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Synthesis and Properties of Interpenetrating Networks

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The preparation and the properties of interpenetrating networks are described. Data are reported on the effective density of branch points, and the dependence of viscoelastic characteristics on temperature, proportions of initial components, and mode of preparation. Results are reported for the morphology and mechanical strength indices. The physicochemical properties of interpenetrating networks can be influenced by inorganic fillers previously introduced into one of the components. A list of 35 references is included.

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I. INTRODUCTION

A promising method for modifying the properties of polymers is to prepare mixtures, which may yield materials combining the properties of diverse component polymers. A special place among investigations of such mixtures is occupied by recent studies[1-15] on the production and properties of interpenetrating networks. These are complicated systems comprising two or more three-dimensional network polymers, not chemically combined but inseparable because of mechanical interlocking of chains resulting from the conditions of preparation.

Interpenetrating networks have now been obtained from analogous[1] or chemically related[3] polymers, as well as from systems differing completely in chemical structure and in mode of preparation[6-8]. Thus their preparation can be regarded as a new method for "mixing" not only definitely incompatible but also network polymers, which enables the properties of the latter to be modified. The production of interpenetrating networks from polymers of the most diverse chemical structure is especially promising, since their combination should give materials with a wide range of properties.

II. PREPARATION OF INTERPENETRATING NETWORK POLYMERS

Two methods are available for obtaining interpenetrating networks. The first method consists in swelling a network polymer (first network) in a liquid polymer or oligomer capable of subsequently setting to form a network of a different chemical type (second network) (Fig. 1). Chemical reaction cannot occur between chains of the two network polymers; it is responsible solely for mechanical interlocking of the unlike chains. This method was applied to poly(ethyl acrylate) and polystyrene[2]: the cross-linked polyacrylate (network *1*) was obtained by photopolymerisation in the presence of benzoyl peroxide and diethylene glycol dimethacrylate as cross-linking agent; the resulting sheets were then swollen in styrene with addition of the above initiator and cross-linking agent, and subsequent photopolymerisation gave cross-linked polystyrene (network *2*) embedded in network *1*. Interpenetrating networks were obtained similarly on the basis of poly(ethyl acrylate) and poly(methyl methacrylate) (with tetraethylene glycol dimethacrylate as cross-linking agent)[3,4,12], polystyrene and polybutadiene[15], and also a styrene–divinylbenzene copolymer[1]. In the last case the copolymer was first prepared in the presence of benzoyl peroxide (first network), and specimens were swollen in a mixture of styrene and divinylbenzene with subsequent polymerisation to give a second network embedded in a matrix of the first network of the same nature.

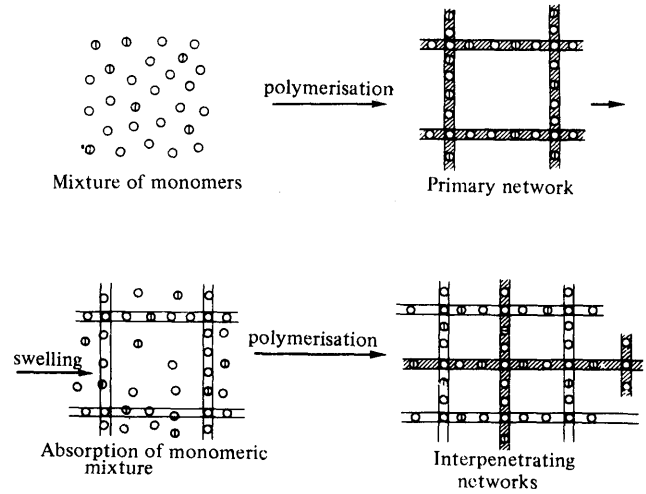


Figure 1. Diagram of first method of generation of interpenetrating networks.

The second method consists in the simultaneous cross-linking of two different polymers already mixed in the same solvent or in suspension. The polymers are selected to ensure mutually independent formation of network structures and to exclude chemical interaction between unlike chains. Frisch et al.[6-10] have used this method to obtain interpenetrating networks consisting of polyurethane based on tolylene di-isocyanate, polyoxypropylene glycol and a polyacrylate, polyurethane and polybutadiene–styrene, and polyurethane and polychloroprene: 50% aqueous emulsions of the polymers containing a cross-linking agent and a stabiliser were stirred vigorously for 1 h, after which films were poured from the resulting composition and kept at a fixed temperature.

The first method of preparation is the more promising, firstly because it permits a more uniform distribution of unlike chains. Secondly, interpenetrating networks can be obtained from the same pair of polymers but with properties varying between wide limits depending on which component is obtained first. This has been shown for cross-linked poly(ethyl acrylate) (network *1*) and a copolymer of styrene with methyl methacrylate (network *2*).[12] If network *1* is synthesised first, and then swollen in a monomer serving as intermediate for the second network, the properties of the resulting interpenetrating networks differ considerably from the "inverse" product obtained when network *2* is synthesised first. We shall discuss the properties of such networks in a later Section.

III. EFFECTIVE DENSITY OF BRANCH POINTS

A fundamental characteristic of the structure of a network polymer is the effective density of branch points, which must therefore first be determined and compared with those in the individual network polymers in order to describe the properties of interpenetrating networks.

Shibayama and Suzuki made such an investigation on interpenetrating networks comprising styrene–divinylbenzene copolymers[1] obtained by the first method to give W_2/W_1 ratios of 1–2 (where W_1 and W_2 are the weights of the first and second networks). The effective density of the network ν_e, determined by means of the equation

$$\nu_e = E/3dRT,$$

where E is the modulus of rubberlike elasticity and d the density of the specimen, was compared with the density of the network ν_T calculated from the ratio of the monomers in first and second networks. Fig. 2 illustrates the dependence of ν_e on ν_T for the first network (line *1*) and for the interpenetrating networks (line *2*). Values of ν_e are evidently higher for the latter, which was attributed[1] mainly to an increase in the number of mechanical contacts on interpenetration of the two networks. The swelling of these specimens in toluene and in acetone was less than those of the individual polymer networks, which confirms the increase in ν_e for the interpenetrating networks. Similar results were obtained by Millar[11] for the same system.

Frisch et al.[6,8,10] have studied the density of cross-linking of interpenetrating networks obtained from chemically different polymers. They determined ν_e by means of the Cluff–Gladding relation[16]

$$\nu_e = \frac{2}{3}\frac{h_0 S}{3A_0 RT},$$

where h is the height of the undeformed swollen cylindrical polymer specimen, A_0 its cross-sectional area, S the slope of the linear dependence of the compression of the specimen on the applied stress, R the universal gas constant, and T the absolute temperature. Frisch suggests that, if ν_e for the interpenetrating networks is greater than the arithmetic mean calculated from the ratio of the initial polymers, the networks should exhibit interpenetrability: i.e. he regards ν_e for the mixed system as a measure of the degree of interpenetrability of the networks.

