Translated from *Uspekhi Khimii*, **55**, 2086-2105 (1986) U.D.C. 547.912.4:547.914

The Physicochemical Properties of Ionomer-containing Interpenetrating Polymer Networks

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The physicochemical properties of interpenetrating polymer networks of a new type, containing an ionomer as one of the components, have been examined. The results of the study of the morphology, viscoelastic properties, mechanical strength characteristics, and adhesive properties have been described. Data on the thermodynamic compatibility of the components in the systems studied have been given.
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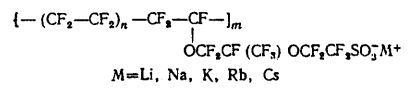
I. INTRODUCTION

In recent years, an increasing number of papers have been published on the synthesis and study of the properties of interpenetrating polymer networks (IPN) and materials based on them.[1-4] This is due to the fact that, in addition to traditional binders for composite polymer materials, increasing use is now being made of complex binders consisting of components of different chemical character, which are second-generation binders, or hybrid binders.[5] A characteristic feature of hybrid binders is that after setting, they themselves are composite polymer materials, since as a consequence of the thermodynamic incompatibility of the components, setting is accompanied by the separation of microphase particles of one of the components, which can be regarded as the filler, distributed in a matrix of the other component.

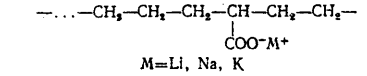
Interpenetrating polymer networks are typical representatives of hybrid binders, whose use makes it possible to achieve much more complex combinations of different polymer structural states in composite materials, providing extensive possibilities for controlling the properties by the action of the filler.

A number of papers[6-15] describe the study of a new type of interpenetrating polymer network, namely systems in which one of the components is an ionomer. Ionomers have been studied particularly intensively in the last 10–15 years. The term ionomer was previously used to describe only copolymers of α-alkenes with unsaturated mono- and dicarboxylic acids, in which some of the acidic groups were neutralised by metal ions.[16] The term ionomer now covers a wider range of polymers. Thus according to one definition,[5] ionomers are polymers whose chains contain a small quantity of ionogenic groups, usually not more than 10 mole %, so that the hydrocarbon chain is the main component, in contrast to poly-electrolytes, which have a high density of ionogenic groups in the chain. Other definitions of the term ionomer have been given; for example, ionomers have been defined[10] as ion-containing polymers in which the concentration of ionogenic groups is insufficient to ensure their solubility in water.

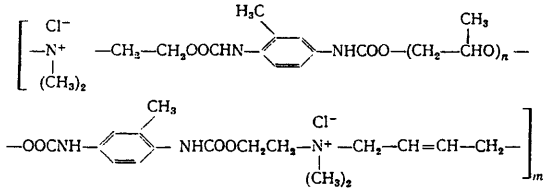
Ionomers based on polymers of different classes have been obtained. For example, fluorinated ionomers with the following structure have been prepared:[17]



The structural formula of an ionomer based on ethylene and acrylic acid[18] is:



Ionomers with quaternary nitrogen atoms in the main chain are often called ionenes.[19] For example, a polyurethane ionene based a glycol oligoether, tolylene di-isocyanate (TDI), 2-dimethylaminoethanol, and 1,4-dichlorobut-2-ene has the following structural formula:[19]



The good operational characteristics of ionomers and the possibility of using them in various branches of technology have led to a considerable increase in studies of their synthesis and properties.

Theoretical ideas on the structure of ionomers are being developed by Eisenberg.[12,13,20,21] According to his ideas, the thermodynamic incompatibility of the salt groups and the polymer matrix, and the electrostatic interaction of the ionogenic groups, lead to the formation of multiplets and clusters. Multiplets consist exclusively of ionogenic groups, and contain a maximum of 8–10 ion pairs; clusters consist of multiplets separated by polymer chains, that is clusters contain both ionogenic groups and polymer chains. According to Eisenberg, cluster formation is observed in ionomers when a certain critical concentration of ionogenic groups in the chains has been reached. This is consistent with ideas on microphase separation in block copolymers and other multicomponent systems where the blocks are thermodynamically incompatible. Experimental studies of various ionomers based on ethylene, styrene, ethyl acrylate, etc.

by electron microscopy, neutron scattering, X-ray diffraction, and infrared spectroscopy[6,20,23] confirm Eisenberg's view that aggregates of two types, multiplets and clusters, exist. This explains the sharp change in a range of physicomechanical and thermophysical properties, such as the viscosity of the melt, the glass-transition temperature T_g, the modulus of elasticity, and the dynamic mechanical characteristics, when ionogenic groups are introduced into polymer chains.

A number of comparatively recent papers[10,11,15,24-30] describe the study of the properties of polyurethane ionomers. Polyurethanes show microphase separation at the level of the flexible and rigid blocks, leading to the formation of systems with a high level of heterogeneity.[22] Moreover, in addition to a chemical bond network, these polymers contain a network of physical bonds, which determines to a large extent the properties of materials based on polyurethanes.[31] The introduction of ionogenic groups into polyurethanes creates an additional, "ionic", network, which has a considerable influence on a range of properties of these systems.

The data obtained to date in the study of the properties of polyurethane ionomers are not unambiguous. On the one hand, in a series of papers[25-28] on the study of segmented polyurethanes in the ionic form by infrared spectroscopy, it was concluded that in these materials the network of hydrogen bonds is broken down, and that hydrogen bonds of a new type are formed, leading to a rearrangement of the segments of the polymer chain and to disordering of the rigid domains; it was also concluded that there is a deterioration in the conditions for self-association of the urethane groups, contrary to the previously proposed[32] scheme based on an increase in the self-association of the urethane groups and the segregation in polyurethane ionomers. On the other hand, other data indicate an increase in the segregation of the blocks of different chemical character when ionic centres are introduced into polyurethanes.[29] An increase in micro-phase separation is assumed to be responsible for the decrease in T_g for the flexible blocks in polyester–polyurethane ionomers, compared with non-ionogenic polyurethanes.[30] The ambiguity in the conclusions about the influence of ionogenic groups on the structure of polyurethane ionomers indicates a need for systematic studies in this field.

The combination of ionomers with polymers with a three-dimensional structure, leading to the formation of ionomer-containing IPN, is a promising method of obtaining new types of composite polymer materials. At the same time, the production of these complex systems unavoidably complicates the structure of the materials by changing the nature of the microphase separation, and hence influences the final properties of the materials. Studies published up to the present on ionomer-containing IPN are examined in the present review.

II. MORPHOLOGY AND STRUCTURE

The determination of the influence of ionogenic groups on the morphology and structure of ionomer-containing IPN is of decisive importance.

A large proportion of the structural studies of IPN containing ionogenic groups, as for IPN of other types, has been carried out by electron microscopy. An electron-microscope study of IPN based on sulphonated cross-linked polystyrene (PS) and polyvinylpyridine (PVP) (see Fig.1) showed that the specimens of all the compositions studied had a cellular structure, indicating phase separation in the IPN.[33,34] When its concentration is high, the sulphonated PS forms a continuous phase with quaternised PVP distributed in it as inclusions with dimensions of 60–80 nm (Fig.1*a*). The size of the PVP domains decreases from 60–80 nm to 30–40 nm on going from specimens with a higher PS concentration to IPN specimens with a component ratio of 1:1 (Figs.1*b* and 1*c*). At medium compositions (Fig.1*c*), both phases are continuous, and with further decrease in the PS concentration, PVP becomes the continuous phase (Fig.1*d*). In this case the size of the PS domains is 10–20 nm. Inversion of the phases takes place with change in the PS/PVP ratio from 1:1 to 1:4.

