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Properties of Epoxy Materials Used for Production of Glass-Reinforced Plastics by the Winding Method

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Abstract—The results of an investigation of the physicomechanical properties of foreign (D.E.R. 330) and domestic (KhT-711) epoxy matrices, including those modified with polysulfone or polyetherimide, are presented. It is shown that the glass-transition point of epoxy compositions based on KhT-711 resin cured with *iso*-MTHPA can reach 190°C and exceeds the glass-transition points of the foreign binders by 15–30°C. The elastic moduli of the compositions based on KhT-711 resin are higher than those of the matrices based on D.E.R. 330 by 40–60%. All the investigated epoxy matrices exhibit seemingly high resistance to the action of acids, alkali, oil products, and water, whereas KhT-711 + *iso*-MTHPA + heat-resistant thermoplastic demonstrate a five to six times lower mass loss than do foreign matrices.

Keywords: epoxy matrices, physicomechanical properties, modification

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INTRODUCTION

In the development of hard-to-recover oil resources, extraction in Arctic conditions, and complicated well stock, oil-producing companies face the problem of corrosion wear of steel pipes. As a consequence, there is a constant need for regular removal of pipelines and production strings, the frequency of which is determined by the corrosion activity of transported media and soil. Pipes made of glass-reinforced plastics seem to be more attractive than steel ones. The strength and operating limits of these items strongly depend on a polymer matrix. As a rule, glass-reinforced plastics are produced using epoxy binders, which can impart not only the required strength, but also resistance to operational factors (temperature, aggressive media, crack resistance, and so on) to a finished product [1, 2]. Often, domestic companies use foreign binders for production of glass-reinforced plastics. In this respect, particular interest is presented by the adaptation of domestic binders, which are not only competitive with foreign materials in their properties, but surpass them. Today, performance characteristics are being improved by using multicomponent polymer systems that include modifying additives in addition to the main resin and the curing agent, which provide them with special properties [3–5]. One promising method for modification of a matrix is the addition of heat-resistant thermoplastics. It has been reported that the introduction of rigid-chain thermoplastics into epoxy matrices substantially improves their crack resistance, resistance to aggressive media, and, in some case, also heat resistance [6, 7]. This work deals with an investigation of epoxy matrices, including those modified with thermoplastic polymers, in order to replace analogous foreign polyepoxides that are used for production of articles from glass-reinforced plastics.

EXPERIMENTAL

The investigations were concerned with binders based on KhT-711 epoxy resin (Khimeks Ltd, Russia) and *iso*-methyltetrahydrophthalic acid anhydride (*iso*-MTHPA) curing agent. To compare the properties of the proposed and foreign compositions, we also used D.E.R. 330 epoxy resin, D.E.H. 650 aromatic amine, and Polypox IPD cycloaliphatic diamine (Dow Chemical Co.) as curing agents. The ratio of the epoxy resin and D.E.H. 650 curing agent was 100 : 26 wt fr, and that for the D.E.R. 330 and Polypox IPD curing agents was 100 : 24 wt fr. PSK-1 polysulfone (NII PM, Russia) or Ultem-1010 polyetherimide (GE Plastics) were used as modifiers for KhT-711 + *iso*-MTHPA composition. PSK-1 and Ultem-1010 heat-resistant polymers were dissolved in KhT-711 epoxy resin at 100–120°C for 2–5 h under continuous stirring. The content of PSK-1 and Ultem-1010 was 10% of the total composition mass. The binder was then cooled to 60–80°C, and *iso*-MTHPA curing agent was added. The ratio of the resin and the curing agent was 100 : 100 wt fr.

Samples based on the epoxy binders were prepared by free silicone-mold casting. Prior to the sample casting, the binder was evacuated for 5–15 min at 50°C to remove air bubbles resulting from stirring. After casting, the binders based on KhT-711 were cured in a stepwise mode: 80°C, 2 h; 110°C, 2 h; and 130°C, 5 h. The curing mode for the binders based on D.E.R. 330 was 80°C, 30 min; 120°C, 30 min; and 180°C, 60 min. After extraction of the samples from the molds, they were mechanically processed on a grinding machine. As a result, two types of samples were obtained for physicomechanical tests. Tests on a dynamic mechanical analyzer were carried out with samples that were rectangular in shape (30 × 5 × 2 mm), and tension tests were performed with blade samples with a working-part section of 2 × 5 mm and a working-part length of 35 mm.

