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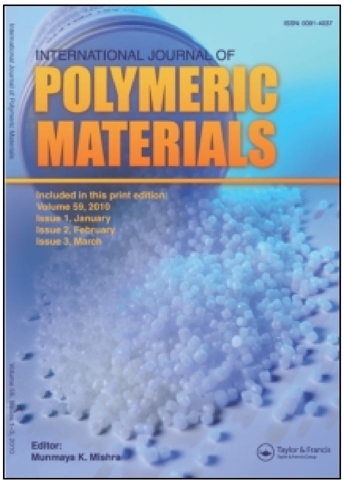

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Kuleznev, Valery N.(1980) 'The Colloidal Structure of Polymer Mixtures. Its Formation and Effect on Properties', International Journal of Polymeric Materials, 8: 2, 117 — 134
To link to this Article: DOI: 10.1080/00914038008077940
URL: http://dx.doi.org/10.1080/00914038008077940

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Intern. J. Polymeric Mater., 1980, Vol. 8, pp. 117–134
0091-4037/80/0802-0117 $06.50/0
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The Colloidal Structure of Polymer Mixtures. Its Formation and Effect on Properties†

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(*Received February 28, 1979*)

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Many polymer applications involve mixtures of polymers. Some of the basic considerations involving colloidal systems are applied to a number of these applications and are shown to be helpful in preparing and processing useful polymer mixtures.

The physical chemistry of polymers belongs to the category of those branches of science which have emerged from colloid chemistry and have become an independent science. The colloid-chemical conceptions of the structure and properties of polymers (mainly, elastomers and rubbers) were most distinctly formulated in the book by B. V. Margaritov "Physical Chemistry of Natural and Synthetic Rubbers" published in 1941. Even at that time not all scientists shared the opinion that polymers are purely colloidal systems consisting of special micelles, in which the specificity of chain molecules is manifested in the properties only through the micellar structure of the polymer. At the same time, as early as the beginning of the twenties propositions were advanced and later well substantiated that polymers are not colloidal systems and that they are simply highly viscous liquids (unless the polymer is crystalline) and that polymer solutions are true thermodynamically stable formations. For many years the colloid-chemical approach to the interpretation of many phenomena observed in polymers were considered old-fashioned. In recent years there has been observed the fusion of the experience (beneficial to both science and practice) accumulated in the

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†Presented at the 10th All-Union Symposium on Polymer Rheology, held June 20–24, 1978, in Perm (USSR).

field of investigation of the problems of both colloid chemistry and polymer chemistry. In this connection, we may cite the words of Academician P. A. Rehbinder taken from the preface to Margaritov's book:[1] "The concepts and methods of the physical chemistry of surface phenomena take full account of the chemical specificity of substances participating in colloidal processes, and therefore it is incorrect to contrast them to purely chemical ideas".

Amorphous polymers are microinhomogeneous, as has been established by numerous investigations. The microinhomogeneity of crystalline polymers is a well-established fact. Typical colloidal systems are also formed in many cases during the processing of polymers. They have a well-developed (with respect to the volume of the polymer) surface, and the presence of an interface undoubtedly determines their properties. An attempt to use the colloid–chemical approach to the understanding of the regularities governing the properties and structure of polymers is not a simple repetition of the old "micellar" concepts; it is a further, new turn in the coil of our cognizance, which even today gives useful scientific results.

We may provisionally pick out three groups of colloidal systems in polymers. The first group includes systems of the "semi-colloid" type. Just like low-molecular-mass semi-colloids (say, soaps), these systems, being microheterogeneous, have not any clear-cut interface and, what is most important, the particles of a semi-colloid do not possess the properties of the macrophases of the same substance. Such systems may include polymers themselves with their supramolecular structure and various levels of microheterogeneity.[2] These systems are often formed as a result of vulcanization. It has been well established at present[3] that ordinary sulphur vulcanizates, which have so far been regarded as homogeneous systems with a network of ordinary chemical bonds, contain in fact microinhomogeneities, probably, in the form of associations of sulphur linkages or a different kind of sulphur or polysulphide particles having a size of the order of several tens of angstroms. The lower limit of the sizes of colloidal particles is known to be 10^{-7} cm, and such a particle consists of 30–100 molecules. This figure is well consistent with the fact that the number of sulphur atoms contained in the nodes of the spatial network in a number of vulcanizates reaches 50–70 sulphur atoms. The formation of a network is affected by the presence of surface–active substances (surfactants). Stable (including thermally stable) rubbers can be produced when account is taken of the colloid–chemical activity of the ingredients. A good combination of physico–chemical properties is also possible if the nodes of the vulcanization network will contain solid particles having a size of hundreds of angstroms, which are chemically bound with the environment of the rubber. Such particles act simultaneously as a vulcanizing agent and a filler.

