylates (PEA) filled with fillers of various chemical nature, the thermodynamic affinity of fillers to IPNs have been estimated from the experimental data on the isotherms of sorption of vapors.[64] From these data, the free energy of mixing IPNs with filler was calculated. The fundamental thermodynamic approach was used, based on the independence of change in thermodynamic functions on the processing regime. The values characterizing the interaction between the polymer and fillers were found from the data on sorption of the low molecular weight liquid for each component separately and for IPN. From the isotherms of sorption, the changes in the chemical potential of the solvent were calculated according to the equation:

$$\Delta\mu_1 = (RT/M)\ln(P/P_o) \qquad [7.16]$$

where M is the molecular mass of the solvent and P/P_0 is the relative vapor pressure of the solvent in the polymer-solvent or filler-solvent system.

To estimate the change in the partial free energy of individual networks or IPNs, $\Delta\mu_2$, the equation of Gibbs-Duhem was used:

$$w_1 \frac{\partial \Delta\mu_1}{\partial w_1} + w_2 \frac{\partial \Delta\mu_2}{\partial w_2} = 0 \qquad [7.17]$$

where w_1 and w_2 are the mass fractions of the solvent and polymer in a swollen system. Value $\Delta\mu_2$ was calculated as described elsewhere.[65]

The change in the free energy of mixing of two networks with the solvent is described as

$$\Delta G_m = w_1 \Delta\mu_1 + w_2 \Delta\mu_2 \qquad [7.18]$$

From the concentration dependence of free energy of mixing of the solvent with pure and filled networks, the values ΔG_I and ΔG_{III} - the free energies of interaction between the unfilled and filled polymer and a large amount of the solvent, were found. Free energy of interaction between the polymer and filler may be calculated as follows:[66]

$$\Delta G_{\text{polymer-filler}} = n\Delta G_I + m\Delta G_{II} + \Delta G_{III} \qquad [7.19]$$

where ΔG_{II} is the change in free energy of mixing filler and solvent, n is the mass fraction of a polymer, and m is a mass fraction of filler in filled specimen.

Values ΔG_{II} were calculated from the isotherms of sorption of vapors by filler. It was found[67] that on adsorption of vapors, the filler transits to the perturbed state which allows one to calculate the change in the chemical potential, $\Delta\mu_{2f}$, for filler. Using equation

$$\Delta G_m = w_1 \Delta\mu_1 + w_2 \Delta\mu_{2f} \qquad [7.20]$$

the free energy of mixing the filler with solvent was found, ΔG_{II}. (The application of thermodynamic cycles in this case does not take into account that in the sys-

Table 7.3: Free energy of interaction with fillers

Polymer	Free energy, ΔG (polymer-filler), J g^{-1} of polymer		
	Fumed silica	Al_2O_3	Polyesteracrylate
Polyurethane	-2.23	-1.17	+1.42
Polyesteracrylate	-0.38	+0.96	+0.31
IPN (PU/PEA=9:1)	-0.92	-4.73	+6.35

tem under consideration, there is mixing of filler neither with polymer nor solvent. Indeed, only the interaction proceeds with the filler surface. Therefore, it would be correct to introduce into the theoretical equations, rather than the amount of filler, expressed in moles or grams, the number of moles of active centers on the surface. This value depends on the dispersity degree of a filler but, unfortunately, it cannot be estimated. This shortcoming of the theory should be borne in mind when discussing results of calculation with application of thermodynamic cycles to filled systems. Such results can only be considered as qualitative.)

The measurements of the free energy of mixing of two networks in IPN have shown that the value is positive in the whole range of composition, i.e., components are not miscible. Maximum of the free energy of mixing is shifted to the region with higher amount of PEA. The results of calculations for the IPN containing 10% of PEA are given in Table 7.3. It is seen that fumed silica has the greatest thermodynamic affinity to PU. No affinity was found when polymeric filler (fine-dispersed, cured PEA) was used.

Data in Table 7.3 show that fumed silica also has affinity to the second component - crosslinked PEA. Free energies of mixing of PEA with Al_2O_3 and dispersed PEA are positive. Thus, the calculations have shown that only one filler has thermodynamic affinity to both network polymers (fumed silica), whereas Al_2O_3 only has affinity to PU, and PEA has no affinity to both networks. It was shown[66] that the change in the thermodynamic functions by reinforcement depends on the filler amounts (possibly due to the already-mentioned factor relative to surface available for interaction.)

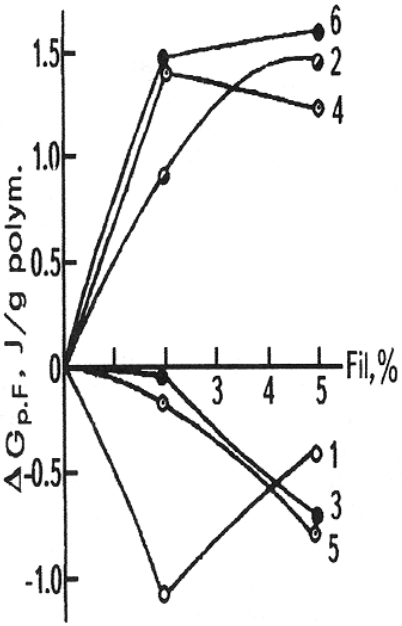

Figure 7.21. Free energy of interaction of polymers with fillers in semi-IPNs (PU-ionomeric PU) with 4 (1,3,5) and 30% ionomer (2,4,6), containing carbon fiber (1,2), glass fiber (3,4) and synthetic high modulus fiber (5,6). [Adapted by permission from Y. S. Lipatov, L. V. Karabanova, and L. M. Sergeeva, *Polym. Intl.*, **34**, 7 (1994)]

Eq 7.20 also was used to calculate the free energy of mixing of fillers with IPN. In this case, ΔG_I and ΔG_{II} are the free energies of interaction of unfilled (ΔG_I) and filled (ΔG_{III}) IPNs with a large amount of solvent. It was found that the free energy of interaction of IPN with fumed silica is negative, and this system is thermodynamically stable. Simultaneously, IPNs filled with polymeric filler are not stable.

The experimental results allow for the conclusion that introducing fillers into an immiscible system may lead to the formation of a thermodynamically stable system only if the filler has affinity either to one or both components of IPN. In this case, we are dealing with the phenomenon of equilibrium compatibilization, i.e., thermodynamic stability increases because of thermodynamic factors. If the filler has no affinity to the IPNs components, only non-equilibrium compatibilization may be observed. This conclusion also follows from the data on IPNs filled with fibrous fillers[64] (Figure 7.21). The results are in agreement with the data on the viscoelastic properties of the same systems. Calculated segregation degree in filled IPNs is much lower for unfilled IPNs. The nature of fillers affects the segregation degree. The lower degree of segregation was observed for Al_2O_3 and the higher for polymeric filler.[68]

The comparison of the data on the segregation degree and on free energy of polymer-filler interaction shows that segregation diminishes both in the presence of fillers having thermodynamic affinity to polymers and for fillers having no affinity. Two mechanisms of compatibilization are supposed to operate here:

an equilibrium mechanism, i.e., increase in the thermodynamic stability of the system, and a non-equilibrium mechanism that is determined by the slowing phase separation due to kinetic reasons. For polymeric filler, only non-equilibrium compatibilization proceeds, and as a result, the segregation degree is higher, compared with other fillers.

From what was said above, it follows that the IPN components have various affinity to solid surfaces, and, therefore, in the course of their synthesis, the processes of selective adsorption at the interface must be observed. In reality, for various IPNs (polyurethane-polyesteracrylate, polyurethane-polybutyl methacrylate), it was found that near the interface, the composition of the surface layer differs from the composition in the bulk. IR-ATIR method was used.[69-71] Supports were glass and poly(ethylene terephthalate). It was discovered that at the interfaces IPN-solid and IPN-air, the surface layers had very different compositions. For PU-PEA IPN, the layer formed at the interface with glass is enriched with PEA, whereas at the interface with air, excess concentration of PU was found. This effect of surface segregation is increasingly more pronounced with diminishing distance from the interface. For the interface with poly(ethylene terephthalate) in IPN based on PU and PBMA, the surface layer is enriched in PBMA. The effects depend on the IPN composition. It was established that the composition of the layers strongly depends on the kinetic conditions of curing.[69]

The changing composition of the surface layers of IPNs, at the interface with a solid, may be explained by the selective adsorption of one component before the gel-point. The selective adsorption initiates phase separation in the system. Depending on the kinetic conditions, the degree of the separation changes, as does the thickness at which the compositional changes are observed. The rate of the microphase separation depends on the component ratio (Chapter 6). Superposition of the chemical processes, selective adsorption, and microphase separation are the main factors determining the properties of the surface layers of IPNs at the interface with a solid. The enrichment of the surface layer in one component (surface segregation) depends also on the free energy of mixing of two networks and on the surface energy of filler. The maximum changes in the composition of the surface layers were observed in such a composition range where the free energy of mixing of two networks had the greatest positive values. It was also established[70] that the difference in the composition of the surface layers depends on the sequence of the component curing, because the conditions for adsorption depend not only on the surface affinity but also on the viscosity of the reaction medium. For simultaneous IPNs, the effect is determined by the correlation between the reaction rates of curing of each network.

For IPN, the surface segregation proceeds in the time interval between the onset of curing and gel point. However, because the phase separation begins very early, the surface segregation occurs simultaneously from two evolved phases before the gel is formed. It was established that for semi- and full IPNs near the interface with a solid of high surface energy, the layers are formed with an excess of the component having a higher cure rate. At the comparable reaction rates of polymerization and polyaddition, the composition of the surface layers does not differ from that in the bulk.

The content of components in the interphase depends on the ratio of networks, ratio of reaction rates of curing of both networks (these rates are interdependent). The effects of surface segregation are also connected with the onset of phase separation, depending on the reaction rates and component ratio.

The composition and structure of the surface layers formed in full IPNs at the interface with a solid also depend on the free surface of solid and initial composition of IPN.

The reasons which lead to the effect of the reaction kinetics on the surface segregation are the following:

- When a composition comes into contact with the surface near the interface between solid and polymer mixture, excess interfacial energy arises, due to the difference in the surface tension of the substrate and the composition. As a result, these components are segregated at the interface, which compensates this difference.
- In the course of curing, the surface layer is enriched with a component whose surface tension more rapidly reaches its limiting value, i.e., has a higher reaction rate.
- The composition of the surface layers depends on kinetic factors. The main role belongs to the sequence of components curing.

We can conclude that the surface segregation in reacting systems such as IPNs depends on:

- reaction kinetics
- phase separation
- sequence of curing of constituent networks.

Surface layers are formed under non-equilibrium conditions, simultaneously with phase separation. Surface segregation is realized on a scale of two microphases enriched with one component of a system with both phases having different compositions.

