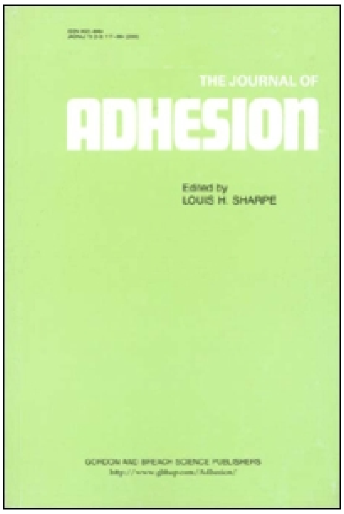

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Some Thoughts About Unsolved Physico-Chemical Problems of Composite Polymeric Materials

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INTRODUCTION

Substantial progress in understanding of the phenomena taking place at the interphase in composite polymeric materials has been made lately.[1,2] The production industry of polymeric composite materials, i.e. polymers with dispersed mineral fillers and reinforced plastics with organic and inorganic fibers is nowadays very highly developed. Advent of the new types of reinforcing fibers—carbon, boron, high-modulus and heat-stable synthetic fibers—along with successes of chemistry in the development of new resins has made possible the solution of a number of important technical problems. However, as a rule, these solutions are not based on clearly established mechanisms of the processes taking place at the interphase between the two components, although these phenomena determine the most important physical and mechanical properties of the compositions, and although the interphase is the region whose properties in large measure control the properties of the material. Despite a great number of works in this field there still exist many unsolved problems. Discussion of some of them is the subject of the present paper.

1. ADSORPTION

It is common knowledge that properties of composite materials are determined by adhesion at the interphase, this adhesion being essential for formation of strong bonds at the interphase.[3] Adhesion is related to the phenomenon of adsorption of polymers on solid surfaces, be they fillers of mineral or polymeric nature (for instance, a reinforcing synthetic fiber). Basic regularities of adsorption of polymers on solid surfaces have been studied in detail.[4] It was found that the surface of a solid during adsorption binds both isolated macromolecules and molecular aggregates or supermolecular formations,[5] present in concentrated solutions, liquid resins and oligomers. The binding conditions of the aggregates and their structure determine the properties and structure of the surface layer of the polymer on the solid surface.[6] Structure of the surface or adsorption layers, formed during formation of the composition, in its turn determines adhesive joint strength, since adhesive joint failure may start just in this border layer.

Though contemporary concepts of adsorption from solutions enable properties of adsorbed layers to be regulated to some extent, this cannot be said about adsorption taking place in the systems containing no solvent. To date, precisely these systems are of particular interest. In preparing filled plastics by any of the known methods, wetting of the surface with the melt and adsorption of the polymer on the surface follows mixing of the components. Such questions concerning adsorption in the absence of the solvent, i.e. how does binding of molecules by the surface proceed from the melt (not from the solution) and what are the peculiarities of the absorbed layer being formed, have not yet been elucidated. We have obtained some data on adsorption from oligomers that enable us to estimate the thickness of the adsorbed layer.[5] Our estimate was based on the apparent volume increase of the disperse phase due to effective growth of disperse particles caused by adsorption; this made calculation of thickness of the adsorbed layer possible. But such problems as adsorption under the conditions, and structure of the adsorbed layers being formed, remain completely undecided. Adsorption from melts, unlike that from solutions, will be possibly determined not only by the melt structure, but by the influence of the surface on the structure formation in the contact boundary area between the melt and the solid surface as well. It means that the influence of the surface can initially change the structure of the melt to produce intermolecular formations and then the surface will adsorb the supermolecular formations. Both processes can run simultaneously. In some way or other one should look for the difference in conditions of formation of the adsorbed layers from the melt and in the structure of the adsorbed layers.

2. STRUCTURE OF THE ADSORPTION AND SURFACE LAYERS

Structure of the adsorption layer itself in any composition preparation technique is another problem to be solved. All the studies of filled systems that have been made before enable one to arrive at a conclusion, namely: under the influence of adsorption forces, the structure of the adsorbed and adjacent boundary layers differs from the structure of the bulk.[4,6] We will distinguish the surface layer, where some physical properties are changed as compared with bulk. The surface layer consists of two layers: the adsorption layer, where macromolecules interact directly with the surface, and the boundary layer, where there is no direct contact between macromolecules and surface; however, molecular properties are changed under the long-range action of the surface. For example, the binding of macromolecules into aggregates on the surface leads to the changes in properties in spite of the absence of direct interaction of all the molecules with the surface. A number of works clearly specify these differences. But only recently some works showing essential structural heterogeneity of the border layer, i.e. different properties at different distances from the surface, have been published. It has been established that in heterogeneous polymeric systems, including all composite materials, heterogeneities of various levels arise due to the effect of the surface on the molecular mobility, molecular packing, structure formation and progress of curing reactions.[7]