Thus the ionomeric IPN examined above, like non-ionomeric IPN, have a cellular structure, but in some cases this structure is not clearly defined, possibly due[33] to some mixing of the two components of the IPN at the molecular level. The chief difference between the morphology of the ionomer-containing IPN being considered and ordinary IPN, however, is that analysis of the photomicrographs of IPN specimens with different compositions has shown that in addition to phase separation of the individual components in the IPN, in the ionomeric components themselves there is additional separation with the production of regions with a higher concentration of ionogenic groups.[33] Thus systems of this type will be provisionally four-phase systems, and not two-phase systems like ordinary IPN.

For IPN based on sulphonated PS and quaternised PVP, the size of the domains obtained experimentally was compared with that calculated using Donatelli's equation:[35,36]

$$D_2 = \frac{2\gamma W_2}{RT\nu_1[1/(1-W_2)-1/2]}$$

where D_2 is the size of the domains of component 2, forming inclusions in component 1, W_2 the weight fraction of component 2, γ the interphase tension between the components of the IPN, ν_1 the density of cross-linking of component 1, R the universal gas constant, and T the temperature. Comparison of the experimental and calculated values of D_2 in relation to the component ratio showed good agreement between theory and experiment only at a PVP concentration of 50% and above. At low PVP concentrations, the theoretical and experimental values differ considerably.

The introduction of ionogenic groups into one of the components of an IPN makes it possible to change the morphology and hence the mechanical properties of materials on thermal treatment. This was shown in a study of the influence of annealing on the morphology of IPN based on a triple copolymer of butadiene, styrene, and methacrylic acid (polymer 1) and a copolymer of styrene with divinylbenzene (polymer 2).[37] Polymer 1 was obtained in both the acidic form and the salt form. In the last case, films of polymer in the acidic form were treated with a 10% solution of sodium or caesium hydroxide; after this treatment, the polymer no longer dissolved in organic solvents, but only swelled, indicating the formation of an elastomer "cross-linked" by physical bonds. Only IPN specimens with medium compositions, with a component ratio of 1:1, were studied. The materials were treated by the method described above, except that to obtain contrast the specimens were treated with osmium tetroxide. Analysis of the electron-microscope photographs showed that in the original IPN the ionomeric component in the acidic form gives a continuous phase, with domains of the copolymer of styrene and divinylbenzene with dimensions of 10–13 nm distributed in it; a small quantity of domains with dimensions up to 70 nm is also present. On annealing (in this case thermal treatment at 110 °C for 24 h), both components of the IPN form continuous phases. When the ionomeric component is in the salt form, annealing gives the same effect, but to a lesser

degree. The observed phenomena are related to the fact that the ionic "cross-linkages", which are thermally labile, become weaker and undergo rearrangement on prolonged thermal treatment, leading to a change in the structure of the IPN and hence to a change in the physicomechanical properties.[37]

This possibility of rearranging ionic "cross-linkages" by thermal treatment has led to the production of thermoplastic IPN in which both components (one of which is an ionomer) are "cross-linked" by physical bonds.[38] One IPN of this type consists of a system based on a triple copolymer of styrene, ethylene, and butene (polymer 1) and an ionomer obtained by the copolymerisation of styrene, methacrylic acid, and isoprene (volume ratio of the components 90 : 10 : 1), followed by neutralisation of the COOH groups with an aqueous solution of NaOH or CsOH (polymer 2).[39,40,41,42] The triple copolymer, in the molecules of which the terminal styrene blocks are physical "cross-linkages", is a thermoplastic elastomer. In the ionomer, the ionogenic groups form domains which are also nodes of the physical network, so that at room temperature the ionomer behaves as a cross-linked polymer, and at high temperatures, as a result of the breakdown of the domains, flow of the material takes place, that is the ionomer behaves as a linear polymer.

Two methods can be used to obtain thermoplastic IPN. In the first method, polymers 1 and 2 are synthesised separately, after which they are blended in the molten state. These are mechanically blended thermoplastic IPN (MBT IPN). In the second method, the IPN are obtained by polymerising polymer 2 in a common solution in the presence of the previously prepared polymer 1. These are chemically blended thermoplastic IPN (CBT IPN). Thus thermoplastic IPN are materials intermediate between IPN and blends of thermodynamically incompatible polymers. The study of the morphology of these materials has revealed certain characteristic features.

Analysis of electron-microscope photographs of IPN specimens with a component ratio of 1 : 1 has shown[40] that when the acidic form of polymer 2 is used in CBT IPN, polymer 2 is the continuous phase. At 100% neutralisation of the methacrylic acid fragments, inversion of the phases is observed; polymer 1 becomes the continuous phase, and polymer 2 (the ionomer) is distributed in it as globules with dimensions of 100–200 nm. At a lower degree of neutralisation (15% and 20%), partial inversion is observed; there are regions in which both phases (polymers 1 and 2) are continuous. The structure of the mechanically blended thermoplastic IPN (MBT IPN) differs slightly from that examined above for the CBT IPN.[41] Thus in the case of the acidic form of polymer 2, although it is the continuous phase with domains of polymer 1 distributed in it (size of the domains 50–150 nm), the degree of blending is less than for the CBT IPN. Here also, inversion of the phases takes place on complete neutralisation, but the dimensions of the domains of polymer 2 show extensive scatter, from 500 nm to 2000 nm with a small quantity of even smaller domains (400–100 nm).

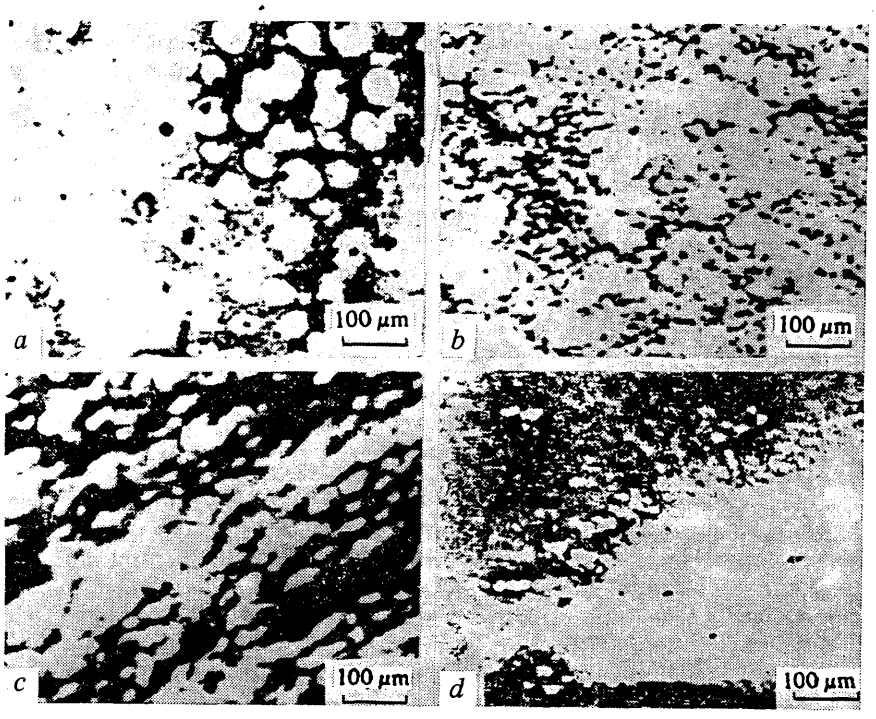


Figure 1. Photomicrographs of ionomer-containing IPN based on cross-linked polystyrene and polyvinylpyridine; PS/PVP ratio: *a*) 76/24, *b*) 58/48, *c*) 50/50, *d*) 20/80.[33]

Individual "islets" of polymer 2 consist of cells with domains of polymer 1 disseminated in them.