7.5.2 VISCOELASTIC PROPERTIES OF FILLED IPNs

Viscoelastic properties of filled IPNs have been studied,[72-74] using various fillers (fumed silica, aluminum oxide, dispersed cured poly(ester acrylate) in the

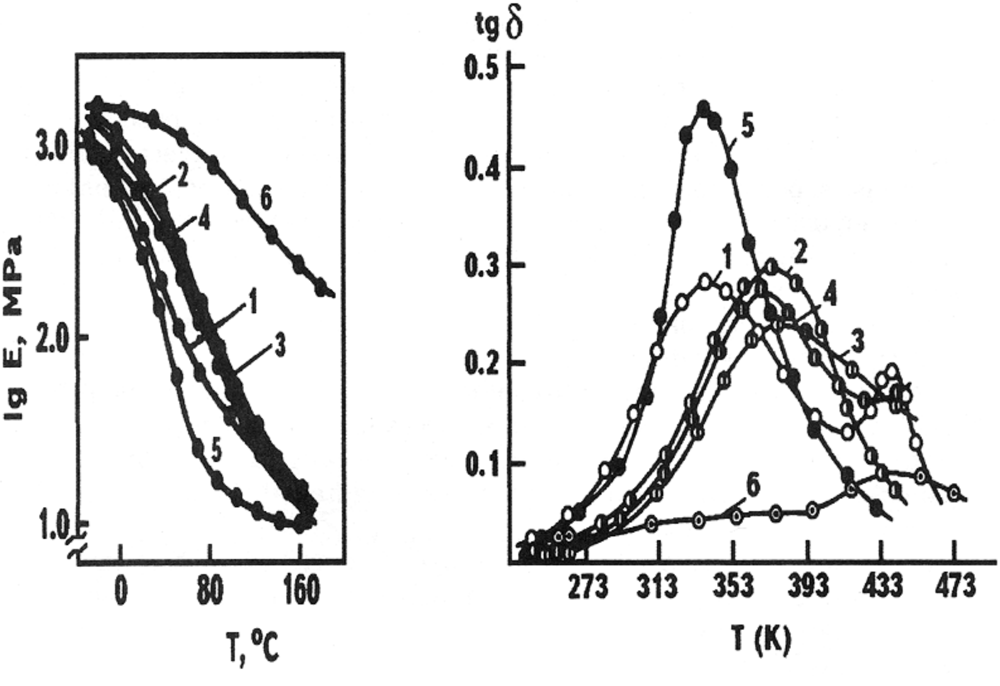

Figure 7.22. Temperature dependence of the elasticity modulus (a) and mechanical loss, tanδ (b) for IPN without filler (1) and with 3% (by volume) of aluminum oxide (2), fumed silica (3), poly(ester acrylate) (4) and for IPN components: PU (5) and PEA (6).

amount of 3%). IPNs based on cross-linked polyurethanes and poly(ester acrylate) have been used. Determination of the free energy of mixing of networks has shown they are not miscible. Figure 7.22 shows the temperature dependence of viscoelastic functions E′ (a) and tanδ (b) for unfilled (curve 1) and filled (curve 2) IPNs. It is seen that the initial system is characterized by the two relaxation maxima of tanδ at 66 and 175°C. Such behavior may be the evidence of the interconnectivity of two networks. The interaction at the phase border seems to be very low, as follows from the high degree of component segregation (Table 7.4). Introducing filler essentially changes the picture of the viscoelastic behavior. From the data given in Figure 7.21 and Table 7.4, it is seen that introduction of filler increases the elasticity moduli in the whole temperature interval. The highest moduli are observed with fumed silica having high surface energy; this effect is less pronounced for other fillers.

Table 7.4: Modulus, E, glass transition temperature, T_g, and segregation degree, α, of filled IPNs based on polyurethane, PU, and poly(ester acrylate), PEA

System	E, MPa at 20°C	E, MPa at 140°C	T_g, °C	α
PU/PEA=90/10	457	21	70	0.83
PU/PEA=90/10 + 3% Al_2O_3	794	22	108	0.46
PU/PEA=90/10 + 3% fumed silica	891	28	104	0.55
PU/PEA=90/10 + 3% PEA	631	23	96	0.69
PU	363	11	66	-
PEA	1514	372	170	-

However, of the greatest importance is the disappearance of two relaxation maxima tanδ (curves 2-4, Figure 7.22), and the appearance of one which is very broad. This effect indicates the essential structural changes in IPN, leading to the broadening of the glass transition region, and shows the increased compatibility of the constituent networks in the filler presence. Increased compatibility also follows from the values of segregation degree (Table 7.4), which is much

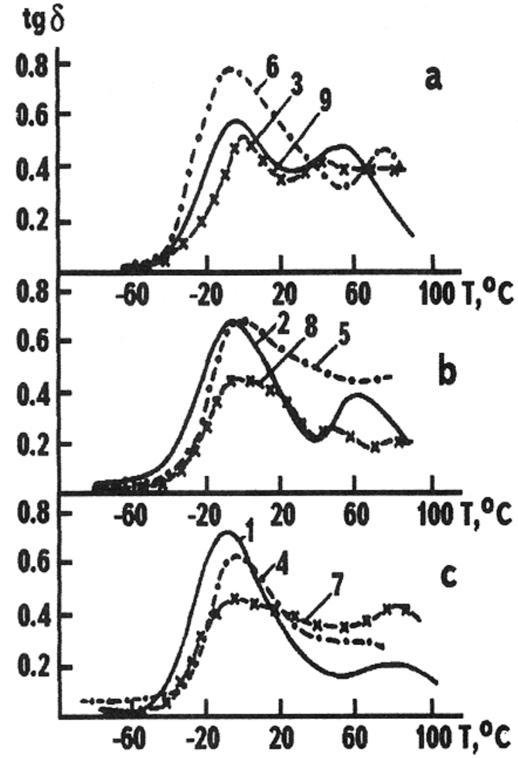

Figure 7.23. Temperature dependence of mechanical loss tangent in IPN's without filler (1-3), with 20% (4-6) and 40% (7-9) at various initiator concentrations: a-0.74.10^{-2}, b-2.96.10^{-2}, c-5.4.10^{-2} mol/l. [Adapted by permission from Y. S. Lipatov, T. T. Alekseeva, V. F. Rosovitsky, and N. V. Babkina, *Polym. Networks Blends*, **4**, 9 (1994)]

lower, as in unfilled IPN. The general trend to increasing compatibility, by introducing fillers, is common for all fillers; despite the extent of the effect, it depends on their nature. It happens to be the highest for an active filler-Al_2O_3, and the lowest for inactive filler - poly(esteracrylate).

Thus, for filled IPNs, the same effect of increased compatibility in the filler presence is observed, which is typical of alloys of linear polymers. These effects are connected with the filler influence both on the phase separation during system formation stage and on the reaction kinetics.

The effect of fillers on the reaction of polymer formation was discussed in Chapter 4. It is evident that introducing a filler during IPN formation should also lead to its influence on the rates of the IPN formation. This influence should affect the possibility of microphase separation. This question was studied[73] for simultaneous semi-IPN based on a crosslinked polyurethane and linear PBMA. The ratio PU:PBMA was 3:1, the ratio IPN:filler was 60:40 and 80:20 by weight. It was established that the onset of auto-acceleration of the butyl methacrylate polymerization increases from 160 min without filler to 220 min in the presence of a filler (talc). After the onset of auto-acceleration, the reaction rate of butyl methacrylate polymerization decreases with the increase of amount of filler. The filler influence on the reaction kinetics was explained based on the so-called cage-effect.[74] This effect stipulates that viscous media prevent the diffusion separation of a radical pair, which results in regeneration of initiator molecules. For filled systems, the effect is revealed by the drop in the reaction rate of PBMA formation in the initial stages of reaction.

The influence of filler on the kinetics of reaction affects viscoelastic properties of filled IPNs.[73] Figure 7.23abc show the temperature dependence of the mechanical loss tangent, tanδ for IPNs (PU:PBMA = 75:25) without filler and in presence of 20 and 40% of talc by weight. It is noticeable that, for unfilled samples, two maxima in mechanical loss are observed. This behavior indicates microphase separation with the formation of two phases, enriched either with PU or PBMA. However, the relaxation maxima show that microphase separation is not complete and depends on the kinetic conditions. The higher the rate of radical polymerization of butyl methacrylate, the greater the difference in glass transition temperatures of the two evolved phases. In addition, filler leads to the broadening of the PU-enriched maximum and to the degeneration of the maximum for the PBMA-rich phase (curves 4-9). At the same time, the loss background between maxima is increased. The data show the inhibition of microphase separation under the influence of filler. Such effects have been discussed in this chapter for filled alloys of linear polymers. The influence of filler on microphase separation in conditions of proceeding reaction may be two-fold: first, it is connected with adsorption at the polymer-solid interface hindering phase separation: second, it may be a result of a change in the kinetic conditions of the reaction. At high reaction rates, microphase separation has insufficient time to develop, whereas at small rates, sufficient time is available.

Considering the effect of filler concentration on the relaxation behavior of semi-IPNs, at an initiator concentration $0.74x10^{-2}$ mol/l (Figure 7.23a), the increase in talc content from 20 to 40% (curves 6,9) reduces the absolute values of the loss maximum for PU-phase and causes a narrowing. The maximum for PBMA is shifted to lower temperatures. At filler concentration of 40%, both maxima in the two-phase system approach each other, compared with the IPN containing only 20% of filler. For the initiator concentration of $2.96x10^{-2}$ mol/l (Figure 7.23b), the reduction of the PU maximum is observed with increasing filler content (curves 5,8). At 20% of filler, the disappearance of the PBMA-phase maximum is observed, whereas at 40%, this maximum is very small (curve 8). At the fastest rate of butyl methacrylate polymerization (Figure 7.23c), the influence of increasing amount of filler on relaxation behavior is more pronounced (curves 4,7). The glass transition temperature of the PU-phase increases by 20^0C, compared with pure PU; the same temperature for PBMA is also higher than for pure PBMA. These data show the essential influence of a filler on the relaxation behavior of both components. The decrease in the rate of butyl methacrylate polymerization has a more pronounced effect on the viscoelastic properties of IPN.

For this system, it is important to compare the degree of segregation in filled systems with those for pure IPNs. It was established that introducing filler sharply decreases the segregation degree, and in two cases, segregation was not observed at all (there is only one maximum in tanδ (curves 4,5)). Generally, when considering the effects of filler and reaction kinetics on viscoelastic properties one should note the following. The segregation degree depends on the kinetics of reaction. The reaction rates and the rates of microphase separation are interconnected. At high reaction rates, microphase separation has insufficient time to proceed and the degree of segregation remains very low. If one of the components of IPN is formed much faster than the other, and the latter remains a viscous liquid, the degree of segregation may be higher, the higher is the rate of the formation of the earlier-forming network. At the same time, the degree of segregation depends on the presence of filler, hindering phase separation.

Thus, the influence of filler on the degree of segregation is twofold: first, filler affects the reaction kinetics, and second, it exerts a hindering action on microphase separation. For increasing unfilled IPNs, the reaction rate of PBMA formation promotes a higher degree of segregation. For filled systems, the data may be divided into two groups, depending on the filler content. At 40% filler, the segregation degree is higher, compared with 40% at the lowest rate of reaction. This result may be explained by a lower hindering effect of filler at its lower content. However, both at 20% and higher reaction rates, the second relaxation maximum does not appear at all. Thus, phase separation is fully suppressed. By introducing filler, the effect of butyl methacrylate polymerization rate is diminished and the main cause of the reduction in phase separation is an adsorption hindrance. Therefore, at 20% filler, the increasing reaction rate prevents separation, whereas in a pure system, the opposite is true. At 40%, when both reaction components are bound to the filler surface, main role in phase separation is adsorption binding. In these IPNs (curves 7-9), the filler preserves the initial structure of the system, and changes in the reaction rate do not influence relaxation behavior and degree of segregation. Thus, depending on the filler content, its influence on reaction rate, determining the phase separation, and on phase separation, governed by preservation of the initial structure, due to adsorption binding, is changed. In such a way, we can conclude once more that the filler directly affects the reaction kinetics, which, in turn, determine the degree of microphase separation in the system. Simultaneously, the filler prevents phase separation and increases the local viscosity in the interphase region. The contribution of each effect on the degree of segregation depends on filler content. However, in all cases the filler exerts a compatibilizing effect on the IPNs and diminishes the degree of phase separation. This case is an example of non-equilibrium compatibilization.

