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Phase Structure of Epoxide-Rubber Systems

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Formation of the phase structure during three-dimensional polycondensation in heterophase epoxide-rubber systems is discussed. Aspects of the phase equilibrium and the interdiffusion of the components in the initial systems and during the chemical reaction are examined. A two-stage mechanism of structure formation is suggested. A relation is demonstrated between the thermodynamic affinity of the components and the final phase structure. Possible methods for obtaining systems having specified parameters are considered. A list of 102 references is included.

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I. INTRODUCTION

Current research on the manufacture and application of polymeric materials is commonly aimed at utilising known polymers by combining or modifying them[1,2]. An urgent task is to improve the physicomechanical properties of vitreous solid polymers (to diminish brittleness, increase resilience, enhance resistance to cracking and creep under the influence of the surrounding medium, and lower thermal shrinkage). A most effective way for solving this problem is to produce heterophase compositions by introducing a modifier as particles of a disperse phase into a vitreous polymer matrix[2-6]. The physicochemical properties of the modified polymers depend significantly[2,4-6] on the proportion by volume and the particle size of the disperse phase and on other parameters of the phase structure. However, research in this field does not yet have a general theoretical basis.

The problem of controlling the properties of heterophase compositions cannot be solved without establishing a quantitative relation between the parameters of the phase structure and the physicochemical properties of the composition, nor without knowledge of the mechanism of formation of the phase structure of modified polymers.

The present Review summaries the results of research on phase-structure formation in epoxide—rubber systems. Problems connected with phase equilibrium and interdiffusion of components during three-dimensional polycondensation of the epoxide oligomer are considered separately.

II. PHASE EQUILIBRIUM IN INITIAL SYSTEMS

When a system includes a region of phase separation the compositions of the phases can be calculated from the equality of the chemical potentials of each component in the coexisting phases, with the condition for phase equilibrium that the Gibbs free energy should be a minimum. For a binary system we have[7]

$$\Delta\mu_1' = \Delta\mu_1'', \ \Delta\mu_2' = \Delta\mu_2''$$

where the primes are used to denote different phases.

Consideration of the thermodynamics of polymer solutions can conveniently start from the Flory—Huggins lattice theory[8-11], in which statistical concepts were used to produce the first quantitative explanation of the thermodynamic properties of the solutions. According to this theory the change in free energy on mixing is given by the expression

$$\Delta G_{mix} = RT[\varphi_1 \ln\varphi_1 + \varphi_2 m^{-1} \ln\varphi_2 + \chi\varphi_1\varphi_2] \quad (1)$$

in which ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer respectively, $m = v_2/v_1$ is the ratio of the molar volumes of polymer and solvent, and χ is a parameter representing the excess free energy of interaction required to transfer one mole of solvent from the pure solvent to the pure polymer phase. The formulae for the changes in chemical potential of solvent and polymer are respectively

$$\begin{aligned} \Delta\mu_1 &= RT[\ln(1-\varphi_2) + (1-1/m)\varphi_2 + \chi\varphi_2^2], \\ \Delta\mu_2 &= RT[\ln(1-\varphi_1) + (1-m)\varphi_1 + m\chi\varphi_1^2]. \end{aligned} \quad (2)$$

Differentiating $\Delta\mu_1$ with respect to ϕ_2 yields the spinodal equation

$$1-(1-m^{-1}+2\chi\varphi_2)(1-\varphi_2) = 0. \quad (3)$$

At the critical point at which the difference between the coexisting phases disappears $(\partial\mu_1/\partial\phi_2)_{p,T}$ and $(\partial^2\mu_1/\partial\phi_2^2)_{p,T}$ vanish. Hence the critical point is characterised by the relations

$$(\varphi_2)_{cr} = 1/(1+m^{1/2}), \quad (4)$$

$$\chi_{cr} = 1/2 + 1/m^{1/2} + 1/2m. \quad (5)$$

From these it follows that the phase diagrams of the solutions are unsymmetrical, and also that $\chi_{cr} \to \frac{1}{2}$ as $m \to \infty$. Flory termed the critical point at which $m = \infty$ the *θ-point*.

Later research established a quantitative relation between critical temperature and degree of polymerisation[12]. The interaction parameter comprises enthalpy and entropy components[9,12-14]:

$$\chi = \chi_H + \chi_S = \frac{\Delta H_1}{RT\varphi_2^2} - \frac{\Delta S_1}{R\varphi_2^2}. \quad (6)$$

As $m \to \infty$ we have

$$T_{cr} = \theta \text{ and } \frac{\Delta H_1}{R\theta\varphi_2^2} = \frac{1}{2} + \frac{\Delta S_1}{R\varphi_2^2} \equiv \Psi. \quad (7)$$

Simultaneous solution of Eqns.(4)-(7) yields

$$\frac{1}{T_{cr}} = \frac{1}{\theta}\left[1 + \frac{1}{\Psi}\left(\frac{1}{m^{1/2}} + \frac{1}{2m}\right)\right]. \quad (8)$$

The Flory-Huggins theory proved extremely useful for analysing a large number of experimental results. Despite all its undoubted merits, however, this theory has several defects. The most significant consists in ignoring the concentration dependence of the parameter χ, and also the changes in volume of the components accompanying mixing. The limited character of the lattice theory was noted repeatedly by Flory, who later suggested an improved theory of polymer solutions[15-17].

A vast amount of information has now been accumulated experimentally on the miscibility of components of binary systems. The majority of this research has been done on systems comprising liquids of low molecular weight and also on solutions of polymers. Polymer–oligomer and oligomer–oligomer systems have been studied least[18-29]. Noteworthy among such work has been the use of thermochemical measurements to calculate[18,19] the concentration dependence of the main thermodynamic functions of mixing for a system comprising an epoxide oligomer and a polymeric butadiene-nitrile rubber. The free energy of mixing proved to be negative throughout the composition range, but the concentration dependence was complicated, showing over a certain range a convex curve characteristic of a metastable state. It was concluded that the systems investigated comprised components of limited miscibility.

Phase equilibrium in systems comprising an oligomeric ester-acrylate and an elastomer has been studied[21,22] by an interference method[23]. Examination of the compatibility of polyisoprene with various ether-acrylate oligomers has established the presence of an upper consolute temperature, with the range of compatibility depending on the number of functional groups in the molecule and also on the chemical nature and length of the oligomeric block. Application of the Flory–Huggins theory gave an analytical dependence enabling such lengths to be calculated at which the acrylate end-groups have no effect on the compatibility of the components.

Table 1. Thermodynamic parameters* of ED-20–rubber systems[29].

Rubber	χ^{298}	χ_S	χ_H^{298}	δ_2, cal$^{1/2}$ cm$^{3/2}$	
				expt.	calc.
PB (M_w = 25 000)	2.22	−0.96	3.18	7.5	7.6
OB-KGG(M_n = 2 200) **	1.48	−0.56	2.04	7.9	7.8
OB-KGG(M_n = 3 100)	1.46	−0.50	1.96	8.0	7.7
OB-KGG(M_n = 4 240)	1.49	−0.42	1.91	8.0	7.7
OB-KG(M_n = 3 100)	1.82	−2.35	4.17	7.1	8.1
PDI-1 (M_n = 3 500)	1.86	−0.64	2.50	7.8	7.9
PDI-3A (M_n = 3500)	1.52	−0.52	2.04	8.0	8.3
SKN-8KKG (M_n = 3 100)	0.75	−0.10	0.85	8.6	8.4

* Relative error in determination of the parameters does not exceed 10%.

