The effect of curing temperature on phase separation, morphology, fracture toughness and impact resistance of epoxy-polysulfone blends and fiber reinforced plastics based on them

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Abstract. The influence of the curing temperature of epoxy-polysulfone compositions on crack and impact resistance of matrices and unidirectional reinforced plastics was studied. It was shown that the structure of cured material depends on the content of PSK-1 and the curing temperature. Stable effect of increasing fracture toughness, as a rule, is observed for matrices with an extended structure of thermoplastic, which is typical for the phase structures of the type "interpenetrating phases". Energy of destruction of fiber reinforced plastics is determined by the fracture toughness of the matrix and its resistance to impact, which depend on the type of structure formed in the curing process.

1. Introduction
Majority of composite materials based on epoxy matrices does not meet the increasing requirements for crack, impact and chemical resistance. At present time complex polymer composition, including modifying additives, are used to create composite materials with increased thermal and shock resistance [1-11]. Active diluents, elastomers, particles of various shapes, sizes and nature, thermoplastic polymers are used as modifying additives. The most effective as modifiers proved rigid-chain thermoplastics (polyetherimides, polyaryletherketones, polyphenylenoxide, polysulfone) [12-16]. With such types of modification it is possible to increase the physical, mechanical and operational properties of reinforced plastics without reduction of heat resistance. The effect of such modification largely depends on the structure of the cured complex compositions [12-16]. At the same time, the design of optimal phase structures remains a very urgent task. To solve this problem, complex studies of phase separation of polymer mixtures, morphology and physical and mechanical properties of cured systems, as well as the establishment of the relationship of strength characteristics and phase structure are required.

In this work the physical and mechanical properties of epoxy-polysulfone matrices and unidirectional winding glass, carbon and organoplastics are investigated and possible mechanisms of their destruction are discussed.
2. Experimental

The study was performed based on epoxy oligomer ED-20 modified with polysulfone PSK-1 (Mn = 35000). The content of thermoplastic phase varied from 5 to 20 wt. % (from the mass of the oligomer). Triethanolaminonate (TEAT) (10 wt. %), 4,4’-diaminodiphenylsulfone (DDS) (30 wt. %), isomethyltetrahydrophthalic anhydride (MTHPA) (90 wt. %) + methylimidazole accelerator (0.5 wt. %) were used as curing agents. The curing programs: TEAT – 8 h at 160 °C; DDS – 6 h at 180 °C; MTHPA – 2 h at 90 °C, then 12 h at 120°C.

The fracture toughness of the matrix G\textsubscript{IR}\textsuperscript{M} was determined by splitting a double-cantilever beam [17]. The energy of destruction of epoxy-polysulfone matrices was determined at a three-point bending mode using a spring impact machine at a loading rate of 4 m/s [17]. The morphology of the fracture surface after splitting of the samples was investigated by scanning electron microscope (PSEM-500). To confirm the existence of continuous phases of polysulfone, cured samples were soaked in dichloromethane for 7 days. After being in the solvent we controlled their appearance.

RVMPN10-400 glass fibers (RPA “Stekloplastik”), Rusar-S aramid fibers (PLC “Khimvolokno”), and carbon Sigrafil C Type fibers (SGL Carbon Group) were used for composite manufacture. Heat treatment of composites were performed in the same modes as the matrix.

For winding composites resins containing a large (10 - 20 wt. %) amount of polysulfone were used. We developed an original technological scheme for composite production, which combines the methods of thermoplastics and thermosets processing. Composites based on the non-modified epoxy matrix were obtained by common method [18]. We were able to produce materials with the high content of fiber (60 - 70 vol %) and low pore content (1-3 vol. %) when the viscosity of the binder does not exceed 6 Pa·s.

On the wound rings and segment cuts, the energy of destruction (E\textsubscript{f}\textsuperscript{CM}) at the shear quasi-static and impact loading was determined [17], as well as interlaminar fracture toughness (G\textsubscript{IR}\textsuperscript{CM}) [19].

3. Results and Discussion

The modification of epoxy binder with polysulfone can be very effective (Fig. 1) for reduction of crack resistance. A significant increase in G\textsubscript{IR}\textsuperscript{M} begins only at a concentration of PSK-1 above 10 wt. % (Fig. 1a). The increase of fracture toughness of epoxy matrices begins with the contents of the PSK-1 greater than 5 wt. %. When 15 – 20 wt. % of PSK-1 was applied the G\textsubscript{IR}\textsuperscript{M} values increased from 3 to 10 times depends on the type of the hardener. The increase in the energy of destruction at impact of matrices cured with TEAT was 20 %; for DDS cured sample – 90 %; for MTHPA cured one – 58 %.

