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DEPENDENCE OF THE STRUCTURE AND PROPERTIES OF UNFILLED AND FILLED COMPOSITIONS BASED ON BINARY MIXTURES OF HARDENABLE THERMOREACTIVE RESINS ON THEIR FORMULA

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Crosslinked materials with different phase structures can be produced in hardening of the binary mixtures of unsaturated polyester resins or mixtures of epoxy resins. The dependences of the mechanical and electrophysical properties on the formula of such mixtures have been determined. The properties of filled compositions based on these mixtures with a two-phase structure, which have been produced by selective introduction of the filler only into one phase of the composition, significantly differ from the properties of filled single-phase mixtures and from the properties of two-phase mixtures produced with a uniform distribution of the filler in both phases.

Commercial thermoreactive resins (TRRs) are frequently used as a basis for production of filled composites. Therefore, it is of interest to study the structure and properties of filled composites based on the mixtures of resins with a two-phase structure, differing in the presence of the filler in the continuous or dispersed phases of the mixture or in both phases simultaneously. The present work seeks to investigate the structure of single-phase and two-phase TRR mixtures and to compare the properties of single-phase and two-phase composites based on them in regular and selective filling.

The objects of investigation were mixtures of styrene unsaturated polyester resins (UPRs) and mixtures of epoxy resins (ERs), including those of:

(a) UPR based on isophthalic acid and neopentyl glycol (VIAPAL VUP 4777 — France) and UPR based on phthalic anhydride and diethylene glycol (PN-1 — Russia); in what follows, called V-47 and PN-1 mixtures;

(b) V-47 and UPR based on orthophthalic polyester (Cristics 196 — Great Britain); in what follows, called V-47 and C-196 mixtures;

(c) ÉD-20 diane ER (Russia) and ÉIS-1 ER based on diglycidyl resorcinol ether (Estonia); in what follows, called ÉD-20 and ÉIS-1 mixtures.

The UPRs were hardened in the presence of methyl ethyl ketone peroxide at room temperature for 24 h and thereafter at 80°C for 8 h. The ERs were hardened in the presence of triethylenetetramine under the same conditions. The products obtained possessed a degree of hardening of 97–98% (for the UPRs) and 92–95% (for the ERs).

Quartz flour (marshalite) with a particle size of 5–10 μm was used for filling of the mixtures; the content of the quartz flour amounted to 20 vol. % of the entire mixture. The limiting packing coefficient of the filler φ_m was equal to 0.54. To produce conducting materials we introduced ground electrode graphite with a particle size to 3–5 μm into them. The concentration of the graphite in the mixtures amounted to 16 vol. % (for ER-based mixtures) and to 8 vol. % (for UPR-based mixtures). Mixing of the resins and introduction of the filler into one phase or another were carried out manually with moderate mixing rates.

The viscosity of liquid resin mixtures was investigated on a Brookfield rotational viscosimeter for constants rates of shear. The mechanical properties of hardened mixtures in tension, compression, and bending were measured on an Instron-1122 dynamometer. The microstructure of the liquid and hardened resin mixtures was studied by the optical-microscopy method on an MBI-6 microscope equipped with a system of phase contrast. The electrophysical prop-

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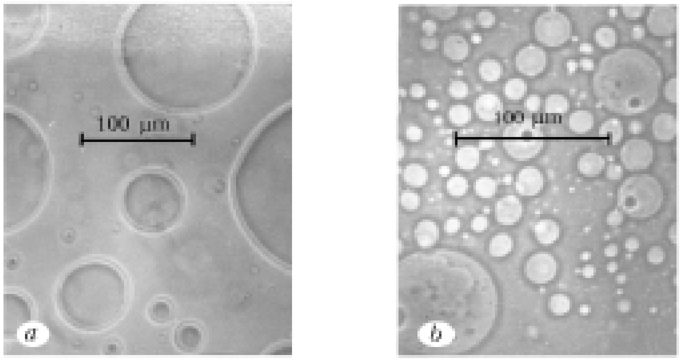


Fig. 1. Structure of two-phase UPR mixtures: a and b) mixtures of V-47 and PN-1 resins with excess of V-47 and PN-1 respectively.