** M_n = number-average molecular mass.

Hydroxylated oligomeric systems have been studied[24] on mixtures of oligo(propylene glycol) with oligo(ethylene adipate), poly(ethylene glycol), and oligobutadiene, of molecular mass M respectively 1050, 2000, 15000, and 2360. Reverse gas chromatography was used to measure the retention volume of the sorbate at various temperatures, and then the thermodynamic parameters of mixing were calculated. Results for the compatibility of the components were compared with those predicted by the classic Flory-Huggins theory and the new Flory theory of liquid mixtures. It was found[24] that the thermodynamics of mixing of the oligomers was qualitatively more correctly described by the new theory. However, the concentration dependence of the thermodynamic functions of mixing proved to be extremely complicated, and quantitative agreement between experimental results and theoretical calculations was not observed, which was attributed to the influence of intermolecular interactions (hydrogen bonding) on structure formation.

Oligosiloxanes and oligoisobutenes showed no significant change in component volumes on mixing[26]. The observed heat of mixing was slightly dependent on temperature, which permitted application of the classic Flory-Huggins theory to this system. A non-monotonic dependence of χ on mixture composition was obtained on the assumption that this parameter was enthalpic in nature. The most important result[26] was the need to take into account a non-combinatorial entropy contribution to χ. The oligobutadiene-oligostyrene system showed[27] qualitative confirmation of the main principles of Scott's theory[28], a development of the classic Flory-Huggins theory to apply to polymer mixtures.

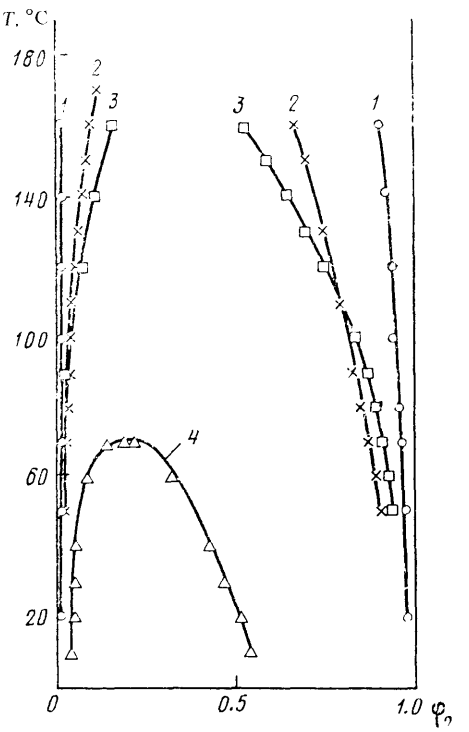


Figure 1. Phase equilibrium diagrams[29] for systems comprising ED-20 with different brands* of rubber: *1*) PB; *2*) OB-KGG with terminal hydroxy-groups; *3*) OB-KKG with terminal carboxy-groups; *4*) SKN-8KKG.

The first investigation of phase equilibrium in systems comprising an epoxide oligomer and an oligomeric rubber established[29] that the introduction of polar groups improves the compatibility of an oligobutadiene (OB) with an epoxide component (Fig. 1). Use of the binodal equation[2]

$$\chi = \frac{\ln(\varphi_1'/\varphi_1'') + (1 - v_1/v_2)(\varphi_2' - \varphi_2'')}{m_1[(\varphi_2'')^2 - (\varphi_2')^2]} \qquad (9)$$

(in which ϕ_1 and ϕ_2 are the respective fractions by volume of ED-20 and an oligomeric rubber, v_1 and v_2 are their molar volumes, $m_1 = v_1/v_0$ with v_0 the molar volume of a segment, and the single and double primes denote symbols corresponding to the two phases in equilibrium) to calculate thermodynamic interaction parameters χ (Table 1) showed a linear dependence on the reciprocal of the absolute temperature. From this relationship χ_H and χ_S were calculated. The equation[30,31]

$$\chi_H = \frac{v_1}{RT}(\delta_1 - \delta_2)^2 \qquad (10)$$

where $\delta_1 = 9.9$ cal$^{1/2}$ cm$^{-3/2}$ is the solubility parameter of ED-20, has been used to calculate values of the corresponding parameter δ_2 for the rubber. Table 1 shows satisfactory agreement with values determined from the theory of group contributions[32]. The carboxylated oligobutadiene (OB-KG) is an exception, apparently owing to marked initial association of the rubber molecules. Such an explanation is supported by the large negative absolute value of χ_S and also by inversion of the binodals of the hydroxylated and carboxylated oligobutadienes at ~100 °C (Fig. 1).

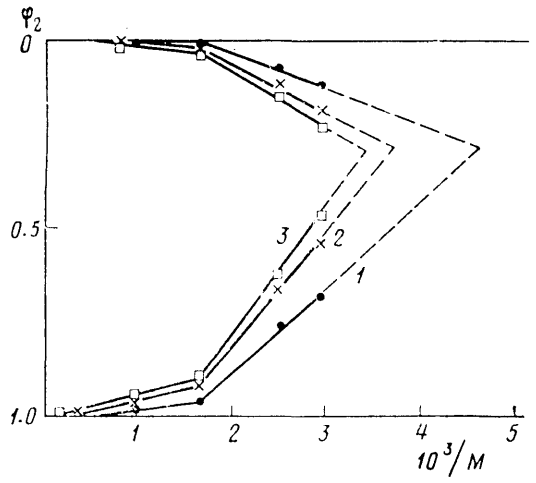


Figure 2. Dependence[6] of solubility of components on molecular mass of epoxide oligomer in ED-20–OB-KGG ($M_n = 2200$) at different temperatures (°C): *1*) 120; *2*) 160; *3*) 180.

Miscibility diminishes with increase in molecular mass of a component, while the upper consolute temperature rises. The influence of molecular mass on phase equilibrium is especially clearly evident in graphs of the dependence of solubility on molecular mass at constant temperature (Fig. 2). On such a diagram two-phase regions are located within the solubility curves, and solutions outside them. With rise in temperature (Fig. 2) and increase in polarity of the oligomeric rubber the region of phase separation becomes smaller. A noteworthy feature of Fig. 2 is the presence of breaks on the graphs. The apparent explanation is that the role of specific intermolecular interactions becomes more important with increase in molecular mass of the epoxide oligomer (EO), which is accompanied by increase in the number of hydroxy-groups in its molecule. The simultaneous improvement in miscibility due to formation of hydrogen complexes partly balances its diminution due to increase in molecular mass of the epoxide. Thus in the presence of specific interactions between the components constancy of δ_{EO} is not a sufficient condition to determine the dependence of the miscibility limits of the components on its molecular mass. The influence of these interactions on the thermodynamics of mixing becomes weaker on passing to lower epoxide oligomers.