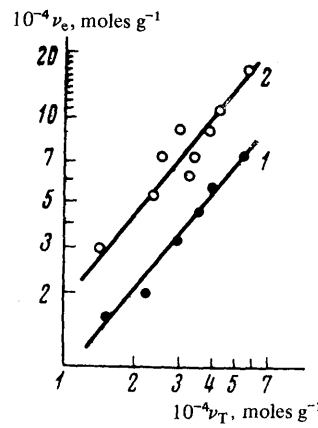


Figure 2. Dependence of ν_e on ν_T for: 1) first network; 2) interpenetrating networks based on styrene–divinylbenzene copolymer.

Table 1. Densities of cross-linking ν_e of interpenetrating networks and of individual components.

System	$10^4 \cdot \nu_e$, mole cm^{-3}	Φ_3, %	System	$10^4 \cdot \nu_e$, mole cm^{-3}	Φ_3, %
Poly(butadiene-styrene)	0.094	—	Polyurethane + polyacrylate	0.392	9.5
Polyacrylate	0.385	—			
Polyurethane	0.350	—	Polyurethane + poly(butadiene-styrene)	0.055	—
Polychloroprene	0.306	—	Polyurethane + polychloroprene	0.390	21.9
			Polyacrylate + poly(butadiene-styrene)	0.342	42.5

The mixed system is considered to comprise three phases—networks *1* and *2* with an intermediate region *3*—the total network density of which is defined as

$$\nu_e = \Phi_1(\nu_e)_1 + \Phi_2(\nu_e)_2 + \Phi_3[(\nu_e)_1 + (\nu_e)_2],$$

where $(\nu_e)_1$ and $(\nu_e)_2$ are the network densities of the individual polymers, and the Φ are the fractions by volume of the different regions, with $\Phi_1 + \Phi_2 + \Phi_3 = 1$. If $\Phi_1 = \Phi_2$, we have $\nu_e = \frac{1}{2}[(\nu_e)_1 + (\nu_e)_2](1 + \Phi_3)$, and therefore $\Phi_3 = [\nu_e - (\nu_e)_0]/(\nu_e)_0$, where $(\nu_e)_0$, the density of cross-linking of the system in the absence of interpenetrability, is given by the arithmetic mean of the ν_e for the individual components. Thus Φ_3 represents the degree of interpenetrability. Table 1 lists values of ν_e obtained by Frisch et al.[6] for the system and for the individual components. In several cases $\Phi_3 > 0$, which suggests interpenetrability, but for the polyurethane–poly(butadiene–styrene) system

$\Phi_3 < 0$, since $\nu_e < (\nu_e)_0$. This is explained by the plasticising action of poly(butadiene–styrene) on the polyurethane network. It was also found that this interpenetrated system swells considerably more than did the individual polymers, which confirms the observed diminution in ν_e relative to the components.

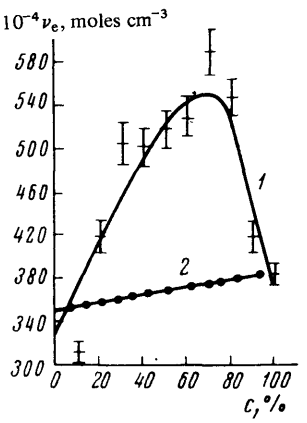


Figure 3. Dependence of effective density of cross-linking of interpenetrating networks on polyacrylate concentration c: 1) experimental; 2) theoretical.

Interesting results on the composition dependence of the density of cross-linking were obtained by Frisch[6] for a polyurethane–polyacrylate system. Fig. 3 shows an extremal dependence of density of cross-linking of the interpenetrating networks on the polyacrylate content. Maximum ν_e is observed at 70% of the latter. The absolute densities of cross-linking are considerably greater than those calculated from the stoichiometric composition. This system will be considered in greater detail in connection with mechanical properties.

IV. EFFECT OF TEMPERATURE ON VISCOELASTIC PROPERTIES

A considerable proportion of research on interpenetrating networks has been concerned with mechanical properties and their temperature dependence. Such an approach provides information on temperature transitions, as well as some indication of the compatibility of the components.

Investigation of the temperature dependence of Young's modulus for the poly(ethyl acrylate)–poly(methyl methacrylate) system[5] has revealed a broad transition region, and dilatometric examination shows also a glass point. Curves representing the variation of the modulus during stretching under creep conditions obtained[4] for the same system show a broad transition region. The range of dispersion of Young's modulus is greater for interpenetrating networks. From the results obtained for this system Sperling suggests that poly(ethyl and methyl methacrylates) are partly compatible components in the formation of interpenetrating networks.

Examination of the relaxation properties of polymer mixtures, e.g. for 50 : 50 mixture of poly(vinyl chloride) and SKN-40 [butadiene–acrylonitrile] synthetic rubber[17], also revealed a single broad transition region.

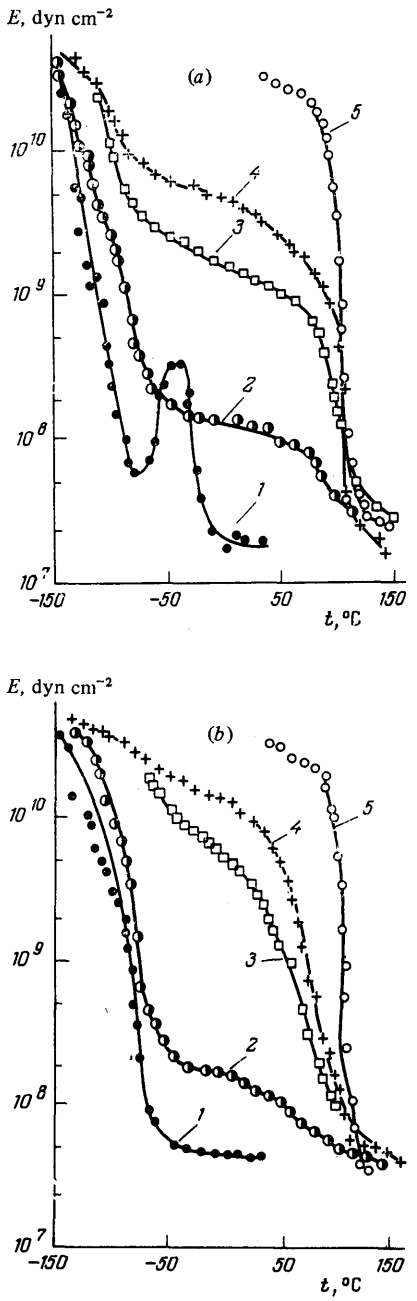


Figure 4. Temperature dependence of Young's modulus for interpenetrating networks containing different quantities (%) of polystyrene: (*a*) first: 1) 0; 2) 24.4; 3) 61.6; 4) 75.7; 5) 100; (*b*) second: 1) 0; 2) 25.6; 3) 56.9; 4) 72.4; 5) 100.