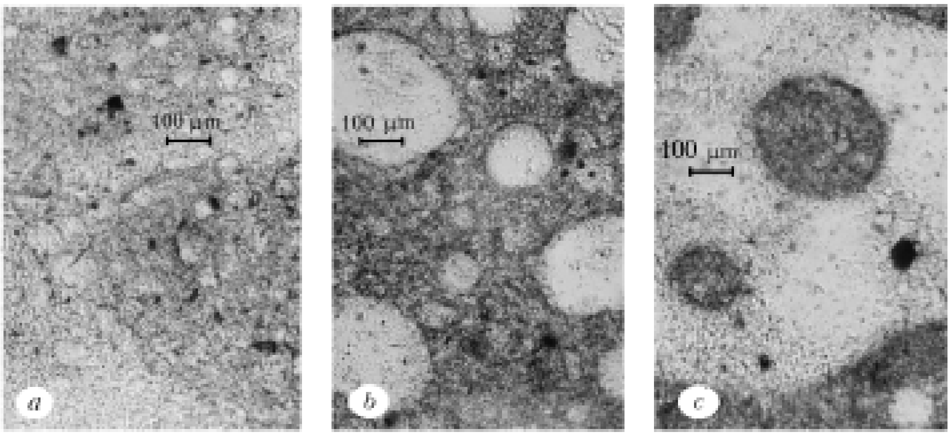
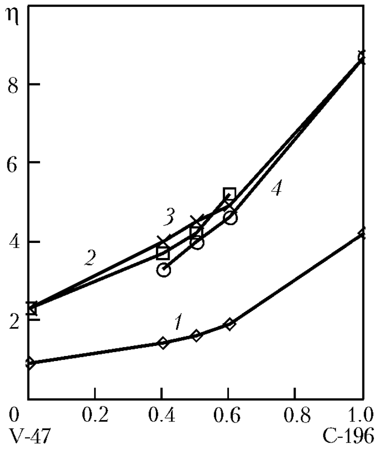


Fig. 2. Structure of filled two-phase V-47 and PN-1 mixtures (1:1): a) the filler has been introduced into both phases uniformly; b and c) the filler has been introduced selectively into the V-47 and PN-1 phases respectively.

erties (specific electrical conductivity) of the mixtures were investigated by a potentiometric method; this method lay in passing an electric current between the "current" electrodes, connected to two ends of a 20 × 20 × 2 mm rectangular sample of composite material, using the so-called potential electrodes.

Structural formation in the mixtures of high-molecular-weight polymers is known to begin with the association of individual macromolecules, formation of heterophase fluctuations and macrophases by them, and subsequent layering due to forcing of foreign molecules beyond the boundary of growing structural elements [1]. When the content of the second polymer component in the mixture is relatively low (fractions of a percent), a disperse structure, usually of the dropping type, develops, in which the component with a higher content forms a continuous phase (matrix) and the component with a lower content forms a dispersed phase. With substantial change in the content of the components in the mixture we can observe the so-called phase "reversal," in which the continuous phase becomes dispersed, and dispersed phase becomes continuous. Mutual solvability, which can disappear with increase in the chain length in hardening, is, rather, a rule for most TRRs differing by molecules of much smaller size. In this case, the processes of possible phase separation, which are determined by the thermodynamics and molecular mobility, the volume content, the viscosity, and other properties of the phases and the processes of hardening, are interrelated [2]. Therefore, the prediction of a single- or two-phase nature for an arbitrary mixture of thermoreactive oligomers is a difficult and frequently impossible problem; direct investigation of their microstructure with a small magnification is the easiest method.