Heterogeneity at the molecular level is connected with restriction of the number of conformations in the surface layer as a result of adsorptive interaction with the surface, and reduction of the number of possible conformations a macromolecule can assume in the boundary layer. Reduction of the molecular mobility in the boundary layers causes changes in relaxation properties and in the packing conditions of macromolecules with respect to volume.[6]

It is, however, essential that according to recent studies the changes are non-monotonic with growing distance from the surface;[8] the pattern of the change could possibly be expressed by a function of a sequence of variables including solid free surface energy, cohesion energy of polymer and chain flexibility.

The primary problem to be solved in this field is to discover correlations between molecular chain parameters, and form up the function of dependence of properties of the boundary layer on the distance from the surface. Here we have an example. It has been fairly well established that glass transition temperature of polymers is a function of flexibility of the chain.[9] Restriction of molecular mobility imposed by the interaction of macromolecules with a surface causes the glass-transition temperature to rise. This interaction is characterized by cohesive energy of the polymer, i.e. by the degree of intermolecular interaction and by the free surface energy of the solid. A phenomenological theory of glass-transition of filled polymers has been developed.[10,11] But a theory quantitatively connecting the change in properties caused by surface influence with molecular characteristics of the surface and molecular parameters of the polymeric chain still does not exist.

In addition to this, the mechanism of the influence of the surface on the layers lying deep and having no direct contact with the surface (transition of influence of the surface from adsorption to the boundary layers) remains unclear. All this boils down to one conclusion: up to now we have collected only a certain quantity of experimentally obtained facts, but a physically substantiated theory is not yet available.

Let us return to the question of structural heterogeneity of polymers, brought about by influence of the surface. Molecular heterogeneity inevitably involves heterogeneity at the supermolecular level, since not isolated but interacting macromolecules (macromolecular aggregates) are concerned. The question of influence of the surface on crystallization in the boundary layers, and formation of the supermolecular structures in amorphous, cross-linked and crystalline systems has been thoroughly enough covered in the literature.[11,12] The studies prove the general thesis of the long-range influence of the surface on structure formation and development of the heterogeneous structure, which is different at various distances from the surface.

These problems, however, have just been posed and in our opinion they cannot be solved with the present level of knowledge in the field. One thing is certain: although the presence of supermolecular structures in amorphous polymers is very probable[13] in spite of some doubts,[14] and although they have been thoroughly studied in crystalline polymers, a quantitative theory linking mechanical properties of polymers with morphology is not available. But theories linking mechanical properties and failure processes with more simple and available parameters—molecular chain characteristics, degree of crystallinity, density, free volume, etc., do exist. Therefore we consider that although study of the morphology of compositional materials is very essential, it cannot answer questions related to establishment of a quantitative relationship between structure and properties. The next heterogeneity level in composite materials—chemical heterogeneity—occurs when curing takes place in the presence of a filler and when, as a result of adsorptive interaction between components of the system and the surface, kinetic or stoichiometric[7,11,15] conditions of the reaction are changed. These changes occur in different ways, depending on the distance from the surface. As a result, the surface layer can have in the case of linear polymer different molecular-mass distribution, and in the case of cross-linked polymer different effective network density depending on enrichment or depletion of the adsorbed layer with the cross-linking agent, or of the component which is principally adsorbed on the surface. Besides, it should be borne in mind that in the case of complex reactions the surface can affect the relative rates of primary and secondary reactions.

We have briefly summarized here the main results obtained from reactions of polymer synthesis in the presence of fillers. It is seen that chemical heterogeneity has been established only qualitatively on some examples, and kinetic models and schemes, making allowance for adsorption influence on kinetic parameters or stoichiometry of the process, have not been worked out.