III. INTERDIFFUSION IN INITIAL SYSTEMS

If the rate of attainment of phase equilibrium is determined by diffusion, mass transfer by such processes is described by the well known Fick's law[33]

$$I = -D\frac{dc}{dx} \qquad (11)$$

in which I (g cm^{-2} s^{-1}) is the material flux, D (cm^2 s^{-1}) the diffusion coefficient, and dc/dx (g cm^{-4}) the concentration gradient. For binary systems the main process is interdiffusion, which is governed by the coefficient D_v. Analysis based on the thermodynamics of irreversible processes shows that the rate of mass transfer in a multicomponent system depends on the chemical potential gradient of each component[34,35]. The relation between the interdiffusion coefficient and the thermodynamic properties of the system is given by the equation

$$D_v = D_i^* \frac{d\ln a_i}{d\ln \varphi_i} = D_i^* \frac{\varphi_i}{RT}\frac{d\mu_i}{d\varphi_i} \qquad (12)$$

where D_i^* is the self-diffusion coefficient of the ith component a_i its activity, and ϕ_i its volume fraction. The self-diffusion coefficient characterises the thermal mobility of the component molecules and is independent of the chemical potential gradient. The specific form of the composition dependence of the interdiffusion coefficient can be obtained by substituting in (12) expressions for the chemical potentials of solvent and polymer in the solution[36]:

$$D_v = D_1^*[1-(1-1/m)\varphi_1 - 2\chi\varphi_1\varphi_2] \qquad (13)$$

$$D_v = D_2^*[1-(1-m)\varphi_2 - 2m\chi\varphi_1\varphi_2]\,. \qquad (14)$$

To the approximation $m \to \infty$ Eqn. (13) becomes

$$D_v/\varphi_2 = D_1 = D_1^*(1-2\chi\varphi_1) \qquad (15)$$

where D_1 is the relative diffusion coefficient. By means of this formula the dependence of χ on mixture composition is calculated from the concentration dependence of D_1 and D_1^*.

Interdiffusion coefficients are usually determined by an optical-wedge method[37]. Analysis of the component concentration distribution curves with respect to distance by the Matano–Boltzmann method gives a solution of the Fick equation describing a non-stationary diffusion process:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D_v\frac{\partial c}{\partial x}\right)\,. \qquad (16)$$

Self-diffusion coefficients are calculated by means of the modified Fujita equation[36]

$$\lg\frac{D_{1,\varphi}^*}{D_{1,0}^*} = \lg\frac{D_{1,1}^*}{D_{1,0}^*}\frac{\beta f_1\varphi_1}{f_2+\beta\varphi_1} \qquad (17)$$

in which $D_{1,\phi}^*$, $D_{1,0}^*$, and $D_{1,1}^*$ are respectively the self-diffusion coefficient at various ϕ values, the extrapolated value of $D_{1,\phi}$ as $\phi_1 \to 0$, and the self-diffusion coefficient of the solvent, $\beta = f_1 - f_2$, and f_1 and f_2 are the fractional free volumes of solvent and polymer respectively. The last two quantities can be found from the temperature dependence of viscosity by means of Doolittle's equation[38]; $D_{1,1}^*$ is usually

determined independently by means of the Einstein-Stokes equation or by the spin-echo method[39,40].

This approach has been used in calculating thermodynamic functions of mixing of the components for an epoxide oligomer-oligomeric rubber system[41]. The observed composition dependence of interdiffusion coefficients for binary epoxide–rubber systems show (Fig.3) that the absolute value of the coefficient increases with the thermodynamic affinity between the components. At temperatures remote from the critical, as in the Ed-20-SKN-14KKG and ED-20-SKN-40KKG systems, the dependence of D_ν on mixture composition is monotonic.

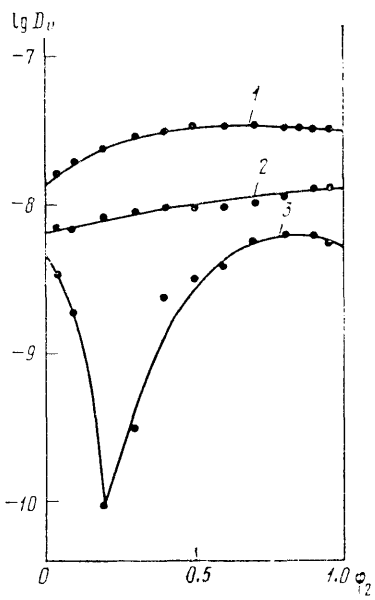


Figure 3. Concentration dependence[41] of interdiffusion coefficient of components at 70 °C in systems comprising ED-20 with different rubbers: *1*) SKN-40KKG; *2*) SKN-14KKG; *3*) SKN-8KGG.

For the ED-20-SKN-8KKG system, which separates into layers at 70 °C (Fig.1), the concentration dependence is characterised by a sharp minimum (Fig.3) in the region of critical compositions. The appearance of such minima is usually attributed to a contribution to the interdiffusion coefficient by a thermodynamic factor (Eqn.12), which tends to zero in the vicinity of the binodal[42]. The coefficient is indeed larger and greater the difference in concentration between the coexisting phases, but such difference is absent at the consolute point[7]. The depth of the extremum diminishes with rise in temperature, and at 130 °C the concentration dependence of χ becomes monotonic.

The plots in Fig.4 show a quite definite concentration dependence of χ calculated by means of Eqn.(16) for epoxide–rubber systems. It is most marked for the ED-20-SKN-8KKG system, which is characterised by the least thermodynamic affinity between the components. A similar effect of the thermodynamic nature of the components on such dependence was found experimentally for solutions of polymers[10,16,17]. With increased content of oligomeric rubber in a binary system with an epoxide the value of χ increases monotonically. An exception is the above ED-20–SKN-8KKG system, curves for which show a clear minimum ($\phi_2 = 0.2$–0.4). The quantity $\partial^2 G_{mix}/\partial\phi_2^2 > 0$ at all mixture compositions in the region of unrestricted miscibility and vanishes at the consolute point[7], and its extremal variation can be assumed to extend over a certain temperature range close to this point. The observed concentration dependence of χ is probably due to this circumstance. In general, one reason for the composition dependence of χ is the formation of association complexes of the solvent in the polymer phase[43,44].

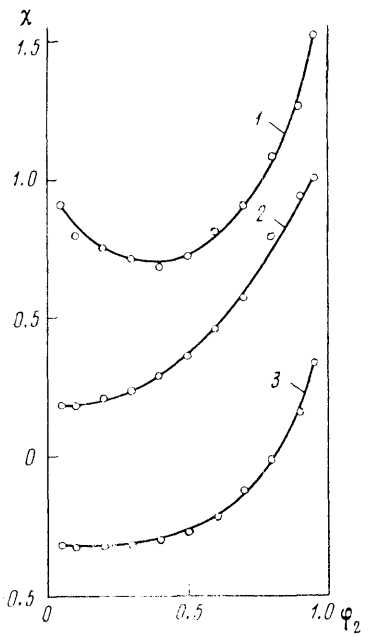


Figure 4. Concentration dependence[41] at 100 °C of χ in binary systems of ED-20 with different rubbers: *1*) SKN-8KKG; *2*) SKN-14KKG; *3*) SKN-40KKG.

Calculation disregarding the concentration dependence(9) for the ED-20-SKN-8KKG system with $(\phi_2)_{cons} = 0.24$ at $T_{cons} = 70$ °C gave $\chi_{cons} = 0.82$. Use of Eqn.(16) for the same conditions gives 0.88, which can be regarded as a more reliable value, since it is almost identical with that (0.87) predicted on the basis of the Flory-Huggins theory (Eqn.5). Calculation by means of a binodal equation apparently gives information on the mean interaction parameter of the components. This method can be usefully applied to estimate χ for systems with similar thermodynamic affinities of the components and in calculations of a spinodal.

