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Regulation of a phase structure at the interface in epoxy—polysulfone systems*

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The influence of technological parameters on the formation of an interfacial diffusion region and a gradient heterogeneous structure during a curing reaction of epoxy—polysulfone system was studied. It was established that the three-step temperature curing process of the modified system allows regulating both the width of the interphase zone and the sizes of the dispersed phases in it.

Key words: phase structure, interface, interdiffusion, dispersed phase, modified epoxy binder.

Epoxy oligomers (EO) modified with thermoplastics, in particular polysulfone (PSU),[1] are widely used in the production of binders for modern composite materials. It has been established that the concentration range of the mixture compositions is limited.[2—5] The thermoplastic content should not exceed ~15 wt.% to obtain a binder with given rheokinetic characteristics,[3] but the greatest effect of improving the deformation and strength characteristics is observed when the PSU content is 15—20 wt.%. This creates certain difficulties in the processing of materials.[3,6]

In order to obtain a composite material with the best properties, we propose to abandon the usual method of introducing a thermoplastic component into the system by dissolving it in a thermosetting resin prior to curing. Instead, it is proposed to lay out alternately the layers of thermoplastic and thermoset, followed by stepwise heat treatment.

Obviously, to implement this approach, it is necessary to study the effect of technological parameters on both the phase structure in local transition zones and the phase architecture of the composite material as a whole.

The main task of this work is to consider the influence of technological (temperature-time) parameters on the formation of an interlayer gradient diffusion zone in the EO—PSU system and the formation of phase structures in it during the curing of the binder.

Experimental

Epoxy diane oligomer ED-20 ($M_n = 380$), polysulfone PSK-1 ($M_n = 35000$), and hardener diaminodiphenylsulfone (DADPS) were chosen as objects of the study. Curing was carried out at 180 °C. Adducts of EO of different composition and degree of curing were obtained by mixing thermoset resin with different amounts of hardener. The degree of curing of the adducts was calculated at a molar ratio of epoxide : diamine = 2 : 1 and confirmed by differential scanning calorimetry. Preliminary, all samples under study were degassed under vacuum at a residual pressure of 100 Pa at room temperature for 3 h.

The solubility and interdiffusion in the EO—PSU systems, the EO—PSU adduct, and the EO—DADPS systems were investigated using laser microinterferometry (ODA-2, Russia). The methodology for carring out the experiments and calculating the compositions of coexisting phases and diffusion coefficients did not differ from that described earlier.[5] In experiments with EO—PSU systems and EO—PSU adduct, a PSU film was placed in the diffusion cell of the interferometer, and in the case of the EO—DADPS system, a hardener powder was placed in the diffusion cell of the interferometer. After thermostating, the cell was filled with EO melt or its adduct. The moment of contact between the phases was recorded visually and was considered as a beginning of the process of intermixing (interdiffusion) of the components. All measurements were carried out in isothermal mode in the temperature range from 20 to 240 °C.

The kinetics of EO curing with DADPS hardener was investigated using DSC. The degree of curing of the adducts was determined by the ratio of exothermic effects on the DSC curves in the experiment for fabrication of the adduct in a dynamic mode at a given ratio of epoxy : diamine and in a similar experiment conducted at a ratio of equivalent weights of epoxy : diamine = = 1 : 1. The measurements were performed using a Netzsch DSC 204 F1 calorimeter (Germany) at a heating rate of 10 deg $\min^{-1}$. The sample weight was 10 mg. It was shown that an exothermic effect indicating the onset of the chemical reaction of the oligomer curing is not observed in the ED-20—DADPS system up to a temperature of 130 °C.

For the preparation of multilayer EO—PSU—EO systems, a PSU film with a 400 μm thickness was placed in a cylindrical crucible previously filled with ED-20 with a hardener taken in a stoichiometric ratio (Fig. 1). At the first stage of the curing