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Structure of a different kind are probably formed in many cases upon addition of small amounts of a number of substances to polymers.[4] Negligibly small amounts, sometimes fractions of a percent, of other polymers or low-molecular-mass substances, introduced into the main polymer considerably change its properties.

The processability of elastomers is improved by addition of 3% of polyethylene; introduction of up to 0.5% of silicone oil into polypropylene directly in the extruder lowers the viscosity of the melt and speeds up the rate of extrusion by several times.[5] By introducing polystyrene in an amount of up to 0.2% into polymethyl metacrylate it is possible to lower the viscosity of the melt by a factor of 10 and to increase the strength of the solid polymer by a factor of 1.5.[6] In all cases the effect indicated is evidently provided by the formation of a special type of critical systems when the substance introduced is at the solubility limit in the polymer matrix. The formation of a system similar to a colloidal system, when the second phase is only starting to form, produces the indicated effect.

The third group includes typical colloidal systems in polymers when the colloidal structure is distinctly observed and when the particles of the disperse phase have an interface and exhibit a set of properties characteristic of the macro-volume of the substance of the particles. Examples of such typical polymer colloids are filled polymers, mixtures of polymers (polymer alloys), impact-resistant polymers, fibre-reinforced polymers. It is known that metals too are not used in the pure state as structural materials; instead, alloys are employed, many of which are structurally colloidal systems. Individual polymers are also always replaced by polymer mixtures and filled or reinforced polymer systems, in which a certain interaction at the polymer–filler or polymer–polymer interface is the decisive condition for the formation of the best set of physico-mechanical properties. Here the condition of the interface makes a direct and noticeable contribution to the formation of a set of properties, which is typical for colloidal systems.

Taking into account the microheterogeneity and sometimes also of the polyphase nature of materials which we usually deal with, the correctness of the statement that "colloid chemistry may be called the chemistry of real bodies"[7] becomes obvious.

The colloid–chemical approach to the interpretation of the regularities governing the properties of real bodies allows us to disclose a certain regularity in the relationship between structure and properties, which is characteristic of both groups of colloids in polymers, irrespective of whether these systems are polymer mixtures or individual polymers having an inhomogeneous structure typical of them. Such a specific feature in the structure of a real body is the combination of regions of strong and weak chemical and intermolecular bonds. Therefore, the process of deformation or, in the

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limit, even of destruction of a polymeric system takes place nonuniformly, in discord to the classical mechanism of propagation of a single, one-direction main crack or a uniform deformation of the entire body in accordance with the continuum mechanics. It is exactly this inhomogeneity of the properties of the body, either brought up or not brought up to the two-phase level during the formation of a body, that results in the improvement of its properties, including its strength properties. The paths of the manifestation of this regularity are varied. We shall now describe some examples.

Dogadkin and his co-workers[8] have found that the fatigue resistance and the tensile strength in vulcanizates are increased in those cases where a combination of "strong and weak, labile vulcanization bonds" is produced in the system during the vulcanization. Implying here that these "bonds" are in fact, as has been pointed out above, particles of colloidal size, it is more correct to regard a combination of strong and weak linkages as a set of spatially alternating strong and weak "microvolumes" of the vulcanizate. Upon application of a load, there occurs an accelerated stress relaxation in regions with a weaker interaction, which makes the stress field more homogeneous and, hence, the entire system more resistant to loads. It is obvious that the assumption of the rearrangement of chemical polysulphide linkages, which has been advanced to account for the observed reinforcing effect, is insufficient since if the system contains a large number of free-radical acceptors the saturation of free radicals with acceptors would be rather probable, which would lead to a considerable destruction of the vulcanization network upon deformation.

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In a mixture of any polymers, there is formed a transition layer at the interface. This layer is formed as a consequence of the segmental solubility at the interface between the phases.[4] A layer of segmental solubility is essentially a microvolume in which the intermolecular interaction is weakened. This is a consequence of the low mutual thermodynamic affinity of polymers, which results in their incompatibility. This weakening has also been shown experimentally[9] as a decrease in the cohesive energy of rubbers as compared with the additive values. The weakened interaction of polymers can be observed not only in the layer of segmental solubility but also in the other regions of the transition layer where the structure in the phase of each polymer is changed as compared with the structure in the bulk of the phase, which thus leads to a decreased density of the substance in the transition layer.[10] Thus, the alternation of "strong and weak" regions in a mixture of polymers takes place even in those cases where the strength, moduli, viscosity or any other characteristic of one phase is close to the same characteristic of the other phase.

For a number of years, Zubov and Sukharevsky and co-workers[11] have shown that during the formation of polymer coatings when the polymer is dissolved in a poor solvent, the film-forming process proceeds through the gel-formation stage. This contributes to the formation of a structure in which the closely packed (more stable!) microvolumes, which are the nodes of the spatial structure of the gel, alternate with weakened microregions. Such as microheterogeneous (but, undoubtedly, one-phase!) structure is retained in the film even after the solvent is removed. The alternation of stable and weakened regions accelerates stress relaxation, probably, as suggested by the authors, as the result of the displacement of stronger microblocks due to their weakened interaction, which is what contributes to the sharp decrease of the internal stresses as compared with those existing in the film having a more homogeneous structure formed from a good solvent.

