RHEOLOGICAL AND PHYSICOMECHANICAL PROPERTIES

OF EPOXY-POLYETHERIMIDE COMPOSITIONS

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The effect of polyetherimide on the viscosity and physicomechanical characteristics of epoxides was investigated. It is shown that the introduction of polyetherimide increases the viscosity of the ED-20 oligomer and enables one to increase the crack resistance of cured resin four times, its impact resistance 1.5 times, and the total impact energy two times. The improvement in these properties is related to structural changes of the composition with increasing concentration of the thermoplastic.

Introduction

At present, the developers of polymer composites are facing the problem on improving their fracture toughness and resistance to impact and vibration loads. A way to increase the impact strength of composite materials is to choose more plastic matrices with high dissipative properties. Earlier, the crack and impact strengths of polymer composite materials were improved by doping matrices (as a rule, epoxy ones) with low-viscosity rubbers [1-3]. However, as a result, the thermal stability of the materials decreased. Recently, the crack resistance of epoxy matrices (and fibrous composites on their basis) and their strength in dynamic loading have been increased by using heat-resistant thermoplastic polymers [4-9]. The purpose of the present study was to investigate the crack resistance and impact strength of polyepoxies modified by one of such thermoplastics — polyetherimide. In addition, the rheological characteristics of uncured systems were examined, which is of importance in choosing the technological parameters for creation of composites.

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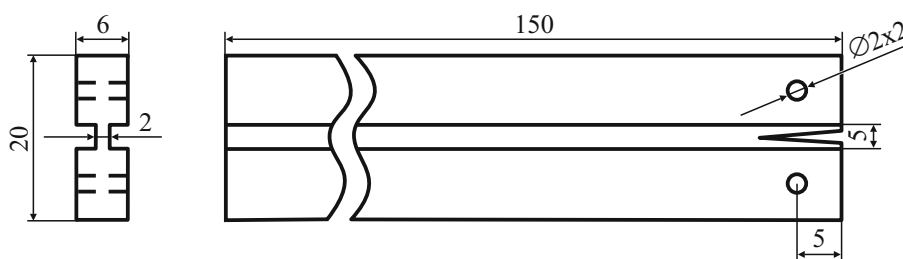
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Fig. 1. Schematic of a specimen for determining the crack resistance.

Experiment

As matrix components, we used an ED-20 epoxidian oligomer and Ultem® 1010 polyetherimide with a molecular weight of 19,000. The epoxy-polyetherimide binders were fabricated by introducing polyetherimide (PEI) granules into the epoxy resin, preliminary heated to 100-120°C, at continuous mechanical mixing for two days at a speed of 10 rpm up to the full dissolution of thermoplastic. The content of thermoplastic in the epoxy resin was 5, 11, 17.5, and 25 wt.%.

As a hardener, we used a 4,4′-diaminodiphenylsulfone (DADPS), added to the blends in the amount of 30 wt.%.

The ED-20 + PEI + DADPS blends were poured into silicone molds; the binder was vacuumized during one hour to prevent the occurrence of defects in the shape of pores; then, the compositions were cured at 180°C for 6 h.

Rheological investigations. The viscosity was measured on a Rheotest-2 rotational viscometer with a measuring cell of "cone–plane" type. Each binder was examined at 10 shear rates in the range from 25 to 250 s⁻¹ at temperatures of 80, 100, and 120°C.

For the tests at temperatures above the room one, the measuring device was thermostated by means of a fluid-circulating thermostat.

The shear stress τ and viscosity η were calculated from the formulas

$$\tau = 3M/2\pi R^3,$$

$$\dot{\gamma} = \omega/\tan\varphi,$$

$$\eta = \tau/\dot{\gamma},$$

where M is torque, R is the radius of cone, ω is its rotational speed, φ is the angle of the wedge-like gap between a rigidly fixed plate and the cone, equal to 0.3°, and $\dot{\gamma}$ is the shear rate [10, 11].

The crack resistance was measured on specimens in the form of rectangular plates. Before the tests, a groove not exceeding 2 mm in thickness and meant for directing the growth of crack, was made on them by milling. Then, by means of a razor, an initial notch was cut to originate a crack at a distance of 8-10 mm from the holes for fastening the specimen to clamps of a tensile machine; the width of the crack did not exceed 0.2-0.3 mm.

After measuring the crack resistance, the halves of specimens were additionally grinded to a width of 5 mm and cut into slices 40 mm in length, which were used to determine the impact strength.