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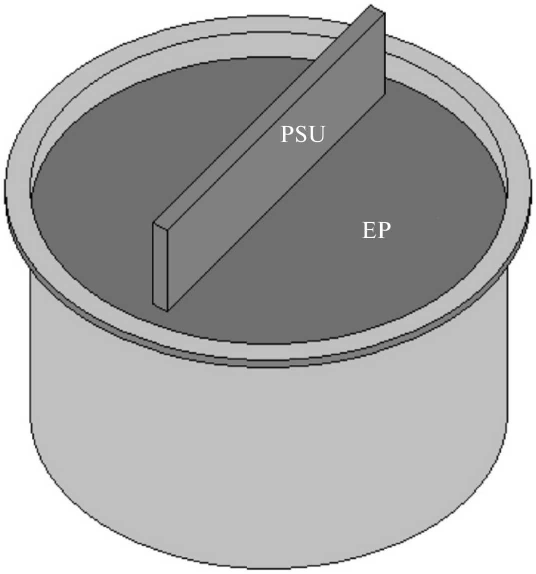

Fig. 1. The scheme of the model experiment EP—PSU—EP, where EP is an epoxy polymer (hardened epoxy oligomer).

process, the assembled cell was thermostated for 30—90 min at 60—120 °C, *i.e.* at temperatures below the temperature of the beginning of the formation of the spatial network. Thus, it was assumed that at this stage a gradient diffusion zone is formed, and its length should be determined by the time and temperature of annealing. In the second stage, the diffusion cell was placed in a heat chamber, where, in an isothermal mode, the composition was cured at 180 °C for 6 h.

The phase structure of the transition zones of the epoxy polymer (EP)—PSU—EP systems was investigated using an electron scanning microscopy (Philips SEM-500, Holland) and X-ray microanalysis (Kevex-Ray, USA). The samples of cured systems were cleaved in the direction of the plane perpendicular to the PSU film. To reveal the phase structure in the diffusion zone of the EP—PSU, the samples were etched in an oxygen discharge plasma using an Edwards Coating System E306A vacuum station (UK) under vacuum for 20 min according to a previously published procedure.[7]

Results and Discussion

Diffusion mixing zones in binary systems. Typical interferograms of interdiffusion zones in the EO—PSU systems, the EO—PSU adduct, and EO—DADPS are shown in Fig. 2. It can be seen that in the EO—PSU, EO—DADPS systems in the temperature range of 20—240 °C, the refractive index distribution profile is determined in the entire concentration range from epoxy oligomer to PSU and DADPS. This indicates the complete mutual solubility of the components.

The behavior of ED-20 adducts is quite different. In this case, in the middle region of the compositions, an interface separating the region of the PSU solutions in the EO adduct from the region of the EO adduct solutions in the PSU is observed. The concentrations corresponding to the composition of the coexisting phases are established and spontaneously maintained on both sides of the interface. This type of interferogram is implemented at all specified temperatures. The specificity of the interdiffusion zones in different experiments lies in the values of the compositions of the coexisting phases and the lengths of the concentration profiles.

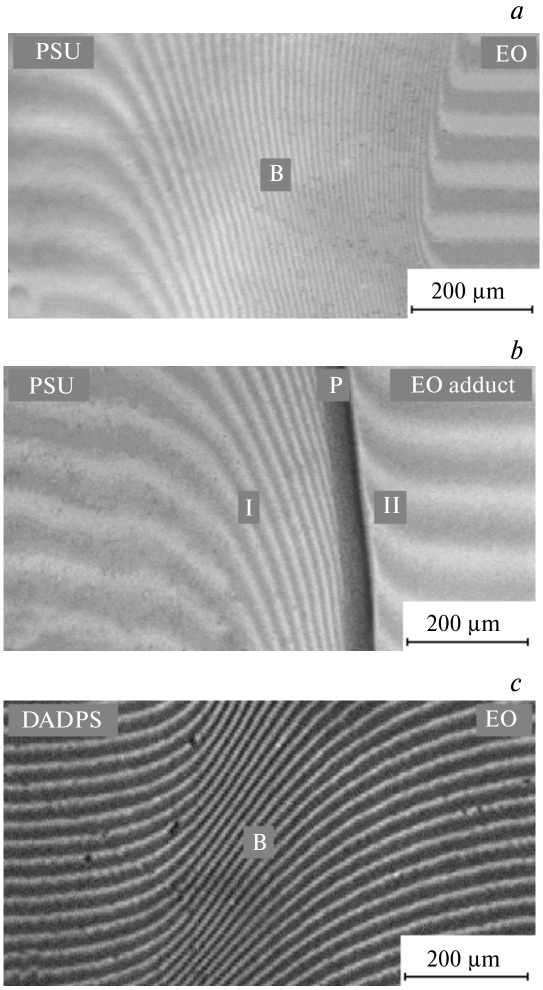

Fig. 2. Interferograms of interdiffusion zones of EO—PSU systems (*a*), EO—PSU adduct (*b*), EO—DADPS (*c*) at a temperature of 180 °C; B is the interdiffusion zone, P is the phase boundary, I is the diffusion zone of the EO adduct in the PSU, and II is the diffusion zone of the PSU in the EO adduct.