The examples given here show that the alternation of microregions with an intensive interaction with regions with a weakened interaction is characteristic of many systems. It is exactly this feature that is characteristic of polymer mixtures. Thus, the specificity of the colloid-chemical approach to the study of the structure and properties of polymer mixtures is determined by the fact that such mixtures are two-phase systems containing alternating microvolumes with enhanced and weakened chemical and intermolecular interactions. By microvolumes we may probably understand both particles of the disperse phase and boundary layers similar to "semicolloid" formations, i.e., which have no characteristic features of an individual phase.

Let us consider some examples of the manifestation of the specific features of the colloid-chemical approach to the investigation of the structure formation and properties of polymer mixtures.

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MIXING THE POLYMERS

The vast majority of mixtures are produced by mixing polymers in mixing apparatus. The mixing process is shown schematically in Figure 1. From this figure it is seen how the filler is dispersed in the polymer. Indeed, if a polymer is placed in the gap between an inner (rotating) cylinder and an outer (immobile) cylinder and a thin layer of a filler is put into the polymer (the thick line in the figure), then, as a result of the rotation of the cylinder the filler will be dispersed in the polymer in the manner shown.

If instead of a filler, a thin layer of another polymer is placed into the polymer, no dispersion will occur in principle and the transition from the spiral filament of one polymer in the medium of the other polymer to the polymer-in-polymer dispersion (the final stage of mixing in the figure) will not be understandable. In other words, the mixing of polymers, according

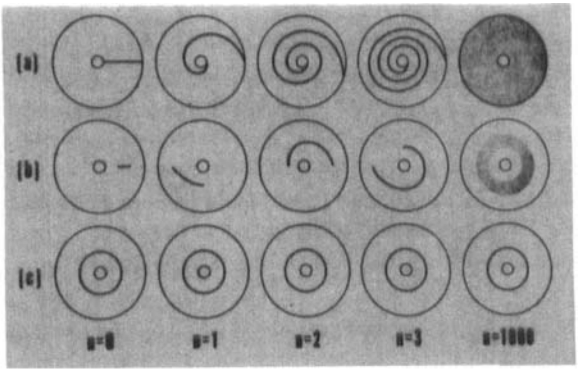

FIGURE 1 The process of laminar, diffusionless mixing in the gap between two coaxial cylinders. The initial orientation of the components and the total shear deformation determine the extent of mixing (according to McKelvey).

to the indicated scheme, must lead to the formation of a fibrous structure and not to the usually observed dispersed structure.

In our opinion, the process of mixing of polymers first formulated in the work written by the present author in collaboration with Miroshnikov[12, 13] may be accounted for by taking account of the instability of the liquid cylinder discovered by Taylor and explained by Tomotika. According to the Tomotika theory, in a liquid cylinder formed in the medium of the other liquid, there arises a perturbation wave which leads to the breakdown of the cylinder into numerous identical drops. The length of the perturbation wave and, hence, the size of the drops produced depend on a number of parameters, mainly on the ratio of the viscosity values. Of course, in the classical works indicated above no account was taken of the presence of viscoelasticity, but in our opinion the relation between the stability of the liquid cylinder of one polymer in the medium of another polymer and the ability of the polymers to undergo mutual dispersion leaves no doubt whatsoever. The fibrous structure formed in a polymer mixture when it is forced through a capillary with subsequent rapid cooling was observed as early as 1969 by the present author and later it was shown that when heated the mixture breaks down into separate drops.

In certain cases, the fibres of one polymer produced in the medium of another polymer can be isolated if the polymer forming the matrix is dissolved in a selective solvent which is inert toward the fibre-forming polymer.[14, 15]

The more stable the cylinder of the polymer being dispersed, the coarser is the polymer-in-polymer dispersion. Indeed, if the cylinder has no chance to break down into drops according to the Tomotika mechanism, then the dispersion can be accomplished only through the mechanical rupture of the

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formed cylinder by changing the direction of shear in the extruder, on rolls, etc. Therefore, the stability of the polymer cylinder must be directly correlated with the size of the particles formed when the polymers are mixed. This correlation is shown qualitatively in Figure 2. In this case the experiments involving the determination of the stability of the cylinder were carried out with immiscible polymer solutions, and for the dispersity of particles to be determined, use was made of mixtures of polymers having a different chemical nature, which was produced by mixing polymer melts in the Brabender plastograph. It is, however, seen that the form of the curves and their position relative to the abscissa are the same both in the case of the stability of the cylinder and in the case of the polymer mixture. Though not final, this is a rather convincing indication that the breakdown of the liquid cylinder formed upon mixing of polymers is an important stage during the formation of the phase structure of the mixture.