The crack resistance was determined on an Instron-1126 testing machine. The specimen (Fig. 1) was fixed in clamps of the machine by means of a special device and stretched at a rate of 1 mm/min. The force increased to a certain value, and then the crack practically instantly grew by some value, but the load decreased. This procedure was repeated several times up to the complete splitting of the specimen (Fig. 2).

After the tests, both halves of the specimen were taken from the device for measuring the width of the splitted surface and the distance between the center of holes for fastening the specimen and the point of onset of the crack (this point was clearly seen from the stripe perpendicular to the direction of crack growth).
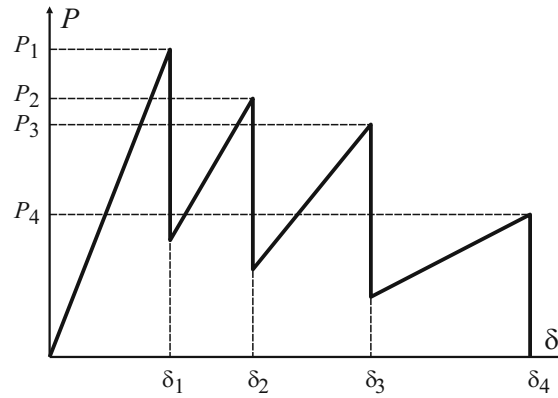
Fig. 2. Graph of the relation between the deflection δ of specimen ends and the load P in measuring the crack resistance [10].

The specific fracture toughness (crack resistance) for each step of crack growth was calculated by using the formula

$$G_{IR} = 2\gamma = P_i \delta_i k / 2 l_i w_i ,$$

where γ is the specific surface energy of crack growth; P_i is the maximum force at an ith growth step of the crack; δ_i is compliance (the deflection of specimen ends at load application points); l_i is distance from the centers of fastening holes to the end of an ith crack; w_i is the mean width of surface upon growth of this crack; k is an experimental constant of specimen, which depends on its rigidity (in our case, $k = 3$ [12]).

In our calculations, the first and the last measurements were excluded, as recommended in [12].

Measurement of impact strength. The tests were carried out on specimens without a notch according to the three-point loading scheme. The specimens were bars with the length of working part $l = 32$ mm, thickness $h = 5$ mm, and width $b = 5$ mm.

Experiments in the conditions of low-speed impact loading were performed on a spring-type unit, created on the basis of a KPS-2 testing machine, at a loading rate of 4 m/s (the impact energy was 13.0 J).

The test results obtained were used to calculate the flexural strength

$$\sigma_{imp} = \frac{3}{2} \frac{Pl}{bh^2}$$

and the total energy necessary for destruction of the specimen

$$A_{imp} = v \int_{t_0}^{t_i} P(t) dt,$$

where v is the speed of striker at the instant of its contact with the specimen; the integral expression is the area under the load–time curve from the initial instant of loading t_0 to an instant of time t_i. In calculating the total energy of destruction, the entire area under the load–time curve was used.

