

ROLE OF INTERFACIAL PHENOMENA IN THE FORMATION OF MICRO- AND MACRO- HETEROGENEITIES IN MULTICOMPONENT POLYMER SYSTEMS

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ABSTRACT

Properties of multicomponent polymer systems (filled polymers, polymer blends etc.) are strongly dependent on interfacial interactions. These interactions may be of physical or chemical nature. For such systems two cases are discussed: (1) the phase boundary is impermeable for polymer (interface solid/polymer), and (2) the boundary is permeable (interface between two incompatible polymers). In the first case at the interface two layers are present, namely an adsorption one where macromolecular segments interact directly with the surface, and a surface layer, including the adsorption layer, the properties of which are changed non-monotonically as a result of the surface forces compared to the properties in bulk. In the latter case, an intermediate layer between the two phases is formed owing to local diffusion.

The study of the adsorption interaction at the impermeable boundary by means of i.r. spectroscopy, e.s.r., n.m.r., electron microscopy, mechanical spectroscopy and thermodynamics shows that an essential change in the surface layer structure takes place as a result of the restriction of the molecular motion, the depth of surface influence being dependent on the interaction energy at the interface and on the polymer energy of cohesion. Non-monotonic changes in properties at different distances from the phase boundary lead to microheterogeneity (difference in density, ratio of amorphous and crystalline parts, transition points etc.). Due to microheterogeneity on the molecular level, the macroheterogeneity on the molecular level appears, containing different types of supermolecular structures and their packing perpendicular to the surface. When the polymer system is formed from monomeric compounds in the presence of the solid phase, the kinetic conditions of reaction and network formation are changed due to adsorption effects and a chemical heterogeneity arises in the system in addition to the structural heterogeneity. The character and distribution of heterogeneities depend on the properties under consideration and on the behaviour of segments or macromolecules as independent kinetic units.

In polymer blends the interaction at the phase boundary is closely connected with the thermodynamic compatibility of components. The local diffusion of segments in the phase boundary region leads to intermediate layer formation with a thickness depending on the segment size and thermodynamic interaction. The structure and properties of the interphase layers depend on the ratio of

the components in the system and their phase condition; all these factors lead to the appearance of different types of micro- and macroheterogeneities, when true compatibility is absent. In the polymer-polymer systems the formation of two different surface layers as a result of interphase interaction may take place; their properties are different from those of each component. In this case, the formation of an additional micro- and macroheterogeneity is connected with the mutual influence of components on their properties in the interphase region. These statements were confirmed in the course of investigation of polymers reinforced with synthetic fibres and interpenetrating networks where the network matrix influences the second network formation similarly to the influence of the filler surface.

Properties of multicomponent polymer systems (filled with mineral and polymeric fillers, polymer blends and other composite materials) are strongly dependent on the interfacial interactions. These interactions cause the appearance of some kind of heterogeneity on different levels. When discussing this problem, we exclude from consideration that type of heterogeneity which is connected with the incorporation into the polymer of some fillers or other polymers as a second phase, because these inclusions have their own physical and chemical properties independent of the presence of the first phase.

In this paper we should like to discuss the appearance of those types of micro and macroheterogeneities which are connected with the differences in the material structure on molecular or chemical levels (microheterogeneity) and with the differences in the supermolecular organization (macroheterogeneity) and in the character and distribution of supermolecular structures.

That is just what we have in mind, speaking about heterogeneity in multicomponent polymer systems. This is the heterogeneity which depends on the interface phenomena.

In the systems under consideration the interface phenomena can be of physical or chemical nature. For such systems two cases will be discussed. First the phase boundary is impermeable for polymer molecules (for example, interface solid-polymer in filled polymers with mineral fillers) and, secondly, partially permeable boundary between two incompatible polymers. In the first case at the interface two layers appear, an adsorption layer where macromolecular segments interact directly with the surface, and the interphase or surface layer, including the adsorption one, the properties of which are changed non-monotonically as a result of the surface forces, compared to the properties in bulk. This surface layer may be characterized by the effective thickness beyond which the deviation of the local properties from their values in bulk becomes inessential¹.

In the second case—for polymer blends and composite materials filled with polymeric fillers—an intermediate layer between two phases is formed owing to local diffusion and segmental solubility² and also due to the adsorption interaction.

Let us consider the role of interfacial phenomena at the impermeable phase boundary in the creation of micro- and macroheterogeneity in a multicomponent polymer system.

First of all we must note that the effective thickness is the value which depends on the properties under consideration and on the properties of segments

or macromolecules as independent kinetic units¹. Therefore the surface layer thickness determined by different methods with respect to different properties can be different. The first level of the microheterogeneity appears when some properties of the surface layer differ from the properties in bulk whereas other properties are the same.