Maintenance of the effect of increasing crack and impact resistance of epoxy-polysulfone matrices in wound reinforced plastics is shown in Fig. 2. The total energy of destruction of the E\textsubscript{f}\textsuperscript{CM} was largely determined by the impact resistance of the matrix. It should be noted that E\textsubscript{f}\textsuperscript{CM} glass fiber reinforced plastics grows faster than carbon fiber composites. Given that the specimens of composites were destructed in the same way (from the shear stresses), it can be assumed that the fracture energy of reinforced plastics significantly depends on the resistance of the matrix to impact and strength at the polymer-fiber interface. Any modification of polymer matrices affects not only their bulk properties, but also the surface ones. It was previously shown [20] that the adhesion properties of modifiers can be much lower than those of the initial matrices.
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Figure 1. Fracture toughness $G_{IR}^M$ (a) and total fracture energy at impact $E_F^M$ (b) of cured epoxy-polysulfone matrices. The type of hardener is shown on the diagram.

However, the adhesive strength in the polymer-fiber system can vary along curves with the maximum or increase monotonically in case of epoxy resins modified with thermoplastics. The adhesive strength of the modified systems was $10 – 30\%$ higher than that of the thermoplastic-free ones.

Figure 2. Comparison of the total energy of destruction of composites $E_{F}\text{CM}$ and full energy destruction of epoxy-polysulfone matrices $E_F^M$. The diagram shows the type of material and the hardener.

Figure 3. The correlation of the fracture toughness of unidirectional composites $G_{IR}\text{CM}$ and epoxy-polysulfone matrices $G_{IR}^M$, cured with TEAT (a) or DDS (b).

Dependence of fracture toughness of reinforced plastics $G_{IR}\text{CM}$ of crack resistance of the matrix $G_{IR}^M$ is presented on Fig. 3. In all cases, there is a correlation of crack resistance of the studied matrices and unidirectional composites on based on them. The growth of energy $G_{IR}\text{CM}$ for glass fiber and organic fiber reinforced plastics is faster than for carbon fiber reinforced plastics.

The points of the studied systems were plotted on the temperature-concentration field (Fig. 4). Schematically, each isotherm built curves of the process of the curing reaction. We have previously shown that heterogeneous region expanded on the scale of concentrations and temperatures with increase of conversion rate ($\alpha$) [16]. It was established using microscopic studies and x-ray microanalysis that all systems were characterized with three types of structures depends on their place in one of the three areas of the phase diagram: I (○) and III (●) were the phase structures of the data type "matrix-dispersion", where the composition of the dispersed particles were close to the PSK-1 and epoxy, respectively, II (●) – were structures of "interpenetrating phases" type.

It was found that at low concentrations of PSK-1 the system was an epoxy matrix with fine phases enriched with polysulfone according to microscopy and elemental analysis. Further increase in the concentration of thermoplastics leads to the formation of a inverted phase structure (which is an extended interpenetrating phase), and at concentrations above 15 wt. % for TEAT cured samples and 20
wt. % for DDS and MTHPA cured ones the formation of a structure where the phase enriched with polysulfone matrix and the disperse phase epoxy oligomer were observed.

Figure 4. Model of evolution of phase diagrams (1, 2, 3) of epoxy-polysulfone mixtures during curing. The points corresponding to the concentrations of the studied systems are shown on the curing isotherms (90, 160 and 180 °C). The arrow indicates the direction of displacement of the upper critical mixing point with increasing conversion rate. For further explanations see the main text.

The scanning electron microscopy and elemental analysis of the cured chips of epoxypolyurethane systems the sizes of the dispersed polysulfone and polyepeoxy phases built and size distribution of particles. For all the compositions studied the particle diameter distributions are close to normal (Fig. 5). From the resulting distributions of the particles diameters determined the most frequent diameters (Tab. 1). It can be seen that for epoxy matrices cured by TEAT or DDS with the dispersed phase of PSK-1 the average size of the polysulfone particles was about 0.5 µm. In the case of the epoxy binder cured by MTHPA, the average size of the dispersed phase of PSK-1 was greater than for the above compositions (0.8 – 1 µm). For the compositions ED-20 + TEAT + 10 wt. % PSK-1, ED-20 + DDS + 20 wt. % PSK-1 and ED-20 + MTHPA + 15 wt. % PSK-1 two types of structures were observed. The first was the dispersed phase enriched with PSK-1, the second was the inverted structure, where the dispersed phase has been enriched with ED – 20 and the continuous phase was enriched with PSK-1. The size of the inverted phases was more than 100 µm. The size of the dispersed phase of PSK-1 varies from 0.5 to 1.78 µm depending on the type of hardener. In the inverted plots of the particle size of the polyepeoxy varies from 1.4 to 21 µm. It should be noted that the bimodal phase distribution enriched with polyepeoxy was observed for the ED-20 + MTHPA + 15 wt. % PSK-1. For this system polyepeoxy particles with an average diameter of 5 µm and 21 µm were found in inverted regions. This distribution
probably indicates several stages of phase separation. The characteristic size of the phase enriched with polyepoxy was in the range from 3 to 17 µm for a fully inverted structures.