Meanwhile, it is quite obvious that the presence of chemical heterogeneity causes the appearance of molecular and supermolecular heterogeneities, which were mentioned above. Consequently, the problem of kinetics and mechanism of reaction in the presence of the surface is one of the most urgent *for the creation of composite materials.*

3. EQUILIBRIUM OF STRUCTURE OF COMPOSITE MATERIALS

The main concepts, cited above, refer equally to systems containing mineral fillers or fibers, as to systems with polymeric fillers, including reinforcing synthetic fibers. In the latter case the principal distinction from the systems containing mineral fillers consists in the existence of a mutual influence of the components on the properties of each other's adjacent boundary layers. *Now we shall deal with another unsolved problem: thermodynamic non-equilibrium in composite materials.*

Thermodynamic theory of binary systems has been developed more widely for a systems of the polymer–polymer type (with polymer fillers) than for the systems with mineral fillers, because of the problems posed by the thermodynamic compatibility of polymers.[16,17] Still, let us begin discussing the problem with systems containing mineral fillers. 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 lower equilibrium. Though it is known that in *glass-like polymers a state of true thermodynamic equilibrium does not* exist, deviations from the equilibrium or quasi-equilibrium state may be of great importance for practical application of composite materials. Therefore, evaluation of the degree of non-equilibrium and the finding of ways to take composite materials to a more equilibrated state is very important.

It should also be remembered that for the degree of non-equilibrium as well as for any other characteristic, there should exist a certain gradient of its value normal to the surface.

At present, three methods are chiefly used to increase the degree of equilibrium, the most common being prolonged thermal treatment, addition *of plasticizers, and treatment of the surfaces of the fillers with agents,* chemically binding with them and producing a plasticizing effect only in the boundary layer, i.e. in the region of the highest non-equilibrium.[18] In terms of composite materials the latter method is the most promising, if the treatment of the filler does not reduce adhesion to it. Thermal treatment, as a rule, does not eliminate the non-equilibrium state in the boundary layer, and plasticizer concentrates chiefly at the polymer-filler interface, affecting properties of the entire system and reducing adhesive interaction. Nowadays, a generally accepted approach to evaluation of non-equilibrium of the system is not available and thermodynamic methods of evaluation are not practically used. No data connecting non-equilibrium with molecular parameters of the system has been reported. As to the systems of polymer–polymer type, kinetic factors and the absence of true thermodynamic compatibility lead to development of metastable states and in some cases to formation of thermodynamically stable disperse colloid systems.[19] For such systems the formation of transition layers is typical, this layer essentially specifying the properties of the system. Formation of the transition layer may be caused by incomplete separation of the system due to kinetic factors or it may be the result of induced emulsification taking place during blending of the polymers, the surface tensions of which are usually alike and the interfacial tensions are very low.[19] The transition layer may be formed through the inhibitive effect of one component on structure formation of the other in the contact region. In all cases, however, the system is thermodynamically incompatible, since the equilibrium state corresponds to the state of complete phase separation of the system without a transition region being formed. This situation can, in principle, be encountered in composite materials, but in reality it is observed very rarely. Thus the problem of evaluation of the thermodynamic state of such systems is particularly essential.

4. ADHESION AND ADHESIVE STRENGTH

Development of a physically substantiated theory of adhesion of polymers to solids is aimed at finding ways of increasing strength of adhesive bonds.[20] In most cases, however, adhesion, a physical phenomenon, considered in terms of interfacial interaction between two components, is viewed as being identical with adhesive strength which should be considered in terms of the general theory of strength of solids.[21]

Adhesion is just the first step in formation of the adhesive joint. This step, closely connected with wetting[22,23] and adsorption at the interface can be considered correctly on the basis of thermodynamic processes at the interface. In this case, the thermodynamic work of adhesion, which can strictly be determined only for the case of adhesion of liquids to solids, is an equilibrium value, characterizing the change of free energy during adhesive bond formation. Evaluation of thermodynamic work of adhesion for the case of two solids, one of them a polymer, can be done only on some assumptions, as direct determination of the surface energy of solids is still a problem to be solved and the notion of surface tension itself, developed for liquids, cannot yet be physically substantiated for solids.[23,24] This follows, in particular, from the fact that cohesive energy, which equals twice the value of surface tension for liquids, will be a very small value for polymers, if existing methods of the surface tension evaluation are to be used.