Effects of the filler influence on the phase separation in forming IPNs also may be connected with the selectivity of component adsorption at the interface with a filler, leading to the redistribution of the reaction system components between the bulk and surface layers.[69] The enrichment or depletion of the surface layers in IPNs depends both on the free surface energy of filler and the surface tension of reacting system components. The greatest changes of the composition in the bulk and in the surface layers are observed in such a composition range, where the positive free energy of mixing components (maximum incompatibility) are observed. These effects influence both the reaction kinetics and the degree of phase separation.

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8

> The mathematicians and physicists
> Have their mythology; they work alongside the truth,
> Never touching it; their equations are false
> But the things **work.** Or,when gross error appears,
> They invent new ones; they drop the theory of waves
> In universal ether and imagine curved space.
> Nevertheless their equations bombed Hiroshima.
> The terrible things **worked.**
> **Robinson Jeffers (1963).**

CONCLUDING REMARKS ON THE MECHANISM OF REINFORCING ACTION OF FILLERS IN POLYMERS

The clarification of the mechanism of the reinforcing action of fillers is of great importance in the improvement of their physical and mechanical properties. The mechanism of the reinforcing action of fillers differs between plastics and rubbers, since, under service conditions, the latter are in elastic (rubber-like) state. We must also bear in mind that the mechanism of polymer reinforcement cannot be explained from any single point of view. To understand it, we have to take into account all factors influencing the properties of PCM: the chemical nature of the polymer and the filler (particulate fillers, fibers, fabric etc.), the phase state of the polymer, the conditions of forming of filled polymer from the melt or in the course of curing, and so forth. However, two main approaches to the mechanism of the reinforcement have been developed, one based on the analysis of the surface phenomena at the polymer-filler interface, and another based on the consideration of mechanical behavior and response to mechanical loading. Both these approaches are interconnected and it is a great pity that the adherents of the mechanical approach (especially for complicated fiber- or fabric reinforced systems) often forget that no reinforcement is possible without, say, adhesion, which is a pure physical phenomenon, or other processes proceeding at the interface.

A large part of investigations dedicated to the mechanism of reinforcement relates to filled rubber vulcanizate [see, for example[1,2]]. Much less attention is paid to the mechanisms of plastics reinforcement.[3,4] In this chapter, we should like to briefly consider only the most important approaches to the problem.

8.1 ROLE OF POLYMER-FILLER BONDS IN REINFORCEMENT

From the discussion in Chapter 2, it follows that both physical and chemical bonds play an important role in reinforcement, determining the adhesion at the filler-matrix interface. Kraus[5] made a detailed study of various aspects of interaction between elastomers and reinforcing fillers, in particular, on the influence of the chemical properties of carbon black particles on the reinforcement. It was found that the character of interaction of carbon black with polymer differs, depending on chemical properties of the surface of the black particles. In particular, there is a possibility of chemical grafting of the polymer molecules onto the surface.

Donne[6] developed ideas on the role of chemical interaction between saturated and unsaturated elastomers and carbon black and found that on the surface of highly reinforcing blacks, only 10% hydrogen atoms are reactive, and increased hydrogen content brings about a rise in the modulus of the rubber. Chemical and adsorption interaction with the surface of the carbon black leads to strong binding of the rubber. The fraction of bound rubber is determined by the gel content of the filler-rubber mixture; the bound rubber content is proportional to the surface area.[7]

Since we are dealing with a number of different effects superimposed on each other, according to Kraus, it is natural to observe a lack of correlation between the bound rubber content and reinforcement. The nature of polymer-filler bonds and their role in the reinforcement of elastomers was considered by Rehner.[8] On the basis of analysis of the deformation properties, it was established that the strength of bonds present in vulcanizates is characterized by a very broad spectrum of forces. From the data on the swelling of filled systems, it is possible to determine the concentration of physical bonds (or attachments) of macromolecules to the surface, which restrict the degree of swelling and the number of chemical crosslinks.

The model proposed by Rehner is based on the idea of the presence of attachments of macromolecules to the surface of the filler particles. The distance between the points of surface contacts is usually lower than that between the crosslinks in the bulk of the rubber, which are not adjacent to the filler particle surface. It was assumed that the points of contact are distributed over the filler particle surface similarly to the centers of closely-packed spheres of equal size. On the layer of such relatively small, closely-packed spheres there is superimposed a layer of large, closely-packed, spherical elements, representing the polymeric medium. The geometric model is, however, far from the real structure of a filled system; in particular, it shows an abrupt transition from the surface layer to the first bulk layer, whereas in the systems, this transition is gradual.

On the basis of the model of the structure of filled vulcanizate and the distribution of points of attachment of macromolecules to the surface, an equation can be obtained linking the parameters of the model with the filler particle diameter, d, and the volume fraction of filler in the mixture, φ, with the ratio R of the total number of links (attachments and crosslinks) in a system (surface attachments to the number of crosslinks in an unfilled system). Unfortunately, the influence of filler on the process of the network formation had not been taken into account, which makes the calculations arbitrary. The calculations are based on the equation:

$$8\lambda_s^3 + 3d\left[1 + \frac{R(1-\varphi)-1}{\varphi}\right]\lambda_s^2 - 11\lambda^3 = 0 \qquad [8.1]$$

where λ_s is the parameter of the model, characterizing the size of the surface layer, and λ is equal to the concentration of crosslinks in an unfilled vulcanizate. On the basis of data on the concentration of links in filled and unfilled vulcanizate, as determined from equilibrium swelling, we can determine λ and R and calculate λ_s. A calculation of the number of surface attachments which was carried out from Eq 8.1 showed that this number depends to a relatively small extent on the nature of black for any particular loading. As a rule, the reinforcement by different blacks differs by less than one order. There is, however, a correlation between the number of attachments and the properties of vulcanizate. The point is that the surface attachments increase the concentration of crosslinks in the layer of polymer adjacent to the surface of the filler.

Calculations have also shown that the fraction of bound rubber contains only a small part of the surface attachments in the vulcanizate. Analysis of the interrelationship of the number of attachments, the crosslink density, and the properties of the vulcanizate indicates that the reinforcement is connected with the concentration of links on, or close to, the surface of the particle.

The nature of the bonds in reinforced plastics was discussed in Chapter 2, where the chemical modification of the filler surface was also considered. Here, we would like to focus on polymeric coupling agents used for adhesion improvement. They bring about a considerable increase in strength of the adhesion joints. For instance, the application of phenol neoprene resin for the treatment of the glass surface, or other combinations of polymers with vinyl groups and synthetic rubber, leads to adhesion bonds, the strength of which greatly exceeds that of the chemical bond of the coupling agents with the glass fiber. Other commercial coupling agents are copolymers of vinyl acetate, poly (vinyl butyral) resins based on allyl esters, etc.[9] To improve adhesion, such polymeric agents may be introduced directly into the polymer binder, forming polymer blends or alloys.

Of special interest may be the case of the modification of the fiber surface by creating, in the surface layers of the fiber, an interpenetrating polymer network.[10] It was established that by swelling, the fiber surface with components capable of the formation of IPNs, followed by curing, leads to the improvement of the ultimate properties of fiber and increases the strength of organoplastics at compression, indicating improvement of adhesion. It is possible that such modification can be achieved by using thermoset binders and thermoplasts as well. In the latter case, due to swelling, the surface of the fiber or film may be considered as a surface of physical network formed, due to the entanglements, between different chains in the surface layers.[11] These approaches were discussed in Chapter 7.

The mechanism of the action of polymeric coupling agents is explained as follows. It is known[12] that during curing at the interface with a solid, high inner stresses arise, which may be so high that they lead to a spontaneous peeling of the cured binder from the surface. The lower the inner stresses, the stronger is the adhesion bond between the surfaces to be bonded. The action of polymeric coupling agents (mainly elastomers are used), leads to formation of a very elastic interlayer between the solid surface of the filler and the cured binder resin.[13,14] The inner stresses, which surround the interface as a result of shrinkage of the binder resin during curing, are partially relaxed.[15] From the same point of view, the use of adhesives, based on IPNs, has many advantages,[16] due to different rates of curing constituent networks, giving the possibility for the relaxation of inner stresses.

In spite of a great deal of experimental data and theoretical approaches, the role of the bonds at the interface is not established. On the basis of the concept of the importance of adhesion in the mechanism of reinforcement, it may be supposed that the significant feature here is the formation of a definite number of strong bonds irrespective of their nature (chemical or physical). The problem is not so much that of the nature but the number of strong bonds, which are necessary to achieve optimum properties. A large number of bonds reduces the mobility of the macromolecules in the boundary layer, increases inner stresses, and, by changing the structure of the surface layer, may lead to the formation of weak boundary layers, which according to Bikerman are centers at which the failure of adhesion joints begins. The bond strength, or the energetic characteristics of the bonds, does not as yet enter into existing theories of reinforcement.

8.2 MECHANISM OF REINFORCEMENT OF RUBBER-LIKE POLYMERS

The reinforcement of rubber and rubber vulcanizates is dealt with, in the literature, with considerable detail.[1,2,17] Here, we would like to consider the questions connected with a role of the surface phenomena in filled systems without discussing in detail mechanical theories of reinforcement. One of the most significant features of the rubber reinforcement by carbon black is its capacity to form chain-like structures in the polymer medium. Rhebinder[18] was the first to have proposed the mechanism of the structure formation in filled systems, taking into account the role of the surface phenomena. It was shown that in the concentrated suspensions of carbon black in a non-polar hydrocarbon medium,[19,20] the three-dimensional coagulation structures are formed by van der Waals forces which bind the filler particles, forming thin interlayers of polymer. The mechanism of structure formation may be described as follows. The surface of filler is always non-uniform, with more or less lyophillic regions, forming a peculiar micromosaic structure. Structure formation is brought about by bringing the particles together to only a small distance (a few molecular diameters) while retaining a thin layer of the dispersion medium (polymer). At the same time, there is an interaction of the three-dimensional structure of two types: the coagulation structure of particles of the solid phase (this network develops, given a sufficiently large number of particles and sufficient degree of loading) and a structural network formed by the dispersion medium itself (i.e., by polymer matrix).

The coagulation structures in question are the most characteristic of systems with a relatively low volume fraction of fillers but with a large amount of fine particles. They are formed particularly readily if the particles are anisodiametric or their surface is of a mosaic-type. For the formation of such structures, the fraction of the surface of the particles, which is occupied by lyophobic regions, i.e., coagulation centers, is bound to be quite low, or else in the opposite case, coagulation leads, not to the development of loose network structures, but to creation of compact aggregates of particles, which would lead to a sharp reduction in the number of free particles (there would not be enough particles to form a three-dimensional network). This indicates the importance of the particle fineness in the filled systems. It is in fact to coagulation structure formation that Rehbinder attributed the reinforcing action of active fillers. If the filler concentration is sufficiently high, polymer, which is adsorbed on the surface, may itself form a three-dimensional network. This network penetrates the whole volume, and, in this case, there is no need for the formation of loose coagulation structures by filler particles. On the other hand, with low filler content, the formation of a coagulation network is necessary for the strengthening of the structure.