Interpenetrating networks based on poly(ethyl acrylate) and polystyrene[2] exhibit different properties from the above system: the temperature dependence of Young's modulus reveals two transitions, corresponding to the respective polymers (at −16 and 75°C). The occurrence of two glass points clearly indicates the formation of two polymer phases in systems of this type. The transition temperatures do not correspond to the glass points of the homopolymers: that of poly(ethyl acrylate) is −22°C, and that of polystyrene 100°C. This was attributed to incomplete phase separation and the existence of an intermediate region in the interpenetrating networks.

Interesting results on the temperature dependence of Young's modulus E were obtained by Sperling for interpenetrating networks based on a crystallising and a non-crystallising homopolymer—respectively polybutadiene and polystyrene—first series[15,18]. A second series of specimens was obtained from non-crystallising polybutadiene with polystyrene. The temperature dependence of the modulus (Fig. 4) reveals for the first series two transition regions, with the glass point corresponding to polybutadiene in the interpenetrating networks higher than in the homopolymer, and that corresponding to polystyrene in the mixed system lower than in the pure polymer. Similar results were obtained for interpenetrating networks based on polystyrene and a polyacrylate.

Incidentally, closer approach of maxima in binary systems was observed when the method of dielectric losses was used to investigate polymers containing polymeric fillers[19], which was attributed to the mutual influence of the components on the molecular mobility of the polymer chains.

Table 2. Incompatibility numbers for first and second series of interpenetrating networks.

Series	Styrene, %	I.N.	Series	Styrene, %	I.N.
First	61.6	0.81	Second	56.9	0.62
	75.7	0.90		72.4	0.65

Interpenetrating networks based on crystallising polybutadiene do not crystallise over the temperature range investigated (Fig. 4*a*), exhibiting merely a steeper fall in modulus with temperature than for the second series. The transition ranges are broader in the latter than in the first series. Sperling suggests that the degree of incompatibility should be assessed from the results. He introduces the concept of "incompatibility number (I.N.)", which can be calculated from the temperature dependence of the modulus by means of the equation

$$\text{I.N.} = 1 - \frac{X_1^{-1} + X_3^{-1}}{2X_2^{-1}},$$

where $X = \mathrm{d}(\lg E)/\mathrm{d}T$, the subscripts *1* and *3* correspond to the two transition ranges, and *2* denotes the plateau between the transitions. The incompatibility number varies from zero for a compatible system to unity for an incompatible system. The values listed in Table 2 show that the components of the first series are more incompatible than those of the second series. The reason is that the polybutadiene in the former series crystallises; the possibility of crystallisation or increase in the degree of order in this series tends to increase the incompatibility number.

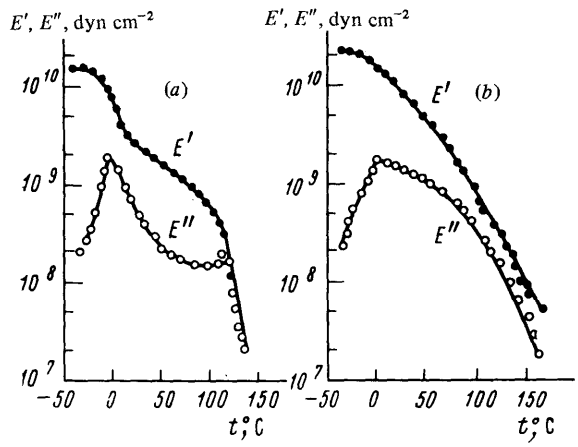


Figure 5. Temperature dependence of E' and E'' for interpenetrating networks of: *a*) 48.8% of poly(ethyl acrylate) plus 51.2% of polystyrene; *b*) 47.1% of poly(ethyl acrylate) plus 52.9% of poly(methyl methacrylate).

Interpenetrating networks of poly(ethyl acrylate) and a copolymer of styrene and methyl methacrylate, with tetraethylene glycol dimethacrylate as cross-linking agent, were chosen[13] for the investigation of viscoelastic properties because the components of the copolymer were chemically different and incompatible polymers, while the polyacrylate and the polymethacrylate were partly compatible, as noted above. It was supposed that the degree of compatibility of the interpenetrating constituents would vary considerably with composition. An additional reason for the choice was that polystyrene and poly(methyl methacrylate) have closely similar glass points (100 and 105°C), so that their copolymer would have a similar glass point, which would simplify analysis of the experimental results. Interpenetrated specimens were obtained with different contents of methyl methacrylate in the copolymer and also with different proportions of the constituent polymers, yielding diverse properties. The temperature dependence of the complex modulus of elasticity for the systems based on poly(ethyl acrylate) and polystyrene reveals two transition ranges for both real and imaginary parts E' and E'' (Fig. 5*a*). The transition corresponding to the former polymer is 10 deg above that for the polystyrene homopolymer. In Sperling's view this indicates some molecular compatibility. With interpenetrating systems based on the polyacrylate and the copolymer the peak in the temperature dependence of E'' becomes broader in the copolymer, and the second transition gradually disappears. Interpenetrating systems comprising the polyacrylate and the polymethacrylate exhibit only one transition in the temperature dependence of E' and E'' (Fig. 5*b*), covering a temperature range around 100°C; these results support the earlier conclusion concerning the compatibility of this system.

With a high content of the elastomeric component—poly(ethyl acrylate)—the real part E' drops rapidly after a low-temperature transition (Fig. 6*a*), but with a low content it varies little with temperature (Fig. 6*b*). From this Sperling deduces that the elastomer forms the continuous phase in the first case, whereas the plastic phase is continuous in the second case.

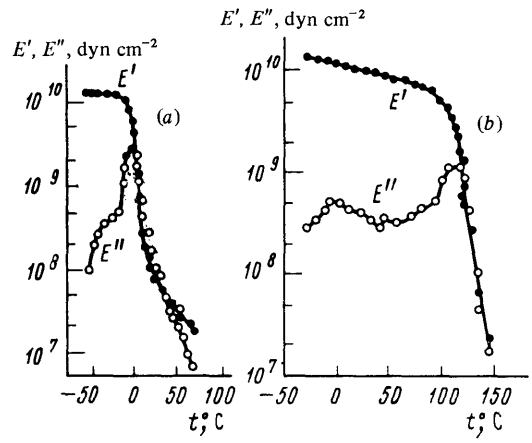


Figure 6. Temperature dependence of E' and E'' for interpenetrating networks of poly(ethyl acrylate) and polystyrene: *a*) 74.4% + 25.6%; *b*) 23.9% + 76.1%.

This worker showed also[13] that the components of the complex modulus and their temperature variation depend on the mode of preparation of the system. The experimental results plotted in Figs. 5 and 6 relate to interpenetrating networks in which the elastomeric part had been synthesised first, and the second network had been polymerised in it (after the monomeric mixture had swollen). But if the second network is prepared first, and then the first network—poly(ethyl acrylate)—is polymerised in it, the resulting "inverse" network exhibits a different temperature dependence of the modulus. The "inverse" system was more rigid than a system obtained by the first method, which indicates the continuity of the polystyrene phase in this network.