But general discussion of the problem in terms of thermodynamics leads to a conclusion that in the case of an impermeable interface, the thermodynamic work of adhesion equals at least the cohesive energy of that component which possesses the lower cohesion energy.[21]

As follows from purely thermodynamic premises, increase of the work of adhesion can be reached through raising the energy of intermolecular interaction in the adhesive which is, in general, in agreement with available experimental data. Thus, one of the ways of increasing adhesive joint strength is to increase the cohesive strength of the adhesive. Simultaneously, the conclusion can be drawn that there is no strict relation between thermodynamic work of adhesion and adhesive strength because in the first case we deal with a thermodynamic equilibrium state, and in the second case with a non-equilibrium failure process. Now we can expect only some correlations, but the failure process itself should be considered within the framework of a statistical theory of strength. Since, in most cases where the adhesive interaction between the components is rather intensive the failure process is chiefly cohesive in nature, increase of the adhesive strength can be reached through regulation of structure of the surface layers and removal of the weak spots where failure begins.[20,25] The unsolved problem remains the same—to forecast the adhesive interaction pattern or even ways to control it. The latter may be achieved by introducing into adhesives some reactive surface-active agents.[26] In this connection it is worthwhile to outline the common practice of using coupling agents leading to the formation of chemical bonds between the surface of an inorganic fiber and a resin.[18]

Notwithstanding the fact that applying coupling agents is so widely used in technology and is very useful, the question of the role of chemical binding of the polymer with the fiber through coupling agents remains open in many respects. Thus far, no quantitative evaluation of the fraction of chemical bonds developing between a coupling agent applied on the surface and a polymer for any system has been done.[27] Moreover, there is no exact quantitative evaluation of the fraction of the applied agent chemically bonded to the fiber. Model experiments yield contradicting results. Furthermore, if for any system the number of chemical bonds between fiber coupling agent and polymer was quantitatively established, it is unclear how these chemical bonds affect strength and other properties. One can expect that some optimum number of such strong bonds should exist, to be most effective. Above or below this optimum, adhesive characteristics will deteriorate because of small number of points of contact, high inner tensions, increased rigidity of chemically bonded chains and analogous effects. On the other hand, other coupling agents are well known which are not inclined to form chemical bonds with the surface, but which strongly affect properties of the system. Here we have an example: in Reference 28 it has been shown that use of vinyl-silane treated kaolin as a filler for polyethylene (PE), essentially improves properties of the composition although silane, a typical coupling agent for polymerizable systems, cannot form chemical bonds with PE. One has also to establish a relation on the one hand between the number of reactive groups of coupling agent on the surface (their reactivity being evidently different from that in the volume because of steric limitations) and on the other hand the density of the polymer network in the surface layer which can vary both due to the above reasons and to the cross-linking with the surface. As to reinforcement by chemical fibers, the picture is utterly different. Chemical fibers and polymer binders possess similar surface energies (surface tension) and belong to materials with low surface energy. Adhesive interaction is realized both by adsorption and diffusion mechanisms. As was shown in Reference 11, the boundary layers of the systems reinforced with chemical fibers experience marked changes of structure and morphology of the fiber as a result of formation conditions of the system and influence of the components on each other. The clear boundary of the fiber vanishes and develops a transition layer, which can cause formation of adhesive bonds of diffused or purely mechanical type. In curing binders in the presence of chemical fibers, especially those which are polymerizable, the possibility of formation of chemical bonds between the fiber and the polymer either due to chain transfer reaction of macromolecules on the fiber or due to interaction of some groups of the macromolecules of the filler with functional groups of polymers of the polycondensed type, should not be overlooked.

The question of grafting of polymers to the reinforcing fibers has been under consideration for a long time, but practically it is far from being solved, since the role of these chemical processes in obtaining the usual systems reinforced with chemical fibers has been studied poorly. Adhesion of binders to fibers, such as carbon, boron and some others has been studied, inadequately, therefore no practical recommendations can be given.

5. "WEAK" BOUNDARY LAYERS

Now in short about this problem. It has been formulated by Bikerman[20,25,29,30] who has shown by his studies that failure of the adhesive joint is in most cases cohesive because of formation of weak boundary layers. Bikerman studied mainly technological flaws, i.e. those whose occurrence is related to particular formation conditions of an adhesive joint. But what has been said above about interphase phenomena in the boundary and surface layers enables us to consider physical processes, resulting from existence of the interphase and not related to technological peculiarities, as one of the main reasons for the formation of weak boundary layers. Formation of various levels of heterogeneity in composite materials[7] is an important reason for appearance of weak boundary layers which, unlike technological reasons, can not be obviated and should always be taken into account in studying processes of formation of adhesive joints.