The formation of chain-like structures in filled rubbers was investigated in detail for a number of filled polymers by Dogadkin.[21,22] It was found that the higher the degree of the development of chain structure of active filler, the higher is the effect of reinforcement. Again, the formation of chain structures of active filler within a medium of rubber polymer implies that the surface of the particles is energetically non-uniform. The energy of interaction of the filler particles in the places of contact is higher than the energy of interaction at the rubber-filler interface. The reinforcing action of the chain structure is explained by the fact that they form the actual matrix on which rubber molecules orient themselves, due to adsorption. The more developed the chain structure, the more its orienting action on the rubber chains becomes evident. The formation of these structures of active filler is an independent factor in the reinforcing of the rubber, since in the breaking of vulcanizates containing active filler, the plane of rupture passes through stronger bonds between the particles of filler, and this hinders breakage.

In the process of deformation of the material, the rubber-black bonds, which have been formed randomly during the mixing rupture and reformed in new positions, securing on the surface of the black the molecules of rubber, are partly oriented in the direction of deformation. As a result, there is a local relaxation, which eliminates local over-stressing. The higher the strength of the bond of the filler with rubber, the greater is the reinforcing action. In subsequent deformation and orientation of the molecules, there is a greater increase in the stress required for rupture. Thus, the balancing of stresses in the course of deformation is one of the reasons for the improvement in strength of filled vulcanizates. The ideas of the existence of chain structure in the filled vulcanizates were not subjected to a quantitative assessment, and accordingly, it is not possible to assess the contribution of these structures to reinforcement.

The influence of the structure of the elastomer on reinforcement is linked with the effects of localization of stresses, because the stress, occurring on the surface of the filler particles, is a function of the elastic properties of the material. This explains the fact that for an equal number of polymer-filler bonds and crosslinks, the reinforcement effects are still different for different rubbers. The predominance of physical interactions between rubber and black corresponds well with the mechanism of equalizing of the stresses on stretching. Stronger interactions would make detachment of the chains from particles of rubber less probable.

There are many works describing the effects of reinforcement with conditions of the vulcanizate rupture and with the crack propagation.[2,23] It is important[24] that rupture takes place along a wavy line from one filler-rubber interface to another. The surfaces of the filler particles, or regions, directly adjacent to them, may be weak places through which failure takes place. The numerous internal defects, which are characteristic of the structure, bring about increased dissipation of energy as a result of the increase in vulcanized volume involved in deformation, and the amount of the dissipated energy depends on the adhesion. Thus, the occurrence of defects (or heterogeneities) may not only weaken adhesion, but also be a reason for the strengthening of the material.

An important role in the rubber reinforcement is played by the Mullins effect,[24] connected with a softening by prior deformation and leading to hysteresis in the energy dissipation. According to Mullins, the hysteresis in filled vulcanizates may be caused by a number of factors, the most important of which are:

- break-up of the secondary formation of filler particles
- rearrangement of the molecular network without break-up of its structure
- break-up of the network structure: rupture of filler-rubber bonds or crosslinks in chemical network.

All these processes may take place simultaneously.

The topological theories of rubber reinforcement have also been considered.[2,25] Bueche's theory[25] is based on the existing strong linkages between the rubber chains and reinforcing filler particles. Immobile crosslink points, formed by these linkages, influence the mechanical properties of vulcanizate. The extent of this influence depends mainly on the number of linkages and their strength, and also on the mobility of filler particles. For low deformations, the simple relationship between the stress, σ, and deformation, α, exists:

$$\sigma = (v_r + v_f)kT(\alpha - \alpha^{-2}) \qquad [8.2]$$

where v_r is the initial number of effective network chains, and v_f is the additional number of chains introduced into the network by the formation of the bonds with the filler particles (in each case, v is the number of chains per unit volume of the rubber + filler). The value of v_f depends on the filler surface area, S, and the average area, s, per active sites. Consequently, it is proportional to the volume fraction of filler, φ, which, in turn, is inversely proportional to the rubber concentration (1 - φ). Hence Eq 8.2 may be written as

$$\sigma = [v_o(1-\varphi) + \beta\varphi]kT(\varepsilon - \varepsilon^{-2}) \qquad [8.3]$$

where β is the proportionality coefficient, and v_0 is the number of effective chains in unfilled vulcanizate. Since $v_f = (S/s)\varphi$, $\beta = S/s$. The calculated values of s were within reasonable limits, from 2 to 40 Å, depending on the type of filler. It is assumed that in the presence of filler, the vulcanization proceeds just as in the unfilled rubber. Otherwise, v_o would have been replaced by a value dependent on the filler concentration.

However, for the majority of vulcanizates, the applicability of Bueche's equation is problematic.[5] This is because of the set of assumptions in the equation, particularly because the existence of surface layers close to the filler particle was not accounted for, as well as the differences in deformability of the chains in the specimen as a whole and close to the filler particle.[26] The layer with a higher concentration of physical and chemical crosslinks also was not taken into account. In a general form, the stress relaxation in the filled vulcanizates is determined by the relaxation processes which are linked to the detachment of the rubber chains from the filler particles, and by regrouping of particles, which takes place at a very low rate.[27]

Mullins, on the basis of the phenomenological analysis of the deformation process, believed that deformation properties can be represented by a model according to which the vulcanizate consists of two phases with the main deformation occurring in the "soft" region, which has the deformation characteristics of an unfilled vulcanizate. The deformation increases the fraction of vulcanizate which is in the soft region as a result of degradation of the relatively unstretched "hard" region. This simple model helps to explain the softening of filled vulcanizates under deformation, and also the sharp increase in the stress vs deformation curve at stretching close to the maximum. A shortcoming of this model is that the postulate of soft and hard regions does not tie up with the actual molecular parameters of polymer.

Since, in the layer of rubber surrounding a filler particle, the value of α is different in the rubber matrix, the following equation was proposed,[28] based on the existence in a filled specimen of two kinds of chains, either attached to the filler or wholly contained in the rubber matrix:

$$\sigma = vkT\left\{(\alpha - \alpha^{-2})\left[1 + \frac{y^2}{1-y} + \frac{Ky^3}{(1-y)^2}\right] + (1-\alpha^{-3/2})\left[\frac{y^2}{1-y} + \frac{Ky^4}{(1-y)^2}\right]\right\} \qquad [8.4]$$

where $y = \varphi^{1/3} = r/R$, r is the radius of a spherical particle of filler included in a larger sphere of radius R (R is selected according to the number of filler particles per unit volume of rubber; multiplied by $(4/3)\pi R^3$, it should equal unity), K is the ratio of densities of the chains linked to filler to chains in the rubber matrix.

The main practical interest regards the cases where deformation does not cause adhesive failure at the rubber-filler interface. In this equation, the terms containing y but not K are connected properly with the filler, while the terms with K are connected with the increase in modulus due to interaction with filler. The equation is applicable only to small deformations. For any given deformation, the reason for breaking an individual chain is its limit of extensibility. The chains broken during the first loading will not influence the magnitude of the modulus in the second cycle of deformation, which is the reason for the Mullins effect. The softening (or decrease in stress) observed at elongation, ε, after rubber has been stretched previously to $\varepsilon_2 > \varepsilon$ is given by equation:

$$\Delta\sigma = K\exp[4.7(a\varepsilon/b)^{1/2}]\{\varepsilon\ln[(\varepsilon_2 b\gamma + \varepsilon_2 - \varepsilon\gamma)/\varepsilon] -$$

$$\ln[(\varepsilon_2\gamma + \varepsilon_2 - \gamma)/(\varepsilon\gamma + \varepsilon - \gamma)]\} \qquad [8.5]$$

where $K = 4.75\mathrm{x}10^{-3}\sigma_r(a/s)^2(\gamma + 1)^{-1}$, γ is a measure of the strength of the bonds which break, given by the ratio σ_r a/kT, σ_r is the stress of chain at the moment of rupture, a is the length of the chain segment, s is the average area of filler surface per rubber-filler bond, and b is a measure of separation of particles of filler, linked to its degree of dispersion within the rubber. It is seen that to apply this equation in experiment work is impossible because of a great deal of values which cannot be found or calculated.

Topological theories, considered in detail in the review by Rigbi,[2] postulate two types of attachments between a rubber matrix and its carbon black filler: a strong type, due to chemisorptive attachments, and a weaker van der Waals type of bond. The former were considered to remain unbroken upon stressing the vulcanizate, but the latter suffered progressive rupture as the stress increases. Various models of deformation have been proposed, based on the model described by Takayanagi,[29] to describe the phenomena observed, but they are strictly mechanical models which do not explain why these phenomena occur.

Rigbi[2,30-32] describes the basic model for the behavior of carbon black in rubber, considering a single macromolecule attached to the filler surface under tension. It is assumed that the polymer chain contacts a carbon black aggregate at one or another point along the macromolecule and on the surface. The points bonding the chain are of various bonding energy. The chains are assumed to be under no average tension. Due to the thermal movements of the chain or its parts, the energy transmitted to one point of attachment may at any given moment exceed some average value of energy, causing the chain to become temporarily detached from one point on the surface and then reattach itself. These detachments and reattachments, which Rigbi calls saltations, occur sporadically. At definite conditions, chains saltate so that a point of attachment moves backwards and forwards in accordance with Eyring's theory of liquid flow, and each jump requires the transfer, to and from the particular portion of molecule, of sufficient energy to surmount an energy barrier. Based on a such concept, the frequency of jumps of one monomer unit in either direction, forward or backward, about the most probable point of attachment may be found.

A case may be considered when a single chain is fixed at two points contacting a carbon black aggregates or two chains link a single aggregate. This consideration may be extended to the case where different structures exist simultaneously within the same space.[2] A macromolecule, attached to carbon black at one point along its length, may be crosslinked to other molecule at one or more points on either or both sides of the carbon black particle, while another may pass fairly close to the black without contacting it and be equally

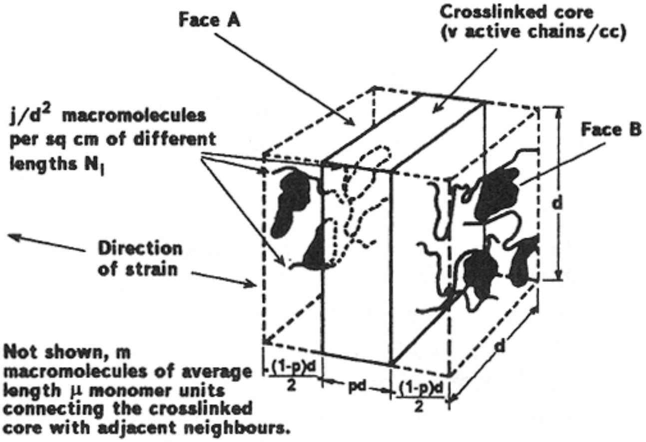

Figure 8.1. Unit cell of model of vulcanizate according to Rigbi. [Adapted by permission from Z. Rigbi, *Adv. Polym. Sci.*, **36**, 21 (1980)]

crosslinked at the distant points. Mathematical relationships have been developed by means of a highly idealized model (Figure 8.1). The vulcanizate is divided into a series of unit cells; in each, a central laminar crosslinked core is found, which contains no carbon black and which extends over the whole width and height of the cell. In the cell there are a number of carbon black particles which are located at the faces normal to the direction of strain and randomly distributed. Also in the cell are protruding macromolecules, bound to the central core and attached to the carbon black by means of mobile attachments. A large number of such cells, placed randomly with the carbon black particles, acting as contact points between the cells, is presumed to describe the behavior of a vulcanizate in all directions.