Thus investigation of the viscoelastic properties of these systems has shown that those based on poly(ethyl acrylate) and polystyrene are almost incompatible, whereas those comprising the polyacrylate and poly(methyl methacrylate) exhibit considerable miscibility. Materials having different degrees of compatibility are obtained by varying the ratio of the components and the content of the polymethacrylate.

In the investigation of the viscoelastic properties of interpenetrating networks of polyurethane and the polyacrylate, Frisch tried to apply to the results a model developed by Takayanagi[20] for mixtures of polymers. The polyacrylate was regarded as a matrix in which the polyurethane was dispersed. He used the equation

$$E^* = \lambda \left(\frac{\psi}{E^*_{pu}} \cdot \frac{1-\psi}{E^*_{pa}} \right)^{-1} + (1-\lambda) E^*_{pa}$$

in which E^*, E^*_{pu}, and E^*_{pa} are the complex moduli of the system, polyurethane, and the polyacrylate respectively. The parameters ψ and λ are related by the formula $\psi\lambda = \Phi_{pu}$, the fraction by volume of polyurethane in the system. The closest agreement with the experimental results is obtained by assigning to λ the values 9.45, 0.620, and 0.88, and to ψ the values 0.667, 0.806, and 0.795 for percentage ratios of the polyacrylate to the polyurethane of respectively 70/30, 50/50, and 30/70. The experimental results were satisfactorily described by one of the models developed for mixtures of polymers.

Sperling et al.[13] also showed that the experimental viscoelastic results for the interpenetrating networks were described satisfactorily in terms of Bauer's model[21], in essence a modified Takayanagi model[20]. The applicability of mechanical models developed for mixtures comprising one polymer dispersed in a matrix of another provides additional indirect evidence that interpenetrating networks constitute a two-phase system.

V. MECHANICAL STRENGTH CHARACTERISTICS

In the preparation of interpenetrating networks it is important to compare their mechanical strength indices with those for the individual polymers, and it is also necessary to monitor the variation of these indices with the ratio of the initial network polymers.

Investigation of the strength properties of the systems based on crystallising and non-crystallising polybutadienes with polystyrene (the first and second series above) has shown[18] that a system having a low polystyrene content behaves as a reinforced elastomer, exhibiting high strength and elongation. Increase to 50% of polystyrene is accompanied by an increase in strength to tenfold that of cross-linked polybutadiene. The maximum elongation at rupture is also greater for the interpenetrating networks than for cross-linked polybutadiene. The former are comparable in strength with a block copolymer of styrene and butadiene, but considerably stronger than the random copolymers. The first series are rather stronger than the second series, as a consequence of the ability of polybutadiene in the former to crystallise when stretched. The impact strength of interpenetrating networks having a high polystyrene content exceeds those of a graft copolymer of the same nature and of a styrene homopolymer by factors of 4 and 15 respectively.

The strength properties of interpenetrating networks of poly(ethyl acrylate) and a copolymer of styrene and methyl methacrylate[13] depend on which network was the first to be obtained. The "inverse" system (with the copolymer obtained first) is considerably stronger than the "straight" system, but maximum elongation at rupture is greater with the latter. Systems of this type, containing a large proportion of the copolymer, have properties almost unaffected by variation in the composition of the copolymer, i.e. by change in the ratio of styrene to methyl methacrylate in it. Such behaviour has been interpreted in terms of the morphology of the networks, as will be described below.

Frisch et al.[6,8] obtained several interpenetrating systems that were usually intermediate in strength between the component networks. In most cases the experimental strength and maximum elongation were smaller than the theoretical values calculated from the composition. The system formed by polyurethane and a polyacrylate was an exception: its experimental strength exceeded the calculated value, and was almost equal to that of pure polyurethane. However, interpenetrating networks of polydimethylsiloxane and a polyacrylate are stronger than either of the component polymers.

Interpenetrating networks of polyurethane and a polyacrylate showed an unexpected variation in strength properties with the content of the latter polymer (Fig. 7): the strength passed at 10% of the polyacrylate through a minimum, and at 75% through a maximum considerably above the strength of pure polyurethane. Frisch attributed the minimum to a decrease in the concentration of hydrogen bonds resulting from introduction of the less polar polyacrylate, which is then functioning as a plasticiser. Subsequent increase in strength is due to a greater number of tangles (contacts) in the system, which tend to "overcome" the diminished concentration of hydrogen bonds. The tangles are assumed to reach a maximum at 75% of the polyacrylate. This is supported by the maximum density of cross-linking at 70% of the polyacrylate (Fig. 3). The density of cross-linking then diminishes, and hence the strength falls. The presence of polyurethane confers great stretchability on this system; in most cases the maximum elongation at rupture determined experimentally exceeds the calculated value.

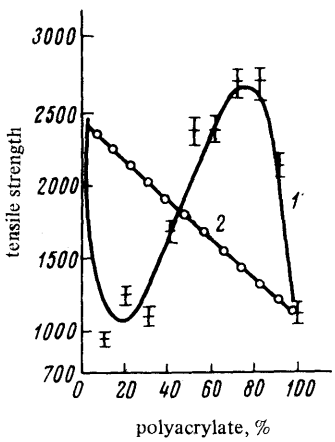


Figure 7. Dependence of tensile strength of interpenetrating networks of polyurethane and a polyacrylate on the content of the latter: 1) experimental; 2) calculated.

The above non-monotonic variation in strength properties and density of cross-linking has been observed in the properties of polyurethanes as functions of the content of inorganic fillers (Aerosil and carbon blacks).[22] In the case investigated by Frisch, the polyacrylate might be regarded as a polymeric filler for the polyurethane. Regarding the properties of interpenetrating networks as those of polymer–polymeric filler systems has been an extremely fertile approach[14], which we shall discuss in detail in connection with the properties of filled interpenetrating networks.

VI. STRUCTURE

Electron-microscopic investigation of the morphology of various types of interpenetrating networks undertaken by Frisch et al. and also by Sperling et al.[12,16] confirms the presence of two polymeric phases deduced from the viscoelastic properties.

Electron micrographs obtained by Frisch et al.[6,8] for a polyacrylate and for polyurethane separately revealed no clearly defined structures, whereas those for the interpenetrating networks exhibited regions differing in optical density, which were regarded as indicating the presence of two phases corresponding to the individual components. Furthermore, the distance between regions of polyurethane embedded in the polyacrylate matrix diminished as the polyurethane content increased from 30% to 50%, and at 70% polyurethane had become the matrix, in which polyacrylate regions were embedded: i.e. inversion had occurred. In this last case the strength was at a minimum (Fig. 7). Increasing the content of the "rigid" phase (the polyacrylate) produces an initial increase in strength, as noted earlier, to reach a maximum at a 70% content. Unfortunately, micrographs were not obtained at higher polyacrylate contents, so that further comparison of the mechanical characteristics with the morphology of the interpenetrating networks is impossible.