The study of adsorption interaction at the impermeable boundary by means of i.r. spectroscopy, n.m.r., e.s.r., electron microscopy, mechanical spectroscopy and thermodynamics shows that there takes place an essential change in the surface layer structure as a result of molecular motion restrictions, the depth of surface influence being dependent on the interaction energy at the interface and the polymer energy of cohesion^{3, 4}. *Figure 1* shows

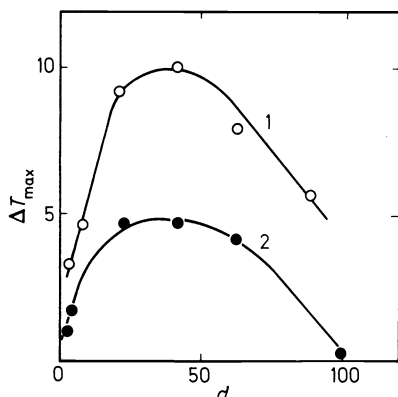
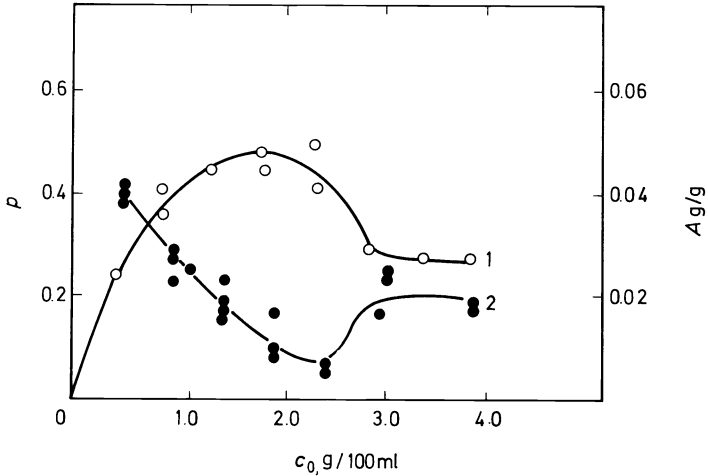


Figure 1. Dependence of shifts of maximum of temperature of relaxation in surface layers on the layer thickness (in comparative units of thickness). 1—epoxide resin, 2—polyurethane.

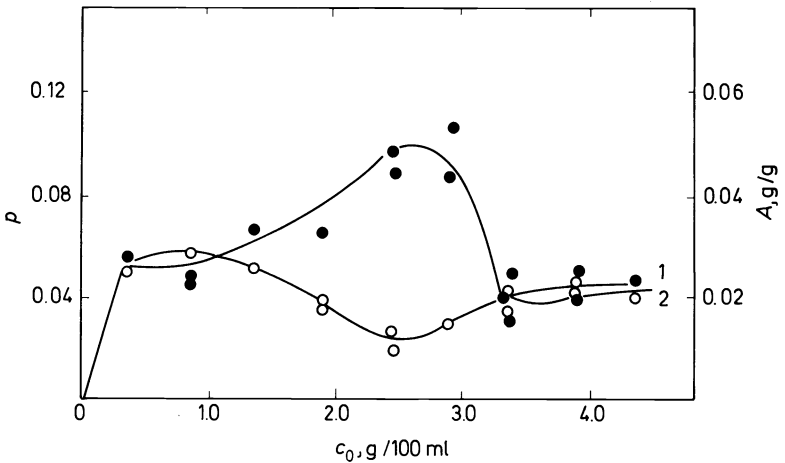
the dependence of the temperature shift of the maximum of dielectric losses, which characterizes the segmental mobility, on the adsorption layer thickness in comparison with volume. The data are given for epoxy resin and polyurethane. It is seen that the change in mobility is non-monotonic. We can explain these data if we suppose, in accordance with current theories, that for the small coverage of the surface, macromolecules form loops with unbonded segments extended into the solution. The interaction between such loops in the course of adsorption or increase in the adsorption layer thickness leads to an increase in intermolecular interactions in the layer and diminishes molecular mobility. Beyond the maximum point according to the ideas developed by us earlier, adsorption of molecular aggregates not of isolated chains takes place here. These aggregates interact with the surface by a smaller number of segments than in dilute solution and the molecular mobility increases again.

Analogous results showing the dependence of the glass temperature in the adsorption layer on its thickness have been found by means of gas chromatography from the temperature dependence of the retention volume. It was found also that in the adsorption layer more than one temperature transition can exist due to the essential microheterogeneity of the layer.

To prove this statement we have determined the fraction of the number of segments in the adsorption layer by means of i.r. spectroscopy for adsorption from solutions of different concentrations. It was shown that in the concentration range where the adsorption of aggregates begins (proved by the method of turbidity spectra) the fraction of the number of segments in the surface sharply decreases (*Figure 2*). This fraction is about 0.03–0.04 in comparison with 0.12–0.15 for adsorption from dilute solution. In this way



(a)



(b)

Figure 2. Adsorption isotherm (1) and fraction of number of segments p in the surface (2) for systems: (a) polycarbonate-dichloroethane-aerosil, (b) polyethylene-glycoladipinate-dichloroethane-aerosil at 20°C.

we can suppose that in the case of aggregate adsorption only a small fraction of segments of macromolecules coming into the aggregate interacts with the surface directly. As distinct from dilute solutions, where the fraction of bonded segments diminishes monotonically with increase in concentration in our case, the case of aggregate adsorption, the fraction of segments in the surface changes non-monotonically. Thus we can see that even in the adsorption layer we are dealing with a non-monotonic change in properties with the increase in the layer thickness. The restriction of mobility, imposed by the surface, determines the change in other properties of adsorption and