A possible condition for production of two-phase mixtures based on liquid TRRs is, for example, the hardening of mutually insoluble resins. Such mixtures have been produced in a wide range of formulas for the UPR mixtures



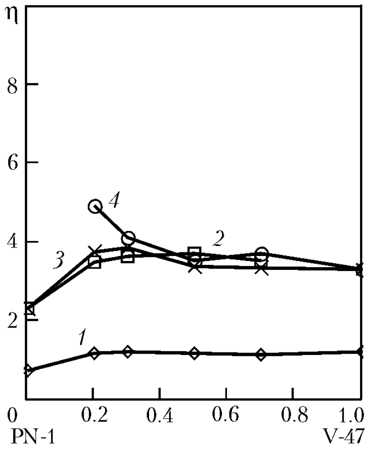


Fig. 3. Viscosity of unhardened single-phase V-47 and C-196 mixtures vs. content of the C-196 resin in the mixture: 1) unfilled mixtures; 2) mixtures with a uniform introduction of the filler into both resins; 3 and 4) mixtures with selective introduction of the filler into V-47 and C-196 respectively.

Fig. 4. Viscosity of unhardened two-phase PN-1 and V-47 mixtures vs. content of the V-47 resin in the mixture: 1) unfilled mixtures; 2) mixtures with a uniform introduction of the filler into both phases; 3 and 4) mixtures with selective introduction of the filler into PN-1 and V-47 respectively.

V-47 and PN-1. The V-47 and C-196 UPR mixtures possessed a single-phase structure in the investigated range of formulas. The ED-20 and EIS-1 epoxy-oligomer mixtures at temperatures higher than 25°C are characterized by a single-phase structure, but the mutual dissolution of these resins is a fairly long-duration process (especially at room temperature) by virtue of their high molecular weight and viscosity; rapid hardening of these resins (15–30 min) causes two-phase mixtures to form.

Thus, it becomes possible to control the phase structure of hardenable TRR mixtures in actual practice and consequently to produce new polymer materials. If such materials are used for production of filled compositions, one can produce materials whose properties are determined by the phase structure of the matrix to an even greater extent.

The microscopic investigation of unfilled compositions based on UPRs has shown that the presence of the second phase is recorded on microphotographs with a 100-fold magnification (Fig. 1). The microstructure of single-phase filled mixtures was characterized by a uniform distribution of filler (marshalite) particles throughout the volume. The structure of two-phase mixtures depended on the method of introduction of the filler into the mixture (Fig. 2). With a uniform filling of two-phase mixtures, their microstructure was characterized by the presence of two phases, each containing a filler. In selective filling of only one phase of the composition, it turned out that the introduction of the filler into the continuous medium of the mixture led to a structure of the "unfilled droplets in a filled matrix" type, whereas the introduction into the dispersed phase led to a structure of the "filled droplets in an unfilled matrix" type. We definitely observed the transition of filler particles from one phase to the other but to a very low extent.

The dependence of the viscosity on the formula of filled compositions based on single-phase mixtures of UPRs turned out to be smooth, irrespective of the method of introduction of the filler (Fig. 3). The relation of the viscosity to the formula of two-phase mixtures was much more complicated (Fig. 4). It turned out to be similar to S-dependences characteristic of two-phase compositions with a dropping structure. Filling of such mixtures led to a change in the type of the plot of the viscosity as a function of the formula of the mixture. For mixtures with a uniform introduction of the filler into each phase we had only an increase in the viscosity without a change in the shape of the curves, whereas in selective filling of the entire filler only into the V-47 phase, we found a substantial increase in the viscosity of the mixture filled (Fig. 4). The reason may be the sharp increase in the viscosity of the V-47 phase, which leads to an increase in the viscosity of the entire mixture or, possibly, the phase reversal with a high content of the PN-1 resin in the mixture. In the latter case, a V-47 filled resin in this range of formulas becomes a dispersed phase with an abnormally high viscosity, which determines the viscosity of the entire mixture (5 Pa·sec for a selec-