Sperling has made an electron-microscopic examination of ultrathin sections of interpenetrating networks of poly(ethyl acrylate) and a copolymer of styrene with methyl methacrylate[13]. The micrographs reveal a complicated cellular structure with cells of ~ 1000 Å, containing a fine structure with regions of ~ 100 Å. With equal quantities of the polyacrylate and polystyrene, the cell boundaries consist of the polyacrylate, while the intracellular region is filled with polystyrene. With equal quantities of the polyacrylate and of the copolymer, the cell boundaries become less well defined with increase in the content of methyl methacrylate in the copolymer, and the regions of fine structure become larger. When the polystyrene units have been completely replaced by poly(methyl methacrylate), no cellular structure is evident on the micrographs, but the system consists of two phases, exhibiting regions of the polymethacrylate and of the polyacrylate. When the ratio of polyacrylate to copolymer is 75/25, i.e. with elastomeric interpenetrating networks, two polymer phases are observed. Initially, when pure polystyrene enters the system, the dimensions of its regions vary between 800 and 1500 Å, while the polyacrylate particles are 100 Å in diameter. On the introduction of poly(methyl methacrylate) units the copolymer particles contract to 200–750 Å, and a fine dispersion of polyacrylate particles in the polymethacrylate is observed when their ratio is 75/25; no cellular structure is detected. When the ratio of polyacrylate to polystyrene (or the copolymer) is 25/75, the morphology varies little with the content of polystyrene or copolymer having a variable quantity of poly(methyl methacrylate). The cellular structure is considerably less well defined than in the previous cases. The strength characteristics remain practically unchanged in the last case, as noted above.

In all the systems poly(ethyl acrylate)—the polymer formed first—constitutes a matrix in which particles of the second polymer phase are disseminated. However, with inverse systems—in which polystyrene, poly(methyl methacrylate), or a copolymer thereof has been formed first—the matrix is a plastic polymer phase in which are distributed particles of the polyacrylate of mean size 150 Å. Thus the morphology of the system is determined by the network produced first, which forms the matrix. Furthermore, the nature of the matrix governs the mechanical strength parameters: if the matrix is the elastomeric polyacrylate, the system is deformed to a

greater extent; conversely, if the rigid component—polystyrene, the polymethacrylate, or the copolymer—was the first to be produced, the resulting system undergoes less deformation.

Investigations of the morphology of polymer mixtures in general have revealed only in certain cases[23] such small particles of polymeric phases ($\leq$ 100 Å) as observed by Sperling for the above systems. This is a specific effect of the first method for obtaining interpenetrating networks, which permits the heterogeneity of the complex system to be diminished. In the second method, used by Frisch et al.,[6,8] considerably larger polymeric phase regions are obtained. These results confirm the above considerations on the advantages of the first method.

Thus the morphological investigations combined with the mechanical properties of the systems indicate that the strength characteristics are determined by the polymer network that forms the matrix. This has been clearly shown by Sperling[12,13] in an examination of the morphological, viscoelastic, and other mechanical properties of interpenetrating networks of poly(ethyl acrylate) and a copolymer of styrene with methyl methacrylate.

Nevertheless, the morphological investigations support the two-phase character of the systems deduced from the viscoelastic properties. The heterogeneity depends on the composition and the mode of preparation; in some cases it is very slight, as noted above. However, these methods of investigation cannot give a criterion of the true, thermodynamic compatibility of the components. Yet hardly any study has been made of the changes in thermodynamic functions accompanying the mixing of network polymers; a few data only are available on the temperature dependence of heat capacity for interpenetrating networks.

VII. CALORIMETRIC AND SPECTROSCOPIC STUDY

The application by Frisch of differential scanning calorimetry to interpenetrating networks of polyurethane and a polyacrylate indicated some interaction between the component polymers[6]. This method gave glass points for the individual polymers identical with those obtained from mechanical relaxation data. In contrast to dynamic mechanical results, however, a single continuous transition was observed for the interpenetrated system, not two glass points. Frisch explained this by specific features of the two methods: whereas mechanical relaxation involves the movement of chain segments, large units—whole molecules or groups of molecules—must be considered in calorimetric measurements. In other words, the presence of a single glass point indicated by viscoelastic results was attributed by Frisch to compatibility or interpenetration of segments, whereas the presence of a transition established from heat-capacity measurements represented mixing of small groups of molecules. In the opinion of the Reviewers the explanation given by Frisch can hardly be accepted as satisfactory. It is more probable that such divergence in the results obtained by the two methods is due to a difference in their resolving power.

No new absorption bands were detected on the application of infrared spectroscopy to interpenetrating networks of polyurethane and the polyacrylate[6]: only bands characteristic of the individual polymers were observed. Hence chemical interaction does not occur between the mixed three-dimensional systems.

VIII. FILLED INTERPENETRATING NETWORKS

It has been noted above that interpenetrating networks can usefully be regarded as containing a polymeric filler. Investigation of the effective density of branch points in network polymers into which inorganic fillers have been introduced at the stage of formation of the three-dimensional network showed[22] that the network is more imperfect in the presence of the large surface area than when polymerisation occurs in the absence of a filler. The reason is that the strongly developed filler surface at the beginning of the reaction may increase the rate of termination of reaction chains at the surface, with a consequent diminution in the frequency of network formation, which becomes more imperfect. Adsorption of growing polymer chains on the filler surface at later stages in the reaction produces a considerable decrease in their mobility, which affects the rates both of growth and of termination. All this tends to result in a more imperfect structure of the three-dimensional network.

In view of the above considerations the Reviewers have compared[14] the properties of individual network polymers containing inorganic fillers with those of filled interpenetrating networks and of such systems filled with Aerosil introduced into one of the polymers. Polyurethane was the first network, and was then swollen in a mixture of styrene and divinylbenzene with addition of benzoyl peroxide and further polymerisation of the second, copolymer network. Determinations were first made of the densities of the specimens and the effective frequencies of branch points both in the initial components and in the interpenetrated system. The experimental densities were intermediate between those of the individual networks, in agreement with results obtained by some workers[4,6] but contradicting those obtained by Millar[11], who found that the density of the interpenetrating networks had increased relative to those of the initial components. The experimental densities were in several cases, in particular with small W_2/W_1 ratios, less than the additive values. With increase in this ratio and in the filler content the experimental density approaches the theoretical value and then exceeds it, which is especially noticeable at high W_2/W_1 ratios and the maximum filler content.

Flory's method[24] was used for the quantitative assessment of the variation in frequency of interpenetrating networks. Dioxan was used for swelling, since the temperature dependence of the volume fraction v_2 of the polymer in the swollen gel showed that the parameters for interaction of the individual network polymers with this solvent were very closely similar at $\psi \simeq 0.30$. Hence this value can be used to calculate the network frequency in the interpenetrated system. The results listed in Table 3[14] show that the experimental effective network densities ν_e/v are always smaller than the additive values calculated from those of the individual networks.