The binodal curves of the phase diagrams of the EO—PSU adduct systems were constructed according to the compositional values of the coexisting phases, measured at different temperatures. These curves are shown in Fig. 3 for adducts of various conversion degrees (α). It can be seen that the solubility of the components in the EO—PSU adduct system increases with increasing temperature, which indicates the presence of an upper critical

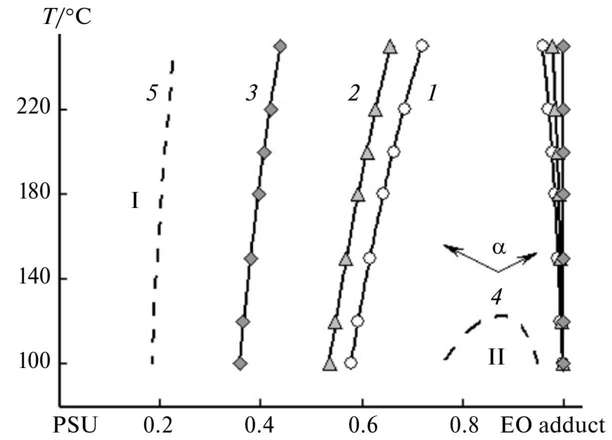

Fig. 3. Phase diagrams of state for the ED-20—PSU adduct systems: α = 0.29 (*1*), 0.33 (*2*), 0.5 (*3*), 0.17 (*4*), 0.63 (*5*). Dotted lines are calculated diagrams; I and II are the areas of true solutions and heterogeneous state, respectively. The arrows indicate the direction of evolution of the diagram with increasing degree of conversion.

miscibility temperature (UCMT) in this system. It can be seen also that with an increase in the conversion degree of adducts α, the heterogeneous region also increases and with $\alpha \to 1$ (which corresponds to the stoichiometric ratio of components in equivalent weights of 1 : 1) crosslinked EP is almost incompatible with PSU (Fig. 4).

Figure 5 shows the kinetic curves characterizing the motion of the diffusion front of EO in the phase of a PSU and the diffusion front of PSU in the phase of an EO. It can be seen that in the diffusion coordinates (x, $t^{1/2}$) the kinetic curves are linear dependencies, which testifies to the diffusion mechanism of components mixing. Translational diffusion coefficients were calculated from the slope of these dependencies. The numerical values of translational diffusion coefficients for epoxy oligomer matrices of various degrees of curing are shown in Fig. 6.

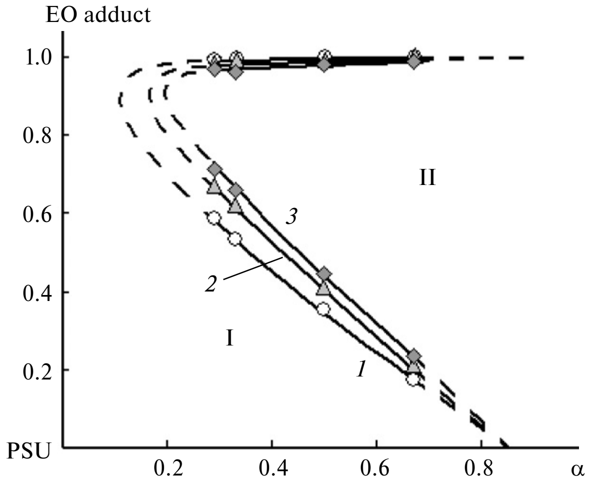

Fig. 4. The dependence of the solubility of the components in the cured ED-20—PSU system on the degree of EO conversion at 100 (*1*), 150 (*2*), 250 °C (*3*); I and II are the areas of true solutions and heterogeneous state, respectively.

It can be seen that for $\alpha > 0.4$, which corresponds to the gelation point, the translational diffusion coefficients sharply decrease, and for $\alpha \to 1$ they approach the value of $1 \cdot 10^{-14}$ cm^2 s^{-1}.