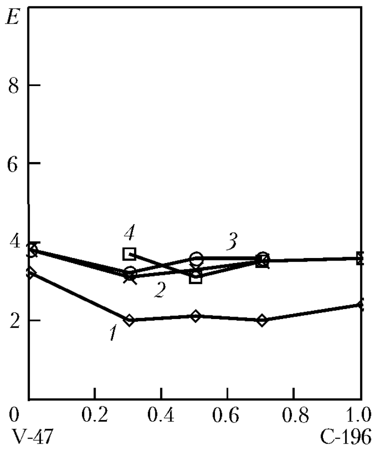


Fig. 5. Elastic modulus in bending of hardened single-phase V-47 and C-196 mixtures vs. content of C-196 resin in the mixture: 1) unfilled mixtures; 2) mixtures with a uniform introduction of the filler into both resins; 3 and 4) mixtures with a selective introduction of the filler into V-47 and C-196 respectively.

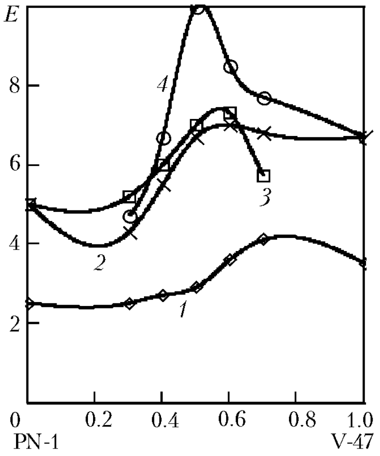


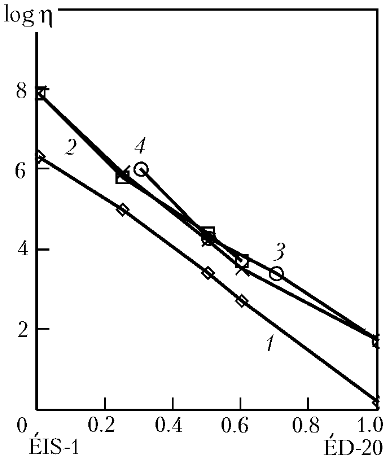
Fig. 6. Elastic modulus in bending of hardened two-phase PN-1 and V-47 mixtures vs. content of V-47 resin in the mixture: 1) unfilled mixtures; 2) mixtures with a uniform introduction of the filler into both phases; 3 and 4) mixtures with a selective introduction of the filler into PN-1 and V-47 respectively.

tively filled mixture instead of 3.5 Pa·sec for a mixture with a uniform filler distribution). It should additionally be noted that the volume content of the filler remained constant in all cases and amounted to 20%.

The change in the elastic modulus of the hardened mixtures largely followed the rheological dependences. From Fig. 5, it is clear that the values of the elastic modulus in bending of the single-phase mixtures of (filled and unfilled) polyester resins change additively to the change in the formula. The dependences of the elastic modulus on the formula of two-phase mixtures significantly differed from additive ones (Fig. 6). For unfilled compositions and those with a uniform distribution of the filler in phases, the dependences investigated were nearly S-shaped. For formulas with a filler introduced into one phase (selectively) the obtained dependences of the elastic modulus on the formula differed from the remaining ones not only quantitatively but qualitively as well (Fig. 6). A change in the formula of the mixtures with a constant concentration of the filler (20 vol. % of the entire mixture) leads to an increase in the specific concentration of the filler in the filled phase. It is natural that the elastic modulus of the filled continuous phase substantially increases, which causes the modulus of the entire mixture to grow. With further decrease in the concentration of the continuous phase in the system we have a phase reversal. The continuous phase becomes dispersed, and its influence on the elastic modulus of the entire mixture sharply decreases. It should be noted that the dependences of the elastic modulus on the formula of the mixture, measured by different methods (in tension, compression, and bending), were in good agreement.