The change in the degree of phase continuity with increase in the degree of neutralisation of the polymethacrylic acid fragments in polymer 2 is an important characteristic of thermoplastic IPN. These changes in structure on going from the acidic to the salt form have been attributed[39-41] to a change in the viscosity of melts of these forms of polymer 2, which has been demonstrated experimentally.[39] The polymer with the lower viscosity, for example polymer 2 in the acidic form, generally tended to become the continuous phase. Increase in the degree of neutralisation led to an increase in the viscosity of the melt of polymer 2, and it became the dispersed phase. The component ratio naturally also has a significant influence on the phase continuity in IPN.

The morphological data for the CBT IPN studied were used to construct a generalised "phase continuity" diagram,[39] characterising the change in the degree of continuity with change in the component ratio in the IPN and degree of neutralisation of the groups of polymer 2.

For many CBT IPN compositions, inversion of the phases, although observed, ofter remains incomplete, that is there is to some extent continuity of both phases, attributed to the fact that the viscosities of the melts of the two polymers in the IPN are approximately equal.[39]

Thus study of the morphology of thermoplastic ionomer-containing IPN has shown that, like ordinary IPN, they have a high degree of heterogeneity, but (particularly CBT IPN) they have a finer structure than ordinary IPN, with smaller domain dimensions than in ordinary IPN and polymer blends. Moreover, the structure of these IPN can be varied over a wide range by varying the concentration of salt groups in the ionomer.

Small-angle X-ray scattering gives more complete information on the polymer structure than electron microscopy; in particular, it makes it possible to determine the size of the heterogeneous inclusions in the range 1–100 nm and other characteristics of the heterogeneity in amorphous systems. This estimation has been carried out for IPN based on the non-ionic form of network polyurethane and a polyurethane ionomer.[43] The ionomer was obtained from polyoxypropylene glycol, 2,4-tolylene di-isocyanate (TDI), 2-dimethylamino-ethanol, and 1,5-dibromopentane.

Analysis of the large-angle diffraction patterns of the individual polymers making up the IPN showed that they are typical amorphous polymers with a more or less developed heterogeneity, resulting from the segregation of the rigid and flexible blocks in the polyurethanes.[22] The degree of segregation can be estimated quantitatively by comparing the theoretical value of the mean-square fluctuation of the electron density $\Delta\bar{\rho}_c^2$ and the mean square fluctuation of the electron density of the real system studied $\Delta\bar{\rho}^2$; the parameter $\alpha = \Delta\bar{\rho}^{2'}/\Delta\bar{\rho}_c^2$ is introduced.[22] The quantity $\Delta\bar{\rho}_c^2$ characterises a so-called "ideal" two-phase system in which the micro-regions have the densities of the pure components, and the thickness of the interphase layer tends to zero. The value of $\Delta\bar{\rho}^{2'}$ depends both on the electron density of the components and on their degree of segregation in the system. The results of calculations of α, $\Delta\bar{\rho}^{2'}$, and $\Delta\bar{\rho}_c^2$ for the individual networks (the non-ionic form of polyurethane and the polyurethane ionomer) showed that the $\Delta\bar{\rho}_c^2$ values differ little; at the same time, $\Delta\bar{\rho}^{2'}$ for polyurethane is 100 times that for the ionomer. Correspondingly, the degree of segregation α for polyurethane is 8 times that for the ionomer. Thus the results indicate that the original networks deviate considerably from the ideal two-phase structure.

The large-angle diffraction patterns showed that the interpenetrating polymer networks based on polyurethane and a polyurethane ionomer are also amorphous polymers. The results of the small-angle X-ray study of the IPN specimens show that there is modification of the heterogeneous structure of the network components as a result of the formation of the system. Firstly, qualitative differences are observed between the diffraction patterns of the original components and the IPN for most compositions studied. The diffraction curves for the IPN are more diffuse, and many curves show two intensity maxima, more or less clearly defined. A particularly marked difference is observed between the diffraction curves for the IPN containing small quantities of the ionomer and the scattering curve for the non-ionic form of polyurethane. It was suggested[43] that the introduction of small quantities of the ionomer into the polyurethane leads, during the production of the IPN, to the formation of micro-regions for which the periodicity of the distribution is determined by the microphase distribution of the polyurethane and the ionomer, leading to the production of the first maximum on the small-angle scattering curves. The second maximum is due to the effect of periodicity at the level of the blocks of different chemical character in the polyurethane. The maxima on the small-angle scattering curves for IPN with medium compositions are very poorly defined. This indicates that the periodicity at the level of the distribution of polyurethane and the ionomer and at the level of the flexible and rigid blocks is broken down to a considerable extent.

To obtain further information on the nature of the heterogeneity revealed in the IPN studied, the experimental values of $\Delta\bar{\rho}^{2'}$ were compared with the theoretically calculated $\Delta\bar{\rho}_c^2$ for different models of the heterogeneous structure.[43] Three models were used to calculate $\Delta\bar{\rho}_c^2$. The first model assumes a microphase distribution with the formation of polyurethane and the ionomer, within which there is complete blending of the flexible and rigid blocks. In contrast to the first model, the second model assumes complete distribution of the blocks of different character in the micro-regions of polyurethane and the ionomer. The third model, like the first two, assumes complete distribution of polyurethane and the ionomer, but unlike the first and second models it assumes that the micro-regions of polyurethane and the ionomer retain the degree of segregation characteristic of the individual networks. The calculations showed that the third model gives the best approximation for the description of the heterogeneous structure of the IPN.

When the third model is adopted, the $\Delta\bar{\rho}_c^2$ values are greater than $\Delta\bar{\rho}^{2'}$, particularly at high concentrations of the ionomer. This indicates that the micro-regions of the phase separation in real IPN are more "diffuse" than assumed by the third model. In other words, the IPN studied show a high degree of blending of polyurethane and the ionomer; this is generally characteristic of those cases where the separation of the phases during the production of the complex polymeric system stops at some intermediate stage. As in individual network polymers, the incomplete separation of the phases may be due to retardation of the movement of the molecular chains during the production of the three-dimensional structure.[22,44] The introduction of ionogenic groups into one of the components, leading to the formation of "ionic" cross-linkages, produces even greater retardation of the phase separation. These suggestions are confirmed by the results of morphological studies of ionomer-containing IPN given in the preceding section.

Thus morphological and X-ray diffraction studies of ionomer-containing IPN indicate that systems of this type have a complex structure with different levels of hetero-

heterogeneity at the level of the components and heterogeneity within each component at the level of the blocks of different chemical character and regions with different concentrations of ionogenic groups. As noted in Ref. 43, the formation of "diffuse" micro-regions of phase separation with a wide range of values of the degree of segregation of the components is possible, depending on the nature of the intermolecular interactions in systems of the given type and on the previous history of these systems.