The tests of the rectangular samples were carried out upon a three-point bending on a Netzsch Artemis DMA 242E dynamic mechanical analyzer. The temperature ranged from 30 to 300°C, and the external load rate was 1 Hz. During the tests, the changes in elastic modulus E and mechanical-loss tangent tanδ were recorded. For each epoxy composition, no less than three samples were tested.

The tension of the blade samples was performed on a Zwick Z-100 testing machine at a constant temperature (25°C) and a loading rate of 1 mm/min. The strain was determined using an extensometer. The resulting loading diagrams were used to establish tensile strength σ_t, elastic modulus E, and fracture strain ε_f. For each epoxy composition, six samples were tested.

In addition, the resistance of the epoxy matrices to the following aggressive media was studied: distilled water, sodium hydroxide (analytical grade), hydrochloric acid (conc., reagent grade), and kerosene (TS-1). The samples used were the capture parts of the blade samples tested for tension. The mass of each sample was about 1 g. To measure the chemical resistance, the samples of epoxy matrices were placed in a vessel with a tightly closing screwing cap with a volume of 20 mL filled with an aggressive chemical medium. The mixture was kept at 23 ± 2°C for 3 days. Then, the samples were taken off, rinsed with water (the samples treated with sodium hydroxide or hydrochloric acid) or hexane (the samples treated with kerosene) to completely remove the chemical reagent from the surface, and dried in an oven at 70°C for 4 h.

The chemical resistance was determined by the formula

$$\Delta m = \frac{m - m_0}{m_0} \times 100\%,$$

where Δm is the quantitative measure of chemical resistance expressed in percent, m if the mass of the sample after exposure to the aggressive chemical medium, and m_0 is the initial mass of the sample.

The binder sample was considered to be chemically resistant to the aggressive medium if $|\Delta m| < 1\%$. The external appearances of the samples were also determined.

RESULTS AND DISCUSSION

Figures 1 and 2 show the dependences of change of elastic modulus E and tanδ depending on the temperature. All the epoxy compositions feature smooth reduction of the elastic modulus with an increase in temperature. When the temperature reaches the phase-transition point from the glassy state to the highly elastic one, the elastic modulus drastically drops. A peak of the mechanical-loss tangent depicted in Fig. 2 indicates a precise phase-transition point. It should be noted that, for KhT-711 + PSK-1 or KhT-711 + Ultem-1010 biphasic systems, the dependences show only one tangent peak. This can be explained by the fact that the glass-transition points of the phases are very close, and this method does not allow one to see a separate phase transition for each component.

Table 1 presents the results of thermomechanical analysis of the epoxy matrices that were investigated. The elastic moduli at room temperature for D.E.R. 330 epoxy resin cured with D.E.H. 650 or Polypox IPD are 2.5 and 2.8 GPa, respectively, and are at the level of most of the epoxy materials. KhT-711 epoxy resin cured with *iso*-MTHPA has an elastic modulus at the level of 4 GPa, which is 30–40% higher than that for the epoxy matrices based on D.E.R. 330. The introduction into KhT-711 of heat-resistant thermoplastics leads to a very small (by 3–7%) reduction in the elastic modulus. However, the values of the elastic modulus for the modified compositions are higher than those for the foreign samples by 30%. The values of the glass-transition points for D.E.R. 330 + D.E.H. 650 and D.E.R. 330 + Polypox IPD epoxy matrices are 176 and 160°C, respectively. It should be noted that these glass-transition points for the epoxy compositions are rather high. For example, for epoxy resins of ED-20 type, one can reach the glass-transition point at no higher than 150°C. KhT-711 epoxy resin shows even higher glass-transition point, which comes to 190°C. The application of PSK-1 polysulfone as a modifier for KhT-711 + *iso*-MTHPA system has almost no effect on the glass-transition point. The result of modification of KhT-711 with polyetherimide seems unexpected. The glass-transition point of this composition drops by 13°C, while the glass-transition point of neat polyetherimide is 210°C. This issue requires further detailed investigations. It should be noted that a drastic drop in the elastic modulus of all the compositions investigated is observed at about 150°C. However, at this temperature, the maximum modulus is observed for KhT-711 composition + *iso*-MTHPA composition, which is 2.01 GPa at 150°C. This composition seems to be more promising from