We have used isoconcentration curves of the temperature dependence of χ to calculate thermodynamic parameters of mixing for the epoxide–rubber systems investigated[41]. The dependence on the reciprocal of the temperature is linear for all compositions, and the temperature coefficient usually increases with the volume fraction of the rubber. From the results molar thermodynamic functions of mixing were calculated for the epoxide–rubber systems by means of Eqn.(2). Results for the systems formed by ED-20 with SKN-8KKG and SKN-40KKG at 100 °C show that the function ΔG_{mix} is negative throughout the composition range (Fig.5). However, the curves differ in character: for the latter system the ΔG_{mix}–ϕ_2 curve (Fig.5*b*, curve 4) is concave

$(\partial^2 G_{mix}/\partial\phi_2^2 > 0)$, which means that the system is thermodynamically stable with respect to phase separation; from the corresponding dependence it can be concluded that the former system is considerably less stable thermodynamically. Indeed, with fall in temperature the ΔG_{mix} curves exhibit a tendency to form a convex segment, which is characteristic of systems having limited mutual solubility. Similar results have been obtained[18,19] for the ED-20–SKN-10 and ED-20–SKN-18 systems, which were regarded as having restricted compatibility. The positive enthalpies ΔH_{mix} (Fig.5) indicate that mixing is endothermic, and dissolution is due to the positive values of $T\Delta S_{mix}$ exceeding those of ΔH_{mix}. As complied above, the entropy of mixing comprises combinatorial and non-combinatorial components. Estimates showed these quantities to be comparable for the systems investigated (maximum difference between them not exceeding 50%), for which reason it is completely unjustified to ignore the non-combinatorial contribution to the entropy ΔS_{mix}.

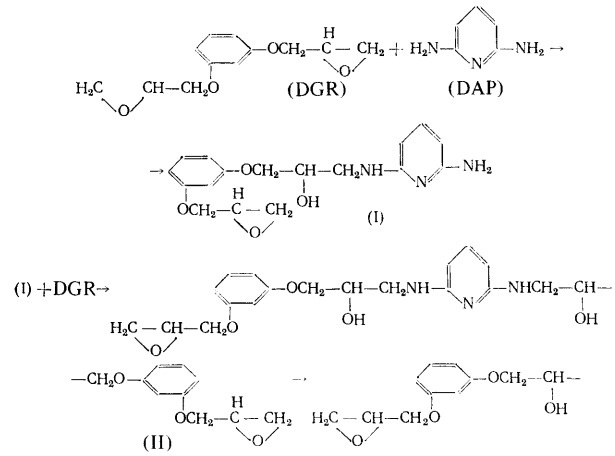
Analysis of the results obtained for all the systems investigated indicates that increase in the thermodynamic affinity between the components due to growth in polarity of the oligomeric rubber increases the absolute values of the free energy ΔG_{mix}, mainly as a consequence of decrease in the enthalpy ΔH_{mix} (Fig.5). For the system with the greatest solubility of the components (ED-20–SKN-40KKG) the enthalpy $\Delta H_{mix} = T\Delta S_{noncomb}$. Mixing under these conditions is due to the combinatorial component $T\Delta S_{comb}$: i.e. the system can be regarded as quasi-ideal.

Thus certain general conclusions can be drawn from the examination of phase equilibria and interdiffusion in the initial epoxide-rubber systems. The Flory–Huggins theory taking into account the non-combinatorial entropy component χ provides an explanation of the dependence of solubility on the thermodynamic affinity between the components.

The thermodynamic stability of the initial systems can be assessed from the quantitative relations between their kinetic and thermodynamic properties.

IV. PHASE EQUILIBRIUM AND INTERDIFFUSION DURING SETTING

The phase state established when the components are mixed undergoes significant changes during the chemical reaction. The reason is a continuous change in the chemical nature of the epoxide component, evident in variation in its thermodynamic properties and increase in the molecular mass:



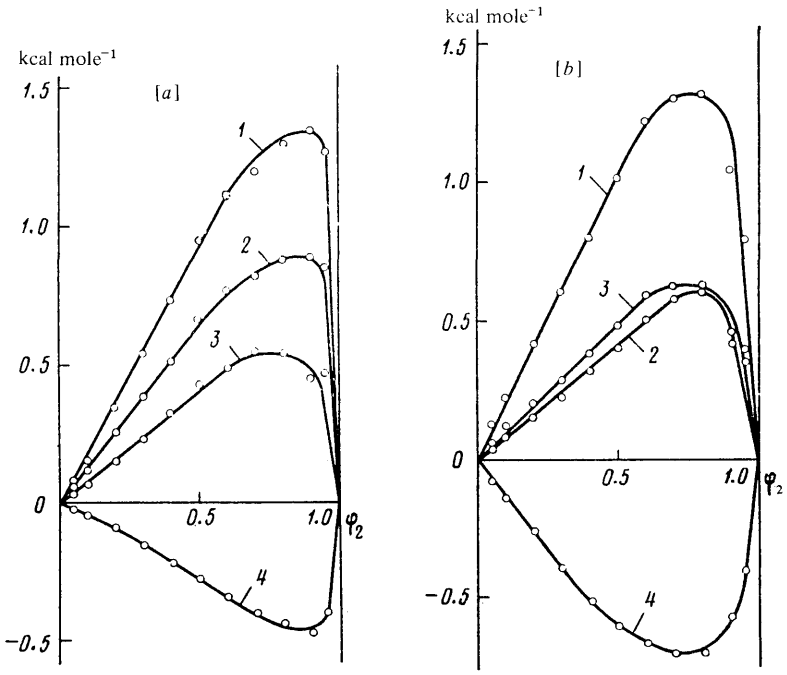
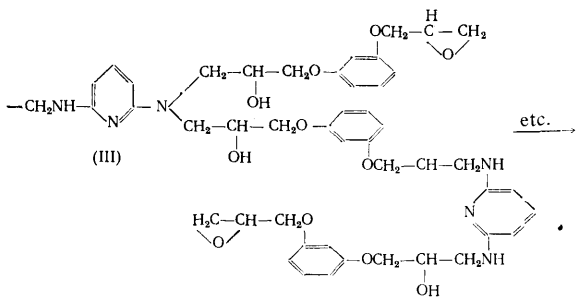


Figure 5. Concentration dependence[41] at 100 °C in binary systems of ED-20 with: *a*) SKN-8KKG; *b*) SKN-40KKG for thermodynamic functions of mixing: *1*) $T\Delta S_{mix}$; *2*) ΔH_{mix}; *3*) $T\Delta S_{mix,non\text{-}comb}$; *4*) ΔG_{mix}.



(III)

Phase equilibrium and diffusion during the three-dimensional polycondensation of an epoxide have been investigated on epoxide–rubber systems based on the diglycidyl ether of resorcinol (DGR) and oligomeric rubbers varying in chemical nature[45]. The hardener used was 2,6-diaminopyridine (DAP).