If m is the number of chains of μ molecular units of length, a, ν is crosslinking density, d is dimension of the unit cell in each direction, and pd (p <<= 1) is the width of core, then the reduced relaxation modulus, E, may be calculated for chains of N_i molecular units from

$$\frac{E}{\nu kT} = \frac{m/\mu + \sum(1/N_i)}{p[(m/\mu + \sum(1/N_i)] + \nu d a^2/3} \qquad [8.6]$$

Individual values of N_i are both time and strain dependent. The relaxation modulus is also a function of the strain, and the model should be capable of treatment by means of temperature-time superposition as well as strain-time superposition. Rigbi has demonstrated some results of calculations according to this model using computer iteration, and obtained relaxation curves for model vulcanizates of various chain length and for the case of redistribution of load between the chains. The model proposed also explains creep behavior, reinforcement, and strength. According to the Rigbi model, the relative movement, called saltation, takes place between elastomer molecules and carbon black during stressing of a vulcanized loaded elastomer. This saltation would relieve local high stresses and result in redistribution of stress, which effectively reinforces the vulcanizate.

Rigbi[2] stated, in his review (1980), that there is actually very little reference made to reinforcement. Very detailed consideration is given to the influence of structure on modulus, to aggregation, agglomeration, polymer-surface interactions, etc. Such a situation exists up to the present time. Rigbi concludes that the reinforcing is connected with the ability of the filler to redistribute the stresses along the macromolecules until they become uniform. The most highly reinforcing fillers are those which show greatest stress softening due to saltation and least softening due to rupture, and this condition results from minimum surface energies, provided that they are sufficient for the black to maintain contact with the polymer molecules.

The reinforcing action of fillers is closely connected with molecular motions in the polymer.[33] The sharp fall in the strength of filled rubbers, when the temperature is reduced below T_g, as compared with unfilled rubber, is linked to the impossibility of relaxation of the stresses present below T_g as a consequence of the difference in the coefficients of thermal expansion of the polymer and filler. This leads to decreased adhesion, and thus, in filled systems, the mobility of the kinetic units influences not only the deformation process and development of defects but also the cohesion. Accordingly, the temperature dependence of the reinforcing action and the strength of filled systems, based on amorphous polymers, are determined by the mobility of chains, irrespective of whether the polymer is elastomer or thermoplast. Development of the mobility leads to an improvement both in the strength and in the reinforcement.

Among other factors influencing the reinforcement of vulcanizates may be noted the shape and size of the filler particles, the character of their dispersion in the polymer matrix, the wetting of the filler by polymer, and adhesion.[34] The role of adhesion in the reinforcement of elastomers and the interpretation of reinforcement as an adhesion effect was first proposed by Voyutsky.[35] The reinforcing capacity of fine-particle fillers can be realized most fully only when their uniform dispersion in the medium is achieved. The differences in shape of particles become evident, mainly in their capacity for forming chain-like structures. Wettability also has a powerful influence on the properties of vulcanizates. Poor wetting by a rubber of agglomerates of particles leads to a weakening of the material because of the formation of structural defects and reduction in the content of filler in adjacent regions.

8.3 REINFORCEMENT OF THERMOPLASTICS AND THERMOSETS

The mechanism of filler action in plastics is not analogous to that considered for rubbers, although a number of concepts developed for vulcanizates can, with various limitations, be applied for filled plastics. Filled plastics usually serve at temperatures below their T_g when high deformations cannot develop. In this case the reinforcement can no longer be explained by changes in the conditions for the relaxation processes, since their role here is very limited.

In thermoplasts and thermosets, the reinforcing action of filler is likewise linked with the formation of thin surface layers with properties different than the properties of a matrix, as considered in the preceding chapters. It may also be assumed that when particulate fillers are used they can form, in the course of production, some coagulated structures analogous to those existing in filled vulcanizates. When we consider the reinforcement of crystallizing polymers, it is necessary to bear in mind the influence of fillers on morphology and formation of spherulites, lamellas, and other structural elements. The formation of fine structures under the influence of filler reduces the length of chains protruding the amorphous phase, and, consequently, their flexibility.

The strength of filled plastics rises with increase in the active surface up to a particular maximum, which corresponds to a full transition of a matrix in a state of the surface layer. Generally, the influence of filler on the strength, as in the case of vulcanizates, may be expressed by means of statistical theories of the distribution of internal defects in a solid. The reinforcing action is related to changes in overstressing of crack apexes, with relaxation of the stress and its redistribution over a large number of centers of growth of microcracks. This causes an increase in the average stress which brings about the failure of the solid. A microcrack, as it develops in the filled polymer, may be stopped by a filler particle, and, consequently, an increase in stress is required for its further development. The more filler available in the polymer, the more hindrances are created against crack development; as a result, the process of failure is slowed down.

If fibers, roving, mat, or fabric are used as reinforcing materials, a major role in the reinforcement belongs to the structure of the insert, its strength properties, and a number of technological factors. However, reinforcement cannot, even in this case, be attributed to purely mechanical factors without taking into account the role of the binder. In such systems, binder ensures uniformity of stress distribution and simultaneous action of all fibers in the reinforced polymer. It binds together the fibers and protects them from the action of an external medium. In this case, a primary importance is attributed to adhesion interaction of polymer and filler. Reinforcement with the use of unidirectional insert may be explained as follows.[3,36] With the application of loading, the fibers elongate, and, at the same time, undergo transverse compression. With deformation in the polymer matrix, a fiber, under transverse compression, is bound to detach from the surrounding thin layer of a binder over the whole surface, or else stretch this layer. Thus, elongation under stretching brings about, in the plane perpendicular to the applied force, a tensile stress preventing elongation of the fiber. This stress is determined by adhesion of the matrix to the surface, and by the properties of the matrix itself. Thus, with deformation, leading to breakdown of the structure, we must overcome not only the overall strength of the reinforcing fiber inserts, but also the forces preventing transverse compression, which are larger than the adhesion joint strength and the elastic properties of the matrix.

The joint deformation with reinforcing fibers and thin films of a polymer were described elsewhere.[37] The fullest utilization of the strength of reinforcing fiber insert may be achieved when, along with high adhesion, the binder possesses a combination of properties which make it possible to ensure joint functioning of the fibers in deformation, and offers the highest "monolithicity" of the system. To ensure joint functioning of the system under stressing, the best ratio of the elastic moduli of the fiber and polymer should be found.[38] For high effectiveness, it is also necessary to ensure a particular relationship between the elongations of the matrix and fiber. If we use strong and stiff binder with elongation at break less than that of the fiber, the failure of the system depends on the failure of the binder. If, however, the matrix is elastic and has high elongation at break, the system fails prematurely, since we do not ensure combined functioning of the majority of the fibers. The matrix must not fail before the fibers, but must possess the capacity of redistributing stresses. We thus see how important elastic properties are in determining the uniformity of distribution of the stresses.

There should be an optimum between the content of reinforcing fibers and their properties.[36] With increase in the relative content of polymer binder in the composition, there is a reduction in strength, since we are reducing the content of reinforcement which plays the main role in taking up the load when stress is applied. On the other hand, with reduction of the content of polymer binder, below a certain limit, the strength of the composite likewise falls, because of inadequate bond strength of the fibers and the disturbances in the conditions ensuring joint functioning of both components. The strength of reinforcing fibers is most fully realized in a plastic given a certain optimum, but not maximum, strength of adhesion. At high adhesion, the failure can occur in the region of elastic defamations at low stress.[39,40] Failure is influenced also by the presence of microscopic defects (weak boundary layers) because the surface of the fibers is not uniform.[41] Sites with zero adhesion are defects which are a significant factor in failure.[42] Stress concentration in the places of voids facilitates the formation of cracks. If the adhesion strength is close to cohesion strength of a matrix, the fibers deflect the advancing crack and the contact of the fibers with the matrix, beyond the plane of the crack, remains unbroken.[43]

There was proposed another view on the mechanism of reinforcement of plastics.[44-46] The main factor in reinforcement is ascribed to the forces of friction at the polymer-filler interface, which determine the possibility of their joint functioning. These forces occur as a result of shrinkage of the polymer on curing. In this case, the elasticity and stressed state of the cured binder in the layers contacting the surface of the fibers are the decisive factors, not the adhesion.[47]

We do not find this point of view convincing, since it cannot explain the role played by the surface treatment of the fillers or by mechanical properties of matrix itself, not to mention thermoplastic, matrix which does not change its volume during processing up to extent the thermosets do. In this case, better properties should be achieved when the greater shrinkage on curing occurs, and this is not true. On the contrary, any stress in the system leads to the occurrence of a non-equilibrium state which has an adverse effect on the mechanical properties.

In the case of polymeric fillers (fibers and particulates), with adequate adhesion at the phase boundary, the failure of filled polymer may be accompanied by deformation of polymeric filler.[48] The capacity of the particles of polymeric fillers or fibers for deformation leads to redistribution of the stresses in the apex of the growing center of failure. The capacity of the filler for adsorbing the energy of deformation increases with an increase of adhesion, and, accordingly, the role of adhesion in the mechanism of reinforcement becomes important. The closer are the cohesion energies of the polymeric filler and the matrix, the more marked the rise in tear strength with an increase of filler content, which is also determined by adhesion.[49] The influence of filler on the energy of failure is also connected with the fact that the particles act as centers of energy dissipation. In polymer alloys used as a matrix, the interphase region may likewise fulfill the function of a filler — a region in which the dissipation of energy occurs together with redistribution of stresses, changing conditions of crack growth. Among the functions fulfilled by the interphase, we may also cite on increase in the heterogeneity of the system. Kuleznev[50] considers that for creation of necessary complex of properties, we require to achieve an optimum degree of inhomogeneity of the composition, since it is known that mechanical inhomogeneity leads to improvement in the properties of many materials, including non-polymeric. Kuleznev assumes the possibility of relaxation of overstressing in the interphase zone whose cohesion energy should be relatively low. Again, as a result, the crack changes its direction of growth repeatedly. Role of the interphase in the transfer of stresses from the elastomeric matrix to the carbon fibers may also be connected with lower molecular mobility at the interface, where interphase exhibits pseudo-glassy properties.[51,52]

In considering the role of adhesion, it is necessary to take into account that the strengthening depends significantly on the conditions of wetting of the filler surface, determined primarily by the conformation of the polymer chain. Along with the progress of resin curing, the conditions of wetting and interaction of polymer and surface deteriorate, because a rigid polymer chain cannot adapt itself to the surface in similar manner as a molecule of small size. Thus, as curing proceeds, the system increasingly becomes a non-equilibrium system, the more so, the stiffer the chain and the higher the possibility of interaction of the polymer with the surface. Moreover, internal stresses are in the resin, determined by the interaction of the polymer with the surface. If the chain is flexible, it "adapts" itself better to the surface, the number of points of its contact increase, and the non-equilibrium of the system is less likely to occur than in the case of a rigid chain. Since the process of establishment of equilibrium is of relaxation character, it is necessary to effect the curing with an optimum ratio of the rates of the chemical reaction and of establishment of equilibrium state in the polymer on the surface. The formation of internal stresses and their relaxation during curing are influenced, to a considerable extent, by interaction with the surface. This leads to a slowing down of the relaxation processes and formation of less equilibrium and more stressed structures.