Electron microscopy. The phase structure was investigated on a Philips SEM-500 scanning electron microscope, equipped with an X-ray microanalyzer having a KEVEX RAY energy-dispersion detector, at 2500x and 320x magnifications.
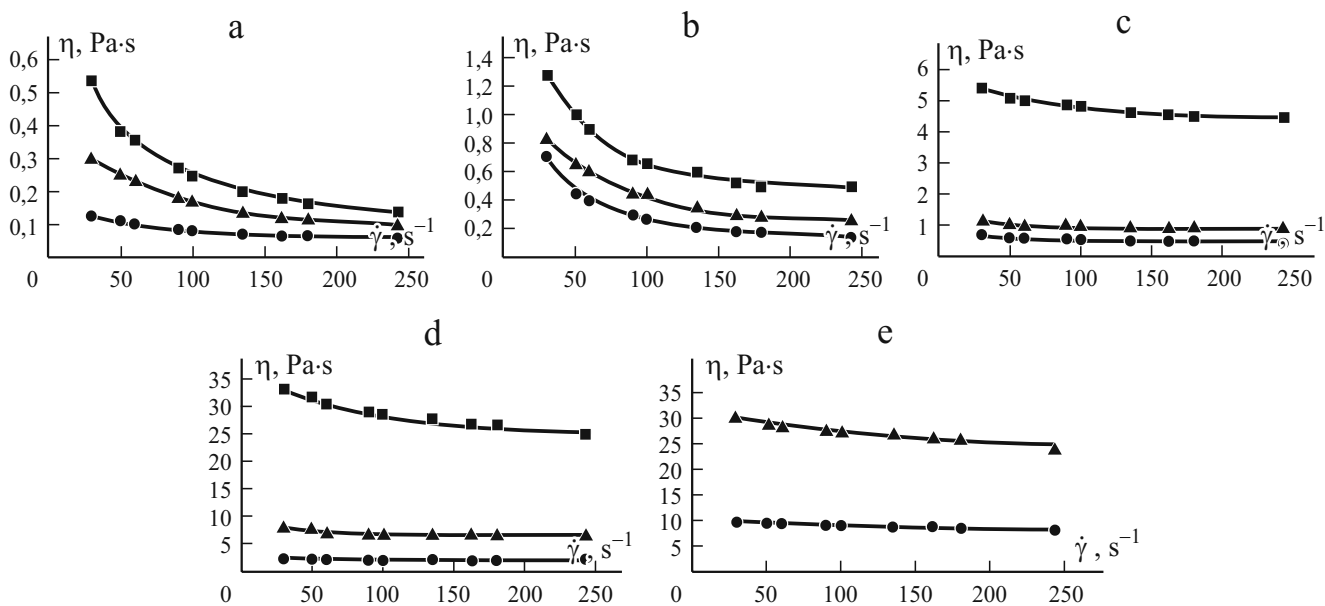
Fig. 3. Relation $\eta-\dot{\gamma}$ for the ED-20 (a), ED-20 + 5 wt.% PEI (b), ED-20 + 11 wt.% PEI (c), ED-20 + 17.5 wt.% PEI (d), and ED-20 + 25 wt.% PEI (e) compositions at $T = 80$ (■), 100 (▲), and 120°C (●).
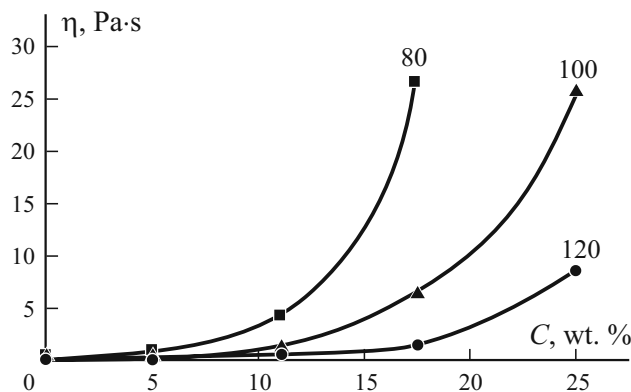

Fig. 4. Relation between the viscosity η and concentration C of Ultem-1010 in the ED-20 epoxy resin at different temperatures (numbers at the curves, °C). $\dot{\gamma} = 100$ s^{-1}.

Results and Discussion

Figure 3 shows the $\eta-\dot{\gamma}$ relations at different temperatures. It is visible that the character of flow does not depend on temperature and shear rate; in all the cases, it is of a non-Newtonian (dilatant) nature, i.e., with increase in shear rate, viscosity decreases. With rising temperature, the character of liquid flow becomes more Newtonian.

Relations between the viscosity of ED-20 + PEI blends and the content of modifier in the epoxy resin at different temperatures are presented in Fig. 4. As expected, the introduction of thermoplastic increases the viscosity of blend compositions, and the higher the content of polyetherimide, the greater the value of η for the modified system. This is typical of all the temperatures considered.