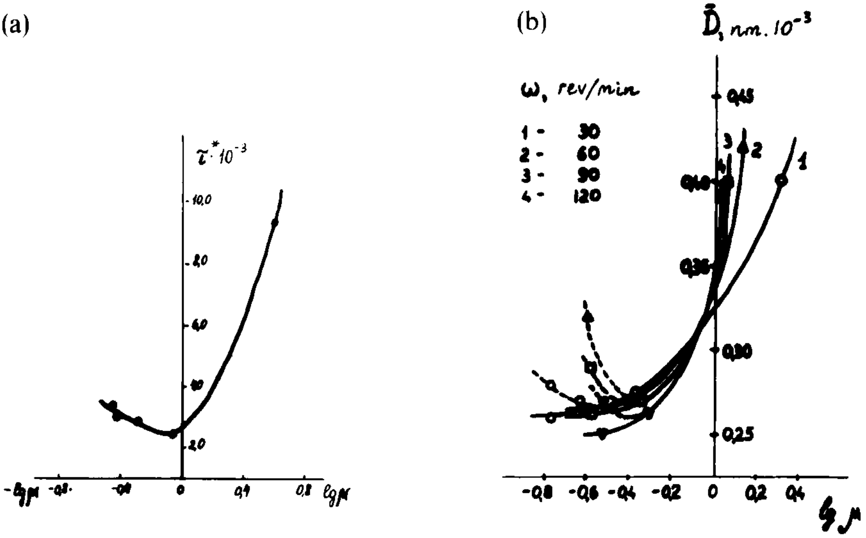

FIGURE 2 The dependence of the lifetime of a liquid cylinder in a liquid medium (a) and the size of particles in a mixture of polymers (b) on the ratio of the viscosities of the disperse phase and a continuous medium. a—a liquid cylinder of a toluene solution of polystyrene (molecular mass from 2.2×10^5 to 1.5×10^6), which is formed in a toluene solution of methylvinylsiloxane polymer (mol. mass 5×10^5); b—a mixture of polymethyl metacrylate and polystyrene (90:10); the dotted line indicates the size of particles in the mixture upon rapid cooling when the elongated particles have had no chance to break down. 1, 2, 3, 4—various rotational speeds of the mixer rotor.

It is exactly from the standpoint of the stability of the cylinder (or the fibre) of one polymer in the medium of another polymer that we can explain the effect of the annealing of the mixture on the particle size and the properties of the polymer. Figure 2b also shows that the annealing of a mixture of

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polymers leads, with a definite ratio of the viscosities ($\mu < 1$), to a decrease of the size of the particles of the disperse phase. This is accounted for by the fact that with the ratio of the viscosity of the cylinder to that of the matrix (μ) being less than unity the cylinder has no chance to breakdown during the mixing time (see Figure 2a) and the cylinder is broken down on additional heating.

The breakdown of the fibres (cylinders) of the disperse phase due to the loss of stability results in a decrease of the anisotropy of the properties, say, the anisotropy of the strength of mixtures of butyl rubber and polyethylene, arising during extrusion (Figure 3), but this does not mean that the elongated particles of the disperse phase have simply relaxed (without breaking down) and assumed a spherical shape. Indeed, the shrinkage of mixtures as a result of heating is mainly governed by the shrinkage of the matrix and is even found to be less in a mixture of polymers than in the polymers taken separately. Thus, after heating and full relaxation the shrinkage of butyl rubber was 67%, of polyethylene, 82%, and in their 3:1, 1:1, and 1:3 mixtures, 67, 60, 50%, respectively.

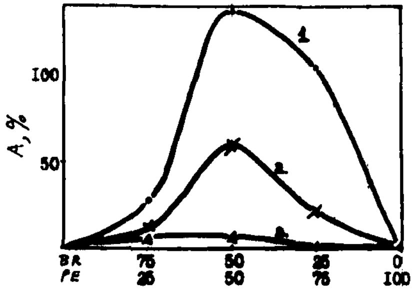

FIGURE 3 The variation of the anisotropy of the strength of mixtures of polyethylene and butyl rubber produced by rolling without subsequent heating (1) and with heating at 80°C (2) and at 140°C (3).

The data given enable us to arrive at an important conclusion: when polymers are mixed, the mixing time must not be neglected, and the main criterion of efficiency should be the total shear deformation in the mixing apparatus. When the rotational speed of the mixer is increased and the mixing time is shortened, there may occur the moment when the dispersity begins to decrease with increasing intensity of mixing.

THE DEPENDENCE OF THE PROPERTIES ON THE COMPOSITION OF THE MIXTURE

Proceeding from the colloid-chemical conceptions of the structure of a

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mixture of polymers, it should be expected that the property–composition relationship would be determined by the structure of the mixture and would coincide in principle with the basic regularities known to exist for low-molecular colloidal systems. Let us demonstrate this by the example of the viscosity and modulus of mixtures.