![Figure 5](image)

**Figure 5.** The distribution of polysulfone (curve 1) and polyepoxy (curve 2) phase diameters for systems cured by TEAT and containing 5 wt. % (a), 10 wt. % (b) and 20 wt. % PSK-1 (c)

We should notice that a significant improvement in mechanical properties was observed for the systems with a concentration of PSK-1 resulted in inverted phase and for structures with large dispersed phases enriched with an epoxy oligomer. Thus, fine (less than 0.5 µm) phases enriched with polysulfone were structures that do not dissipate the crack energy, as the crack propagates through the epoxy matrix bypassing the dispersed phase. Macro (>10 µm) phase significantly improves the physico-mechanical characteristics of the matrixes. This is mainly due to the fact that in such epoxy – polysulfone compositions the matrix is a plastic phase (enriched with thermoplastics) and consequently the crack propagation should inevitably be associated with the destruction of the plastic phase.

**Table 1.** Particle sizes distribution of phases enriched with polysulfone or polyepoxy.

| Hardener | Concentration of PSK-1, wt. % | 5 | 10 | 15 | 20 |
|----------|------------------------------|---|----|----|----|
|          | Phase PSK-1 | Phase ED-20 | Phase PSK-1 | Phase ED-20 | Phase PSK-1 | Phase ED-20 | Phase PSK-1 | Phase ED-20 |
| TEAT     | 0.47         | -             | 1.78        | 6.58         | -             | 17.24        | -             | 10.55        |
| DDS      | 0.38         | -             | 0.42        | -             | 0.56         | -             | 0.47         | 1.41         |
| MTHPA    | 0.81         | -             | 1.01        | -             | 1.10         | 5.021.1      | -             | 2.90         |

To confirm the existence of a continuous phase enriched with polysulfone the cured samples were kept in dichloromethane. It was assumed that the polysulfone would dissolve and the samples would lose their initial shape. The result of the exposure of epoxy-polysulfone matrices in a solvent is shown...
on Fig.6. It can be seen that unmodified epoxy matrices were destroyed due to residual stresses regardless of the type of a hardener, and therefore the curing temperature.

![Image](image_url)

**Figure 6.** Appearance of the epoxy-polysulfone binder, cured with TEAT (1), DDS (2) and MTHPA (3), after soaking in dichloromethane. The numbers on the figure are concentrations of PSK-1

For epoxy-polysulfone samples corresponding to region I on temperature-concentration phase diagrams (Fig. 4) were completely destroyed. The dispersed phase of polyepoxy was found on the surface of the solvent according to x-ray spectral analysis. In the case of the dispersed phase of the polysulfone (region III), the samples retain their initial shape and cavities on their surface were visible where the dispersed phase enriched with PSK-1 has been washed. The samples containing interpenetrating phases (region II) were swollen (no complete destruction was observed). The only exception was the composition of the ED-22+DDS modified with 5, 10 and 15 wt.% of PSK-1. These samples have fully retained their shape and have not been destroyed, thus showing excellent resistance to organic solvent.

4. Conclusion

We showed the effectiveness of the use of epoxy-polysulfone matrices to increase crack resistance and shear strength at low-speed impact of unidirectional winding composites based on fibers of different chemical nature. The study of the morphology of the fracture surface showed that the final form of the structure depends on the content of PSK-1 and the curing temperature. It was established that a stable effect of crack resistance increase is usually observed for matrices with extended thermoplastics structure, which is typical for phase structures of the "interpenetrating phases" type (region II in Fig. 4). The fracture energy of reinforced plastics is largely determined by the crack resistance of the matrix and its resistance to impact which depends on the type of structure formed during the curing process. With data on the evolution of phase diagrams in the curing process, Phase diagram presented allows to predict some physical and mechanical properties of the specific systems cured at specified conditions.

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