At a temperature of 120°C, with increase in the concentration of polyetherimide, the viscosity of the composition increases 6.5 times (from 0.07 to 0.45 Pa · s) at a 11% content of PEI, and, at $C = 25$ wt.%, it grows 120 times. With decrease
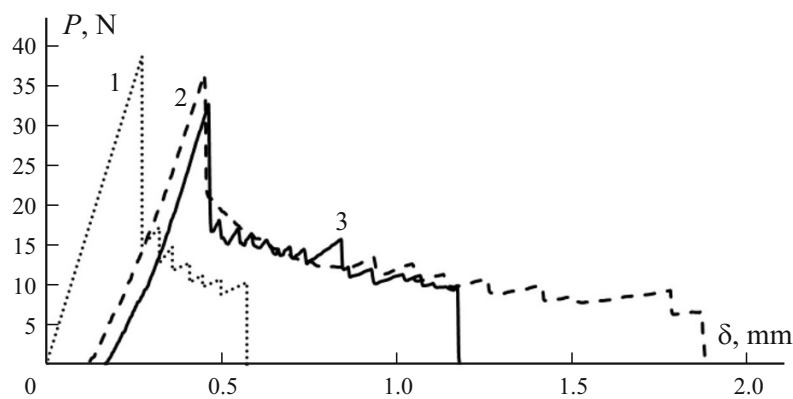
Fig. 5. Typical loading diagrams in measuring the crack resistance of epoxy specimens modified with PEI: $C = 0$ (1), 11 (2), and 25 wt.% (3).
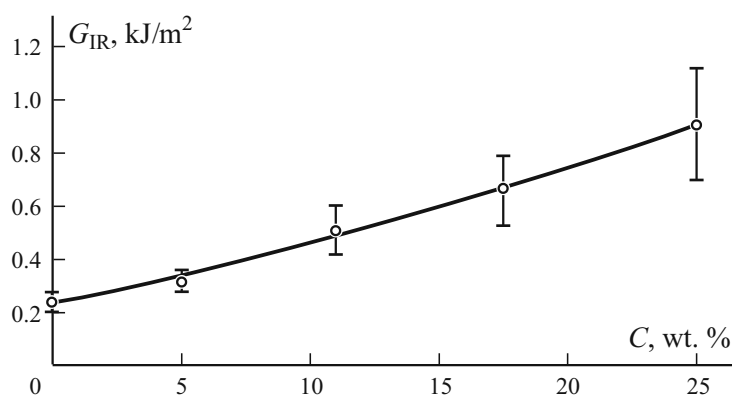

Fig. 6. Relation between the crack resistance G_{IR} of compositions with ED-20 and the concentration C of Ultem-1010 polyetherimide.

in temperature to 100°C, the value of η starts to grow stably already at small concentrations of polyetherimide. At a content of thermoplastic of 11 wt.%, the viscosity grows sixfold, but at 25 wt.% — 370 times. A further decrease in temperature down to 80°C entails a sharper increase in viscosity, and at 25 wt.% PEI in the epoxy resin, the value of η could not be measured at all. It follows from here that, in creation of fibrous composites based on epoxy binders with a high content of PEI, it is necessary to keep the winding temperature above 120°C so that to perform a qualitative impregnation of reinforcing fibers.

Figure 5 depicts the typical P–δ diagrams observed in measuring the crack resistance of the compositions. Attention is engaged by the fact that the character of the diagrams practically does not depend on the structure of specimens. This factor indicates that the character of growth of cracks in the specimens is the same. The fracture occurs unevenly, i.e., the crack grows only at the instant when the load in the material reaches its critical value; at the instant of cracking, the load drops instantly. Practically in all cases, with each growth step of the crack, the level of the load taken up decreases.

The height of the first peak, both for the "pure" and modified polyepoxies, is practically at the same level: the changes do not exceed 10%. Further, the load taken up drops more than twofold: the second and the third peaks for the ED-20+DADPS and ED-20+PEI+DADPS specimens are at the same level, too. Further, the growth of crack and decrease in the load on the specimens consisting of pure polyepoxy proceed much faster than for the modified ones: the forces necessary for the growth of cracks in epoxy-polyetherimides are by 30-50% higher than those in epoxies. In this case, an increase in the concentration of PEI leads to the emergence of a greater number of peaks (on the average, 10-12 against 5-7 for the unmodified resin). The changes observed can be associated with changes in the phase structure of the polymer, namely with transition of PEI from dispersion in the mass of epoxy to the state of an extended layer and, consequently, to a less brittle destruction of specimen.
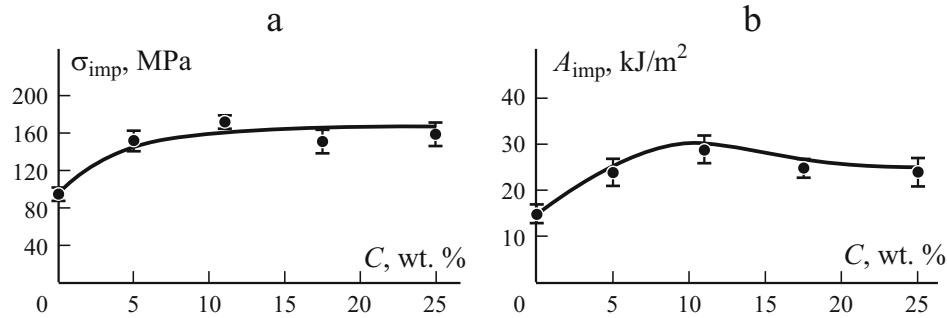
Fig. 7. Impact strength σ_{imp} (a) and the total impact energy A_{imp} (b) as functions of the concentration C of Ultem-1010 in the ED-20 epoxy resin.