It is known that viscosity has the property of logarithmic additivity, i.e., there is an additive dependence of the logarithm of viscosity of a mixture of low- or high-molecular compounds on its composition. This circumstance has been noted by Frenkel,[16] who pointed out that in the presence of any special interactions in a mixture of liquids, as compared with the interactions taking place in the individual components, to the additive value of viscosity there is added the term reflecting the extra interaction of the components in the mixture:

$$\ln \eta = \tfrac{1}{2}N_1^2 \ln \eta_1 + \tfrac{1}{2}N_2^2 \ln \eta_2 + N_1 N_2 \ln \eta_{12}$$

where N_1 and N_2 are the mole fractions of the components; η_1 and η_2 are their viscosities, and η_{12} is the quantity characterizing the interaction of components 1 and 2.

The formula of logarithmic additivity is rather difficult to check out on mixtures of polymers since there are few compatible polymers and the formula is evidently inapplicable to emulsions, and most of polymer mixtures are just emulsions.

Among the few representatives of polymer mixtures, a mixture of cis-polyisoprene and Na-butadiene synthetic rubber is (evidently, without doubt) "compatible"; the rubber is a strongly branched and highly irregular polymer of butadiene.[17] We can hardly suppose that between polymers which have structurally similar units (say, polybutadiene and polyisoprene) there may occur an additional strong interaction differing in intensity from the interaction taking place in the polymers themselves. Such a mixture of polymers which are similar in chemical nature (and is a single-phase mixture) must follow the rule of logarithmic additivity.

The results of investigation of a mixture of polyisoprene and synthetic butadiene rubber are presented in Figure 4. Indeed, the logarithm of the viscosity of the mixture is proportional to its composition, which reflects the single-phase structure of the mixture. For many single-phase systems, including solutions of the mixture indicated there is observed the rule of logarithmic additivity.

For ordinary two-phase mixtures, provided that the polymers do not differ in their narrow molecular-mass distribution, there is observed a relationship between viscosity and composition, which is concave toward the side of the composition axis, as shown in Figure 5. This is the most typical shape of the curve, well known to every investigator who has dealt with the

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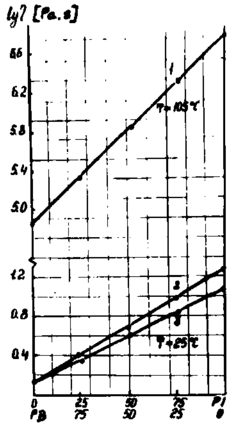

FIGURE 4 The dependence of log η on the composition of a mixture of polyisoprene and synthetic branched butadiene rubber. 1—a mixture obtained by evaporation of the solvent (the shear stress log $\tau = 4.5$ N/m^2, 2, 3—4% benzene solutions of the mixture at log $\tau = 0.2$ (2) and log $\tau = 1.6$ (3).

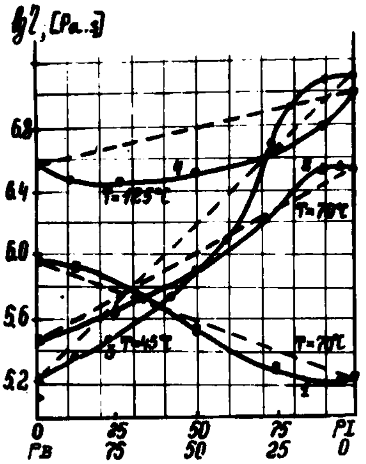

FIGURE 5 The dependence of log η on the composition of a mixture of polybutadiene and polyisoprene with narrow MMD produced by mixing on rolls (1), by evaporation of the solvent from mixtures of solutions (2), by coprecipitation from solution (3) and a mixture of polymers of wide MMD produced by evaporation of the solvent from the solution of the mixture (4).

rheology of polymer mixtures. From colloid chemistry it is however known that the relation between the viscosity of an emulsion of the liquids differing in viscosity and the composition has an S-shape, the inflection on the curve corresponding to the moment of phase inversion; the method itself of plotting the indicated dependence of viscosity may serve as a good characteristic of the changes in the emulsion structure that occur with change of its composition.

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Figure 5 also shows that for polymers of narrow MMD the viscosity-composition dependence is really S-shaped. This is characteristic of various polymer mixtures, including those which are not shown in the figure. It thus appears that an S-shaped curve of viscosity vs. composition is typical for mixtures of polymers of narrow molecular-mass distribution, and a curve concave toward the composition axis is typical for mixtures of polymers of wide MMD. The only difference between such polymers is, of course, that (from the rheological standpoint) polymers of narrow MMD do not exhibit viscosity anomaly, being Newtonian liquids. It may be thought that it is exactly viscosity anomaly that is responsible for the fact that the viscosity–composition relationship does not characterize the structural changes in the mixture, which take place when the composition undergoes change. Experience has shown that viscosity anomaly in a mixture of polydisperse polymers is really enhanced as compared with the anomaly of each of the polymers entering into the composition of the mixture.