Thus, it can be assumed that in a three-component system (EO + DADPS)—PSU—(EO + DADPS) during the curing of the EO + DADPS solutions a heterogeneous structure will be formed in accordance with the phase state diagram (see Fig. 3).

Gradient zone curing. Figure 7 shows schematically the structural and morphological changes in the concentration profile in the system (EO + DADPS)—PSU at different stages of the formation of the gradient zone before and after the start of the epoxy matrix curing process. It can be seen that at the stage of forming the diffusion zone at a temperature below the curing temperature of the EO + DADPS solution, the concentration distribution profile is determined, as noted earlier, over the entire range of compositions from EO + DADPS to PSU, which indicates the complete mutual solubility of the components (see Fig. 7, *a*).

At the initial stage of curing, phase decomposition is accompanied by the formation of a phase boundary inside the concentration profile. The position of phase boundary corresponds to the position on the critical concentration profile (see Fig. 7, *b*). A further stage of curing at 180 °C is accompanied by the formation of a gradient phase structure simultaneously in the thermoset enriched and in the thermoplast enriched areas (see Fig. 7, *c*).

As it was shown by us earlier,**[4,5]** the compatibility of the components during the curing process decreases and amorphous separation with UCMT is observed at a degree of conversion (α) of 0.29 in solutions of ED-2—PSU. A further increase in the degree of conversion leads to an expansion of the heterogeneous region of the diagram of state (see Fig. 3) and, at α = 0.85, the system disintegrates into coexisting phases close in composition to pure components (see Fig. 4). In this case, at the point of gelation, occurring at α = 0.4, there is a sharp decrease in the coefficients of interdiffusion (see Fig. 6).

Thus, at the stage of curing the system with a conversion degree from 0.17—0.29 to 0.4, the transition zone grows under conditions of a change in diffusion coefficients and the onset of phase decomposition; for $\alpha > 0.4$, the diffusion zone is stabilized and the ongoing phase decomposition leads to the formation of nanodisperse structures.

Figure 8 shows the structure of the interlayer diffusion zone of a model system containing PSU film. It can be seen that a diffusion zone, characterized by a gradient phase structure, is formed at the interface. The structure has two main areas, namely, on the left is a matrix enriched with PSU, with a gradient in size of the dis-

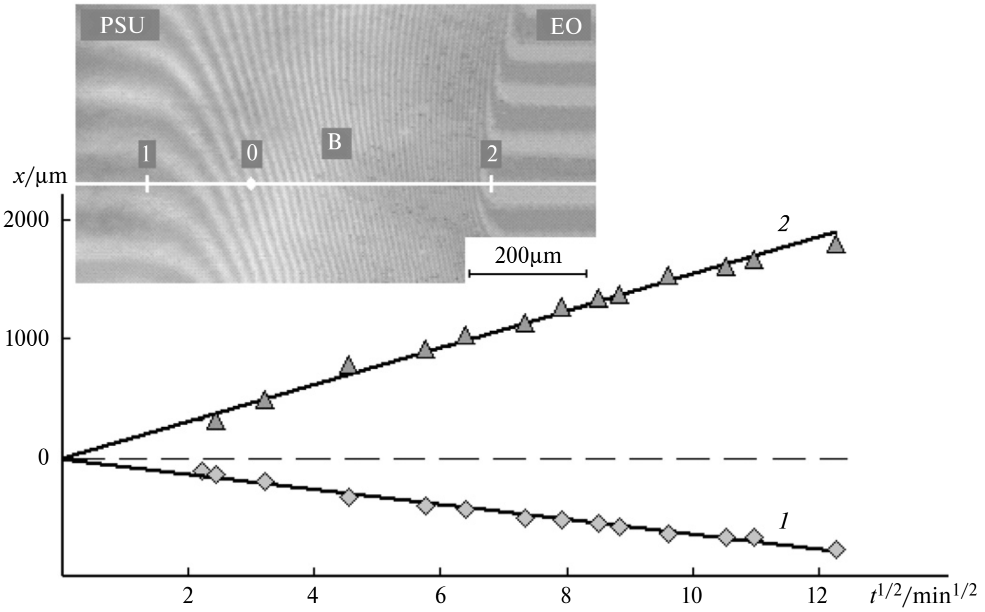

Fig. 5. Interferogram of the interdiffusion zone and kinetics of the movement of the fronts of limiting concentrations in the ED-20—PSU system at 180 °C. Line *1* corresponds to the diffusion front of EO in PSU, line *2* corresponds to the diffusion front of PSU in EO. The kinetic straight lines (*1* and *2*) of the movements of the concentration fronts correspond to the isoconcentration planes 1 and 2 indicated on the interferogram; 0 is the reference point in the laboratory coordinate system, B is the interdiffusion zone.