Also, we have studied the distinctive features of the dependences of the mechanical properties on the formula of the mixture of ÉD-20 and ÉIS-1 ERs. The investigation of the dependence of the viscosity of unhardened ÉIS-1 and ÉD-20 mixtures has shown (Fig. 7) that it is similar to a logarithmically additive dependence in a wide range of formulas. Filling of such a single-phase composition, including the selective one, only leads to a regular increase in its viscosity. Based on the data obtained, we can assume that ÉIS-1 and ÉD-20 mixtures possess a single-phase structure in the form of both pure and filled compositions. It should be noted, however, that evaluation of the rheological properties of the compositions, by virtue of their extremely high viscosity, was carried out at a temperature of 50°C, when the resins under study are compatible and the composition is single-phase indeed.

The microscopic investigation has shown that at room temperature (and particularly at an even lower temperature: 10–15°C), the resins lose mutual solubility and particles with a size less than 1 μm are recorded in the micro-



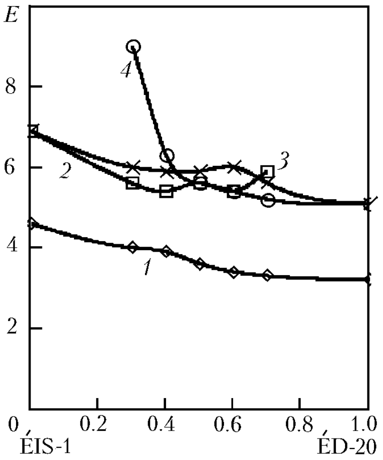


Fig. 7. Logarithm of viscosity of unhardened single-phase ÉD-20 and ÉIS-1 mixtures vs. content of ÉD-20 resin in the mixture: 1) unfilled mixtures; 2) mixtures with a uniform introduction of the filler into both resins; 3 and 4) mixtures with a selective introduction of the filler into ÉIS-1 and ÉD-20 respectively.

Fig. 8. Elastic modulus in tension of hardened two-phase ÉD-20 and ÉIS-1 mixtures vs. content of ÉD-20 resin in the mixture: 1) unfilled mixtures; 2) mixtures with a uniform introduction of the filler into both phases; 3 and 4) mixtures with a selective introduction of the filler into ÉIS-1 and ÉD-20 respectively.

scope field. Furthermore, mixing of the ÉIS-1 and ÉD-20 resins, by virtue of the extremely high viscosity of the former (higher than 3500 Pa·sec), leads to their mutual solubility only in a fairly long period of time (2–4 h). Therefore, a rapidly prepared and hardened mixture of these resins turns out to be two-phase due to the fact that the hardening is more rapid than the mutual dissolution. This observation was confirmed in investigating the mechanical characteristics of the ÉIS-1–ÉD-20 mixture in tension.

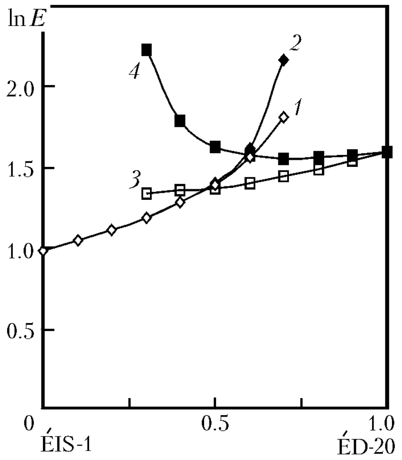
As is clear from Fig. 8, the physicomechanical indices of unfilled mixtures change not quite additively to the formula. A comparison of the dependences of the elastic modulus on the formula of filled compositions with a uniform distribution of filler particles in the composition and in the case of selective filling enables us to infer that the phase structure undoubtedly exerts an appreciable influence on the properties of filled compositions. This is demonstrated by the 50% increase in the elastic modulus of the compositions with selective filling of the ÉD-20 dispersed phase (to 9 GPa) as compared to the composition with a filler uniformly distributed in phases (6 GPa).