There is no doubt that a phase inversion also takes place in a mixture of polydisperse polymers. Thus, Figure 6 is a plot of the elastic modulus vs. the composition of a mixture of the rubbers under study. In order to increase the difference between the moduli of the components, investigations were carried out at a temperature intermediate between the glass-transition temperatures of the components. The dependence of the modulus on the composition appears to be S-shaped. This means that in a mixture of polymers, including polydisperse polymers, in a solution or in a melt, there takes place a phase-inversion, which is clearly seen from the change of the modulus and may not affect the relation between the viscosity and composition of the mixture.

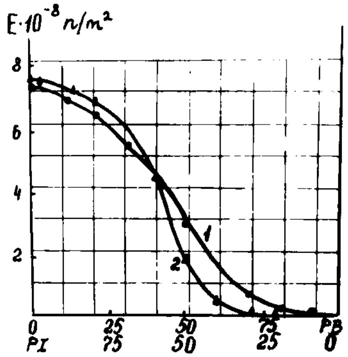

FIGURE 6 The dependence of the compression modulus on the composition of a mixture of butadiene rubber and polyisoprene of wide MMD (1) and narrow MMD (2). The test temperature butadiene rubber and polyisoprene of wide MMD (1) and narrow MMD (2). The test temperature: −92°C (1) and −90°C (2).

The data given on the property–composition relationship for a mixtures

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of polymers show to what extent the attempts to compare the experimental property–composition curve with the additive relation are unsubstantiated. The most general form of the property–composition curve for a mixture of polymers is S-shaped since it reflects the inevitably occurring phase-inversion when the ratio of the components is changed. Of course, this statement does not apply to the properties of the mixture, which are determined at large values of deformation, as, for example, the tensile strength is often determined. Large deformations lead to a strong change in the structure of the mixture, and the phase-inversion may hardly influence the property–composition relationship.

The transition layer and its effect on the properties of the mixture. Transition layers at the interface between the phases exist at all times. Gibbs in his works on the thermodynamics assumed the presence of a transition layer and assigned to it a thickness and certain parameters intermediate between the values of the parameters of the co-existing phases. The thickness of the transition layer may be very large even for low-molecular-mass systems. An example is the dependence of the thickness of a transition layer of fatty acids in aqueous solution at the interface with air on the length of the hydrocarbon radical, plotted on the basis of the data obtained by Rusanov and co-workers.[18] The distance from the interface, where the structure of the solution of a fatty acid differs from the bulk structure may reach hundreds of angstroms (see Figure 7). Deryagin[19] has demonstrated the presence of a

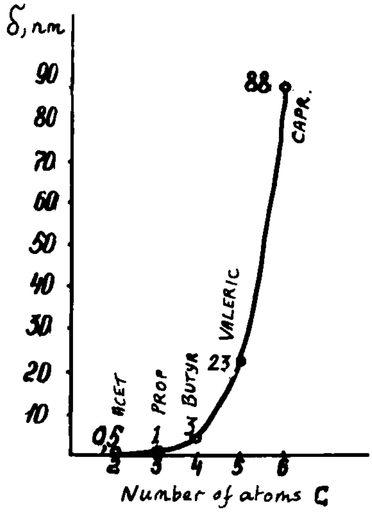

FIGURE 7 The thickness of the surface layer of a liquid solution of fatty acids versus the number of carbon atoms in the acid molecule.

transition layer in dimethylsiloxane oligomers at the interface with steel. A number of investigators, in the first place Lipatov and his co-workers,[2] have shown the presence of a transition layer in polymers at the interface with a solid surface, including the interface with a filler particle.

Thus, there are no grounds for discussing the question of the presence of a transition layer at the polymer–polymer interface in a mixture; it is more important to determine its sizes and to study its structure. In our opinion, at the interface of polymers there may exist various types of transition layers, including those which are characteristic of any interface between a polymer and a solid. The most specific layer for systems of this type is the layer resulting from the segmental solubility of polymers at the contact interface.

The physical significance of the phenomenon consists in that the boundary macromolecules have no chance to assume the conformations taken by the macromolecules in the bulk. Therefore, the boundary macromolecules are "not rich in entropy". If a polymer is brought into account with another polymer, there exists the possibility of transfer of segments of boundary macromolecules of one polymer into a layer of another polymer. Such a transfer is explained by the fact that with decreasing molecular mass down to sizes comparable with the size of a segment there occurs a sharp increase in the polymer-in-polymer solubility.[20] The change in the conformation of boundary macromolecules may take place only as a result of the diffusion of macromolecular segments; the results of determinations of the polymer-in-polymer solubility show that the transition of segments from one layer to another is quite possible. We should only stress that the phenomenon of segmental solubility is a surface phenomenon, i.e., it is determined by the change of the surface thermodynamic potential, and therefore the relationship between segmental solubility and mutual solubility is a qualitative relationship.

