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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Modification of Heat-Resistant Epoxy Matrices with Acryl-Containing Oligomers

Yu. N. Smirnov, E. A. Dzhavadyan, B. A. Komarov, L. M. Bogdanova, V. A. Lesnichaya, A. I. Efremova, and B. A. Rozenberg

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Moscow oblast, Russia

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Abstract—With the aim to enhance the crack resistance and impact resilience of heat-resistant epoxy polymeric matrices for high-strength composites, modification of epoxy resins with new poly(ether acrylates) and their adducts with amines was studied.

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Modern polymeric composite materials (PCMs) should exhibit not only high specific elastic and strength characteristics, but also high levels of dynamic and static fatigue properties, vibration and crack resistance, and impact resilience, i.e., properties associated with the capability of a polymeric matrix (PM) and its phase boundary with a reinforcing material in PCM to dissipate a mechanical load [1]. For this purpose, PM should exhibit increased relaxation ability and hence higher molecular mobility. At the same time, the polymeric matrix should exhibit high heat resistance (and hence high glass transition point), which implies decreased molecular mobility in PM. Therefore, a topical problem in PCM studies in search for an optimal molecular mobility in PM with the aim to enhance crack resistance and impact resilience without a decrease (or with a minimal decrease) in the heat resistance of PCM.

There are several ways to accomplish this goal [2]. The most widely used approach consists in decreasing the defectiveness of PM structural organization by using individual components or their blends [3–5].

The widely used way to enhance the strength of epoxy binders is introduction of low-molecular-weight liquids: plasticizers and antiplasticizers [6]. However, in so doing, the PM heat resistance considerably decreases. Similar result can also be attained by introduction into epoxy binders of rubber additives. The mechanism responsible for their strengthening effect has been extensively studied [7–14].

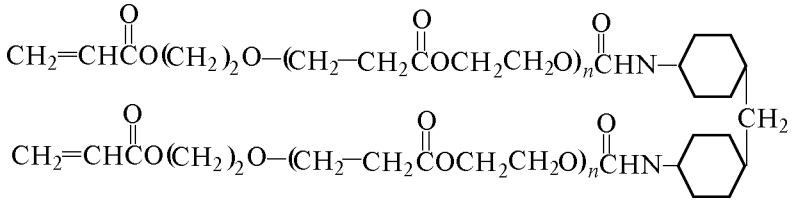
The more promising approach, from the viewpoint of preserving heat resistance, is introduction of thermoplastic polymers into a thermosetting matrix [15–18] and preparation of gradient PMs [19]. Other interesting approaches are chemical construction of a PM with a star-shaped structure with several arms originating from a common center [20] and use of hyperbranched network structures [21], mesomorphic thermotropic polymers (“molecular composites”), and interpenetrating and semiinterpenetrating networks [23–25]. This approach provides wide possibilities for creating heterophase composites with an optimal size of particles uniformly distributed in the bulk of the glassy phase.

In this study we examined the possibility of using polyacrylates for modification of some commercial grades of heat-resistant epoxy binders with the aim to enhance their plasticity and crack resistance.

EXPERIMENTAL

The base binder was ENFB-2M, a commercial product. As modifiers we used poly(ether diacrylate) (PEDA) and its piperazine (PP) adducts synthesized by the Michael reaction [24, 25]. The modifiers were synthesized at the Institute of Problems of Chemical Physics. Depending on the ratio of functional groups (double bond and amino

group), the reaction yields: at equifunctional (1 : 1) ratio, poly(ether amine) with terminal acrylate and amino groups (adduct 1); with an excess of diacrylate (1.1 : 1), poly(ether acrylate) with increased distance between two terminal double bonds (adduct 2). The structure of PEDA modifier is shown below:



The extent of curing of the initial binder and the effect of modifiers on this parameter were evaluated calorimetrically in isothermal and scanning modes with DAK-1 and DSC 822e (Mettler–Toledo) calorimeters. The following temperature schedule was chosen for curing of the epoxy compound: T_{c1} 80°C, 0.5 h; T_{c2} 120°C, 2 h; T_{c3} 180°C, 5 h.