Such weak spots can be caused both by purely technological factors, i.e. circumstances of preparing the adhesive joint, and by physical and chemical factors. Among the latter, the most important role is played by the wetting of the surface with an adhesive and the effect of the surface on the adhesive curing process in a thin layer and on the physico-chemical properties of thin adhesive films.[30]

These processes result in formation of microheterogeneities in the surface layers at the molecular, supermolecular and chemical levels and can be beneficial or detrimental to formation of a strong, flaw-free joint. The above-discussed concepts are useful in most cases also to the matter of adhesive interaction between two polymers, where thermodynamic incompatibility of the components determines the usual physical character of interaction at the interphase, and formation of the transition layer is caused either by the effect of a component on the properties of the boundary layer of the other component, or by thermodynamic or other physical factors.

6. ALLOYING OF POLYMERS THROUGH SMALL ADDITIVES

Much attention is being paid lately to properties of polymers modified through small additions of other polymers. In a great number of works it has been shown, on the example of amorphous and crystalline linear polymers, that addition of small amounts of other polymers in the absence of thermodynamic compatibility or cocrystallization essentially changes the entire complex of physical and mechanical properties of polymers both in the solid and molten state.

Attempts are being made to interpret the mechanism of the alloying effect of various additives in terms of colloid–chemical concepts.[19] These concepts are as follows: with small additives the interphase is a region where adsorption of low-molecular fractions of the bulk polymer takes place and, as a result, the entire volume of the material will be enriched with fractions of higher molecular weight with high values of surface tension.[31,32] As is known from thermodynamics the cohesive energy equals twice the value of surface tension. Hence enrichment of the volume with fractions of high surface tension causes, in terms of thermodynamics, increase of cohesive energy. The same effect can be caused by very small (up to 2%) additions of a filler.

Consequently, colloid-chemical processes provide explanation for the mechanism of the alloying effect. Another explanation can be linked with redistribution within the system because of incompatibility of free volume and appearance of "excess" free volume in the interphase. Anomalies observed in behaviour of the systems filled with small quantities of mineral fillers enable us to consider that there must be a common mechanism of the effect of small additives (of polymer or nonpolymer nature) on properties of polymers.

A general theory of the phenomenon is not yet available; what is required are more experimental investigations to gather evidence (which is scanty) and development of general theoretical concepts.

7. SURFACE TENSION OF POLYMERS

We have many times here dealt with the surface tension of polymers, which is essential from the point of view of adhesion of polymers to one another, wetting, equilibrium thermodynamically established work of adhesion and so on.

The problem of thermodynamic establishment of the surface tension of polymers or their surface energy is also very important for understanding the mechanism of formation of transition layers.[33]

The problem will not be discussed now, for it has been covered in detail elsewhere.[24] We shall only note related, undecided problems. While the problem of theoretical description of surface tension of polymeric solutions can still be regarded as one based on contemporary concepts of properties of polymeric mixtures, theoretical concepts in the field of surface tension of solid polymers are rather scarce and are not based on sufficient theoretical and structural substantiation. Determination of surface tension is based on the approaches applicable both to polymers and nonpolymers, as to common organic glasses. Specificity of structure of polymeric bodies and macromolecules has not yet been taken into account.

One can note at least two conditions that will substantially determine surface properties of polymers. They are—flexibility of the chain formed of links containing both polar and nonpolar groups, and polydispersity. The first factor should, according to H. Frisch,[33] lead to change of the configurational pattern of macromolecules in the surface layer and thus to change its density, expansion coefficient, etc.[33] These effects may cause substantial non-uniformity of the field of surface forces and show inapplicability of the simple hypothesis of additivity of polar and dispersion components. This same factor may cause changes of the surface properties at various purely physical interactions. Polydispersity of polymers with equal average molecular mass will also contribute much to the value of surface tension because of differences in surface activity and surface tension of separate fractions. It will equally affect surface tension of polymeric solutions. Thus in an elaborately developed thermodynamic theory of polymeric solutions and solids there exists a deficiency concerning thermodynamics of surface phenomena. Of the latter there has been developed only a theory of adsorption of polymers from solutions and adsorption by polymers.[4,5] Intense development of physical chemistry of composite polymeric materials, whose main properties depend on the effects taking place at an interphase, will hopefully stimulate progress in the study of surface tension of polymers and related problems.

Considerations reported in the present paper show that the field under discussion has its achievements and enables many various phenomena to be qualitatively explained.

Unfortunately the existing concepts of some mechanisms of the phenomena do not always agree, and sometimes they contradict each other.

As a Russian poet Valery Brjusov said, "Truths are numerous and often they contradict each other". The task we are facing is to find common mechanisms and ways of quantitative description of the phenomena, whose mechanism is qualitatively quite clear.

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