Theoretically, the presence of segmental solubility has been shown in the works of Helfand and Tagami[21] and the presence of a transition layer, in which a layer of segmental solubility is a constituent, has been observed by many investigators during direct electron-microscopic observations.[4]

The presence of a layer of segmental solubility, the thickness of which evidently varies from several tens to a few hundreds of angstroms, is responsible for the formation of a fluctuating network at the boundary layer; this network is formed by entanglements of different macromolecules. Such a layer has been shown schematically earlier[22] and is a well-known fact. The formation of a fluctuating entanglement network in a layer of segmental solubility has different effects on certain properties of a mixture of polymers, depending on the difference between the flexibilities of the boundary macromolecules of polymers. This effect can easily be traced out with a mixture of monodisperse polymers (with narrow molecular-mass distribution).

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We may suppose that the viscosity anomaly in two-phase polyisoprene-polybutadiene and polybutadiene-polystyrene mixtures is high. This follows from the simple reasoning that during the flow of an emulsion, and a mixture of incompatible polymers is really an emulsion, the drops of the emulsion must undergo deformation and the viscosity must decrease due to a decrease in the cross-section of the drops of the disperse phase. Experiment shows, however, that solutions of a mixture of polybutadiene and polystyrene at a concentration not much higher than the phase-separation point, do not exhibit viscosity anomaly, like solutions of individual polymers of narrow MMD. From the works of Dreval and Tager[17] it is known that in a solution of polymers at a certain concentration there is formed a fluctuating network; below this concentration there does not exist such a fluctuating network in solution. We have carried out special experiments to determine the concentration at which a fluctuating network is formed in polymer solutions. It has been found that for polymer solutions and mixtures the concentration at which a fluctuating network is formed is about 18%.[17] This allows us to draw a number of important conclusions. First, a fluctuating entanglement network forms in solutions independently of whether we deal with a solution of one polymer or a solution of a mixture of polymers, even in those cases when this mixture is two-phase, i.e., we deal with an emulsion of a solution of one polymer in a solution of another polymer. Second, this viscosity anomaly arises only in solutions of a mixture of polystyrene and polybutadiene at a concentration higher than the concentration at which a network is formed. This means that viscosity anomaly is caused not by the presence of a two-phase structure but by the breakdown of weakened nodes of the fluctuating network in the boundary layer of nodes formed by entanglements of diverse macromolecules. A two-phase solution with a concentration of 10% exhibits no viscosity anomaly, but this phenomenon is inherent in a solution with a concentration of 20% (higher than 18%!). (see Figure 8).

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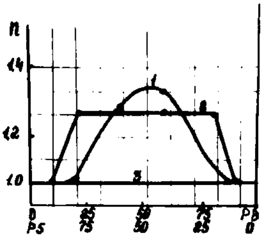

FIGURE 8 The flow index "n" versus the composition of a mixture of polybutadiene and polystyrene of narrow MMD. 1—20% solutions; 2—a mixture produced by evaporation of the solvent; 3—a mixture of LINEAR, PB and PIP.

Solutions of a mixture of polybutadiene and polyisoprene do not show viscosity anomaly at a concentration higher or lower than the critical concentration at which a network is formed, in spite of their two-phase structure in a given concentration range. This phenomenon can be explained by the fact that the flexibility of macromolecules of the polymers in question is practically the same and a fluctuating network in the boundary layer is formed by macromolecules which, though dissimilar, do not practically differ in flexibility, and therefore the network is homogeneous throughout the bulk of the solution with respect to the strength of fluctuating nodes both inside the drops of the disperse phase and in the matrix and transition layer. The homogeneity of the network is provided by the absence of viscosity anomaly in the emulsion of the polymer solution. The data obtained point unambiguously to the dependence of the rheological properties of a mixture of polymers on the structure of the transition layer. The presence of regions with weakened bonds, such as the transition layer in a mixture of polymers, determines the dependence of viscosity on shear stress in this system.

There is a further characteristic manifestation of the properties of the transition layer as a region of weakened bonds in the system. This is its well-known effect on the fatigue resistance of polymer mixtures.