Additive calculation of the solubility parameters of the chemical conversion products of an epoxide oligomer showed[45] that they remain almost unchanged up to high degrees of converson. However, increase in the number of hydroxy-groups in the epoxide component during the reaction favours specific interactions in the setting system. The presence of such interactions and the increase in molecular mass of the epoxide are probably responsible for the change in phase state during the reaction. The character of the phase equilibrium and the rate of its attainment at different stages in the hardening of the epoxide can be assumed to be the main factors determining the mechanism of structure formation.

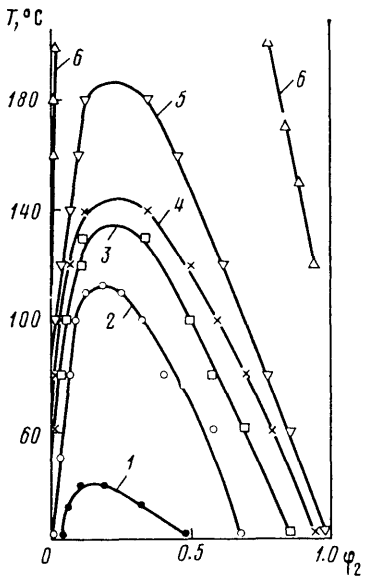
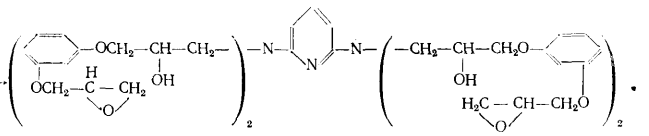


Figure 6. Phase equilibrium diagrams[45] of (DGR-DAP)–PEF-3A system for different degrees of conversion (%): *1*) 31; *2*) 37; *3*) 40; *4*) 42; *5*) 44; *6*) 53.

Analysis of the position of the binodals in the epoxide–rubber system at the stage of mixing of the components shows that increase in the thermodynamic affinity of the rubber for the epoxide in the sequence SKN-8KKG < SKN-14KKG < PEF-3A leads to expansion of the region of homogeneous mixing, in agreement with earlier results. Change in phase equilibrium during chemical reaction was studied on model systems representing products of the hardening of diglycidyloxybenzene by various quantities of pyridinediamine that are completely consumed:

DAP + 4 DGR →



(IV)

The model systems adopted—DGR + (IV)—are not adequate, of course, to describe the actual products of hardening (I–III) and can be regarded merely as qualitative analogues of the real systems, employed for the phenomenological description of the change in phase state under the influence of chemical reaction.

Polycondensation of the epoxide oligomer is accompanied by expansion of the region of phase separation (Fig. 6); the solubility curves shift to higher temperatures, and the solubility of the components becomes infinitesimal when a certain degree of chemical conversion of the epoxide is reached. Analysis of the results revealed a relation between the initial compatibility (i.e. before the start of reaction) and the rate of change of miscibility during reaction. Breakdown of the stability of the epoxide solution in the setting system takes place at different stages of chemical conversion of the epoxide depending on the initial compatibility. As a consequence, change in the phase state of the system occurs at different rates of conversion of the epoxide (Fig. 7).

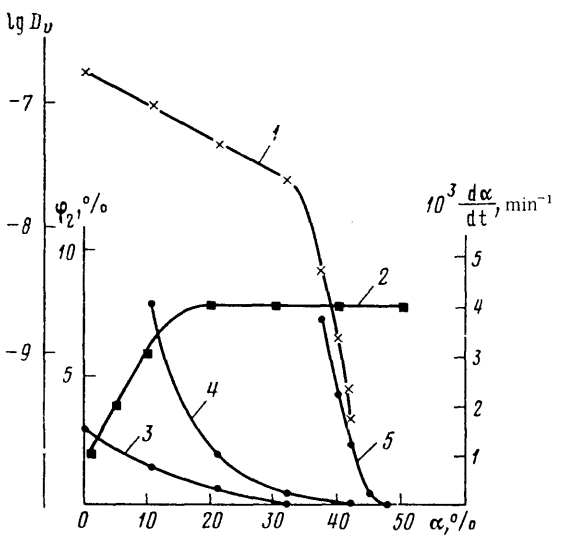


Figure 7. Variation[45] of parameters during hardening at 90 °C in binary systems of DGR–DAP with different rubbers: *1*) interdiffusion coefficient, PEF-3A; *2*) rate of reaction, PEF-3A; 3) solubility of SKN-8KKG; 4) solubility of SKN-14KKG; 5) solubility of PEF-3A.

Fig. 8 illustrates the temperature dependence of the interaction parameter calculated from the binodal equation for the (DGR-DAP)–PEF-3A system. A significant difference in the type of dependence is evident for systems at the stages of

mixing of the components and of chemical conversion of the epoxide. The dependence of the enthalpy of mixing (the temperature coefficient of χ) over a wide temperature range evident in the latter case cannot be explained by ignoring the concentration dependence of χ, since averaging χ with respect to composition leads to its linear dependence on the reciprocal of the temperature, as shown earlier on binary systems. The reason for the anomalous behaviour of setting systems must most probably be sought in their tendency to develop specific interactions. The increase in the enthalpy of mixing as the temperature is lowered suggests that the predominant form of specific interaction is association of oligomeric epoxide molecules, which ultimately impedes mutual dissolution.

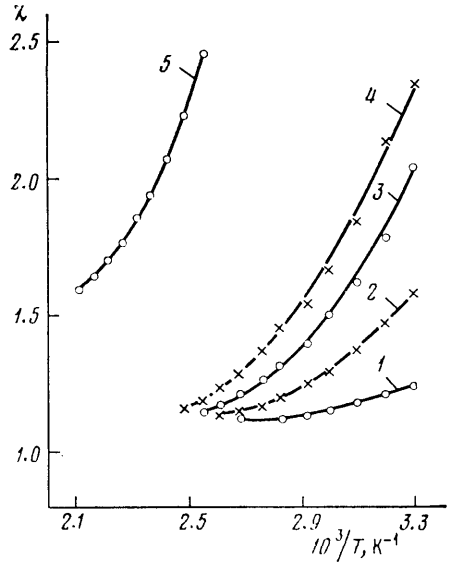


Figure 8. Temperature dependence[46] of χ in (DGR-DAP)–PEF-3A system at different degrees of conversion (%): *1*) 37; *2*) 40; *4*) 44; *5*) 53.

The diffusion method described previously[36] has been used to determine thermodynamic functions of mixing in a hardening epoxide–rubber system of type (DGR-DAP)–PEF-3A. The character of the concentration dependence of the interdiffusion coefficient is found experimentally to change during the course of polycondensation of the epoxide oligomer, from a monotonically increasing to a non-monotonic function of composition with a break in the region of two-phase mixtures[46]. Analogous results have been obtained in a study of diffusion in systems formed by an epoxide oligomer with a hardener and with a plasticiser[47]. The appearance of minima and breaks on the concentration curves during the chemical conversion of the epoxide is due to diminution in the mutual solubility of the components and separation of the hardening system into layers.

The concentration dependence of the interaction parameter calculated by means of Eqn.(16) for such systems with different degrees of hardening of the epoxide oligomer is qualitatively the same as the corresponding dependence at the mixing stage. It is more marked for a system containing the epoxide oligomer at a higher degree of conversion, which is consistent with the hypothetical formation of molecular association complexes of the solvent in the polymer phase[43,44].