II. THERMODYNAMIC PROPERTIES

The introduction of ionogenic groups into one of the components of IPN, even when they are of similar chemical character, leads to thermodynamic incompatibility of the components in the IPN.[45] This has been demonstrated for IPN containing polyurethane and a polyurethane monomer; the composition dependence of the thermodynamic compatibility of the components was studied, the coefficients of self-diffusion of the solvent calculated, the fraction of the free volume and the change in it with change in the component ratio in the IPN determined, and the influence of the filler on the thermodynamic interaction at the interface examined.[45,46,47] The polyurethanes were based on the adduct of trimethylolpropane and tolylene di-isocyanate (TMP + 2,4-TDI) and a copolymer of propylene oxide and tetrahydrofuran[33] or polyoxytetramethylene.[45] The ionomers used were a polyurethane ionomer with a three-dimensional structure based on polyoxypropylene glycol (MM 3000), 2,4-TDI, 2-dimethylaminoethanol, and 1,5-dibromopentane[45] (ionomer A) or a linear ionomer based on polyoxytetramethylene, 2,4-TDI, and potassium dihydroxybenzoate[45] (ionomer B).

An analysis of the isotherms for the sorption of organic vapours by specimens of these IPN and the individual components made it possible to calculate the thermodynamic parameters. Thus the concentration dependence of the mean free energy of mixing of the solvent with the individual networks and the IPN, and the method proposed by Tager,[48] were used to calculate the change in the free energy of mixing of the polyurethanes and the polyurethane ionomers in the IPN. The results of the calculation are given in Fig. 2. ΔG_m is positive throughout practically the entire range of compositions, that is the components of the system are thermodynamically incompatible. The greatest separation into phases is observed for medium compositions (in the case of ionomer A) and at low concentrations of ionomer B in the polyurethane. An exception is the range corresponding to small quantities of added ionomer A, where ΔG_m is negative, that is the components are compatible. Compatibility in restricted ranges of this kind is observed for many heterogeneous systems.[49,50] The components of the polyurethane–linear ionomer (ionomer B) system, that is in the semi-IPN, are incompatible throughout the composition range (curve 2 in Fig. 2); the degree of incompatibility increases with increase in the proportion of ionomer. Thus even when the components of the IPN are very similar in chemical character, the introduction of ionogenic groups into one of the components leads to thermodynamic incompability of the components, producing the heterogeneity of the systems as a result of phase separation during the formation of the IPN.

As already noted, the interpretation of most experimental data on the properties of ionomers is based on the idea that multiplets and clusters are formed.[21] The ability of the ionomer to undergo association will probably have a significant influence on the phase separation processes in ionomer-containing IPN. The introduction of even small quantities of polyurethane into an ionomer with a linear structure[46] will apparently lead to a sharp increase in the degree of association of the latter. Polyurethane, added in small quantities, probably cannot form a continuous network, for the reasons examined in Ref. 51, and it will be distributed by diffusion as individual fragments in the bulk of the ionomer, facilitating self-association of the ionomer in the IPN system. Self-association of the ionomer B is also facilitated by its linear structure, which gives greater mobility of the segments (compared with the three-dimensional ionomer A) and leads to the formation of associates of ionic groups.

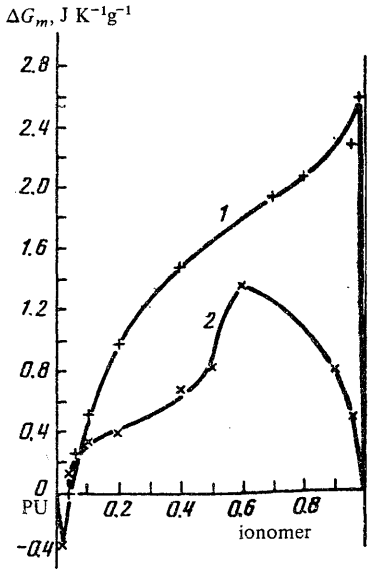


Figure 2. Composition dependence of ΔG_m for IPN based on polyurethane (PU) and ionomers A (1) and B (2).[45]

The self-association of the ionomer apparently intensifies the microphase separation in the IPN. As a result, the concentration dependence of the free energy of mixing of the components shows a maximum for small quantities of added polyurethane (see Fig. 2). At a higher concentration of polyurethane in the semi-IPN (medium compositions and the range of low concentrations of the ionomer in polyurethane), self-association is probably observed to a smaller extent, since the formation of the three-dimensional structure of the polyurethane, which is the matrix in these composition ranges, retards the process of phase separation in the IPN. The conditions of phase separation in these composition ranges are apparently close to those in IPN not containing ionomers.[52,53]

Microphase separation in the IPN leads to a redistribution of the free volume.[45–47] Quantitative treatment of data on the sorption of the vapours of substances with low molecular weight by IPN specimens using Fujita's theory[54,55] enabled the authors cited[45–47] to calculate the fraction of free volume in the ionomer-containing IPN.

The results are given in Fig. 3. For IPN containing the cation-active ionomer with a three-dimensional structure (ionomer A), at low concentrations of the components, the value of $f(T)$ is lower than the additive value, but for

intermediate compositions the IPN specimens show an increased proportion of free volume; for the IPN containing the anion-active ionomer (ionomer B), $f(T)$ deviates from the additive value towards higher values throughout the composition range, that is the IPN have a higher proportion of free volume.

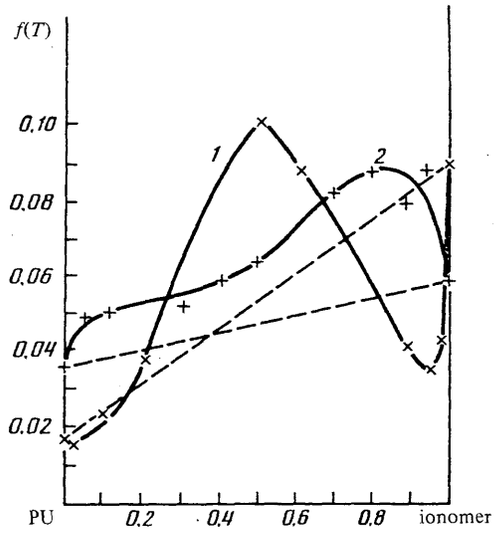


Figure 3. Dependence of the fraction of the free volume $f(T)$ on the component ratio for IPN containing ionomer A (curve *1*) and ionomer B (curve *2*); the broken lines give the additive relationships.[46]

Comparison of the concentration dependence of $f(T)$ and ΔG_m shows two common extremal points (curves *1* in Figs. 2 and 3), a minimum at low fractions of the ionomer A in the IPN, and a maximum at medium compositions, that is the compatibility range has a lower proportion of free volume than the individual components, and the range of greatest separation of the phases in the system corresponds to an excess of free volume. The self-association of the cation-active ionomer in the IPN system, leading to an increase in the segregation of the components in these systems, is apparently less marked than in the case of the anion-active ionomer (at least in the range of low concentrations of one of the components), since for the individual ionomers the formation of associates is more characteristic of the anion-active ionomers, as noted earlier. This is possibly due not only to the nature of the salt centres but also to the fact that ionomer A has a network structure, and ionomer B a linear structure. In this connection, phase separation accompanied by the formation of loose intermediate regions is more characteristic of the IPN with the linear ionomer (ionomer B),[3] leading to the production of an excess free volume throughout the composition range (curve *2* in Fig. 3).