The concentration dependence of crack resistance of the compositions is close to linear; with increasing content of PEI, the values of G_{IR} grow monotonically (Fig. 6). As a result, the values of G_{IR} of the compositions containing 25 wt.% polyetherimide reach 0.91 kJ/m^2, which is 3.5 times greater than those for the unmodified cured resin.

The filling of ED-20 resin with polyetherimide raises the impact strength σ_y 1.5 times (Fig. 7a); the total energy A_y necessary for the destruction of specimens increases twofold (Fig. 7b).

Most likely, the increase in the impact strength can be explained by the high impact strength of pure polyetherimide [13]. This leads to an increase in the values of σ_{imp} from 96 for a pure polyepoxy to 160 MPa for the modified specimens. The concentration dependence of the total energy necessary for destruction is described by a curve with a maximum at 10-13 wt.% PEI.

Figure 8 shows the microphotos of chips of specimens containing different amount of thermoplastic and destroyed during the measurement of their crack resistance. Depending on the degree of filling of epoxy with the thermoplastic, some distinctions in the morphology of the cured compositions are observed.

For example, for specimens of "pure" epoxies (see Fig. 8a) and the specimens containing 5 wt.% PEI (see Fig. 8b), a clear front at the end of growth of the crack is observed. As a result of delamination, the smooth surface of the specimen becomes developed owing to the decreased growth rate of the crack upon decay of its growth energy and realization of plastic deformations in the specimen.

With addition of the thermoplastic, the surface becomes more "developed". This is caused by the formation of disperse particles due to the phase disintegration initiated by the emergence of thermodynamic incompatibility as a result of decreased molecular mobility in the process of chemical reaction of cure. The further growth in concentration of thermoplastic to 11-17.5% (see Fig. 8c,d) leads to the disappearance of the front of crack growth and to an increase in the size of dispersed inclusions enriched with thermoplastic.

Quite a different structure is formed in the composition containing 25 wt.% PEI (see Fig. 8e). It is seen that the system is macroinhomogeneous and occurs in the region of phase reversal. In this case, the "darker" macrophase is enriched with epoxy, while the "lighter" one — with PEI. As seen at a greater magnification, the "darker" macrophase has a structure similar to that of the blend shown in Fig. 8b, whereas the "lighter" one contains a dispersed phase in the form of spherical particles 2-4 μm in size arising owing to the secondary phase disintegration.