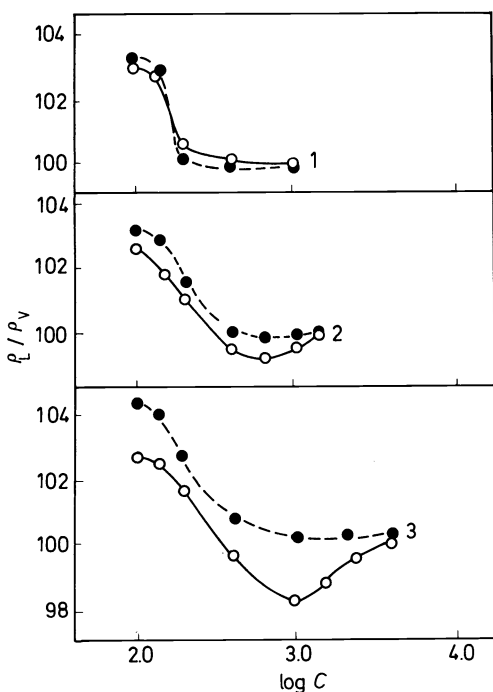


Figure 3. Ratio of densities in the surface layer ρ_s and in volume ρ_v as a function of the relative layer thickness $\log C$. Broken line—on the surface of polytetrafluoroethylene; solid line—on quartz; 1—polydimethylsiloxane, 2—polystyrene, 3—polymethylmethacrylate.

surface layers. The diminishing in the relaxation rate makes worse the molecular packing which also can be changed non-monotonically. These changes in molecular packing density can be evaluated by the molecular probe method and are determined by the nature of solid and energy cohesion density and flexibility of polymer chains. Figure 3 shows the change in molecular packing densities for these polymers on to two surfaces of high and low surface energy. Polymers were selected in such a way that two of them had an equal cohesion energy and different chain flexibility whereas another pair had

different cohesion energy at the same flexibility. (As a measure of flexibility we used the ratio of a mean square distance between the chain end in a theta solvent and in a freely joined chain.)

Figure 3 shows the ratio of the effective densities of the layer ρ_l and of the matrix ρ_v for different distances from the surface of high surface energy (quartz) and low energy (polytetrafluoroethylene). Here polystyrene (PS) and polymethylmethacrylate (PMMA) have the same flexibility, whereas PS and polydimethylsiloxane (PDMS) have the same cohesion energy. It is seen that for all polymers there is a typical increase in the density near the phase boundary independent of the nature of the surface. The difference in the surface influence on density is most pronounced for PMMA and least pronounced for PDMS. For flexible chains having a weak interaction with the solid surface, a monotonic decrease in density takes place, whereas for more rigid chains of great cohesion energy the character of the density change is more complicated. Here the region with higher density is replaced by a region with looser packing than in the bulk volume, the density of volume being achieved later. For surfaces with a low energy only decrease in density for all polymers is observed whereas for high energy surfaces the effect of loosening the packing takes place. The layer thickness where the surface influence is still noticeable is higher for the more rigid polymer with higher cohesion energy and is smallest for flexible chains with weak interaction. The data discussed above show that the properties of polymer layers change non-monotonically in the direction from the solid surface. This allowed the conclusion to be drawn about the arising of property microheterogeneity on the molecular level. The character of microheterogeneity and the distance from the surface, at which its influence is noticeable, are dependent on the cohesion energy of the polymer. Figure 4 shows an increase in the glass temperature on the surface layer as a function of the cohesion energy density. Earlier it was shown that the glass temperature of filled polymers may be described by the equation

$$T_g = T_{g,0} + \Delta T_v$$

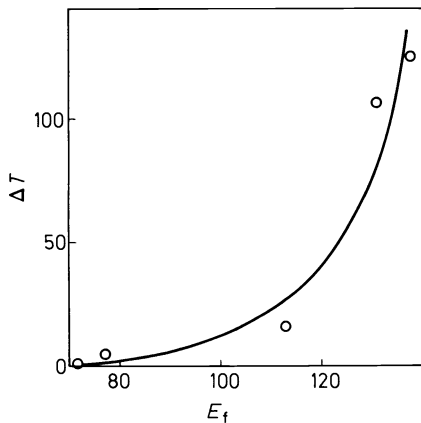


Figure 4. Dependence of ΔT on the cohesion energy E_f .

where $T_{g,0}$ is the initial glass temperature, ν is the fraction of polymer in the surface layer, ΔT is the increase in T_g at $\nu = 1$. The value ΔT , as seen from *Figure 4*, is dependent on cohesion energy⁴. For polymers with a low cohesion energy the formation of surface layer does not essentially influence their properties, and ΔT is small. When the intermolecular interaction in the polymer is strong enough, the transfer into the surface layer even of a small part of the polymer leads to a distinct change in glass temperature or molecular mobility. Thus the cohesion energy density determines the long range action of the surface on the molecular mobility. Where it is high, the influence of the surface due to strong intermolecular interaction is spread to more remote layers. In an opposite case such transfer of the surface influence is less probable. Thus the adsorption interaction at the phase boundary and the transfer of the influence from macromolecules which are directly bonded with the surface to more remote molecules give rise to a non-homogeneous change in properties or the microheterogeneity on the molecular level.