Summarizing the above, the conclusion can be drawn that the main parameters determining the strength of particulate and fiber-reinforced plastics are:

- the elasto-mechanical equilibrium of the two phases
- wetting of the surface and the strength of the adhesion bond at the interface
- the non-equilibrium structure of the interphase and surface layers.

Although it is well-known that both amorphous and crystalline polymers have a very complicated supermolecular structure, almost no attempts have been made to connect the reinforcement to the interaction between filler and structure formation. Such an idea was put forward,[51] but for a long period of time it was not used in the explanation of reinforcement. The development of the concept of supermolecular structure of polymer indicates that in studying the structure and properties of filled polymers, it is necessary to account for the interaction with the surface not of individual macromolecules but of supermolecular structures of various types. The interaction with the filler surface of any molecules participating in formation of aggregate leads to a binding by the surface of other molecules available. As a result of this interaction, there is a limitation of the mobility not only of the chains coming into direct contact with the surface, but also other chains in this aggregate. On the other hand, the interaction of polymer molecules with a surface, even in the course of formation of filled polymer, leads to change in the conditions of formation of supermolecular structure and their relative interplay.

Bozveliev[53-57] studied many systems filled with particulate fillers, using matrices with well-developed supermolecular structures. He believes that the properties of filled amorphous thermosetting and thermoplastic polymers (including crystalline polymers) should be explained by taking into account their supermolecular structure. Such an approach allows one to explain many unexpected results. It was shown that dependencies on filler concentration of the tensile strength, yield stress, Young modulus, average density, and degree of crystallinity of the polymer component in filled plastics have many maxima and minima,which cannot be explained on the basis of current theories (an example is given in Figure 8.2).

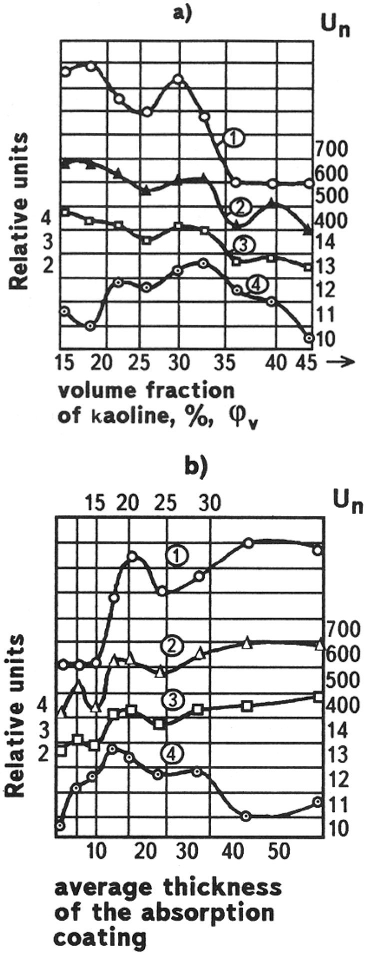

Figure 8.2. Dependence of the change in the properties of phenoplasts on the kaolin volume concentration (a) and on the average thickness of the adsorption coating (b): 1-specific volume electric resistance, 2-flexural strength, 3-impact strength, 4-electrical strength. [Adapted by permission from L. Bozvellev, *Ph. D. Thesis*, Sofia, 1990].

Bozveliev studied the model of filled polymer containing a critical amount of filler which causes an abrupt change (worsening) of the composite properties. At a critical loading, some individual particles have their surface layers adjacent to each other, which determines the conditions of deformation. The individual dispersed particle is not identical with the filler particle; it represents a combination of the latter and adsorption layers of polymer bond to the filler surface by adhesion forces. The binding polymer (phenolaniline-formaldehyde resol resins, modified with nitrile rubber or poly(vinyl chloride)) has a structure formed from globules of a definite statistical average size, which does not change substantially with the degree of filling. It was assumed that the physical structure consists of a new type of particles in contact with each other. These particles are composed of filler (kaolin) particles (or aggregates) completely covered by adsorption layers of globular matrix polymer. The spaces between these close-packed particles are filled with globular coatings, and its thickness can be easily calculated.

To explain the periodicity of properties, a mechanism of periodical changes in the structure and the thickness of the adsorption globular coating by filler is assumed (Figure 8.2). This change is related to a periodical formation of a whole number of monoglobular adsorption coatings of the resin in the filler particles, and, for this reason, the latter could be considered as particles of a new type of filler. The monoglobular coating may create an oriented layer of other globules, which appear periodically. The periodical appearance of this intermediate layer of oriented globules, connected with increasing amount of the filler, determines periodical changes in properties, passing through minima and maxima. The model proposed allows one to explain unusual dependencies of many properties on the filler content but does not consider physical reasons for their appearance.

8.4 NON-EQUILIBRIUM STATE OF POLYMER COMPOSITE MATERIALS

In this book, we have considered the formation of filled polymers in a microheterogeneous system in terms of equilibrium thermodynamics, resulting from reversible transition in the system. However, the processes of formation of disperse polymer systems often occur under conditions far from equilibrium. As early as 1979, we tried to attract attention to this problem,[58] and later analyzed it in more detail.[59] These are the materials which can be described by the features of the thermodynamics of small systems. The extensive thermodynamic functions depend non-linearly on their dimensions. For example, the energy of any thermodynamic system is a non-linear function of distance from the interface. This effect,which is unimportant in large volume of the system, plays a major role in dispersed systems where structural elements (adsorption layers, interphase, fine particles of filler) are too small, and, therefore, their dimensions are taken into account in the thermodynamics of small systems.

The usual processes of the formation of a solid polymer body, i.e., any solidification of polymer (curing, crystallization, vitrification) take place as a non-equilibrium process.[60] Glensdorf and Prigogine[61] showed that the concept of the thermodynamics of irreversible processes could be extended to states that are far from equilibrium, where continuous changes in entropy, and entropy increase, are observed. They found it necessary to draw a clear distinction between equilibrium and dissipative structures. The latter are maintained as a result of exchange of either energy or matter under extremely non-equilibrium conditions. In contrast to equilibrium structures, which can be homogeneous and unlimited in their dimensions, dissipative structures are formed under conditions far from those of equilibrium, where diffusion flows are a non-linear function of thermodynamic forces. Lindenmeyer[60,62] has concluded that both crystallization and glass formation should pass through the formation of non-homogeneous dissipative structures. Glass is an “extreme” dissipative structure in which all latent heat has been dissipated in the form of internal energy of a solid body. The structure of glass should consist of high-energy regions, which are formed as a result of dissipation of energy released during solidification in adjacent low-energy regions. The processes of spinodal decomposition can be formally regarded as the process of formation of dissipative structures.

In preceding chapters, it was emphasized that filled polymers and polymer alloys are non-equilibrium systems, due to the formation of the surface (adsorption) layers at the interface which are not in the state of thermodynamic equilibrium or formed due to incomplete phase separation. Reduction of molecular mobility in the boundary layers and development of less dense packing in boundary layers, in terms of thermodynamics, are indicative of transition of the system into a state of less equilibrium.

Recently, Chakraborty and coworkers[63-66] have shown that, at strongly interacting polymer-solid interfaces, the quasi two-dimensional glass-like structures are formed which are non-equilibrium, connected with non-equilibrium conformations of adsorbed chains.

It is known that in glassy polymers, a state of true thermodynamic equilibrium does not exist. It was pointed out that deviations from the equilibrium state may be of great importance for practical application of composite materials. Therefore, the evaluation of the degree of non-equilibrium and the finding of ways of bringing composite materials to a more equilibrated state are very important. It should also be remembered that, for the degree of non-equilibrium as well for other characteristics, there should exist a certain gradient of its value normal to the surface. However, a generally-accepted approach to evaluation of non-equilibrium of the system is not available, and the thermodynamic methods of evaluation are not practically developed. No data connecting the non-equilibrium state with molecular parameters of the system have been reported. All the data presented in this book allow us to relate polymer composite materials to a non-equilibrium system where dissipative structures are formed.

In this respect, the concepts developed by Wessling[67-72] are of great importance, and connected with the mechanism of formation of a filled system and reinforcement.

All theories of reinforcement of plastics by particulate fillers and corresponding equations (see Chapter 5) assume the statistical distribution of the discontinuous phase in a continuous matrix, although this has not been experimentally verified.[67] The assumption that during distribution in the dispersion process, the particles or dispersed phase become statistically distributed, is identical to the increase of entropy. If we treat such systems as equilibrium, as proposed by Wessling,[67] their properties should be predictable. But experimental data show that most polymeric systems, including filled ones, exhibit unpredictable behavior, sudden change in properties, and even totally unexpected phenomena.

To explain the conflict of experiment with topological equilibrium theories, Wessling proposes a new viewpoint based on the non-equilibrium thermodynamics and self-organization phenomena.[67,68] The main principle formulated by Wessling[69] consists of the definition of the non-equilibrium character of polymer dispersions (which all filled polymers relate to), and the interpretation of the experimental findings (phase separation, dispersion-flocculation, phase transition) as dissipative structures. Wessling summarizes his concept as follows.[67] The high energy input necessary for preparing a multiphase polymer system pushes these systems far from equilibrium. At a critical concentration, the energy input and the entropy export are so far above their critical value that a self-organization process occurs in the form ofphase transition. From a mechanical point of view, the following steps are taking place:

- the adsorption of a monomolecular polymer layer on the dispersed phase (in Chapter 1, it was shown that adsorption is not necessary of monomolecular character)
- the phase separation of all dispersed and polymer-coated phases, arranging themselves into the form of thin but broad and elongated layers ("seams") (this supposition coincides with the concept of the formation of chain structures formed by particles in the polymer medium[21])
- the formation of flocculated chains, resembling snakes that have swallowed several golf balls (Figure 8.3), plus branching of these flocculated chains, so that many particles have a common adsorbed layer around them and small voids between them.

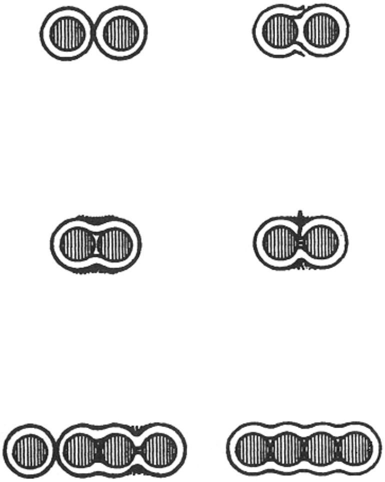

Figure 8.3. Scheme of flocculation mechanism according to Wessling. [Adapted by permission from B. Wessling, *Polym. Eng. Sci.*, **31**, 1200 (1991)]

The theoretical evaluations made by Wessling allowed him to make the following conclusions:

- the entropy of mixing for the preparation of multiphase polymer systems seems to be very high (in the range of 50-250 MJ/mol)
- an entropy increase by some 10^{17} bits was estimated to occur. Because the entropy increase is supercritical, a sudden self-organization of dissipative structure is observed.