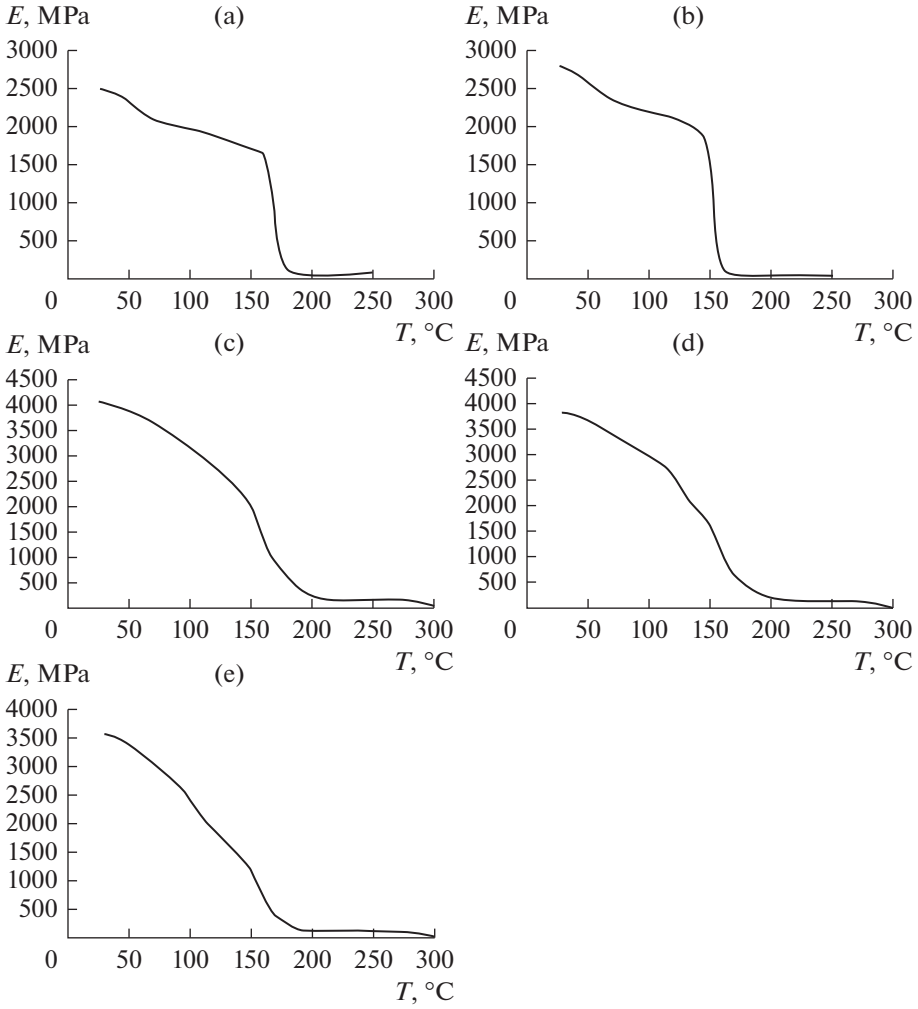

Fig. 1. Dependence of elastic modulus E on temperature for the epoxy matrices (a) D.E.R. 330 + D.E.H. 650, (b) D.E.R. 330 + Polypox IPD, (c) KhT-711 + *iso*-MTHPA, (d) KhT-711 + *iso*-MTHPA + PSK-1, and (e) KhT-711 + *iso*-MTHPA + Ultem-1010.

the viewpoint of realization of heat resistance compared to the other matrices considered. Presumably, the optimization of the curing process of a finished product will allow us to improve the system's heat resistance further.

Figure 3 shows typical loading diagrams of epoxy matrices during tension. From these diagrams, it is obvious that D.E.R 330 + D.E.H. 650 and D.E.R. 330 + Polypox IPD epoxy matrices possess a small region, which corresponds to elastic deformation, and a large region of inelastic deformation, which is expressed in a nonlinear growth of the stress with increasing strain. The epoxy matrices based on KhT-711 resin are deformed in the elastic manner almost up to the point

Table 1. Glass-transition points and elastic moduli of the epoxy matrices defined by DMA

Composition	Elastic modulus at 25°C, GPa	T_g, °C (according to tanδ)	Elastic modulus at 150°C, GPa	T_g, °C (according to E)
D.E.R 330 + D.E.H 650	2.55	176	1.65	155
D.E.R 330 + Polypox IPD	2.79	160	1.96	145
KhT-711 + *iso*-MTHPA	4.04	190	2.01	150
KhT-711 + *iso*-MTHPA + PSK-1	3.82	187	1.67	148
KhT-711 + *iso*-MTHPA + PSK-1 + Utem-1010	3.57	177	1.18	150