The dependence of the interaction parameter on the reciprocal of the temperature is linear over the range 90–130 °C whatever the proportions of the hardening epoxide oligomer and the rubber[46]. As with the initial systems, the temperature coefficient increases with the proportion of the rubber. Its absolute value at a constant volume fraction of the rubber is almost independent of the degree of conversion of the epoxide oligomer. Molar thermodynamic functions have been calculated for mixing the rubber PEF-3A with epoxide oligomers of different degrees of chemical conversion. The changes in chemical potential of both components decrease in absolute magnitude during the chemical reaction: i.e. the thermodynamic affinity of the components diminishes. A consequence is a decrease in the absolute magnitude of the molar free energy of mixing (Fig. 9).

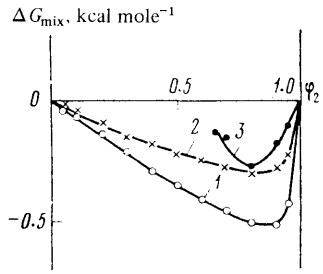


Figure 9. Concentration dependence[46] of ΔG_{mix} in (DGR-DAP)–PEF-3A system at 90 °C for different degrees of conversion (%): *1*) 0; *2*) 21; *3*) 42.

Analysis of the results[46] has shown that the solubility remains endothermic in character during hardening of the epoxide oligomer, with the enthalpy of mixing little changed. This means that the change in free energy of mixing during the reaction is due mainly to the entropy factor. For the initial systems the change in free energy has been determined predominantly by the enthalpy component. The entropy of mixing in turn changes during hardening of the system mainly because of the non-combinatorial term. From this it can be concluded that over the temperature range investigated the hardening system exhibits a tendency to form a solution having a more ordered arrangement of the molecules.

Thus study of phase equilibrium and interdiffusion during hardening of an epoxide–rubber system has shown that the Flory–Huggins theory describes satisfactorily the thermodynamics of the process only over a narrow temperature range. The thermodynamic stability of a solution of an oligomeric rubber in a hardening epoxide oligomer is determined mainly by the entropy factor. The role of specific interactions becomes greater with hardening of the epoxide.

V. MECHANISM OF FORMATION OF PHASE STRUCTURE

The mechanism of phase separation is determined by the relative rates of transition of the system into a non-equilibrium state w_{neq} and for structural relaxation w_{sr}.[48] When $w_{neq} < w_{sr}$, heterophase fluctuations increase with time while remaining unchanged with respect to composition: i.e. the system comprises two phases from the very start. Such a mechanism of phase separation is termed *nucleation*. When $w_{neq} > w_{sr}$, the system stratifies by a spinodal mechanism without formation of heterophase nuclei. For a long time,

right until phase separation, the structure comprises a single phase with fluctuations of composition, which increase with time. A characteristic feature of structures formed by spinodal stratification is the spatial coherence of each phase and the absence of isolated inclusions. Such a mechanism of phase separation is observed comparatively rarely and has been little studied hitherto. Separation by a nucleation mechanism has been studied in greater detail[10,49-98]. Generation of particles of a new phase (nucleation) can take place homogeneously (within a single phase), heterogeneously (e.g. on the surface of the vessel or trace impurities[53-55]), and also by "self-nucleation"[56-59].

The first theories of the homogeneous formation of nuclei[60-63] were based on the postulate that the factor governing nucleation is the relative supersaturation $\Pi = c_{sup}/c_{sat}$, the ratio of the concentrations of supersaturated and saturated solutions. The rate of nucleation is related to the supersaturation by the formula

$$w_{nu} = K_1 \exp[-K_2/(\ln\Pi)^2] \qquad (18)$$

in which K_1 and K_2 are constants. In view of the strong dependence of the rate on the supersaturation it was suggested[62,63] that a critical supersaturation Π_{cr} existed, below which the rate of formation of nuclei was so small that it could be neglected, i.e. $w_{nu} = 0$. Supersaturation is necessary to accumulate the energy required to surmount the barrier ΔG_{nu} associated with formation of nuclei (creation of an interface). The maximum free energy ΔG_{nu} corresponds to the critical size below which a nucleus cannot grow.

Theories of homogeneous nucleation were subsequently improved[64-67]. The rate of generation of a new phase in a condensed system was shown to depend not only on the degree of supersaturation but also on the rate of diffusion of material through the interface. For example, the rate of generation of crystals is described by the equation[67]

$$w_{nu} = (NkT/h)\exp[-(\Delta G_{nu} + \Delta G_D)/kT] \qquad (19)$$

in which N is the number of molecules in 1 cm^3 of liquid, k Boltzmann's constant, h Planck's constant, and ΔG_D the activation free energy of diffusion. The principles underlying the theories of homogeneous nucleation were used to develop theories of heterogeneous nucleation and "self-nucleation" of a new phase. The kinetics and the mechanism of growth of the nuclei have been investigated in greatest detail for crystallisation[64,68-73]. The development of isothermal crystallisation can be expressed[71-73] by the formula

$$a_t = 1 - \exp(-Kt^n) \qquad (20)$$

where a_t is the fraction of the material that has crystallised by time t, and K and n are constants. The rate of growth of a phase structure in a viscous condensed system is proportional to the diffusion coefficient D and the concentration gradient dc/dx resulting from supersaturation[74]:

$$w_{gr} \sim D\frac{dc}{dx} . \qquad (21)$$

The total rate of formation of the new phase is determined by the rate of nucleation and the rate of particle growth[74]:

$$w_{ph} = w_{nu} w_{gr}^n . \qquad (22)$$

Such are the general laws of formation of a new phase in various heterophase systems.

In real heterophase polymer systems, which are of the greatest interest, chemical reaction and phase separation often take place in some measure simultaneously, and exert a strong mutual influence. We shall examine some examples of such processes. Heterophase polymerisation processes of dispersion[75], suspension[76], emulsion[10,77-79], and precipitation[80-87] types have been investigated in some detail.

The main conclusion from the diffusion theory of dispersion polymerisation[75] has been the relation

$$w_{nu} = w_{init}[1 - \pi r^2 N (2P_{cr}D/K_p[M])^{1/2}] \qquad (23)$$

where w_{init} is the rate of initiation, r the particle radius, N the number of particles in unit volume, P_{cr} the critical degree of polymerisation necessary for nucleation of the growing macroradical, D the mean diffusion coefficient for the growing radical, k_p the polymerisation rate constant, and [M] the monomer concentration. The equation for the critical degree of polymerisation relates the final number of particles formed to the solubility of the polymer, dissolving power of the medium, and the critical relative supersaturation:

$$P_{cr} = -\ln\varphi_p \Big/ \left(\chi - 1 - \frac{v_0}{v_m}\ln\Pi_{cr}\right) \qquad (24)$$

with ϕ_p the fraction by volume of the polymer, v_0 the molar volume of a monomer unit, and v_m the molar volume of the solution. Other theoretical approaches have been made to the description of dispersion polymerisation, but none gives more than a qualitative explanation of the observed relations between particle size, polymer solubility, dissolving power of the medium, and quantity of stabiliser.