The effective density of branch points for the system investigated is "intermediate" between those of the individual networks: it exceeds the density of polyurethane and is less than ν_e/v for the copolymer. These results were explained on the basis of the above views and earlier ideas on the structure of filled polymers[25,26]. Interpenetrating networks can be regarded as filled systems in which one of the networks is a continuous network polymeric filler for the other. An attempt can then be made to describe the properties by the effect of a filler on the structure of a network formed in its presence. It had already been established that the structure of a polymer network produced in the presence of a solid surface always

Table 3. Theoretical and experimental values of $10^4 \nu_e/v$ for interpenetrating networks of polyurethane (first) and a styrene–divinylbenzene copolymer (second).

Aerosil, %	$10^4\left(\frac{\nu_e}{v}\right)$ Individual networks, expt.			$\frac{W_1}{W_2}$	1% Divinylbenzene			$\frac{W_2}{W_1}$	2% Divinylbenzene			$\frac{W_2}{W_1}$	3% Divinylbenzene		
	first	second +2% +3% divinylbenzene			$10^4\left(\frac{\nu_e}{v}\right)_{expt.}$	$10^4\left(\frac{\nu_e}{v}\right)_{theor.}$	$10^4\frac{\Delta\nu_e}{v}$		$10^4\left(\frac{\nu_e}{v}\right)_{expt.}$	$10^4\left(\frac{\nu_e}{v}\right)_{theor.}$	$10^4\left(\frac{\Delta\nu_e}{v}\right)$		$10^4\left(\frac{\nu_e}{v}\right)_{expt.}$	$10^4\left(\frac{\nu_e}{v}\right)_{theor.}$	$10^4\frac{\Delta\nu_e}{v}$
0	5.0	14.0	30.0	0.305	5.4	7.0	−1.6	0.283	6.2	7.8	−1.6	0.289	6.6	11.9	−5.3
	—	—	—	0.349	5.1	7.1	−2.0	0.268	5.9	7.9	−2.0	0.308	6.2	12.2	−6.0
0.5	—	—		0.412	4.0	6.1	−2.1	0.175	4.6	6.0	−1.4	0.242	5.0	9.8	−4.8
	4.0	9.0	12.0	0.447	3.9	6.4	−2.5	0.256	4.7	6.3	−1.6	0.240	4.4	9.8	−4.4
								0.305	4.2	6.6	−2.4	0.297	4.5	10.7	−6.2
								0.494	4.7	7.7	−3.0	0.500	4.7	13.7	−9.0
1.0				0.492	5.9	7.5	−1.6	0.289	—	7.8		0.328	5.9	12.3	−6.4
	5.0	10.0	13.0	0.554	5.5	7.5	−2.0	0.462	6.6	8.6	−2.0	0.666	6.2	16.3	−10.1
												2.985	7.1	24.6	−17.5
1.5				0.425	6.3	7.5	−1.2	0.149	6.7	7.0	−0.3	0.14	6.9	8.5	−1.6
	6.0	11.0	18.0	0.498	6.3	7.7	−1.4	0.443	7.2	8.6	−1.4	0.697	6.7	16.4	−9.7
								0.501	7.0	8.9	−1.9				

differs from that of an unfilled polymer: for example, the effective network density of a polymer formed in the presence of a dispersed filler is usually less than the network frequency of the unfilled polymer. In the production of interpenetrating networks the second network, i.e. the styrene–divinylbenzene copolymer, is formed in the presence of an existing first network (polyurethane), i.e. in the presence of a solid surface. As in a filled polymer, therefore, defects may appear here in the network owing to a diminished quantity of chemical branch points and the generation of "free ends" in the network. The effective density of branch points in the second network, formed in the presence of the first network, will therefore be smaller than the frequency of the individual second network.

Nevertheless, chain entanglements are formed during polymerisation, which act as additional network branch points, and hence increase the total density of branch points in the interpenetrating networks. The experimental ν_e/v will be greater or less than the additive value depending on which of the effects predominates, and in some cases equality may be expected. In view of the above considerations the suggestion by Frisch that ν_e/v be regarded as an index of the compatibility of the components in the interpenetrating networks cannot be accepted unreservedly: the components may be partly compatible even when $(\nu_e/v)_{exp} < (\nu_e/v)_{theor}$.

Inspection of Table 3 shows also that the difference between experimental and theoretical values of ν_e/v increases with the content of cross-linking agent in the second network, and especially with the content of the latter in the system, i.e. with increase in W_2/W_1. A similar type of variation in ν_e/v is found for interpenetrating networks containing an inorganic filler previously introduced into the first network: the difference between experimental and theoretical values increases with the content of the second network and with its "hardening" resulting from increase in its content of cross-linking agent—divinylbenzene.

Both these factors—increase in the content of divinylbenzene in the second network and increase in the ratio W_2/W_1—tend to increase the number of rigid phenyl groups in unit volume, which prevents formation of chemical branch points in the interpenetrating network and also "hardens" the chain segments between the branch points, preventing formation of physical branch points by the interaction of polar groups. The latter effect is very significant, since it had been established earlier[27] that the proportion of physical links in polyurethane networks is very large. However, the introduction of rigid blocks, as occurs in the system described here, decreases this proportion. All these increase the divergence between experimental and calculated ν_e/v. Thus the effective density of cross-linking of interpenetrating networks is determined by the chemical structure of the initial components and also by their proportions.

Temperature transitions in these systems have been studied by measuring dielectric losses at 300 Hz over a wide temperature range (from −130 to +120°C)[14]. The styrene–divinylbenzene copolymer does not exhibit a maximum value of tan δ within this range. Results are therefore reported for the temperature dependence of tan δ for the polyurethane network and for the interpenetrating networks with a constant W_2W_1 ratio and different quantities of filler (Fig. 8). A maximum in tan δ corresponding to dipole–segmental losses of cross-linked polyurethane (Table 4) is observed at −10°C, and shifts to −4°C on introduction of the maximum quantity of filler, owing to the restriction of segmental mobility of the chains between the branch points of the polyurethane network. This is consistent with effects observed earlier[28].

Increase in the filler content in the interpenetrating networks displaces $\tan\delta_{max}$ to higher temperatures. A similar effect is produced by increasing the degree of cross-linking in the second network. Thus an analogy can be drawn between the effects of the filler and of rigid blocks of the second network on the molecular mobility of the chains between branch points of the first network. The combined effect of these factors shifts the maximum losses from −10 to 0°C: i.e. a considerable decrease in segmental mobility of the chains occurs between branch points in the first network. The absolute value of tan δ is greatly diminished, which also indicates increased chain rigidity in the first network.