It should be noted once again that the total volume concentration of the filler remained equal to 20 vol. % in all of the mixtures but, as the ratio of the resins in the mixture changed, the fraction of the filler in a phase into which it has been introduced changed in proportion to the change in the formula. Taking this into account, we calculated the elastic moduli of mixtures of such a type according to the Lewis–Nielsen model [3] to allow for the influence of the filler in the filled phase:

$$E_{\mathrm{rel}} = \frac{1 + AB\varphi}{1 - BC\varphi}, \tag{1}$$

where $A = 1.8$, $B = \dfrac{E_{\mathrm{f}}/E_{\mathrm{matr}} - 1}{E_{\mathrm{f}}/E_{\mathrm{matr}} + A}$, $C\varphi = 1 - \exp[-\varphi/(1 - \varphi/\varphi_{\mathrm{m}})]$, and E_{rel} is the relative elastic modulus; E_{f} is the elastic modulus of the filler, and E_{matr} is the elastic modulus of the polymer phase of the filler system.

The index obtained was introduced into the Takayanagi–Kawai equation [1] to allow for the influence of both phases on the elastic modulus of the entire mixture:



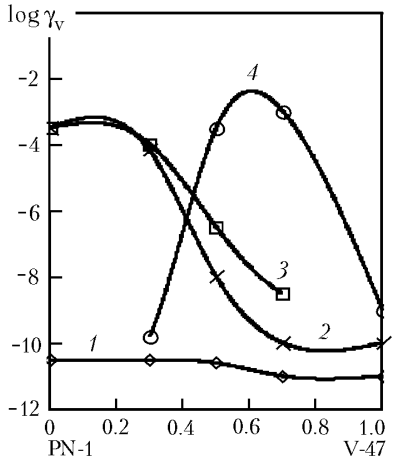


Fig. 9. Model dependences of the logarithm of elastic modulus on the formula of a mixture for oligomer mixtures selectively filled in different manners in introduction of the filler: into EIS-1 resin, representing a dispersed (1) or continuous phase (2); into ED-20 resin, which is a dispersed (3) or continuous phase (4).

Fig. 10. Negative logarithm of electrical conductivity of hardened two-phase V-47 and PN-1 mixtures vs. content of V-47 resin in the mixture: 1) unfilled mixtures; 2) mixtures with a uniform introduction of the filler into both phases; 3 and 4) selective introduction of the filler into PN-1 and V-47 respectively.

$$E_{\mathrm{rel}} = \frac{3E_1 + 2E_2 - 3(E_1 - E_2)\varphi_2}{3E_1 + 2E_2 + 2(E_1 - E_2)\varphi_2}, \qquad (2)$$

where E_1 and E_2 are the elastic moduli of the continuous and dispersed phases in the polymer mixture respectively.

The dependences calculated according to this model for the elastic moduli of mixtures with different structures are presented in Fig. 9. It is clear from them that, introducing a filler into each phase selectively, we can change the properties of this phase and consequently the properties of the entire composition. As applied to the mixtures of EIS-1 and ED-20 resins, it should be noted that ED-20 resin apparently remains the continuous phase in the mixture in a wider range of formulas, irrespective of the method of introduction of the filler. With decrease in the content of this component in the mixture, i.e., with increase in the actual degree of filling of this phase, its elastic modulus substantially increases. The elastic modulus of the entire mixture increases, too. It is natural that the model proposed is based on the absence of migration of the filler from phase to phase, as has been shown above for UPR mixtures.

Thus, it can be inferred that, introducing a filler selectively into each phase, not only can we change the properties of the phase to be filled but we can also significantly change the indices of the entire system as well. Also, we have revealed the dependence of the basic physicomechanical indices on the method of introduction of the filler. Additional proofs of the significant influence of the phase structure of filled TRR mixtures on their properties have been obtained in investigating the electrical conductivity of hardened mixtures. Conducting graphite powder (so-called electrode graphite) was, of course, selected as a filler in this case. The electrical conductivity of the mixtures naturally increased with dosage of the graphite in the resins. For filling of epoxy compositions we found the optimum volume content of graphite (16 vol. %); for filling of polyester compositions it turned out to be sufficient to introduce 8 vol. % of graphite.