Really, if we consider the long range effect of the surface, we can see it is high enough. *Figure 5* shows the dependence of the effective network density for polyurethane on the layer thickness on surfaces of different nature⁵. In polyurethane systems the effective network density is determined mainly by physical interactions between polar groups, not by chemical crosslinks. It is seen that for a system with an essential contribution of physical crosslinks to network density the interaction with the surface leads to an increase in density (the molecular weight between crosslinks diminishes). This effect is dependent on the surface nature and disappears only at a distance from the surface of about 160 nm. Thus the microheterogeneity is pronounced on a large scale. It has been shown that for crystalline polymers the same adsorption effects may cause the inhibition of crystallization in the surface layers, the degree of crystallinity being dependent on the nature of the surface. In this way the degree of crystallinity in the surface layer can be changed; this also means a change in the structural microheterogeneity. Thus, the existence of phase boundary and interface phenomena determine the appearance and development of non-equilibrium states due to molecular motion restrictions and to the formation of a less perfect structure. Both types of microheterogeneity spread from the surface to different distances. It is worth noting that all these changes allow us to evaluate the effective thickness of the surface layer, the value of which depends on the property under consideration.

We have discussed above some cases of heterogeneities in systems where the solid phase was incorporated into the polymer in the melt or viscoelastic state. However, multicomponent polymer systems may be prepared in the course of hardening reactions in the presence of solid particles. These cases are of great practical importance. Here some additional effect of heterogeneity may take place. The highly developed surface of the solid may influence kinetic conditions of the reaction in the surface layer. This is especially important for network polymers which are formed from oligomers⁶.

The adsorption of oligomer molecules and growing chains change the conditions of chain growth and termination. This leads to the formation of an imperfect network structure with lower effective network density. It has been shown that for complicated reactions, for example, the reaction of polyurethane synthesis, it is possible to change the rates of primary and

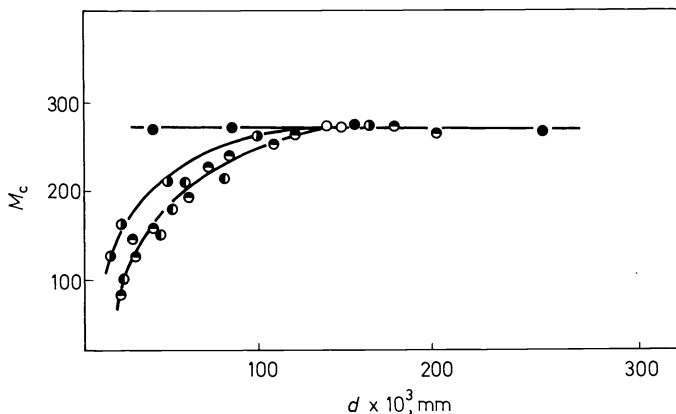


Figure 5. Dependence of molecular weight M_c between crosslinks for polyurethane coating on the distance from the surface for different surfaces.

secondary reactions, which determines the deviation of the chemical structure of the network in comparison with its volume. Due to adsorption interaction it is also possible that any part of reacting functional groups become inactive in reaction and the chemical structure changes again. We must also have in mind that in such systems the selective adsorption of a reaction component may take place and the difference in their distribution arises in the surface layer and volume. As a result the surface layer may be enriched or impoverished by some components, for example, by the crosslinking agent. Here again both kinetic conditions and stoichiometric conditions are changed. Depending on the real system, the more imperfect and rigid or elastic network can be formed at the interface. Thus, in parallel with heterogeneities on molecular and structure levels, an additional chemical heterogeneity arises, which in its turn leads to an additional heterogeneity of polymer on all levels and at different distances from the surface.

The next level of heterogeneity is the structure macroheterogeneity of the polymer matrix, or heterogeneity on the supermolecular level. When considering the properties of filled polymers it is necessary to take into account that interaction with the surface can not only isolate macromolecules but also their aggregates and other types of supermolecular structures. Their formation in the presence of solid at different distances from the surface also proceeds in a different way in comparison with volume. This process is also ruled by the cohesion energy of the polymer and by the free surface energy of the solid. It was established, for example, that in crosslinked amorphous polyurethanes the process of supermolecular structure formation is dependent on the surface nature up to distance from the surface 200 nm^5 . At the same time the size of globules and the character of their aggregation and distribution change also. For a crystalline solid the influence of the different crystal planes on the structure of the polymer⁷ has also been observed. The surface influences especially strongly the character of supermolecular structures in crystalline polymers. It has been discovered that the surface can increase

the crystallization rate of the polymer or hinder the process; it also influences the size distribution of some structures. Thus, due to the existence of an interface with the solid the conditions of supermolecular structure formation in the surface layer can be essentially changed and additional structural macroheterogeneity of the polymer appears. Now we do not know exactly what role is played by the different levels of heterogeneity in the formation of mechanical and other properties of multicomponent polymer systems; their influence on many characteristics is not known yet either. We can think that due to the microheterogeneity some properties can be improved. For example, the increase in the elasticity of a surface layer may lead to diminution in inner stresses. In general we can say that the optimal properties of a heterogeneous system can be achieved at a definite level of heterogeneity.

Let us now consider the formation of heterogeneity on micro- and macro-levels in polymer mixtures and blends. In these polymer-polymer systems the interfacial interaction is determined first of all by the thermodynamic compatibility of components.