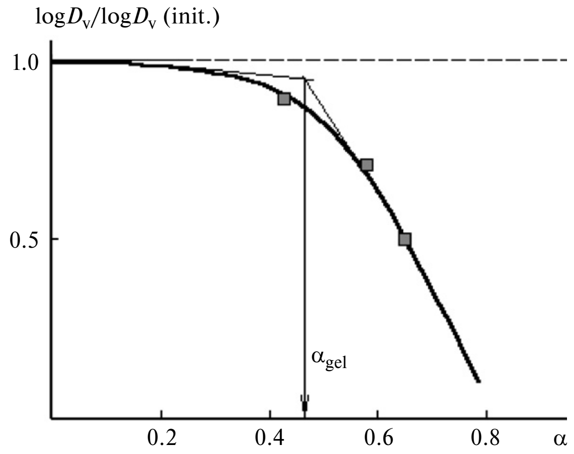

Fig. 6. The dependence of the relative diffusion coefficient of PSU in ED-20 on the degree of oligomer conversion.

persed phase enriched with EO, and on the right is a zone enriched with EO with finely dispersed phase particles enriched with PSU.

The concentration zones and the corresponding values of the conversion degree of the onset of phase decomposition are shown schematically on the micrographs of the phase structure of the gradient diffusion region. The decrease in the size of the dispersed phase particles as the composition in the gradient diffusion zone approaches the pure components is explained by both a decrease in the concentration of the second component and lower interdiffusion coefficients at higher conversion rates.

We present below the results of experiments using model EP—PSU—EP samples at different temperature—time regimes to analyze their influence on the structural characteristics. Typical micrographs of structural changes in diffusion regions formed on both sides of PSU film, placed in EO and cured with preliminary exposure at 120 °C for 90 min, are shown in Fig. 9. It is seen that the system has the following areas: I is the diffusion zone of PSU in the EO with a width a, II is the diffusion zone of EO in the PSU with a width b, III is the concentration point of intersection of the isotherm at 180 °C by the binodal dome (UCMT) during curing (see Fig. 9, *a*).

It can be seen that region I is characterized by a matrix—inclusion type structure (see Fig. 9, *b*). The size of the inclusion does not exceed 1 µm. According to X-ray microanalysis, the matrix in this area consists mainly of EP, the inclusions are PSU particles. The concentration of PSU in this region varies from 15 to 0 wt.%, and the phase composition is described by changing of the right branch of the binodal curve (see Fig. 3) during the curing process.

Curing in region II (see Fig. 9, *c*) is described by the left branch of the binodal curve (see Fig. 3). The local microanalysis of the dispersed phase in the form of spherical particles showed that the spherical inclusions contain mostly EP, while the dispersion medium is PSU.