According to Wessling, many complex characteristics of polymer systems may be explained using the principles proposed, called the "dispersion theory".

For conductive fillers (carbon black), Wessling[70] proposed a model explaining a sudden increase of the conductivity at a critical volume concentration of filler, φ_{crit}. The main aspects of this model consist of the formation of a strongly-adsorbed monolayer of matrix molecules. At the critical point, φ_{crit}, which is determined by the interfacial energy at the particle/adsorbed shell interphase, the dispersed phase flocculates (separates from the matrix) and forms branched, elongated chains. The process dispersion-flocculation, as a phase transition, seems to be reversible; at φ_{crit}, it occurs in the form of an oscillation. This phase transition explains the sudden change in many properties: dispersed phase is suddenly converted from a fully dispersed stage to a flocculated stage. The critical concentration at which this phase transition occurs is crucially dependent on the properties of the interphase (the interfacial energy) and temperature. It was shown that the free Gibbs energy of dispersion is positive and dispersion entropy is negative, leading to formation of highly-developed structures. Therefore, the systems with dispersed and flocculated phases exist far away from thermodynamic equilibrium. The theory developed by Wessling[67-71] is based on a general non-equilibrium consideration and may be applied both to filled polymers and polymer blends. He substantiated the conditions of instability causing dispersion structure to be formed in heterogeneous polymer systems. This seems to be a very great achievement in the theory of heterogeneous polymer systems, and, for the first time, it allows one to establish critical parameters above which a dispersion structure is formed. Of great interest is the establishment of the conditions at which "bifurcation" occurs and the system leaves the thermodynamic branch.

The qualitative description of the model is broadly supported by experimental evidence.[70] The later theoretical explanation of this qualitative model is experimentally proven, insofar as the necessary energy input ("excess interfacial tension") can be measured during dispersion of a given phase in a given polymer matrix. The non-equilibrium phase diagram, with the phase separation and flocculation description, and especially the non-equilibrium energy level,[68] is experimentally well supported. On the other hand, the theoretical description is

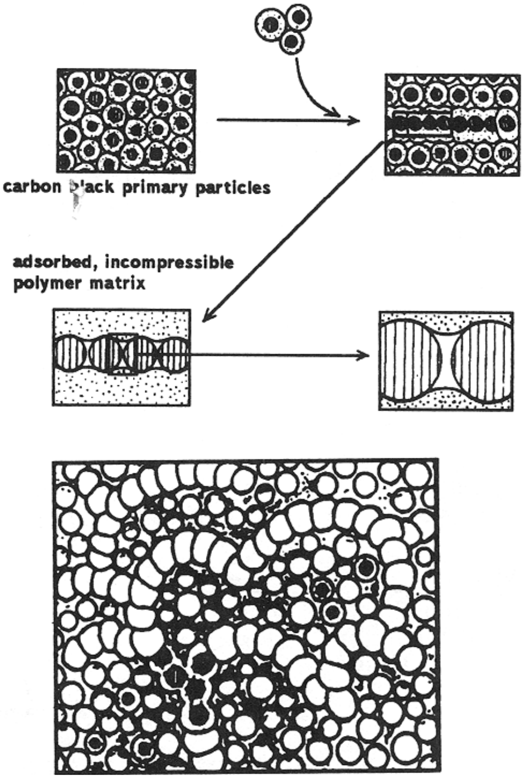

Figure 8.4. Flocculated particles, forming chains.[70]

only the first attempt,[68,69] as well as the analogous conclusion for impact-modified systems.[71]

On the basis of the developed theory, Wessling[71] describes the fracture mechanism in the systems formed by dispersed rubber phase in the continuous polymer matrix (polymers filled with polymeric fillers). The rubber phase, dispersed in a polymer matrix, is divided into mesoscopic particles (microdroplets), thereby creating a relatively high amount of surface to be wetted by the polymer matrix. Polymer chains, building the inner surface area of the polymer matrix, are essentially different from the free polymer of the matrix. This is the reason for the segregation of the rubber phase, including the adsorbed polymer chains forming flat, elongated layers. Above a critical volume concentration, the previously well-separated rubber particles form flocculates, whereby the originally isolated adsorbed surface layers of the polymer matrix chains, around the rubber particles, partially desorb and join to a joint tubular layer around the flocculated rubber particles (Figure 8.4). The rubber droplets may form a continuous segregated rubber phase and their coating layers, so we are dealing with a bicontinuous structure, one continuous phase being the original brittle polymer matrix, the other continuous phase formed from the layers and incorporated flocculated network structures.[71]

During the sudden impact, as Wessling describes this process, local heat originates, plastic deformation occurs, and microcracks cause propagation through the system. The local shear will cause cavitation, followed by redispersion of the flocculated network structure, forming droplets of completely coated rubber and destroying the continuous flocculated network, which was formed during the processing of the polymer blend above critical volume concentration (Figure 8.5). The crack propagates along the interface between the adsorbed polymer matrix layer and the free polymer matrix, which is brittle. The energy dissipation mechanism is the energy necessary for the redispersion of the flocculated system. The crack propagation at the brittle interface, between the non-adsorbed polymer matrix and the adsorbed matrix, allows the

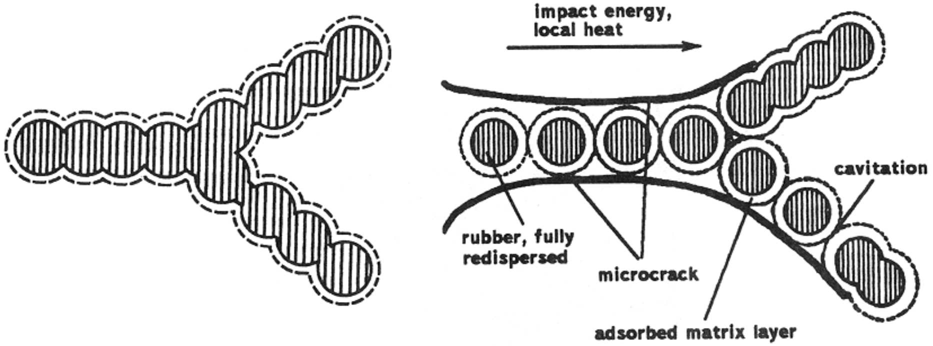

Figure 8.5. Fracture mechanism and energy dissipation according to Wessling. The flocculated rubber network is becoming redispersed by the impact energy; the crack is propagating at the interface between free matrix and adsorbed polymer matrix layer; cavitation occurs at the point where redispersion begins. [Adapted by permission from B. Wessling, *4th Eur. Conf. Polym. Blends*, Capri, 1993]

crack always to find an new adsorbed polymer layer, which might be able to redisperse a new portion of the flocculated chain. As Wessling states, it is important that crack propagation and energy dissipation are based on changes within continuous dissipative structures. It seems probable that the analogous mechanism may be used to describe the fracture of polymers filled with particulate fillers.

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EPILOGUE

“There are many truths and often one contradicts another. It is necessary to understand and accept... The truths have been dying..” These words belong to the great Russian poet and writer Valery Briusov (1870-1924). We cannot help but accept this statement, which explains many possible contradictions in approaches to reinforced polymer systems. In saying good-bye to the reader, the author would like to recall some more of Briusov’s words: “Only truth, in which one may doubt, is valuable.” Maybe this opens new Rubicons for all of us?

NOMENCLATURE

α	conversion degree; segregation degree; thermal expansion coefficient; deformation; half angle of grove
α^*	experimental value of expansion coefficient of filled polymer
α_1	thermal expansion coefficient above T_g
α_g	thermal expansion coefficient below T_g
β	expansion coefficient of coil, Cole-Cole parameter; wavenumber
Γ	adsorption; amount of polymer adsorbed in segment unit; amount of vapor sorbed at pressure P
γ	surface tension; dimensionless surface concentration of polymer
γ_l	surface tension of liquid
γ_{12}, γ_{sL}	interfacial tension
γ_c	critical surface tension of wetting
γ_i	mean deformation
γ_m	surface tension
γ_s	surface tension of filler; surface tension of solid
δ	solubility parameter; thickness of the surface or interphase layer; angle of mechanical or dielectric losses; half-thickness of interlayer between two particles
δ_A, δ_B	solubility parameters
$\langle\delta_m\rangle$	mean maximum thickness layer
$\tan\delta$	mechanical loss tangent
ε	dielectric permeability; strain; energy of the chain attachment to the surface; elongation
ε_c	deformation of filled specimen
ε_i	deformation of interphase layer
ε''_{md}	maximum energy of the dense part
ε''_{ml}	maximum energy of the loose part
η	viscosity
η_1, η_2	parameters of adhesion
η_0	initial viscosity
$[\eta]$	intrinsic viscosity

$[\eta]^{**}$	intrinsic viscosity corresponding to a limit of molecular mass M^{**}
Θ	contact angle
θ	temperature; coverage of the surface on adsorption; angle of incidence
θ_o	surface coverage by solvent molecules
θ_{ex}^{p}	excess amount of adsorbed polymer expressed as a number of equivalent monolayers
λ	wavelength; parameter of Takayanagi model
λ_{fi}	hydrostatic pressure at filler-interlayer interface
λ_{im}	hydrostatic pressure at interlayer-matrix interface
λ_{opt}	optimum spinodal decomposition wavelength
λ_s	model parameter characterizing the size of the surface layer
μ	chemical potential; Poisson ratio; parameter characterizing central part of profile
μ_c	Poisson ratio for isotropic heterogeneous composition
$\mu_f(r^*)$	chemical potential of bound polymer
μ_i	chemical potential
μ_p	chemical potential of free polymer
ν	crosslink density; fraction of polymer in the surface layer
ν_1	frequency of bond formation
ν_2	frequency of bond degradation
ν_h	molar volume of holes
$\nu_{h,o}$	molar hole volume in unfilled polymer
$<\nu>$	mean number of bound segments
ξ	screening length
ξ_b	correlation length
ξ_{fi}	composite strain
ρ	density; electron density
ρ'	mean density
ρ_d	density of disordered regions in filled semi-crystalline polymer
ρ_o	density of disordered regions in bulk
ρ_p	density of polymer
ρ_s	density of surface layer; density of disordered regions in

	surface layer
$\rho'(x)$	local density
σ	stress; interfacial tension; flexibility parameter; free surface energy; interfacial energy
σ_a	adhesion strength
σ_f	critical stress of fracture
$\sigma_{o\,dist}$	disturbing stress
σ_p	tensile strength
τ	average relaxation time; shear rate; average aggregate size; infinite shear stress; shear stress
Φ	volume fraction of polymer
Φ^*	volume fraction of polymer in solution bulk
Φ_1	volume fraction of polymer in the adsorption layer
Φ_s	fraction of polymer in contact with surface
Φ_1^o	volume fraction of solvent in the adsorption layer
Φ_*^o	volume fraction of solvent in solution
Φ_v	viscoelastic loss function
ϕ	concentration of a polymer in solution; parameter of Takayanagi model; parameter of Girifalko-Good equation
ϕ^*	crossover concentration in solution
ϕ_F	volume fraction of filler
ϕ_f	filler concentration
$\phi(z)$	function of concentration profile
ϕ_x	filler concentration
φ	volume fraction; volume fraction of filler
$\varphi_{A\cdot}, \varphi_{B\cdot}$	volume fractions of components which behave like continuous media
$\varphi_{A\perp}, \varphi_{B\perp}$	volume fractions of components which behave as dispersed phase
φ_{crit}	critical fraction of filler
φ_f	unoccupied volume available for polymer
φ_i	volume fraction of chain
φ_M	volume fraction of filler at maximum dense packing
φ_m	limiting packing density; limiting loading; maximum volume fraction of filler particles