The polymer nature of both components supposes that at the interface the diffusion of segments of one polymer into another can take place. This diffusion is determined by thermodynamic conditions and is one of the most important factors of the formation of the intermediate or interphase layer. It has been long known that in general polymers do not form compatible systems. That means the formation of two independent phases in the systems, as a result of phase separation. Such structural heterogeneity is a result of the method of producing the polymer blends (we shall not discuss here the exceptional cases of compatibility). The polymer blends can be of two types. In the first case it is a two-phase system where both phases are continuous and it is impossible to say which polymer can be considered as the matrix and which as the disperse phase. In another type one polymer may be considered as the polymer filler distributed in a definite way in the polymer matrix. However, in both cases the interfacial phenomena lead to the same results—to the appearance of micro- and macroheterogeneity of the types already discussed in connection with the problem of mineral fillers. The difference in the behaviour of these two systems is that in the latter case a mutual influence of both components on their behaviour in the intermediate layer is possible. Some experimental data obtained by us show that the more rigid polymer may act as the solid surface where the molecular motion restriction of the second component takes place. In this case for the second more flexible component all the types of heterogeneity discussed above can arise. When the hardening reaction proceeds in the presence of the second polymer phase, chemical interaction between two components may occur as a result of chain transfer for polymerization, or interaction with functional groups may take place for polycondensation. These chemical reactions lead to the formation of graft polymers in the intermediate layer and to the appearance of a new type of microheterogeneity on the molecular, chemical and structural levels. As in polymer-polymer systems the phase boundary can be considered to be permeable, the softer component may in its turn influence the structure of the adjacent surface layer of the more rigid components, the molecular mobility in which may be increased. In this way mutual influence of components on their surface layer in the intermediate

region takes place. It is of great importance especially in those cases where the process of polymer matrix formation proceeds in the presence of polymer filler. At the initial stages of such reaction the process is like the similar process in the presence of mineral fillers. However, both components of the reaction mixture and polymer formed influence the properties of polymer filler⁴.

We have also discovered the phenomenon of inversion of the mutual influence of the components which occurs when the polymer-filler at the initial reaction stages diminishes the molecular mobility of the forming polymer-matrix; after the end of the process the lessening of molecular motion in the polymer filler takes place under the influence of the hardened polymer matrix. In such complicated processes at the different stages of the reaction there appears the distribution of the intermediate structures and of the heterogeneities on different levels—molecular, chemical and super-molecular.

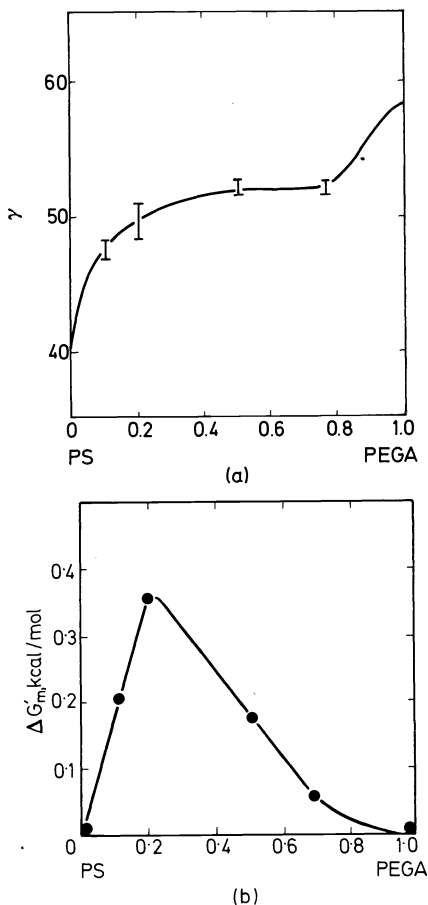


Figure 6. Dependence of surface tension γ (a) and excess free energy of mixing (b) for mixtures of polystyrene–polyethyleneglycoladipinate at different ratios of components.

Microheterogeneity may be also a consequence of the local diffusion of segments in the phase boundary regions and of the local solubility on the segmental level, following the ideas of Kulesnev and Voyutski². According to their point of view, polymers are incompatible in respect of macromolecules and compatible in respect of segments. The segmental solubility in the interphase region leads to differences in the properties of this region and constituent components. Thus of the many factors which lead to the additional heterogeneity, the segmental solubility is one of the most important. Another reason for intermediate layer formation can be the usual adsorption interaction of the component at the interface, that means the intermolecular interaction.

The thickness of the intermediate layer is dependent on the segment size and thermodynamic interaction. The structure and properties of the interphase layers depend on the ratios of the components in the system and their phase condition. All these factors lead to the appearance of different types of heterogeneity when true compatibility is absent. The local diffusion at the interface leads also to the microheterogeneity in the intermediate layer, because the component concentration in this layer will be gradually changed.

It is worth noting that in a wide range of factors which rule the appearance of heterogeneity, an essential role can be played by the difference in the surface activity of the components, or in their surface tension. In *Figure 6* the dependence of the surface tension of polymer blend on its composition can be seen. The initial polymers—polystyrene and PEGA (polyethyleneglycoladipinate)—have essentially different values of surface tension. It is interesting that there exists a sharp change in the blend surface tension in the range of composition where only a small amount of the second component is added. In the intermediate composition range there are no essential changes in surface tension. As in the case under consideration PS has a high surface activity, an enrichment of the blend surface layer with PS takes place. The analysis of experimental data and the determination of the excess free energy of mixing (*Figure 6*) for the blend of different compositions allowed the conclusion to be drawn that it is necessary to take into account another peculiarity of the interphase phenomena in polymer blends—a non-monotonic change in properties depending on the composition due to the difference in the surface activity. Seeing that in the blends the segregation into two phases usually takes place we can draw an important conclusion, namely, that the structure of the intermediate layer will also be changed in a non-monotonic manner. When we discuss the role of local solubility in the properties of the intermediate layer, we must bear in mind that this effect cannot explain high values of the layer thickness which can be determined experimentally. The real heterogeneity of the intermediate layer spreads to larger volumes than could be predicted, if we assume that that thickness determined by high solubility cannot be more than the segment length.