The addition of a filler to the composition in the production of the IPN introduces its own characteristic features into the thermodynamic properties of these systems. Thus the introduction of small quantities (2–10%) of carbon fibres into IPN based on polyurethane and ionomer A leads to a decrease in their sorptive power;[47] the sorption decreases irregularly with increase in the concentration of the filler. This may be due to the competing action of two simultaneous processes: the formation of a more compact boundary layer and polymer–filler bonds, leading to a decrease in sorption, and the production of defects in the network (a decrease in the number of chemical nodes, "free" ends in the network) formed in the presence of the filler, leading to an increase in sorption.[51] Another noteworthy feature is that in the formation of two polymer networks in the presence of a filler for which the networks have different affinities, selective adsorption of one of the polymers will take place; this will lead to a change in the composition of the boundary layers in the final IPN structure produced, at the same time changing the extent of the sorption of the vapours of low-molecular-weight substances by the filled IPN.

For the case of a decrease in sorption in filled polymers compared with non-filled polymers, a thermodynamic cycle has been proposed[56] for estimating the extent of the reaction of the polymer with the filler.

ΔG^*_{p-f}, that is the free energy of formation of the polymer–filler bond, which is a measure of the interaction of the polymer with the filler, is determined experimentally from the isotherms for the sorption of the vapours of organic solvents by the free polymer, the filler, and the filled polymer.[56] ΔG^*_{p-f} is calculated using the equation:

$$\Delta G^*_{p\text{-}f} = \Delta G_1 + n\Delta G_2 - \Delta G_3$$

where ΔG_1 and ΔG_3 are the free energies of the reactions of the polymer and the filled polymer with a large quantity of solvent, and ΔG_2 the free energy of the reaction of the filler with a large quantity of the solvent.

Calculation showed[47] that for the polyurethane–carbon fibre system, the free energy of the polymer–filler interaction ΔG^*_{p-f} is negative in the range of filler concentrations studied. This indicates that the system is thermodynamically stable. For the polyurethane ionomer, only the composition with a low concentration (2%) of carbon fibres was found to be thermodynamically stable. Further increase in the filler concentration leads to destabilisation of the system, and the free energy becomes positive. Polymer–polymer contacts become energetically more favourable than polymer–filler contacts. Thus the ionomer macromolecules are less effectively adsorbed on the carbon fibres than the polyurethane macromolecules.

For filled IPN, the sign of ΔG^*_{p-f} depends on the component ratio at which the filler is introduced into the composition; at low concentrations of the ionomer (up to 10%) in the filled IPN, ΔG^*_{p-f} is negative, that is the system is thermodynamically stable; at an ionomer concentration of 30% or more, ΔG^*_{p-f} is positive, that is the system is destabilised. Here it is evidently necessary to take account of the influence of the filler on the microphase separation taking place during the formation of the IPN. According to the ideas developed in Ref. 5, in the formation of composite materials based on hybrid binders, the rate of the microphase separation and the degree of segregation in the hybrid binder depend on the reaction of the components with the filler. Thus if the filler reacts preferentially with one of the components, the rate of the microphase separation increases, and the degree of segregation should be greater. This probably takes place when carbon fibre is introduced into a polyurethane–polyurethane IPN containing 30% or more of the ionomer, where ΔG^*_{p-f} is positive. At low concentrations of the ionomer, in spite of a possible increase in the rate of the microphase separation under the influence of the filler, ΔG^*_{p-f} remains negative.

IV. THE SWELLING OF IONOMER-CONTAINING INTERPENETRATING POLYMER NETWORKS

The swelling of ionomer-containing IPN obtained by sequential setting have been studied;[33,34,57] the ionogenic groups were introduced into one of the components of the IPN [57] or into both components.[33,34] The swelling of the IPN based on cross-linked polystyrene (network 1) and the copolymer of ammonium acrylate with ethyl acrylate (network 2) was carried out using toluene (a "good solvent" for network 1) and water (a "good solvent" for network 2). The experimental values of the swelling were compared with the values calculated using the additivity rule and assuming that the networks do not influence one another. All the IPN specimens studied undergo appreciable swelling in water and toluene, but to a much smaller extent (smaller by a factor of 3-6) than that calculated from the additivity rule. In the opinion of the authors cited, this behaviour indicates indirectly that both networks in the IPN system are continuous.[57]

Detailed studies have been made[33,34] of the swelling of cross-linked polystyrene, polyvinylpyridine, and IPN based on them, with and without ionogenic groups of different types; the anion-containing component of the IPN was obtained by sulphonation of the phenyl ring of polystyrene, and the cation-containing component by quaternisation of the pyridine ring by treating polyvinylpyridine with methyl fluorosulphonate solution.[33,34] The data on the swelling of the IPN and its components, not containing ionogenic groups, were analysed using the Flory–Rehner[58] and Thiele–Cohen[59] equations. The last equation was derived from the Flory–Rehner equation for application to homo-IPN, that is IPN based on two or more polymers of the same chemical character, so-called "Millar IPN".[60] The final form of the equation is

$$\ln(1-v_1-v_2)+v_1+v_2+\psi_s(v_1+v_2)^2=V_s(\nu_1)'(1/v_1^0)^{2/3}\times \times(v_1^{1/3}-v_1/2)-v_s(\nu_2)'(v_2^{0\,2/3}v_2^{1/3}-v_2/2) \quad (1)$$

where ν_1 and ν_2 are the volume fractions of polymers 1 and 2 in the swollen state, ν_1^0 and ν_2^0 the same in the non-swollen state, ψ_S the molar volume of the solvent, ν_1' and ν_2' the density of cross-linking of polymers 1 and 2 in mole cm^{-3}, found from the Flory–Rehner equation, and $(1/\nu_2^0)^{2/3}$ a correction coefficient (front factor) for the change in the internal energy on swelling.

In the analysis of the data on the swelling of IPN not containing ionogenic groups, the experimentally determined values of the volume fraction of the polymer in the swollen IPN specimens, ν, were compared with the values calculated from Eqn.(1), in which $\nu = \nu_1 + \nu_2$. It was concluded that in the IPN studied, in the swollen state at least, there is no additional chemical and physical cross-linking, which might have been expected on formation of the IPN. The addition of ionogenic groups to IPN based on polystyrene and polyvinylpyridine introduces its own characteristic features into the behaviour of the specimens on swelling. Thus for swelling in water at different pH values, the magnitude of ν (the maximum swelling) is greatest in weakly acidic or neutral media for all IPN compositions.[33] The value of ν increases with increase in the concentration of quaternised polyvinylpyridine, that is sulphonated polystyrene undergoes swelling to a greater extent than quaternised PVP. The addition of NaCl to water leads to different behaviour of the IPN, depending on their composition: specimens enriched in sulphonated PS, as before, give the minimum values of ν in neutral and weakly acidic media; specimens enriched in quaternised PVP give a maximum value of ν (that is minimum swelling) in these media. The observed differences in the swelling of ionogenic IPN, depending on the composition of the "solvent", are attributed to the shielding effect produced on the addition of, in this case, Na^+ and Cl^- ions, which influence the electrostatic repulsion of the ions in the actual network.[33,60] Thus the introduction of ionogenic groups into the IPN makes it possible to vary the degree of interaction of these systems with the solvents over a wide range by changing the composition; this is important when IPN are used as ion-exchange resins and membranes.