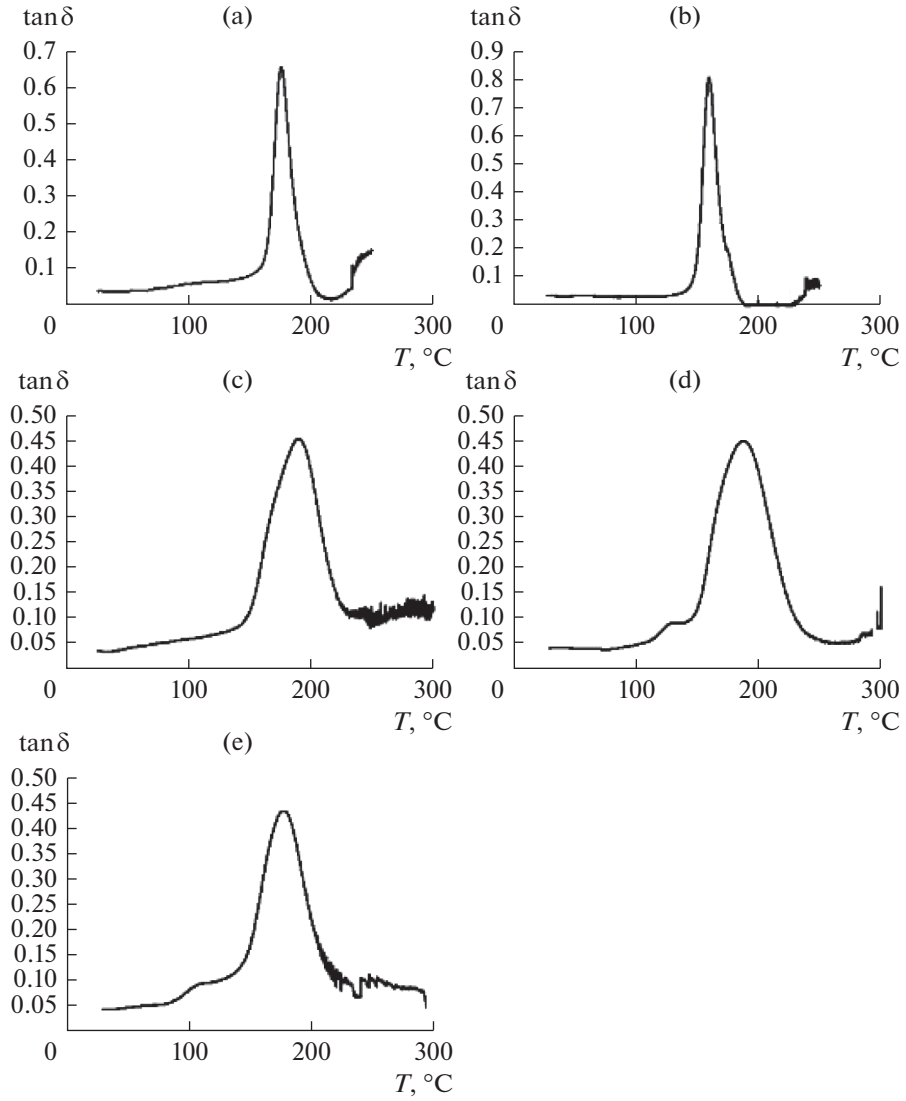

Fig. 2. Dependence of mechanical-loss tangent tanδ on temperature for the epoxy matrices (a) D.E.R. 330 + D.E.H. 650, (b) D.E.R. 330 + Polypox IPD, (c) KhT-711 + *iso*-MTHPA, (d) KhT-711 + *iso*-MTHPA + PSK-1, and (e) KhT-711 + *iso*-MTHPA + Ultem-1010.

of fracture. The modification of KhT-711 with heat-resistant thermoplastics does not lead to a fundamental change in the loading diagrams. Table 2 shows the results of the tests of epoxy matrices. The strength of the investigated epoxy matrices does not depend on the curing agent or modifier type and comes to about 70 MPa. Such a tensile strength is characteristic of most polyepoxides. Upon dynamic mechanical analysis, the elastic modulus of D.E.R. 330 + D.E.H. 650 and D.E.R. 330 + Polypox IPD is 40–60% lower than those for the matrices based on KhT-711. It should be noted that the foreign epoxy matrices are more prone