Let us consider now some results of our electron microscope investigation of heterogeneity genesis in the course of the intermediate layer formation. The mixtures of polystyrene (PS) and polyoxymethylene (POM), and polyethylene (PE) and polycaproamide (PA) were studied. Their morphology immediately after extrusion shows the existence of a sharp phase boundary between two phases [*Figure 7(a)*]. POM is distributed in the PS matrix in the

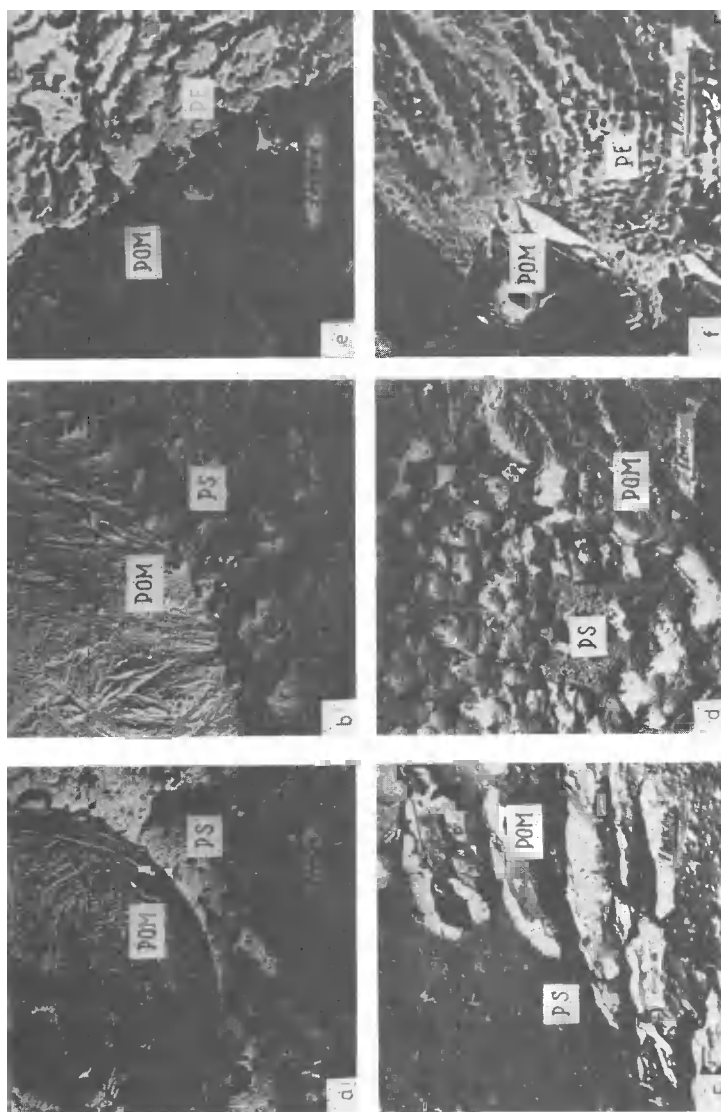


Figure 7. Changes of phase boundary between components in polymer blends as a result of heat treatment. Polyoxymethylene-polystyrene (a) initial, (b) after 30 min at 150°C, (c) 60 min and (d) 60 min at 190°C. Polyoxymethylene-polyethylene (e) initial, (f) 60 min at 150°C.

form of spherical inclusions, lamellar paracrystalline structure being seen on their surface. The main structural element of PS here is globular. After heat treatment at 150°C for 30 min the boundary between two components loses its sharpness and in different parts of the mixture we can see the structural elements of POM included into the PS matrix. A similar picture was observed also for the second system. The following heat treatment leads to the formation of the phase boundary in the form of a broken line with deep protuberance (Figure 8). Naturally, the intermediate layer which is formed

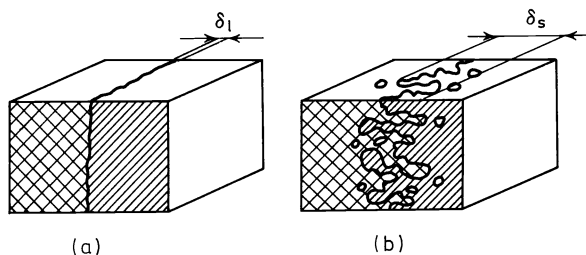


Figure 8. Intermediate layer in contact zone of polymer mixtures (a) initial state, (b) possible distortion as a result of heat treatment.