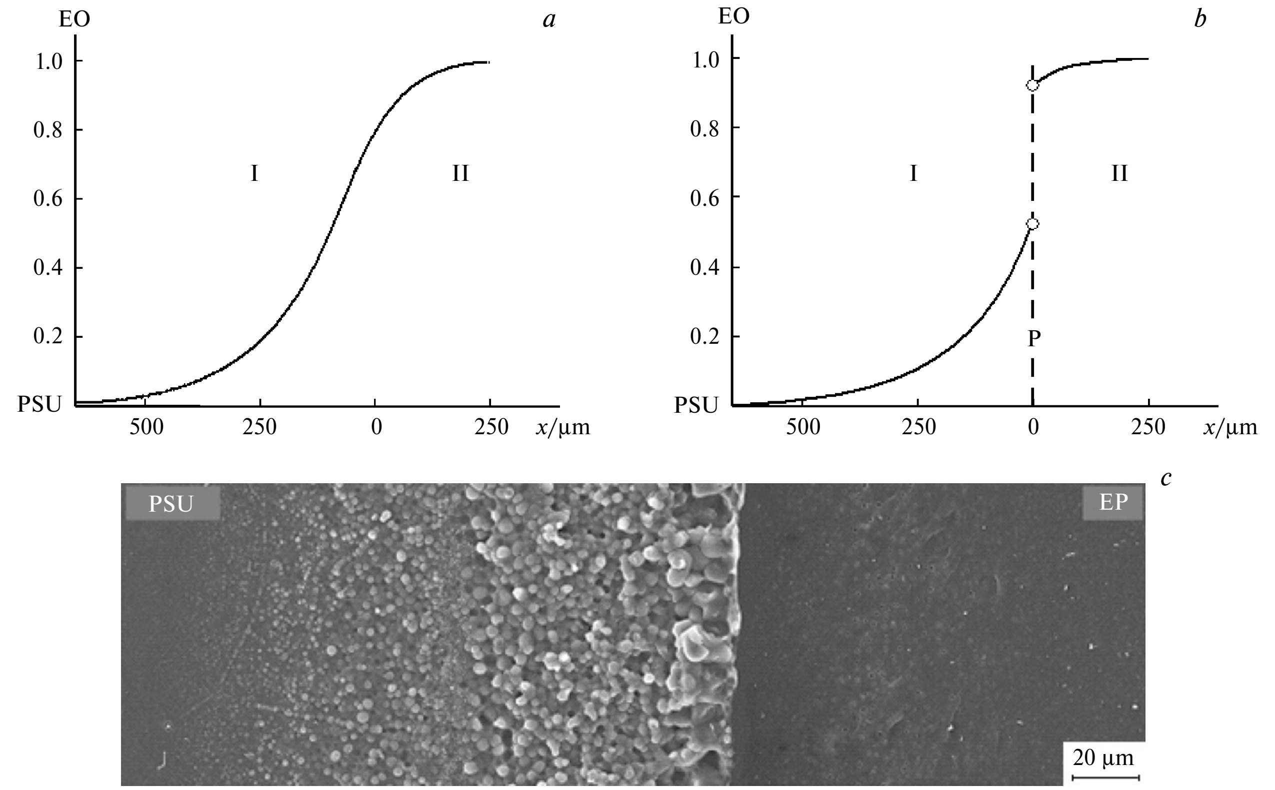

Fig. 7. The evolution of concentration profiles at the stage of forming the diffusion zone (*a*), at the initial stage of EO curing (*b*), and phase structure after thermal annealing at 180 °C (*c*); P is the phase boundary, I is the diffusion zone of EO in PSU, II is the diffusion zone of PSU in EO.

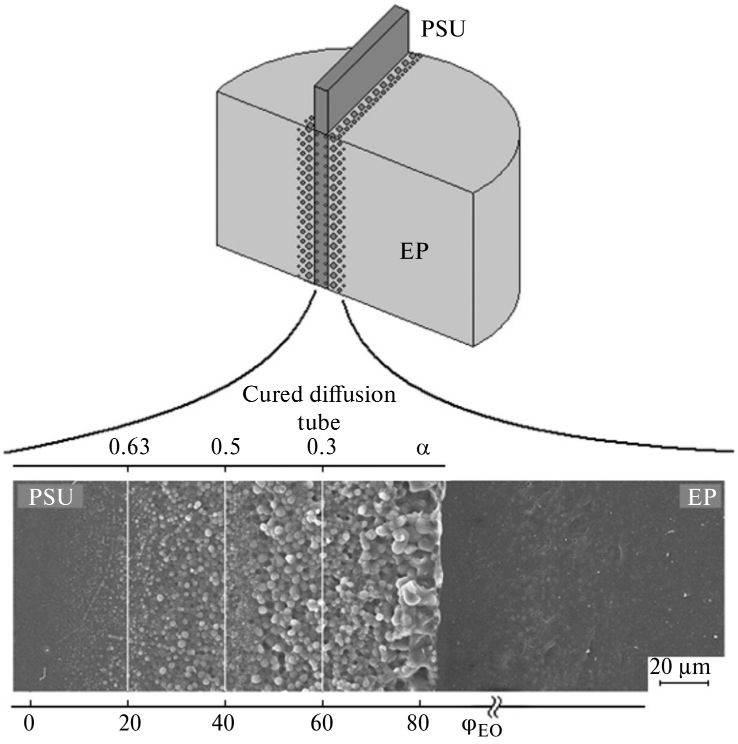

Fig. 8. Scheme of the sample model epoxy—polysulfone system for the study of the interlayer diffusion zone and its SEM image.