χ	thermodynamic interaction parameter
χ_{AB}	thermodynamic interaction parameter between two polymers
χ_S	polymer-solid thermodynamic interaction parameter
χ_s	parameter characterizing total change of enthalpy
χ_c^{do}	adsorption energy parameter for adsorption of displacer from solvent
χ_c^{pd}	adsorption energy parameter for adsorption of polymer from displacer
χ_c^{po}	adsorption energy parameter for adsorption of polymer from solvent
Ψ	energy of crack propagation; parameter of structural rearrangement
ω	frequency
ω_g	transition frequency
$\overline{\omega}_o$	specific adsorption frequency
A	adsorption; coverage of the surface; adhesion strength; density of deformation energy of lattice
A_{121}	parameter of intermolecular interaction
A_f	deformation of filled specimen
A_p	the amount of polymer adsorbed at concentration c
A_{ps}	the amount of polymer adsorbed at saturation
a	size of monomeric unit; cube linear dimension; activity
$\dot{a}$	rate of crack propagation
Δa	absolute deformation of cube
B	parameter of Vogel equation
b	effective length of segment
b_i	statistical segment length
C	concentration; fraction of long chains
C^*	critical crossover concentration
C^{**}	crossover concentration between semi-diluted and concentrated regimes
ΔC_0	change in heat capacity of glass transition temperature for unfilled polymer
C_1 and C_2	Mooney constants

C_B	concentration of solution
ΔC_c	change in heat capacity at glass transition temperature for filled polymer
C_β	average count for a great number of fracture regions
C_m	β-ray count for metal surface
C_n	β-ray count for adhesive surface
C_P	heat capacity
ΔC_p	difference of heat capacities of polymer in melt and glassy state
c	concentration
D	diffusion coefficient; particle diameter; thickness of adsorbed layer
D_A	differential enthalpy of adsorption
d	cubic lattice period
E	Young modulus; elastic modulus; field intensity
E_C	modulus of composite; cohesion energy; composite modulus
E_c	modulus of composite
E_f	modulus of filler
E_i	modulus of interphase
E_m	modulus of matrix
E_P	polymer modulus
E_p	modulus of unfilled polymer
E_x	composite modulus
F	Helmholz free energy; force; number of moles of filler
ΔF	free energy of activation
F_{12}	force of interaction
f	adsorption energy; form factor
f_G	fractional free volume
f_i	bond energy
G	Gibbs free energy; shear modulus, crystallization rate
G_2	free energy of sorption by filler
G_{AB}	free energy of mixing of two polymers
G_c	work of deformation; shear modulus; dynamic modulus of composite
G_{cryst}	rate of crystallization

G_e	limiting value of shear modulus
G_f	dynamic modulus of disperse phase
G'_f	real part of complex shear modulus of filler
G_m	dynamic modulus of matrix
G'_p	real part of complex shear modulus of polymer
G_R	spherulitic crystallization rate
$G(t)$	shear modulus at time t
ΔG	Gibbs free energy; change in free energy of formation of filled polymer
ΔG_1	change in free energy on independent sorption of solvent by free polymer
ΔG_2	change in free energy on independent sorption of solvent by filled polymer
ΔG_3	change in free energy of sorption by unbound polymer
ΔG_4	change in free energy associated with reduction of adhesion
ΔG_A, ΔG_B	free energies of mixing
ΔG_{mix}	Gibbs free energy of mixing
H	enthalpy; distribution function of relaxation times; sample thickness
ΔH^*	energy of single contact
ΔH_1	heat of interaction equilibrium of melt with solvent
ΔH_{23}	heat of wetting
ΔH^{AB}	enthalpy of acid-base interaction
H_b	boundary layer thickness
ΔH_c	configurational contribution
ΔH_g	heat of polymer transition from metastable state
ΔH_p	heat of interaction of equilibrium melt with solvent
ΔH_{po}	enthalphy of desolvation per molecule of adsorbed monomeric unit
ΔH_{pp}	energy of interaction of adsorbed polymer molecules
ΔH_{ps}	enthalpy of bonding per mole of monomeric units
ΔH_r	heat of mixing
ΔH_s	heat of interaction of filled polymer with solvent; heat of dissolution
ΔH_{so}	heat of wetting per mole of active sites

ΔH_v	contribution of volume change on mixing
h	film thickness
h_e	enthalpy term of interfacial energy
h_i	depth of groves
h^{**}	distance between chain ends at molecular mass, M^{**}
$<h^2>$	mean end-to-end distance
$<h^2>^{1/2}$	mean-square distance between chain-ends in non-ideal solvent
$<h_o>^2$	mean square distance between the chain-end for freely-joined chain
$<\bar{h}_0^2>^{1/2}$	mean-square distance between chain-ends in ideal solvent
$<\bar{h}_o^2>^{1/2}$	mean-square distance for model of freely-joined chain
$<h_\theta>^2$	mean square distance between the chain end in θ-solvent
$\bar{h}$	Planck constant
I_f	intensity of filler spectral lines
I_p	intensity of polymer spectral lines
K	bulk modulus; complex function of segment molecular mass; surface roughness coefficient
K_1	constant characterizing the interaction of polymer molecules with each other
K_p	rate of nuclei formation
L	distance between two filler particles; specimen length; average distance between filler particles; interface thickness
L_e	mean length of tails
L_r	specimen length at rupture; mean length of loops
L_o	initial length of specimen
L_t	mean length of trains
$<L>$	effective thickness of interlayer between two particles
l	length of deformation
M	molecular mass
M_C	critical molecular mass between entanglements
M_c	critical molecular mass
M_e	average molecular mass
M_m	molecular mass of monomeric unit
M_N	number average molecular mass

M_W	weight average molecular mass
M_Z	Z-average molecular mass
m	amount of polymer
m_i	relative length of chain
m_{il}	mass of constituent in lower phase
m_{iu}	mass of constituent in upper phase
m_T	total mass
N	polymerization degree; number of monomeric units of adsorbed molecules; total number of lattice sites
N′	number of adsorbed molecules
N^*	number of contacts of chain segments with active centers of the surface
N_A	Avogadro number
N_i	degree of polymerization
N_o'	number of adsorbed solvent molecules
N_R	number of spherulites in a volume unit
N_s	number of adsorption centers
n	number of surface sites covered by polymer segments
n_1	number of groves; refractive index of element; number of moles of polymer before filler incorporation
n_2	number of pores; refractive index of sample; number of moles of polymer not affected by filler
n_3	number of moles of polymer adsorbed on filler surface
P	pressure, polarizability
ΔP	depth of radiation penetration
P_0	pressure in bulk
P_b	number of segments connected with surface
P_d	number of segments in denser area; disjoining pressure
P_{dh}	excess of phase pressure in thin liquid film near the interface
P_l	number of segments in looser area
P_m	hydrostatic pressure
P_N	normal part of pressure
P_s	number of segments non-connected with surface
P_T	tangential part of pressure
p	fraction of bound segments; peeling force; fraction of polymer

	segments
$\overline{\overline{\Delta}}p^{2\prime}$	density variations
$\overline{\Delta}p^{2\prime\prime}$	electron density fluctuations
R	relative reinforcement
$2R(\beta)$	amplification factor
R_g	radius of inertia of Gaussian coil; size of macromolecular coil in melt
r	radius of particle; separation distance; radius of filler particle
r_1	rate of polymer adsorption
r_2	rate of polymer desorption
r_1^o	rate of solvent adsorption
r_2^o	rate of solvent desorption
r^*	radius of bound polymer
r_A, r_B	number of segments
r_f	radius of filled particle
r_o	radius of filler
S	entropy; specific area; contact area; spreading coefficient; adsorbent volume; interphase surface; surface available for interaction; entropy term of interfacial energy
S_0	specific surface of filler
S_h	entropy change relative to hole formation
S_m	enthalpy of melting
ΔS_m	entropy of melting
s_R	surface area of spherulite
S_t	unitary surface area of a true contact surface
T	temperature
T_2	temperature of the second order transition
T_G	glass transition temperature
T_{g1}	PBMA T_g
T_{g2}	epoxy resin T_g
T_{g12}	interphase region T_g
T_{gc}	glass transition of filled polymer
T_i^*	temperature reduction parameter
T_M	melting point
T_m	melting point

$T_{m(d)}$	melting point of crystal
$T_{m(\infty)}$	melting point of macrocrystal
T_m^o	equilibrium melting point
$\Delta T_{g\infty}$	maximum shift in T_g
T_{sp}	temperature at spinodal
T_β	specific temperature of secondary transition
t	time; time of contact
U	inner energy; activation energy
U_i	energy of bonds
U(r)	energy function
ΔU_s	enthalpy change due to adsorption
V	molar volume; total volume of system
V_a	specific volume of amorphous phase
V_{as}	specific volume of amorphous phase in surface layers
V_c	molar volume of polymer at T_g
V_s	specific volume of interphase
v	volume; excluded volume
v_f	specific volume of filler; volume fraction of filler
v_g	real volume
v_i	volume fraction of interlayer
v_m	volume fraction of matrix
v_o	specific volume of unfilled polymer; occupied volume
v_p	volume of unfilled polymer
$v_{p,f}$	volume of filled polymer
v_R	rate of radial growth of spherulite
v_r	volume of segment
v_s	specific volume of polymer in surface layer
v_∞	volume of at the most dense packing; equilibrium volume
v_β	specific volume of secondary transition
W	amount of filler by mass; energy of segment interaction
W_a	thermodynamic work of adhesion
W_{CA}, W_{CB}	cohesion energies
W_c	thermodynamic work of cohesion
W_{crit}	critical mass of filler
W_p	energy of viscoelastic losses

w	weight fraction
Z	coordination number; total number of surface contacts
Z'	total number of solvent contacts
Z_m	energetic term
X	crystallinity degree
x_1	average energy of a single bond
x/m	gain in weight due to vapor adsorption
ATR	attenuated total inner reflection
DSC	differential scanning calorimetry
ESR	electron spin resonance
IR	infrared
IRS	infrared spectroscopy
LCST	lower critical solution temperature
NMR	nuclear magnetic resonance
RTL	radio thermoluminescence
UCST	upper critical solution temperature
WLF	Williams-Landell-Ferry
EVC	copolymer of vinyl acetate and ethylene
IPN	interpenetrating polymer network
PBMA	poly(butyl methacrylate)
PCM	polymeric composite material
PDMS	poly(dimethyl siloxane)
PE	polyethylene
PEA	poly(ester acrylate)
PMMA	poly(methyl methacrylate)
PS	polystyrene
PU	polyurethane
PVA	poly(vinyl acetate)
PVC	poly(vinyl chloride)

Index