A structural investigation of this system was made also under a UEMV-100V electron microscope by the

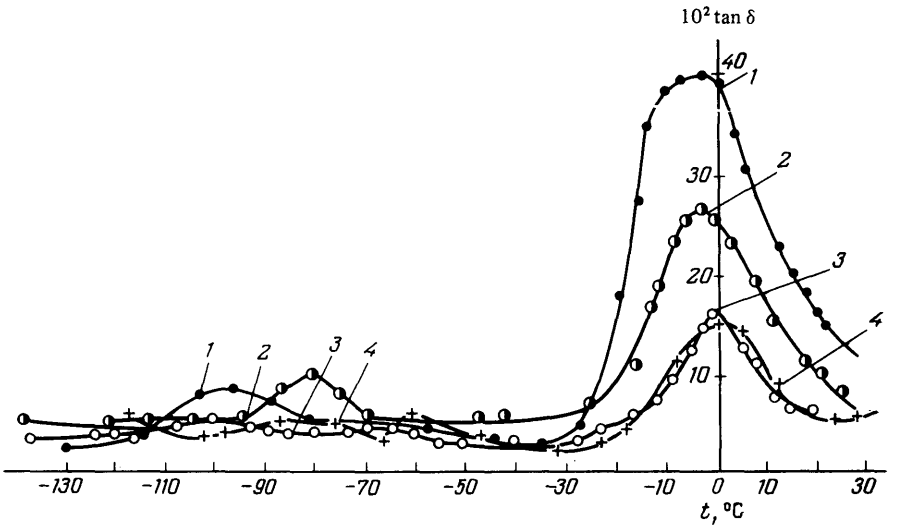


Figure 8. Temperature dependence of tan δ for interpenetrating networks of polyurethane and a styrene–divinylbenzene copolymer for different ratios W_2/W_1 and Aerosil contents (%): 1) 0.3 + 0; 2) 0.3 + 0.5; 3) 0.3 + 1; 4) 0.7 + 1.

Table 4. Dependence of temperature of maximum losses T_{max} (°C) on quantity of filler in polyurethane (first network) and in interpenetrating networks with $W_2/W_1 = 0.5$.

Aerosil, %	First	Divinylbenzene,		Aerosil, %	First	Divinylbenzene,	
		1%	3%			1%	3%
0.0	−10	−11	−5	1.0	−5	−6	−1
0.5	−3	−9	−3	5.0	−4	−2	0

replica method with preliminary treatment in the oxygen plasma of a high-frequency discharge[29]; the individual networks were also examined. A polyurethane rubber is characterised (Fig. 9*a*) by clearly defined globules of size 0.2 μm and by the presence of interglobular regions. The styrene–divinylbenzene copolymer exhibits smaller globules (0.05 μm), which are considerably less well defined (Fig. 9*b*). Specimens of the interpenetrating networks contain coarser globules (0.4 μm) than in the first network, separated by interstructural regions (Fig. 9*c*). The globules are considerably farther apart than in the first network.

From these results it was concluded that formation of the second network in the presence of the first is accompanied by an increase in the distance between the globules in the latter as the interglobular regions become filled with the copolymer. At the same time the globules themselves become larger (Fig. 9*c*). Thus during swelling of the first network in the mixture of monomers, the latter penetrates not only into the interglobular regions but also into the globules themselves, in which copolymerisation also takes place. Thus introduction of the second network has a significant influence on the structure of the first, leading to increased heterogeneity of the system.

In contrast to the structural investigations made by Sperling and by Frisch, the Reviewers examined[14] the

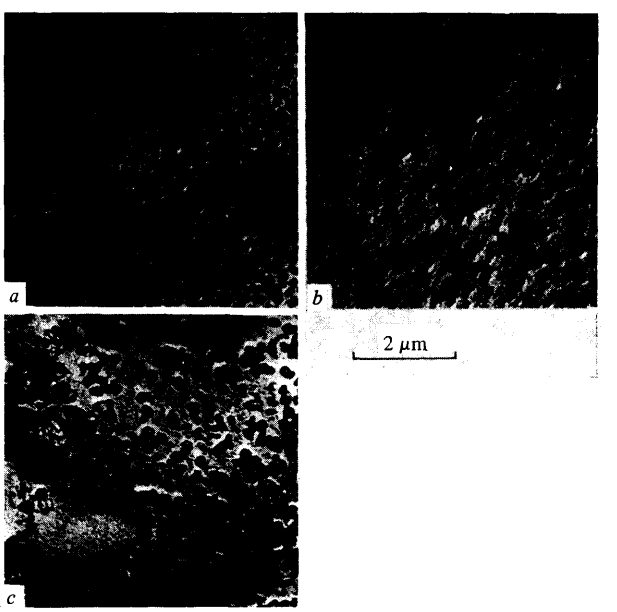


Figure 9. Micrographs of platinum–carbon replicas of the surfaces of: *a*) polyurethane rubber; *b*) styrene–divinylbenzene copolymer; *c*) interpenetrating networks of (*a*) and (*b*).

effect of a filler (Aerosil) on the structure of the first network and on the interpenetrating networks obtained from it. Introduction of 1% of Aerosil into polyurethane suppresses the formation of large globules in the first network (Fig. 10*a*), so that the resulting system containing the filler previously introduced into the first of the constituent networks differs from the unfilled system (Fig.

10*b*) in having less clearly defined structural inhomogeneity. Thus the introduction of a filler into interpenetrating networks may change significantly the structure and probably the physicomechanical properties.

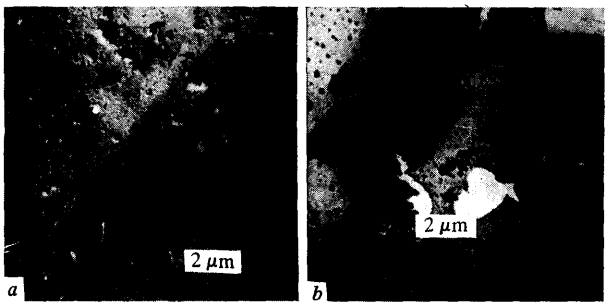


Figure 10. Micrographs of platinum–carbon replicas of surfaces of: *a*) polyurethane rubber filled with 1% of Aerosil; *b*) interpenetrating networks of polyurethane and of a copolymer, filled with 1% of Aerosil, of styrene and divinylbenzene.

The physicochemical and mechanical properties of a polymer are largely determined by the density of packing of the macromolecules. When applied to network polymers, this becomes the density of packing of chain segments between chemical branch points. Any change in intermolecular interactions in the system leads to a change in the density of packing of the macromolecules.

Table 5. Specific surfaces and cohesive energy densities of individual and interpenetrating networks containing various quantities of Aerosil.

Network (W_2/W_1) plus Aerosil	Surface, $m^2 g^{-1}$	Energy, cal cm^{-3}
First (polyurethane)	24.20	84 ± 1.5
Second (styrene–divinylbenzene)	4.96	95 ± 1.5
Unfilled 0.3	21.10	100 ± 1.5
0.3 + 0.5%	16.12	100 ± 1.5
0.3 + 1%	11.16	–
0.3 + 0.5%	8.37	–
0.66 + 1%	4.03	–
2.98 + 1%	2.03	–
Unfilled 0.443	–	100 ± 1.5

The variation in the porosity of the interpenetrating networks of polyurethane and the styrene–divinylbenzene copolymer, both filled and unfilled, was investigated by the Reviewers[14]. Since the second network is formed in the presence of the already formed first network (filled and unfilled), the process obviously being accompanied by adsorption of growing chains at the surface of the filler and of the first network, changes must be expected in the porosity and other parameters of the polymer.