Table 2. Properties of the epoxy matrices during tension

Composition	σ_t, MPa	E, GPa	ε_t, %
D.E.R 330 + D.E.H 650	72 ± 2	3.0 ± 0.1	7.7 ± 0.8
D.E.R 330 + Polypox IPD	68 ± 2	2.9 ± 0	8.0 ± 0.7
KhT-711 + *iso*-MTHPA	75 ± 4	5.4 ± 0.3	4.7 ± 0.4
KhT-711 + *iso*-MTHPA + PSK-1	74 ± 3	4.3 ± 0.2	5.9 ± 0.4
KhT-711 + *iso*-MTHPA + PSK-1 + Utem-1010	77 ± 7	4.9 ± 0.4	4.8 ± 0.6

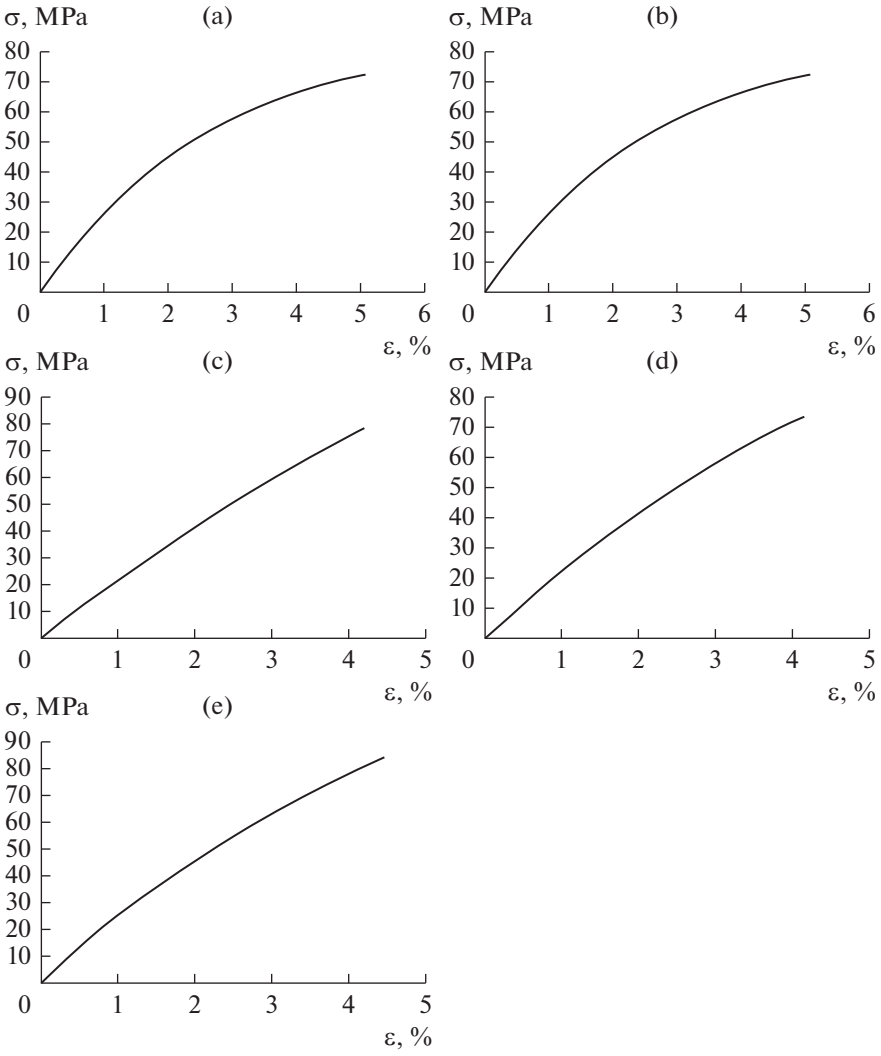

Fig. 3. Typical σ–ε tension diagrams for the epoxy compositions (a) D.E.R. 330 + D.E.H. 650, (b) D.E.R. 330 + Polypox IPD, (c) KhT-711 + *iso*-MTHPA, (d) KhT-711 + *iso*-MTHPA + PSK-1, and (e) KhT-711 + *iso*-MTHPA + Ultem-1010.

to deformation. The ultimate fracture strain comes to about 8%. Epoxy matrices based on KhT-711 resin are less prone to deformation. The ultimate strain comes to about 5% and is almost independent of the type of the modifying additive.