It is in the system containing 25 wt.% PEI, i.e., in the presence of the structure corresponding to that of "phase reversal" type and in those with large dispersed phases, that the tendency to a sharper increase in the values of G_{IR} is observed. Thus, the finely dispersed (smaller than 1 μm) phases enriched with polyetherimide are structures which do not dissipate the energy of a crack, since the latter grows in the epoxy matrix, bypassing the dispersed phase. The macrophases (exceeding 10 μm) considerably improve the dissipation characteristics of polymer blends.
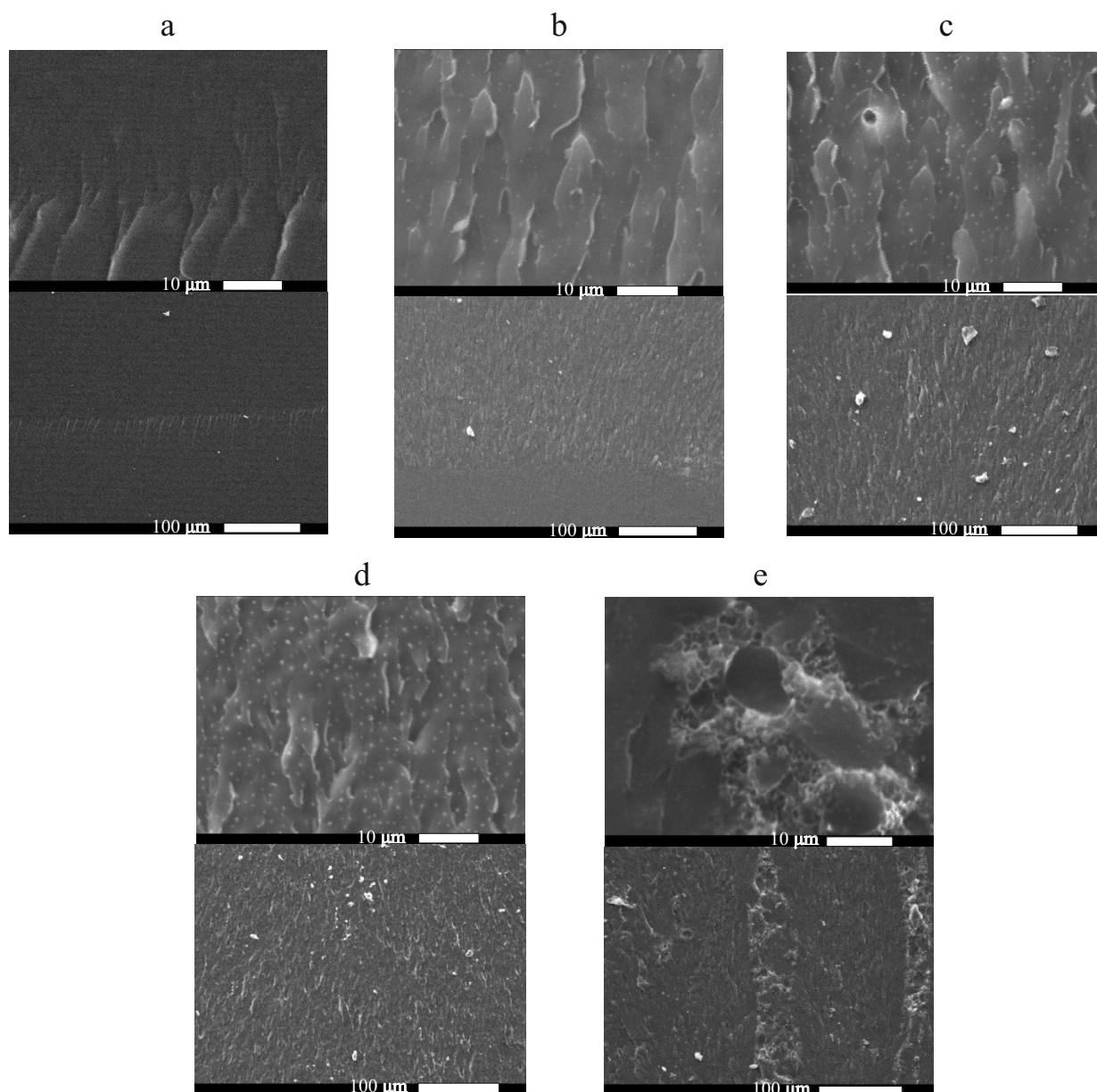
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Fig. 8. Microphotos of chips of specimens of modified epoxies cured with DADPS, after measuring the crack resistance, at different magnifications for the compositions ED-20 (a), ED-20 + 5 wt.% PEI (b), ED-20 + 11 wt.% PEI (c), ED-20 + 17.5 wt.% PEI (d), and ED-20 + 25 wt.% PEI (e).

Conclusions

In the present study, the effect of modification of an epoxy polymer with a heat-resistant thermoplastic (poly-etherimide) on its rheological and physicomechanical properties is investigated. It is shown that the introduction of PEI into the matrix can significantly (by up to several orders of magnitude) increase the viscosity of the binder. This occurs upon addition of 17.5 and 25 wt.% PEI. It is recommended to employ the results obtained in choosing the optimum conditions of winding of fibrous composites.

With increased concentration of thermoplastic, the crack resistance GIR grows 3.5 times, namely from ~0.26 in an unmodified epoxy resin to 0.91 kJ/m^2 upon introduction of 25 wt.% PEI into the resin.

The impact strength σ_{imp} also monotonically grows from 96 to 160 MPa, i.e., by 65%. The impact energy increases twofold.

The results obtained in investigating the surface morphology of the specimens obtained by splitting a double cantilever beam show that an increase in the concentration of polyetherimide leads to structural changes in the epoxy-polyetherimide blend: structures like "phase reversal" are formed, which positively influences the physicomechanical properties of cured compositions.

Thus, it is shown that the doping of epoxies with heat-resistant thermoplastics makes it possible to markedly improve their resistance to impacts and to the propagation of cracks. We believe that such a modification will allow one to also raise the specific fracture toughness of fibrous composites fabricated on the basis of such matrices.

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