Filling of two-phase polyester-resin mixtures (Fig. 10) has shown that the dependences of the electrical conductivity of the mixtures obey the same laws as those established for their mechanical characteristics. The electrical conductivity of unfilled hardened resins turned out to be extremely low. A substantial growth in the electrical conductivity was observed for the mixtures with a uniform introduction of the filler into both phases, particularly, for PN-1 resin. Selective introduction of the filler into the V-47 phase lead to a considerable (of seven decimal orders) growth

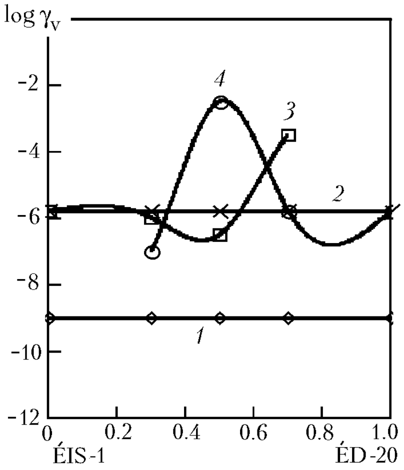


Fig. 11. Negative logarithm of electrical conductivity of hardened two-phase ÉIS-1 and ÉD-20 mixtures vs. content of ÉD-20 resin in the mixture: 1) unfilled mixtures; 2) mixtures with uniform introduction of the filler into both phases; 3 and 4) selective introduction of the filler into ÉD-20 and ÉIS-1 resins respectively.

in the electrical conductivity of the mixtures. An analogous filling of the PN-1 resin phase did not give such an abrupt increase in the electrical conductivity of the mixture, apparently because of the higher electrical conductivity of this mixture in the presence of graphite.

The electrical conductivity of two-phase mixtures based on ERs (Fig. 11) obeyed the same laws that had been found for mixtures based on unsaturated polyesters. The sharp increase in the electrical conductivity of hardened mixtures with increase in the "specific" concentration of graphite in the phases in selective filling of course gave a smaller effect but, nonetheless, was more than three decimal orders. Further increase in the dosage of one component of the mixture led to a phase reversal, as a rule, and consequently to a sharp (of orders of magnitude) drop in the electrical conductivity of the mixtures. The results obtained confirm the two-phase nature of hardened mixtures based on ÉIS-1 and ÉD-20 ERs, which has been found in investigating the mechanical characteristics.

As a result of the investigation carried out, it has been established that the use of selective filling of two-phase TRR mixtures enables us to attain a remarkable effect unknown earlier: a sharp increase in the elastic modulus or the electrical conductivity with substantially (2–3 times) lower dosages of the fillers usually ensuring the manifestation of this property upon the introduction of them into individual resins. This makes it possible to improve the economy or processability of filled composites based on liquid TRRs. The improvement in the economy can be predicted by using smaller dosages of expensive fillers, for example, conducting ones, whereas the processability can be improved due to the relatively low viscosity (in an unhardened state) of filled compositions possessing a high elastic modulus after hardening. This confirms our assumption that new-type composites, whose improved properties are ensured by changing their phase structure, can be created.

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NOTATION

A, coefficient in the Lewis–Nielsen equation [1] ($A = K_e - 1$, where K_e is the Einstein coefficient); B and C, coefficients in the Lewis–Nielsen equation [1]; E, elastic modulus, GPa; γ_v, specific volume electrical conductivity, $\Omega \cdot$m; η, viscosity of the composition, Pa·sec; φ, volume fraction of the filler in the composition; φ_m, coefficient of maximum packing of the filler in any volume; φ_2, volume fraction of the dispersed phase in the polymer mixture [2]. Subscripts: v, volume; m, maximum; rel, relative; matr, matrix; f, filler; 1 and 2, continuous and dispersed phases.

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