The simple relation

$$w_p = K_p(N/2)[M] \qquad (25)$$

was established[78] for the dependence of rate of emulsion polymerisation on number of particles. It was subsequently found that this equation provides a satisfactory description of the polymerisation only of those monomers that dissolve their own polymers, e.g. styrene, butadiene, isoprene. The emulsion polymerisation of vinyl chloride and acrylonitrile, which do not dissolve their own polymers, takes place on the surface of particles, not within them. These processes are described in terms of the theory of Medvedev and Sheinker[79], according to which the rate of polymerisation is proportional to the total particle surface. Furthermore, neither theory[78,79] has proved applicable to the emulsion polymerisation of ethylene and vinyl acetate.

Precipitation polymerisation may be accompanied by crystallisation of the polymer[64,88]. The resulting crystals then have a special morphology (fibrillar and acicular), and their macromolecules have extended conformations. Crystallisation in turn influences polymerisation, changing its rate and mechanism.

The copolymerisation of styrene with rubber in bulk or in the block-suspension modification merits separate consideration[84]. The resulting copolymers have a peculiar phase structure: rubber particles surrounded by a thin film of grafted butadiene–styrene copolymer are dispersed in a polystyrene matrix; the particles are inhomogeneous, containing a large quantity of occluded polystyrene as still finer inclusions. The polystyrene particles are occluded by the rubber phase at the moment of phase inversion (occlusion of the first kind) and also during further copolymerisation by separation from the rubber phase of the polystyrene formed (occlusion of the second kind).

A special case of phase separation is observed in the formation of a network structure by polymers[89]. This phenomenon, which has been studied in detail by Dusek[90-93], has been termed *microsyneresis*. It is evident in the separation of liquid (solvent, monomer, oligomers) from swollen cross-linked macromolecules as a consequence of diminution in their swellability due to intramolecular cross-linking of the macromolecules in the course of three-dimensional polymerisation. To describe the thermodynamics of microsyneresis Dusek started from the equation

$$\mu_i - \mu_i^0 = (\Delta\mu_i)_{mix} + RT v v_i \left[\varphi_p^{1/3}\frac{\langle r^2\rangle_d}{\langle r^2\rangle_{sw}} - \frac{1}{2}\varphi_p\right] \qquad (26)$$

in which μ_i and μ_i^0 are the chemical potentials of swollen and unswollen polymers respectively, $(\Delta\mu_i)_{mix}$ is the change in chemical potential of the polymer on mixing, ν is the concentration of elastically active chains, v_i is the molar volume of the solvent, ϕ_p is the fraction by volume of the polymer, and $\langle r^2\rangle_d$ and $\langle r^2\rangle_{sw}$ are the mean square distances between the ends of the network in dry and swollen polymers respectively. Dusek took into account also the variation in entropy of mixing and in chain distribution with degree of swelling. Substitution in Eqn.(26) for $(\Delta\mu_i)_{mix}$ from the Flory-Huggins theory (2) yields a condition of phase separation depending on χ and ν. Hence there should exist critical values of χ and ν on attaining which (in the course of three-dimensional polymerisation) the system begins to stratify. In spite of the availability of experimental results consistent with the theoretical calculations, the legitimacy of the postulates made by Dusek in the calculations is open to doubt[89]. This arises from disagreements concerning the form of the elastic potential[94,95], and also to the absence under real conditions of the proportionality between the dimensions of the network during swelling and the volume of solvent absorbed that is assumed in the calculations.

Thus formation of a new phase complicated by chemical reaction is difficult to describe quantitatively. Existing theories of these processes have not yet reached a stage of development at which a clear physicochemical model could be used to predict the number, size, and shape of the particles formed under any specified conditions.

Table 2. Degrees of conversion α_{sep} at which phase separation begins in (DGR-DAP)–rubber systems[98].

Rubber (%)	PEF-3A (0.2)	PEF-3A (0.5)	PEF-3A (1.0)	PEF-3A (3.0)	PEF-3A (5.0)	SKN-8KKG (0.1)	SKN-8KKG (0.2)	SKN-14KKG (0.2)
α_{sep}*	0.46	0.45	0.44	0.42	0.39	0.30	0.30	0.39
α_{sep}**	0.50	0.49	0.46	0.43	0.41	0.41	0.39	0.46

* Determined from phase equilibrium diagrams.
** Determined from light-scattering data.

Investigation of the formation of a phase structure in epoxide–rubber systems began quite recently[45,98]. Views on the mechanism for a heterophase polymer system were based on results for the phase equilibrium, interdiffusion of components, and kinetics of particle growth of the disperse phase. The scattering of light[99] and the turbidity spectrum[100] were used to examine the kinetics. The phase structure of a hardened system has been studied by electron microscopy[101]. The start of phase separation in the hardening system was established from the kinetic curves of light-scattering intensity. Comparison of these results with Fig.7 revealed that phase breakdown takes place at a later stage than would follow from the phase equilibrium diagram (Table 2). The difference may be due to inadequacy of the model for the real system, but also may have thermodynamic causes. Chemical conversion of the epoxide oligomer disturbs the condition of thermodynamic stability of the solution, corresponding on the phase equilibrium diagram to passage of the binodal through a point determined by the concentration adopted and the hardening temperature. However, separation of heterophase particles begins not at the solution composition corresponding to the limiting solubility of the components but on the attainment of some critical degree of supersaturation.

The variation in mean particle size of the disperse rubber phase during hardening, indicated by the turbidity spectrum, is extremal (Fig.10). The observed course of the kinetic curves can be attributed to the appearance at a certain instant of a fraction of smaller particles.

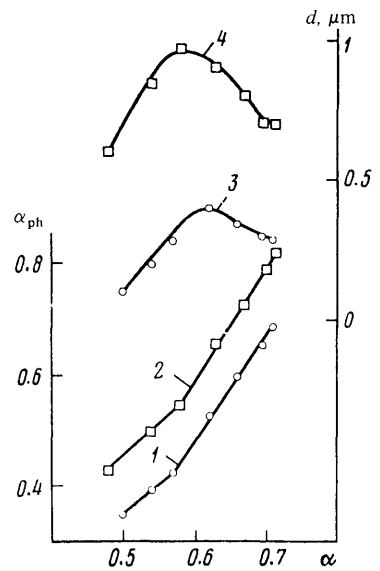


Figure 10. Dependence at 90 °C [98] of degree of phase conversion and mean particle size of disperse phase on extent of chemical reaction for the (DGR-DAP)–PEF-3A system containing different initial rubber contents (%): *1*) conversion (0.5); *2*) conversion (1.0); *3*) particle size (0.5); *4*) particle size (1.0).

Comparison of the particle-size distribution curves for the disperse rubber phase in the hardened systems with the phase diagrams at the mixing stage (Fig.11) indicates that the structure of the hardened composition is related to the compatibility of the initial components. Indeed, the rubber SKN-8KKG, which is poorly compatible with the epoxide oligomer, has the widest particle-size distribution. The use of systems that are most remote from the consolute temperatures, e.g. EO-PEF-3A, narrows the distribution significantly. All the compositions investigated have a bimodal particle-size distribution of the disperse phase. The bimodal character is retained with increase in the volume fraction of the oligomeric rubber. The ratio between coarse and fine particles changes: the mean particle size increases.

The peculiarities of the phase structure of a hardened modified composition—the presence of discrete, spatially unconnected rubber particles dispersed in an epoxide matrix—indicate a nucleation mechanism of heterophase formation. The passage of the particle-size distribution curve of the rubber phase through two maxima apparently indicates a two-stage formation of the phase structure.