due to segmental solubility does not change, its configuration being changed (Figure 9). Experimental facts allowed a conclusion to be drawn that at higher temperatures where plastic deformation can be easily realized, the diffusion processes in the boundary region have different rates depending on the structure of contact regions, either amorphous or crystalline. The development of stresses in the contact zone may lead to the dislocation of some structural elements and their aggregates. Thus, in the boundary region there are such places where the local distortion of phase boundaries is possible due to their phase heterogeneity, and transfer of finite volumes of one polymer into interstructural regions of another polymer takes place. For this case we have proposed a scheme of the initial contact and its distortion in the course

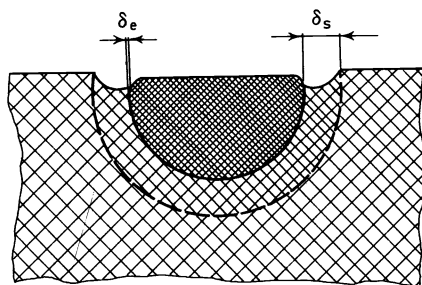


Figure 9. Scheme of connection between polymeric filler and polymer matrix. δ_e is the intermediate layer thickness for segmental solubility only; δ_s is the thickness of a quasi-intermediate layer where structural elements of polymer in contact are present.

of heat treatment (Figure 9). Here δ_s is the intermediate layer thickness for the case of segmental solubility and δ_e is the effective thickness of the intermediate layer in which elements of both polymers are present. As a result, the general model of the intermediate layer at the interface polymer/polymer may be presented by the scheme in Figure 10 on the right. On the left the scheme of the layer is presented, which takes into account only segmental

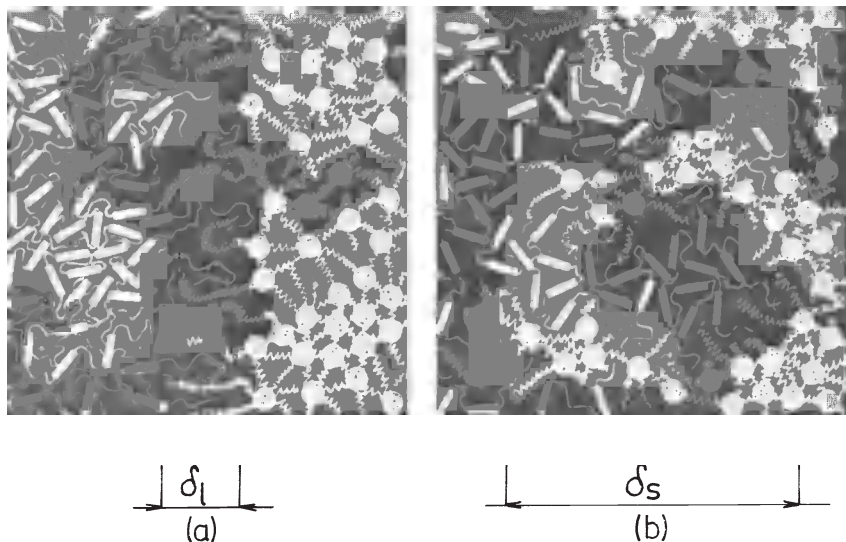


Figure 10. Intermediate layer model at the interface between two components (a) for the segmental solubility only, (b) for structural element dislocations.

solubility. According to the scheme on the right in the effective intermediate layer some microvolumes of one polymer are incorporated into the matrix of the second polymer, the true intermediate layer thickness being constant. The scheme of the intermediate layer structure can explain also the fact of the deviation in the properties of the mixture from those predicted according to the free-volume theory. Earlier we have proposed the modified Simha-Boyer equation for heterogeneous polymer systems, where segregation of different block and microseparation into two phases take place. For this case⁸

$$\Delta\alpha_1 T_{g1}/w_1 = \Delta\alpha_2 T_{g2}/w_2 = \text{constant}$$

where T_{g1} and T_{g2} are the glass temperatures of components, $\Delta\alpha$ is the difference in the volume expansion of the mixture below and above the transition temperature and w_1 and w_2 are the volume fractions of polymers. The value of the constant in the equation determined the free volume fraction at the transition temperature. The Simha-Boyer equation in its usual form very well describes the properties of filled polymers with mineral fillers.

As for the incompatible polymer mixtures it has been shown in our investigations that in spite of their incompatibility (the constancy in the position of temperature transitions of both components), the modified

equation does not describe the properties of the real systems. Therefore we can assume incomplete segregation, and the existence of some degree of interaction between the two phases. The experimental data allows us to conclude that in the intermediate region both increase and decrease in the packing density for individual components may take place due to heat treatment and the effect of excluded volume at the interface. An analysis of the equation