From an analysis of the results of the study of the swelling of IPN specimens consisting of a copolymer of styrene with divinylbenzene (ST + DVB) and a copolymer of methacrylic acid with divinylbenzene (MA + DVB), an attempt was made[61] to obtain a criterion of the degree of interpenetration in IPN. The IPN indicated were obtained by sequential setting; specimens of the ST + DVB copolymer were first obtained, after which they were swollen in an MA + DVB monomer mixture, followed by polymerisation of the system. The IPN were obtained in the H^+- and Na^+-forms, and the swelling of the individual components and the IPN in a series of solvents was studied. Determination of the density of cross-linking from the swelling data showed that the experimental values of ν_e (the effective density of nodes in the network) of the IPN specimens are much greater than the values calculated from the additivity rule. From the assumption that the IPN is a heterogeneous system provisionally consisting of three phases (the phases of the individual components and the intermediate range), and an analysis of the swelling data, the following criteria for the degree of interpenetration in IPN were proposed:[61] 1) the difference between the sum of the specific volumes of the gels of networks 1 and 2 and the specific volume of the IPN gel

$$\Delta V = V_1\cdot v_1(1-P_1)+V_2\cdot v_2-V_i(1-P_i) \quad (2)$$

and 2) the difference between the volume fraction of the copolymer in the IPN gel and the sum of the volume fractions of the copolymers in the gels of networks 1 and 2:

$$\Delta v_g = v_{g_i}-(v_{g_i}\cdot v_1+v_{g_i}\cdot v_2) \quad (3)$$

where V_1, V_2, and V_i are the specific volumes of networks 1 and 2 and the IPN, ν_1 and ν_2 the volume fractions of networks 1 and 2 of the IPN, P_1 and P_i the porosities of network 1 and the IPN, and ν_{g_1}, ν_{g_2}, and ν_{g_i} the volume fractions of the copolymer in the gels of networks 1 and 2 and the IPN.

The proposed criteria, like Frisch's interpenetration criterion,[62] are applicable only when the number of nodes in the networks of the individual components is identical to that for the components in the IPN system; this is not observed in practice, since IPN are micro-filled systems,[3] to which all the ideas developed for filled polymers are applicable.[51] Thus the proposed interpenetration criteria can be criticised. The most appropriate criterion of the degree of interpenetration is apparently the degree of segregation, as noted above (see section II).

The fact that the experimental values of ν_e and the other parameters deviate considerably from the values calculated from the additivity rule for ionomer-containing IPN [61] indicates not only and not so much an increase in the degree of interpenetration in IPN, but also and more particularly the characteristic features of systems of this type determined by the increased self-association of the ionomeric component in the IPN system. This question will be discussed later.

V. MECHANICAL AND RELAXATION PROPERTIES. TRANSITION TEMPERATURES

The study of the composition dependence of the mechanical properties of ionomeric IPN revealed the same regularity as for IPN of other types and mixtures of linear polymers, that is the extremal character of the change in properties with change in the component ratio. Thus an IPN consisting of polyurethane and a polyurethane ionomer[46] showed an extremal increase in the tensile strength at low concentrations (5%) of the polyurethane ionomer.[43] The breaking strain also showed an unexpected increase. An extremal change in properties with change in composition is a general regular feature of binary systems: mixtures of linear polymers, IPN, semi-IPN, and filled polymers. The reasons for this phenomenon are undoubtedly related to the characteristic features of the structural changes in the composites with change in their composition, but in spite of a number of attempts to explain the observed extremal values for different systems, no general explanation of these phenomena has yet been given.

The method of preparation of ionomer-containing IPN has a significant influence on their mechanical and relaxation properties. This has been demonstrated for thermoplastic IPN: chemically and mechanically blended IPN based on copolymers of styrene, ethylene, and butene (copolymer 1) and styrene, methacrylic acid, and isoprene (copolymer 2) (CBT IPN and MBT IPN respectively) differ in various mechanical properties. Both CBT IPN and MBT IPN with the ionomeric component in the acid form have lower strength values than IPN with the ionomeric component in the salt form.[40] When copolymer 2 is neutralised, the resulting more rigid component (the ionomer) acts as a characteristic filler for copolymer 1, leading to an increase in the mechanical strength of the IPN. CBT IPN have a higher tensile strength and a greater elongation at rupture, but a lower modulus of elasticity, compared with MBT IPN. This change in mechanical properties was related[18] to the morphology of these IPN; thus the lower modulus of elasticity of the CBT IPN was attributed to the greater degree of dispersion of copolymer 2 (the ionomer) in the matrix of copolymer 1.

The relaxation properties of the above systems have also been studied.[40,41] Data on the temperature dependence of the imaginary part E'' of the complex modulus E^* established that the individual copolymer 1 has two glass-transition temperatures; the first, at −60 °C, is due to the presence of blocks of ethylene and butene, and the second, at 102 °C, is due to glass formation by the styrene blocks. The ionomer shows one glass-transition temperature at 140 °C. These three glass-transition temperatures also appear on the curves giving the temperature dependence of E'' for CBT IPN, without any deviations; this indicates that there is little blending at the molecular level of the components in the systems considered, in contrast to polyurethane–polyurethane ionomer systems,[43] discussed above.

The mechanical properties of these IPN have been described using the theoretical models of Takayanagi, Budyanskii, Davis, and Kerner.[40] The experimental data are most accurately described by Davis' equation, which assumes that both phases in the two-phase system are continuous. For MBT IPN, continuity of both phases is probably more characteristic, since Davis' equation provides a better description of the mechanical properties for MBT IPN than for CBT IPN. This correlation is illustrated directly by the electron microscope data given in the previous section, which show "double" continuity of the phases.

Systems related to ionomer-containing IPN are those in which one of the components is a polyelectrolyte such as acrylic acid and its derivatives. These systems[63] and their relaxation properties have been studied. They are IPN and semi-IPN based on polyoxyethylene (POE) and polyacrylic acid (PAA), obtained by sequential setting. Polyoxyethylene with a molecular mass of 7800–9000 was dissolved in a mixture of the monomer, a cross-linking agent (DVB), and an initiator (benzoyl peroxide), after which the polymerisation was carried out. This gave semi-IPN. The complete IPN were obtained by swelling the previously cross-linked POE in a mixture of the monomer and the cross-linking agent, followed by polymerisation. Study of the dynamical mechanical properties of the semi-IPN and total IPN obtained showed that the curves giving the temperature dependence of E'' and tan δ for specimens with medium compositions or compositions close to them have a single maximum, indicating that there is one temperature transition in systems of this kind. Thus the specimens studied consist of single phases. For specimens in which PAA predominates, and in particular for the semi-IPN with 75 mass % PAA, two maxima are observed; one corresponds to that for the IPN with the equimolar component composition, and the other corresponds to the glass-transition temperature of PAA. For the complete IPN with approximately the same composition, a sharp second maximum is not observed; the curve shows only a slight shoulder. For semi-IPN and IPN enriched in POE, one broad transition is observed, with a maximum at a temperature slightly below the melting point of POE.