Analysis of the results suggests a mechanism of formation of a two-phase structure in a hardening epoxide–rubber system with two stages—nucleation of a new phase and its subsequent growth—involved in transition to a non-equilibrium

state. The rate of growth of nuclei is determined by a parameter equal to the product of the interdiffusion coefficient and the concentration gradient. This gradient is in turn related to the degree of supersaturation of the solution, which is proportional to the rate of chemical reaction of the epoxide oligomer. Fig.7 illustrates the experimental variation in rate of chemical conversion and in interdiffusion coefficient of the components with the degree of conversion of the epoxide. Since this coefficient and the concentration gradient vary in opposite senses, the rate of growth of nuclei is an extremal function of duration of hardening. At the start of the process particle growth is limited by the rate of chemical reaction.

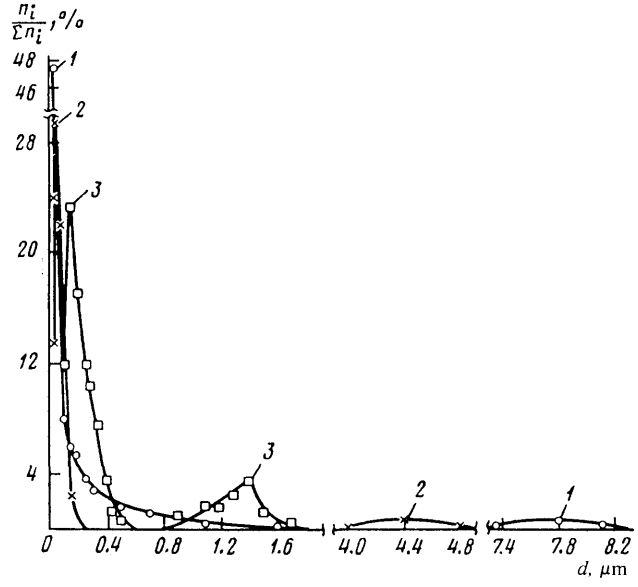


Figure 11. Particle-size distribution curves[45] of disperse phase in hardened systems comprising DGR-DAP with different rubbers: *1*) SKN-8KKG; *2*) SKN-14KKG; *3*) PEF-3A.

The compatibility of the components of an epoxide—rubber system determines the time at which nucleation of a new phase begins (Fig.7). If primary nucleation takes place at a stage limited by the concentration gradient dc/dx, the increase in supersaturation of the solution during polycondensation of the epoxide oligomer is balanced by diffusion in the direction of the centre of growth. A feature of this stage is the coarsening of heterophase particles by "diffusion consumption" of finer particles. Compensation of supersaturation breaks down at a stage determined by the interdiffusion coefficient: as the latter decreases, the radius of the diffusion sphere around the growth centre diminishes. A consequence is the appearance and growth at the periphery of this sphere of regions of localised supersaturation, in which formation of new growth centres—secondary nucleation—results from further chemical change. A mechanism of two-stage nucleation is confirmed by the kinetics of particle growth of the disperse rubber phase. Decrease in the mean heterophase particle diameter is apparently also due to secondary nucleation (Fig.10).

Two-stage formation of the phase structure is evident also in the variation in number of heterophase particles during hardening. The first stage involves a sharp drop in the number as a consequence of intense "diffusion consumption" of extremely fine particles. Increase in the number of particles of the disperse phase at the second stage is due to secondary nucleation. This may be due to diminution in the ability of the cross-linked macromolecules to swell during three-dimensional polycondensation, by analogy with microsyneresis[97]. This hypothesis is supported[98] by the experimental dependence of degree of phase conversion on extent of chemical reaction in the system (Fig.10). Breaks in the curves occur in the region of a critical extent of chemical conversion ($\alpha_{cr} \approx 0.58$):[102] i.e. secondary nucleation begins in the region of gel formation.

The suggested mechanism of structure formation enables us to elucidate the type of relation between the thermodynamic compatibility of the components and the phase structure of the hardened modified compositions. The particle size of the disperse phase is determined by the rate and the duration of growth. The free energy of mixing of the initial epoxide—rubber system determines the "reserve" of thermodynamic stability of the solution towards separation into layers. The greater the affinity between the components the longer the life of the hardening solution and the later does the first nucleation take place: i.e. increase in the compatibility of the components leads to a shortening of growth time and hence a decrease in particle size at the first stage. The size of the particles separating after the first nucleation (second peak in the particle-size distribution curves of the heterophase—Fig.11) does indeed diminish with increase in compatibility. Furthermore, a high degree of supersaturation in systems of well miscible components leads to earlier onset of diffusion control. As a result, both the rate and the time of growth of particles of the disperse phase that separate after the second nucleation (first peak on the distribution curves) increase. Hence the particle-size distribution of the disperse phase becomes narrower with increase in thermodynamic affinity between the components.

Thus the remoteness of the system from the consolute temperature affects the evolution of phase transitions and ultimately determines the character of the phase structure.

VI. CONCLUSION

The laws of structure formation established in this Review enable certain conclusions to be drawn on possible ways of controlling the phase structure. Among factors determining the latter are the thermodynamic properties of the components and the conditions of hardening of epoxide-rubber systems.

Increasing the thermodynamic affinity between the components may effect a narrower particle-size distribution of the disperse phase. In the limit, with systems having components of high miscibility, the solution may remain stable up to the point of gelation. Two-stage formation of the phase structure will then become a single-stage process, with a consequent unimodal particle-size distribution of the heterophase. In this case the particle size diminishes when the components are more compatible[6]. By combining components differing in chemical nature and also varying their molecular masses it is possible to regulate between wide limits the mean particle size and polydispersity of the rubber in the hardened systems. It is noteworthy that the mean size and the polydispersity of the heterophase particles are related in such a way that increase in one of them leads to an increase in the other, and conversely.

Varying the temperature conditions of hardening has a more complicated influence on the mechanism of structure formation. Raising the reaction temperature both increases the rate and shortens the time of particle growth. The particle size of phase inclusions is determined by the influence of temperature on each of these factors, so that the temperature dependence of the particle size of the rubber should be extremal.

With rise in reaction temperature the primary nucleation takes place at a higher degree of conversion. The time at which secondary nucleation begins depends on the ratio of the activation energies of chemical reaction and diffusion. Thus with rise in temperature the two successive nucleations must be expected to approach each other in degree of conversion, as a result of which the polydispersity of the particles should diminish. If it is assumed that secondary nucleation is associated with gel formation, change in the reaction temperature should not displace the start of diffusion control. The polydispersity will then be less dependent on temperature.

Change in the functionality of the initial oligomers has a significant influence on the critical extent of conversion, which constitutes yet another factor affecting polydispersity. Increasing the rubber concentration leads to an increase in the mean particle size of the disperse phase without significant change in polydispersity. Thus the most effective method for regulating the particle size and polydispersity of the rubber during hardening of an epoxide–rubber system is to vary the chemical nature of the components.

Research on heterophase polymer compositions should be aimed at establishing a quantitative theory of formation of the phase structure, which will contribute to a deeper insight into the relation between the chemical nature of the initial components and the phase structure of the polymer compositions. On the basis of the quantitative relations between these factors it will become possible to control the physicomechanical properties of the multicomponent materials, which will lead to further progress in this promising field of polymer science.

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