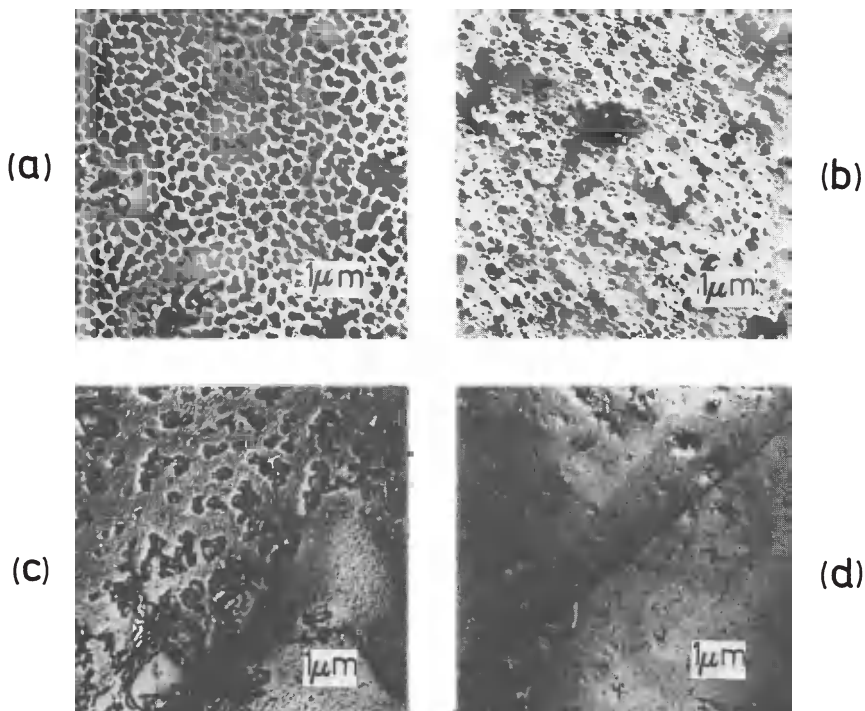


Figure 11. Electron micrographs: (a) polyurethane network, (b) copolymer styrene-divinylbenzene network, (c) interpenetrating network, (d) interpenetrating network in presence of one per cent aerosil in the matrix network.

(which we omit) shows that microsegregation leads to the appearance of excess free volume in the intermediate layer which is distributed between the two phases. In this way a change in the free volume distribution takes place and an additional microheterogeneity arises. These ideas are in accordance with the structural data and with a model of the intermediate layer, formed due to the dislocation of structural elements into the interfacial region. An interpenetrating network can be considered as a special case of the multicomponent polymer system. These systems are also micro- and macroheterogeneous due to the reaction conditions. Here we should like to draw attention to one more type of heterogeneity in the interpenetrating network which has not yet been discussed. The lack of additivity in properties

of such systems, as has been shown by us for the interpenetrating network from the polyurethane matrix and the copolymer styrene–divinylbenzene, may be explained by the influence of the matrix network on the structure of the second network in the course of its formation. The surface of particles of the matrix network may influence both the molecular mobility of growing chains and the character of their packing in the second network. As a result the 'defectivity' of the second network will differ from that for the free network and will be different at different distances from the interface with structural elements of the network matrix. In this respect all considerations can be applied to the interpenetrating network which have been discussed for interfacial phenomena in filled polymers. This statement was proved by data concerning the influence of the mineral filler on the interpenetrating network properties. It was shown that the filler influences the molecular mobility in the network matrix like the second network. By considering the interpenetrating networks as a filled microheterogeneous system and evaluating the role of interface phenomena one may explain some properties of such systems which cannot be done in terms of polymer mixtures. An electron microscope study of that network showed (*Figure 11*) that the formation of the second network leads to an increase in the size of structural elements in the first network (globules). The distance between them also increases due to swelling in the course of formation and filling up the interstructural region with the second network. Thus the incorporation of the second network very considerably influences the morphology of the network matrix, the structural heterogeneity being increased. The filling of the interpenetrating networks can change the heterogeneity restraining the structure formation and decreasing the general structure heterogeneity of the polymer phase.

In conclusion we should like to discuss briefly one of the aspects of structural microheterogeneity in block-copolymers which has not been considered earlier. The structure of block-copolymers is a two-phase one where blocks of different nature form domains, clusters and other distinct microregions. The study of temperature transitions in polyurethane block-copolymers allows us to conclude that some kind of local compatibility may be possible for different blocks. On the basis of our observations we may suggest that a sort of intermediate region exists containing different blocks. However, the relative amount of these intermediate regions should sharply decrease in the course of segregation processes in various blocks. There exists mutual interference of component blocks which manifests itself by a sort of averaging of kinetic flexibilities of polyurethane molecules. In segmented polyurethanes the intermolecular H-bonds are formed not only between the urethane groups in stiff blocks, but also between urethane groups of stiff blocks and ether linkages of soft blocks. This in turn hinders a more pronounced segregation of blocks differing in flexibility and causes the formation of intermediate microregions containing different blocks. Such intermediate regions may be formed by adjacent fragments of different blocks each of which is influenced by another. Stiff block aggregates which can be considered as polymeric filler influence the mobility of segments in the soft blocks of the same chain, whereas soft blocks may have a plasticizing effect on the stiff ones. The incorporation of inorganic fillers in block

copolymers is of great interest due to their different effects on microregions formed by still and soft blocks. The filler surface appears to selectively interact with blocks different in polarity. The incorporation of fillers results in decreased interaction between both soft and stiff blocks, and this effect promotes further segregation of stiff blocks into domains. Thus in block-copolymers there exists an intermediate region composed of different blocks apart from soft and stiff block containing domains. Formation of such intermediate regions leads to an additional microheterogeneity in block-copolymer systems.

In conclusion we can say that the difference disappears again between polymer chemistry and colloid chemistry, or physical chemistry of surface phenomena. Now we come again—as 20–30 years ago—to the ideas about heterogeneities in the polymer structure. In connection with this we would like to end our paper with words written in 1920 by a great Russian poet Valerij Brjusov: ‘Science put in front its face of Gorgona (Medusa), all truth is dissolved in micellae’.

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