The phenomenon of increased fatigue resistance upon repeated deformations of polymer mixtures was discovered in 1957 with the vulcanizates of a mixture of natural and butadiene-styrene rubbers,[23] and later the fact of enhanced fatigue resistance was detected in mixtures of butadiene-nitrile and polybutadiene rubbers.[24] The dependence of the fatigue resistance upon repeated deformations for a pair of butadienenitrile and polybutadiene rubbers is shown in Figure 9. It is seen that the fatigue resistance of the vulcanizates of the polymer mixture exceeds by several times that of the individual polymers. With an appropriate choice of the vulcanizing group the difference in fatigue resistance between the mixture and each of the individual rubbers may be several decimal orders. The same phenomenon is observed with mixtures of polyethylene and polypropylene and with many other polymer mixtures. It is characteristic that other mechanical properties, such as the strength on a single extension, the internal friction modulus, the resistance to aging, vary without maxima and minima on the curves, which allows us to account for the increased fatigue resistance by the decreased internal friction, increased strength or increased resistance to thermal aging or by other usual factors. It is apparent that in this case, just as in the combination of "strong or weak bonds" in vulcanizates, the dynamic strength increases owing to the relaxation of stresses (more exactly, overstresses) in microregions with "weakened linkages", i.e., in the transition layer characterized by a decreased cohesive energy.

A combination of strong and weak bonds in the system leads to an increase

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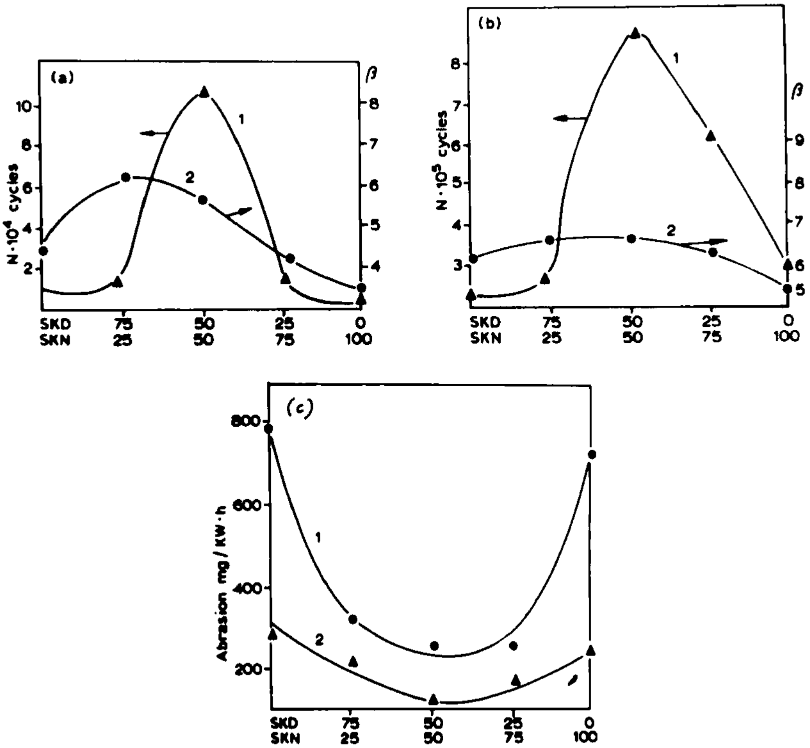

FIGURE 9 The fatigue resistance of unfilled (a) and filled (b) vulcanizates: 1—twisting with flexure; 2—the fatigue coefficient; (c) the wear resistance of the specimens on a metallic gauze; the specimens are the same as in Figure 9a.

of wear resistance (Figure 9b). If the wear resistance is determined upon movement of a polymer along a smooth surface or metallic gauze, the wear will be due to fatigue and, hence, the wear resistance must also depend in the first place on the resistance to repeated deformations. From Figure 9 it is seen that the wear resistance on a metallic gauze varies, on the whole, in the same qualitative way as the fatigue resistance, which is also the result of the presence in a mixture of polymers of microvolumes with "weakened bonds".

Experiment shows that at a higher fracture rate, when the crack is propagating at a high velocity, it passes both through the matrix and the particles of the disperse phase. At a low rate of crack growth it goes round the particles of the disperse phase. This is practically an indication of the highest possibility of stress relaxation in the transition layer, i.e., the most effective influence of a combination of strong and "weakened bonds" on a set of mechanical properties. Therefore, the effect of mutual reinforcement in a mixture of polymers manifests itself in the dynamic deformation regime,

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when the propagation of cracks occurs slowly and the fracture is gradually accumulated from cycle to cycle.

CONCLUSION

The material discussed in this work, in spite of conciseness, allows us to arrive at the conclusion that the application of the colloid-chemical concepts to mixtures of polymers is fruitful. This refers to the formation of phase structures in the preparation of mixtures and to the transformations of these structures during processing, which is accompanied by the appearance of a considerable anisotropy of properties due to the deformation of the particles of the disperse phase—up to the formation of fibres. The colloid-chemical approach to the evaluation of the structure and properties of polymer mixtures points to the S-shape of the property–composition curve as the most typical one since this form reflects the phase inversion that usually takes place in the system with the change of the composition of the mixture. Of great importance is also the conclusion that one of the most general features of the structure of mixtures of polymers is the combination of microregions with a more or less intensive inetarction, and such a structural inhomogeneity as a consequence of the two-phase nature of the system is thought to be an important factor leading to the improvement of the strength properties of polymer mixtures.

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