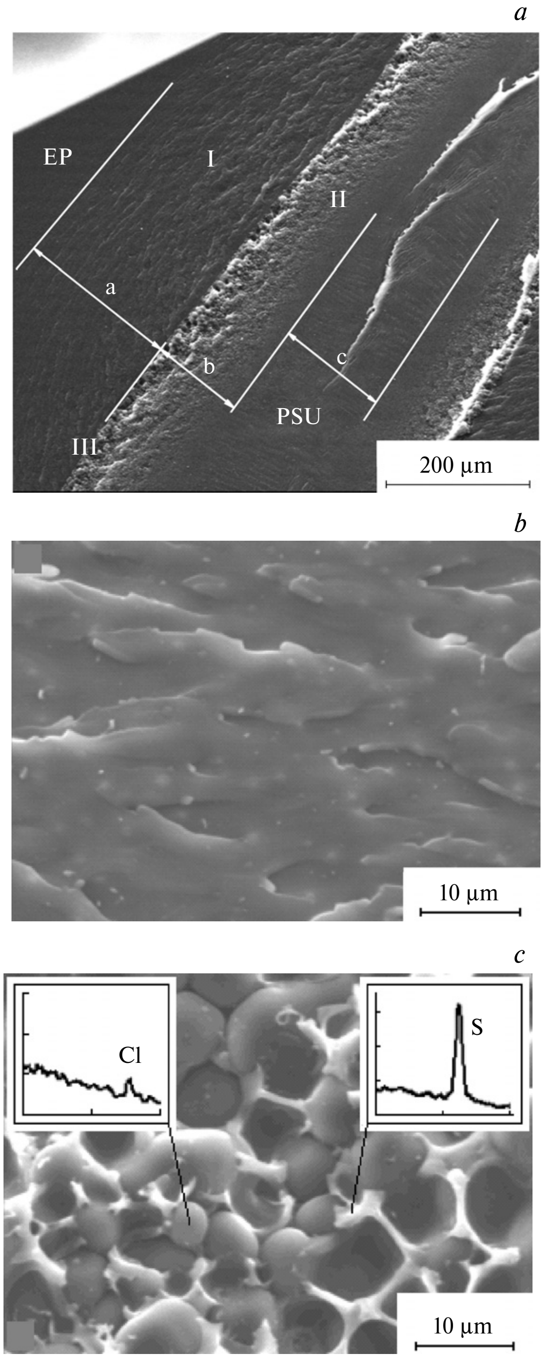

Fig. 9. Micrograph of the EP—PSU—EP model system with preliminary exposure at a temperature of 120 °C for 90 min; the thickness of the initial PSU film is 400 µm (*a*); morphology of regions I (*b*) and II (*c*) of an EP—PSU mixture. The insets show fragments of the spectra of the characteristic X-ray radiation from microphases.

Region III is located between areas I and II and is a concentration region (about 15 wt.% of PSU) in the temperature-concentration field of the phase diagram, in which the curing isotherm intersects with the UCMT of the binodal dome. In fact, a structure of the type of "interpenetrating phases" should be formed in this region. However, under given conditions for carrying out the experiments, this region is characterized by a very small length.

The sizes of the diffusion zones (a and b, see Fig. 9, *a*) were estimated by the presence of dispersed phases recorded using a scanning electron microscope, by X-ray spectral analysis of the Kα line S, and by the change in the nature of the damage in the region I. It can be seen that the width of region I containing the dispersed phase enriched with PSU exceeds the size of region II, the matrix of which is enriched with PSU, and the dispersed phase is enriched with EP.

Thus, the proposed method of the formation of composite material allows obtaining a multilayer system with a complex gradient architecture concentrated in the transitional interfacial region. We assume that such a structure in a multilayer system will allow the implementation of various mechanisms for the dissipation of crack growth energy. When a crack hits region I, the crack growth energy is dissipated on small PSU phase particles with the sizes not exceeding 1 µm. The change in the nature of the destruction is clearly seen in the micrograph (see Fig. 9). Upon transition to region II, the crack will fall into the PSU matrix, bending around the dispersed EP phase particle. Such multi-layered system allows us to count on high physicomechanical characteristics.

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