These results are interpreted in terms of the formation of complexes between POE and PAA molecules as a result of the production of hydrogen bonds between the COOH groups of the acid and the oxygen atoms of POE.[63]

The question of the association of PAA and POE during the polymerisation of acrylic acid in the presence of POE was examined earlier[64–66] by one of the authors of Ref.63. It is suggested that dynamic mechanical analysis shows that the formation of a single-phase system in IPN and semi-IPN with medium compositions and compositions close to them is due to complex formation. IPN with a low concentration of PAA, according to Ref.63, show microphase separation of POE domains and domains of POE + PAA complexes; IPN with a high PAA concentration show microphase separation of domains of PAA and the complexes. The degree of microphase separation or segregation is greater for the semi-IPN than for the complete IPN, and this is attributed to preliminary cross-linking of the POE during the preparation of the complete IPN. The interpenetration of the components and the formation of interpolymer complexes probably also explains the decrease in the crystallinity of POE in the system of semi-IPN and complete IPN.[63]

Analysis of the strength properties of IPN based on POE and PAA [63] or on polymethacrylic acid[67,68] revealed a characteristic feature of systems of this kind, of practical importance: for low mechanical strain, considerable elongation of the IPN specimens is observed, due to the possible dissociation of the POE + acid complexes and their rearrangement under the influence of the strain.

The characteristics of the reaction between the components and the molecular mobility in IPN based on polymers of related character (polyurethanes) have been studied.[69] NMR spectroscopy was used to study the temperature dependence of the second moment of the absorption line ΔH_2^2 for IPN based on polyurethane (PU) and a polyurethane ionomer (PUI). The latter was obtained by the reaction of oligotetramethylene glycol, TDI, and sodium dihydroxybenzoate.

The curve giving the temperature dependence of ΔH_2^2 for PU showed three main transitions: transition I in the low-temperature range (−130 °C) due to the defreezing of the molecular mobility of the methyl groups:[70] transition II, which begins at −90 °C and is due to the retarded rotation of the methylene groups; and transition III at −10 °C,

apparently due to the start of the segmental movement of large parts of the molecules,[71] possibly sections of the polyurethane chains between the transverse cross-linkages. Unlike PU, the PUI does not show sharply defined temperature transitions: ΔH_2^2 decreases gradually with increase in temperature. For the IPN specimens, transitions I and II are preserved, but transition II is displaced to lower temperatures with change in the ionomer concentration. Transition II, observed at low concentrations of the ionomer, becomes "blurred" with increase in the quantity of the latter.

The preservation of the IPN of the transitions characteristic of the individual components indicates that two phases are present, in spite of the similarity in the chemical character of the components. In the two-phase system there may be intermolecular interactions of different kinds between the components. The nature of the interaction between PU and the PUI in the IPN was therefore estimated from the magnitude of $(\Delta H_2^2)_{int}$, determined as follows:

$$(\Delta H_2^2)_{int} = (\Delta H_2^2)_{expt} - (\Delta H_2^2)_{theor}$$

where $(\Delta H_2^2)_{theor}$ is the second moment of the absorption line of the two-component system, calculated from the additivity rule. The quantity $(\Delta H_2^2)_{int}$ may take positive or negative values if there is an intermolecular interaction between the components of the system, in spite of the absence of chemical transformations. In the absence of interactions, $(\Delta H_2^2)_{expt} = 0$. Calculations showed that the values of $(\Delta H_2^2)_{int}$ for all IPN specimens at the lowest temperature used (−130 °C) are negative, indicating that the molecular mobility of the IPN is greater than that of the individual components. The study of the thermodynamic compatibility of the components in IPN of this type (see section II) showed that the components are incompatible (the free energy is positive). Thus the system studied, like non-ionogenic IPN, shows separation of the phases during its formation, leading to the production of an intermediate range, which, as in non-ionogenic IPN, has a loose structure, as indicated by the negative values of $(\Delta H_2^2)_{int}$.

Calculation of the activation energy of the transitions in the IPN and its components showed that the value of the activation energy E changes non-additively and irregularly with change in composition. For non-ionogenic IPN, the value of E for the transitions also changed irregularly with change in composition; for all IPN specimens, however, the value of E was always less than the additive value and less than the values for the individual components;[72] this was attributed to the formation of a loose intermediate range, facilitating molecular movement in it. In ionogenic IPN, the value of E is lower than the additive value only for IPN specimens containing up to 20–30% of the ionomer. At high concentrations of the ionomer, E is greater than the additive value.

These results were interpreted[69] using the theory of multiplet and cluster formation in ionomers, developed in a number of studies.[6,21,73,74] The ability of the ionomer in the IPN to undergo self-association possibly intensifies the microphase separation. At the same time, the formation of a loose intermediate region, having an excess free volume, facilitates the self-association of the ionomeric component in the IPN system, compared with the individual ionomer. The association of the ionogenic groups is probably the decisive factor in the change in molecular mobility in the IPN when it contains ionomer concentrations of 20–30%, so that E is greater than the additive value. At lower concentrations of the ionomer, when the matrix is PU, the self-association of the ionomeric component is not so marked, and the molecular movement in the system is determined chiefly by the existence of the intermediate range. In this case E is lower than the additive value.

A study of the temperature transitions in an epoxide resin–polyurethane ionomer system (based on polyoxypropylene glycol, TDI, dimethylaminoethanol, and dibromopentane)[75] showed that for IPN of all compositions, two transitions are observed, lying in the region of the glass-transition temperatures of the component networks. In the IPN, however, the glass-transition temperatures are displaced along the temperature scale, as indicated in Fig. 4. The temperature of the transition, which is due to the glass transition of the epoxide resin (curve *1* in Fig. 4), in the IPN changes with change in composition along a curve which has two minima at concentrations of each component of about 10%. The second transition, which lies in the negative temperature range and is due to the glass transition of the polyurethane ionomer (curve *2* in Fig. 4), is displaced to higher temperatures with increase in the proportion of resin in the IPN.

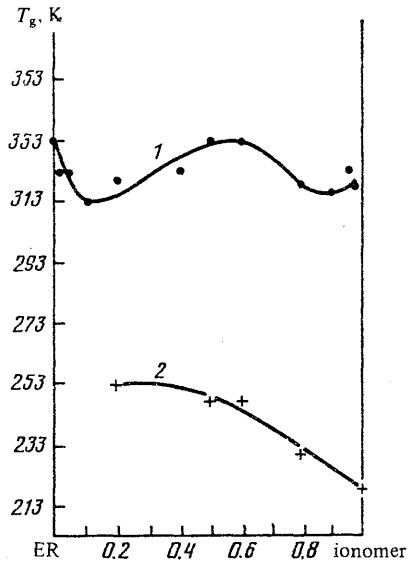


Figure 4. Change in the glass-transition temperature with change in composition for IPN based on polyurethane and epoxide resin (ER): *1*) glass-transition temperature of the epoxide resin, *2*) glass-transition temperature of the polyurethane ionomer.[75]

The results were interpreted[75] in terms of the degree of completeness of the processes of microphase separation and the degree of segregation. At a low degree of segregation, leading to the formation of an appreciable proportion of interphase regions, as in the case of blending at the molecular level, the temperature transitions characteristic of the individual components may not be observed.[76] The presence of two glass-transition temperatures in the IPN indicates, however, that there is a fairly high degree of segregation of the components even at low concentrations of each of them. In the range of medium concentrations, however, where the glass-transition temperature of the epoxide resin in the IPN is approximately equal to that for the pure epoxide resin, the degree of segregation is probably very high, and the phase separation is extensive.