The variation in the porosity was assessed from the sorption of hexane, which is inert towards the interpenetrating networks, and can thus be used to determine the specific surfaces of these polymers[30,31]. Fig. 11 shows that all the isotherms are sigmoid. The BET equation can be applied to such isotherms to calculate the specific surface, which serves here as a measure of porosity[31]. The calculated results (Table 5) show that the first network has a considerably larger specific surface than has the second. Values for the interpenetrating networks are intermediate between those for the individual networks, but closer to the specific surface of the second network.

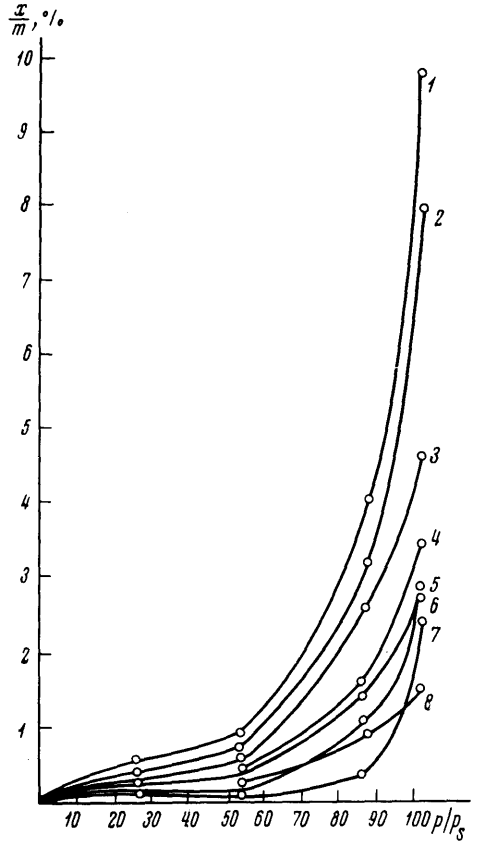


Figure 11. Isotherms for the sorption of hexane vapour by individual and interpenetrating networks with different W_2W_1 ratios and contents (%) of Aerosil: 1) unfilled polyurethane; 2) 0.3 + 0; 3) 0.3 + 0.5; 4) 0.3 + 1; 5) 0.3 + 5; 6) 0.66 + 1; 7) 2.98 + 1; 8) unfilled copolymer of styrene with 3% of divinylbenzene.

The specific surface decreases, i.e. the porosity diminishes, with increase in the ratio W_2/W_1 and in the Aerosil content of the first network. The specific surfaces of the system and of the second network are so small that these polymers can be regarded as non-porous sorbents in Kiselev's classification[32], whereas polyurethane appears as a finely porous sorbent.

Thus entanglements of chain segments of these two networks with a high content of the second network polymer have a considerable effect on the porosity of the system.

This may cause an increase in the density of specimens at high W_2/W_1 ratios, so that the experimental density becomes greater than the theoretical value, as noted above. On the other hand, the density of cohesive energy for the interpenetrating networks is rather greater than those of the individual networks (Table 5). Hence intermolecular interaction is greater in such systems than in the separate networks.

Comparison of the properties of filled and unfilled interpenetrating networks indicates that, if interpenetrating networks are regarded as a filled system in which one component network is a filler for the other, the ideas developed by the Reviewers[22,25,26] on the effect of a filler on the structure of a polymer network can be applied to such systems. We must remember that we are then dealing with a polymeric filler, and must bear in mind that, in contrast to systems with mineral fillers, not only are the properties of the polymer matrix influenced by the filler surface but the properties of the polymeric filler itself also change[19].

The above account shows that the problem of preparing interpenetrating networks and studying their properties is only in an initial stage of development, although the possibilities of the practical application of such materials can already be foreseen. Solution of the fundamental problems of production still lies in the future. In conclusion, therefore, we would like to discuss briefly certain aspects suitable for immediate investigation.

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The primary problem in the synthesis of interpenetrating networks is the mechanism of formation of the second network in the matrix of the first, in view of the chemical and structural heterogeneity of any network polymer[33]. If our model based on the analogy with filled polymer systems is accepted, the matrix will clearly change significantly the conditions of formation of the second network at the interface with the first, and hitherto this has been almost entirely ignored. It is quite obvious that the second network, produced in the first, will never be identical in structure with the network of the same polymer obtained under comparable conditions (of temperature, proportions of components, etc.). Formation of the second network takes place from the very start in the highly viscous medium of the swollen first lattice, i.e. actually under gel conditions. Thus the second network will begin to be formed immediately at the gel point, as it were, but how the gel of the second network will actually be formed, what will be the parameters of this gelation (the extent of reaction at the gel point, the molecular-weight distribution, etc.), is still obscure. By analogy with filled systems the supermolecular structure of the first network will also influence formation of the second network. Therefore additivity of the properties of the two networks cannot in principle be expected: where it is observed, the reasons must be sought.

If the second network is formed by a polymerisation mechanism, chain transfers to molecules of the first network are entirely probable, so that chemical bonding of the two networks is possible even when such bonding should not occur in view of the nature of the two systems. The role of such reactions and the degree of bonding of the networks are still to be elucidated.

The process is complicated also by thermodynamic incompatibility and separation into two phases during formation of the second network. The morphological data reported indicate that the second network is actually formed in interstructural regions of the first, so that structure formation is taking place under complicated conditions. The diagrammatic representation of the structure (Fig. 1), therefore, does not correspond to the actual situation, and perhaps we should speak not of interpenetrating networks but of "parallel" or "coexisting" networks. The structural approach to network formation developed previously[33,34] will therefore be especially fertile.

An important task of research on structure and properties is to establish the effect of the extent of swelling of the first network, the temperature, and the thermodynamics of the "solvent", monomers of the second network, etc. It is necessary also to assess the thermodynamic interaction between the two networks and the possibility of formation of a transition layer and combined supermolecular structures (structural incompatibility), since many properties are determined by the inhomogeneity of the resulting system; as with mixtures of polymers, optimum properties will develop at a certain degree of structural heterogeneity.

Thus we have been the first to detect by reverse gas chromatography the formation of a transition region in interpenetrating networks of polyurethane and a styrene–divinylbenzene copolymer, and have estimated the enthalpy of mixing as a function of the ratio of the networks[35]. However, formation of this region does not indicate compatibility of the component networks, since the experimental enthalpy of mixing was positive. We must therefore speak rather of forced compatibility in such systems. The appearance of a transition region is probably connected with the mechanism of the formation of interpenetrating networks.

Further research is thus required to elucidate specific aspects of the formation and the structure of interpenetrating networks which govern their properties and potential applications.

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