The results of investigations of the epoxy matrices towards the action of aggressive media are presented in Fig. 4 and Table 3. From Fig. 4 it is obvious that the external view under action of aggressive media did not change, i.e., the samples did not reveal the traces of etching or deposition of chemical substances. This is confirmed by the change in the mass of the samples after exposure, which is presented in Table 3. For all types of polymer matrices, the change in mass was less than 1%, which testifies to the high chemical resistance of the epoxy matrices investigated. It should be noted that KhT-711 epoxy matrix modified with heat-resistant thermoplastics remains almost unchanged under action of aggressive media. Thus, the changes of

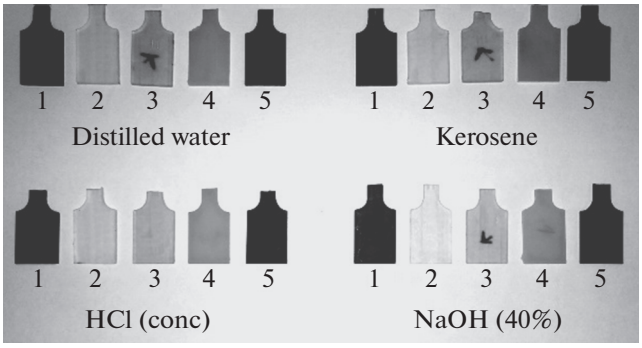

Fig. 4. Effect of aggressive media on the external appearance of samples made from the epoxy compositions (1) D.E.R. 330 + D.E.H. 650, (2) D.E.R. 330 + Polypox IPD, (3) KhT-711 + *iso*-MTHPA, (4) KhT-711 + *iso*-MTHPA + PSK-1, and (5) KhT-711 + *iso*-MTHPA + Ultem-1010.

Table 3. Chemical resistance of the epoxy matrices

Composition	Aggressive medium	Change of the external view	Δm, %
D.E.R 330 + D.E.H 650	Distilled water	Without changes	–0.1
D.E.R 330 + Polypox IPD			0.02
KhT-711 + *iso*-MTHPA			0.05
KhT-711 + *iso*-MTHPA + PSK-1			0.07
KhT-711 + *iso*-MTHPA + PSK-1 + Utem-1010			–0.01
D.E.R 330 + D.E.H 650	Sodium hydroxide (analytical grade)		–0.15
D.E.R 330 + Polypox IPD			–0.28
KhT-711 + *iso*-MTHPA			–0.2
KhT-711 + *iso*-MTHPA + PSK-1			–0.06
KhT-711 + *iso*-MTHPA + PSK-1 + Utem-1010			0
D.E.R 330 + D.E.H 650	Hydrochloric acid (conc., reagent grade)		0.58
D.E.R 330 + Polypox IPD			0.45
KhT-711 + *iso*-MTHPA			0.06
KhT-711 + *iso*-MTHPA + PSK-1			0.04
KhT-711 + *iso*-MTHPA + PSK-1 + Utem-1010			0.04
D.E.R 330 + D.E.H 650	Kerosene (TS-1)		–0.18
D.E.R 330 + Polypox IPD			–0.16
KhT-711 + *iso*-MTHPA			–0.2
KhT-711 + *iso*-MTHPA + PSK-1			–0.05
KhT-711 + *iso*-MTHPA + PSK-1 + Utem-1010			–0.02

the mass of these samples upon exposure to hydrochloric acid, sodium hydroxide, and kerosene came to 0.02–0.05%, which is within the level of statistical error. The foreign resins exhibit a larger change in mass: upon exposure to acid, the mass change reaches up to 0.5%, that in kerosene up to 0.2%.

CONCLUSIONS

The physicomechanical properties of foreign and domestic epoxy matrices were studied. It was shown that the glass-transition point of the epoxy compositions based on KhT-711 and *iso*-MTHPA can reach 190°C and exceeds the glass-transition point of the foreign binders by 15–30°C. The tensile strength of the epoxy matrices investigated comes to 75 MPa and corresponds to the strengths of most of epoxides. The elastic modulus of the compositions based on KhT-711 is higher than that for the matrices based on D.E.R. 330 by 40–60%. All the epoxy matrices investigated exhibited high resistance to acids, alkali, oil products, and water. The water absorption of all the compositions considered did not exceed 0.07%. It is worth noting the high resistance of KhT-711 + *iso*-MTHPA + heat-resistant thermoplastic composition to acids and oil products compared to the basic matrices. In this case, the mass loss is five to six times lower than that for the basic systems. The set of the resulting physicomechanical properties of the matrices based on KhT-711 epoxy resin allows one to predict the high prolonged strength of a glass-reinforced plastic.

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