Thus the formation of ionic "cross-linkages" in IPN as a result of the introduction of ionogenic groups into one of the components has a significant influence on the mechanical and relaxation properties. This is apparently related to the increase in the degree of segregation of the components of the system due to the increase in the association of the ionogenic groups in the IPN compared with the pure ionomer. The association of the ionogenic groups is also possibly responsible for the marked difference between the experimental and theoretical values of ν_e (see section III), as follows from Ref.61; the associates of ionogenic groups are characteristic nodes of the network, leading to an increase in ν_e.

The question of the formation of multiplets and associates in individual ionomers of different character is still being discussed in the literature. Analysis of the results of studies in this field indicates that the nature of the ionogenic groups has a decisive influence on the association: associates are detected for polymers of different classes with anion-containing ionomers; associates are less frequently detected in cation-containing ionomers. This field is now being intensively studied.[6,20]

VI. ADHESIVE PROPERTIES

Adhesives and coatings based on IPN show good adhesion to supports of different kinds;[3,4] no systematic studies of the adhesive properties of these coatings, or of coatings based on ionomer-containing IPN, have been described, however. The use of an ionomer as one of the components of the IPN to obtain adhesives and coatings will apparently make it possible to obtain materials with good adhesive power and low hydrophilic character (compared with the individual ionomers).

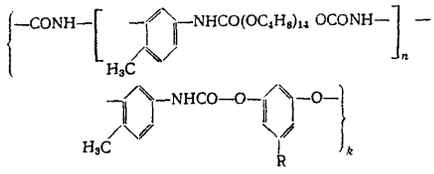
Influence of the nature of the counter-ion and the concentration of salt groups on the adhesive strength (N m^{-1}) of coatings on substrates of different character*.

Type of salt	Steel			Glass		
	n=1	n=2	n=3	n=1	n=2	n=3
Lithium salt	340	220	180	280	210	140
Sodium salt	280	200	170	230	160	130
Potassium salt	220	200	100÷95	210	180	130

Type of salt	Dural			Brass		
	n=1	n=2	n=3	n=1	n=2	n=3
Lithium salt	220	170	95	320	240	220
Sodium salt	160	140	100	310	180÷200	200÷220
Potassium salt	90	120	75	212÷200	180	110

*Temperature of formation of the coatings 80 °C.

The adhesion to various supports (steel, brass, glass, Dural) has been studied[77] for coatings based on IPN consisting of network polyurethane and polyurethane ionomers with the general structure



where n = 1, 2, 3; R = COOLi, COONa, COOK; and k is the degree of poly-addition. The study of the influence of the concentration of salt groups in the chain of the ionomers studied on the strength of the adhesion (at separation) showed that increase in the concentration of salt groups in the structure of the polymer chain (that is decrease in n) increases the adhesive strength of the ionomeric coatings for all supports studied (see Table). The fact that a significant increase in the adhesive strength of the ionomers is observed only at a high concentration of salt groups in the composition makes these polymers unsuitable as protective coatings, because of their highly hydrophilic nature; their use as one of the components of the coating gave good results, however.[71]

Fig.5 gives typical curves showing the change in the equilibrium work of adhesion for coatings based on ionomer-containing IPN with change in composition. At low concentrations of each component, an extremal increase in adhesion is observed; this is particularly clearly defined at low concentrations of the ionomer. At the same time, the coatings are only slightly hydrophilic, and this is important from the practical viewpoint. The extremal point on the graph giving the dependence of the hydrophilic character on the concentration composition of the IPN probably corresponds to the range of concentrations at which the ionomeric component becomes the continuous phase.

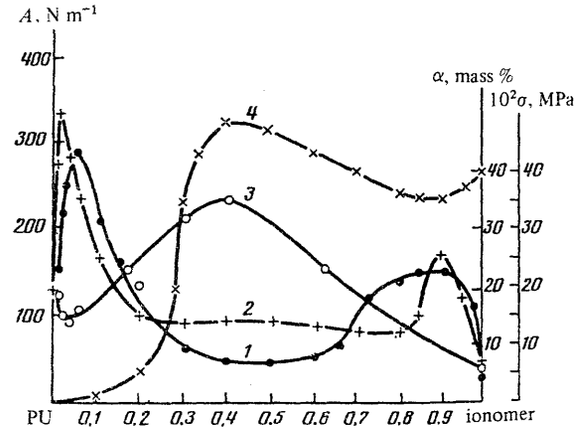


Figure 5. Dependence of the quasi-equilibrium work of adhesion A (*1*, *2*), hydrophilic character α (*3*), and internal stresses σ (*4*) on the component ratio.[77]

In the production of coatings, the influence of the solid surface of the support is superimposed on the process of IPN formation, that is selective adsorption of a particular component on the surface is possible, leading to an irregular distribution of the components in the boundary layer of the coating. Thus analysis of the surface tension values, and also data on the temperature dependence of the adhesive strength of the above coatings, indicated[77] that the polar groups of the ionomeric component are oriented on the surface of the substrate, leading to an increase in the adhesion of the coating. The principal feature of the dependence of the strength of adhesion on the composition of the IPN, however, is the presence of extremal points.

Up to a certain composition, the microregions of one of the components, distributed in the matrix of the other component, apparently act as a reinforcing filler, leading to an

improvement in various characteristics of the materials based on IPN, in particular the adhesion of coatings. In the range of medium and similar compositions, however, inversion of the phases is observed, that is the component acting as the micro-filler gradually becomes the matrix; in this range there is generally a deterioration in both the mechanical and the adhesive properties (see curves *1* and *2* in Fig. 5). The gradual transformation of the filler component into the matrix component produces strained structures, as indicated, for example, by the marked increase in internal strain in the coatings (curve *3* in Fig. 5). This in turn leads to a decrease in the strength of adhesion.

Thus the use of an ionomer as one of the components in the production of coatings based on IPN makes it possible to obtain coatings whose adhesive strength is considerably greater than that of the individual components. A more detailed explanation of the reasons for this phenomenon requires further studies on a wider range of systems.

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The above analysis of published data indicates that the introduction of ionogenic groups into IPN systems leads to a significant change in the mechanical, structural, and relaxational properties of materials based on these IPN. In contrast to non-ionogenic IPN, where a change in properties is achieved only by varying the component ratio in the system, in the case of ionomer-containing IPN it is possible to vary the properties of the materials obtained more widely by changing the quantity and nature of the salt groups in the ionomeric component of the IPN. Information on the preparation and study of ionomeric IPN began to be published only in the last 5–7 years. Reports indicate,[78] however, that studies in this field are being extended; the synthesis of new IPN with ionogenic groups in both components, with opposite charges, is being suggested. Methods are being developed for obtaining IPN in which interpolymer complexes are formed.[67,68]

The use of polymers of more complex chemical character with active groups in the chains as components of IPN naturally complicates the production of the system, and alters its final properties considerably. A comparative study of IPN consisting of polymers of the same chemical character with and without ionogenic groups has not yet been carried out, however. Nevertheless, judging from the above results of structural studies of ionomer-containing IPN, the conditions of the chemical reactions, and also the conditions of microphase separation, in these systems will differ from those in non-ionogenic IPN. The task of the immediate future is to carry out studies in these directions.

Thus ionomer-containing IPN represent a new type of hybrid binder, whose use will make it possible to develop more complex combinations of different polymer structural states and to create new possibilities for controlling the physicomechanical properties of polymeric materials based on them.

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