The glass transition point was determined with a DSC 882e differential scanning calorimeter (Mettler–Toledo) and by the thermomechanical method with a UIP-70 device at a heating rate of 2.5 deg min^{-1} under a load of 0.2 MPa. The tensile and crack resistance tests were performed with a Zwick TC-FR 010 TH universal testing machine. Tensile tests were performed with 3 × 5 × 60 mm bars according to ASTM D 882–95a standard and with dumbbells according to GOST (State Standard) 11262–80. In tensile tests we determined the tensile elastic modulus E_t (MPa), breaking tensile stress σ_t, (MPa), elongation at break ε_b (%), and fracture energy W_f (J m^{-2}). The crack resistance K_{1C} (MPa $m^{1/2}$) was determined with flat samples of size 3 × 6 × 27 mm with a triangular cut in accordance with ASTM D 5045–96 standard.

All physicomechanical tests were performed on a series of six samples with a scatter from 5 to 9%. The figures show the mean values of the parameters.

The test results in relation to the modifier concentration are shown in Figs. 1 and 2.

As seen from Fig. 1, the weakest modifying effect with respect to these parameters is attained with PEDA (curve *1*).

With adduct 1 used as modifying additive (Fig. 1, curve *3*), at its amounts of up to 5 wt %, an increase in the breaking tensile stress is close to that observed with PEDA, whereas with 5–10 wt % adduct 1 σ_t sharply increases, reaching a maximum with 12.5 wt % adduct 1.

With adduct 2 used as modifying additive (Fig. 1, curve 2), the breaking tensile stress sharply increases in the range of modifier concentrations from 0 to 5 wt %, after which the curve flattens out. The limiting value of σ_t obtained with adduct 2 exceeds by 20% the value attained with PEDA as modifier.

With all the modifiers tested, in the entire examined range of their concentrations, the fracture energy and crack resistance appreciably increase (Fig. 2).

Additions of the examined modifiers do not noticeably affect the elastic modulus of the polymer in the entire range of modifier concentrations (Fig. 3).

The glass transition point of the polymer in modification with adduct 1 does not decrease at a modifier concentration

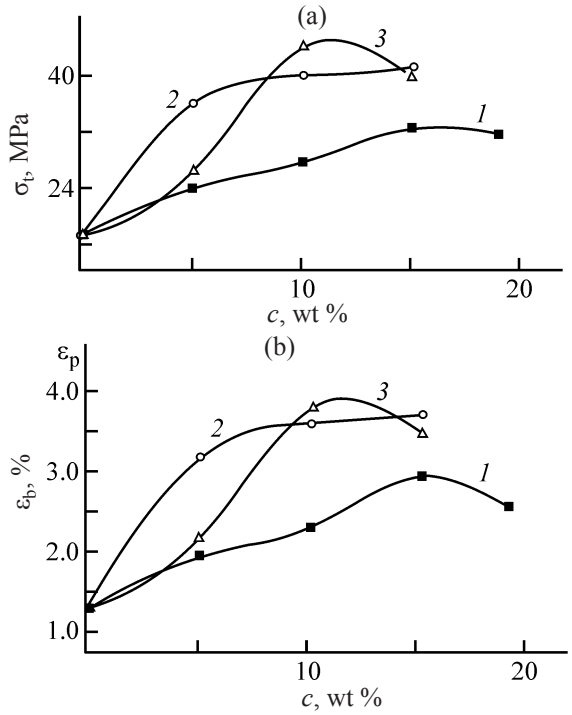


Fig. 1. (a) Breaking tensile stress σ_t and (b) elongation at break ε_b as functions of the modifier concentration c: (*1*) PEDA, (*2*) adduct 2, and (*3*) adduct 1.

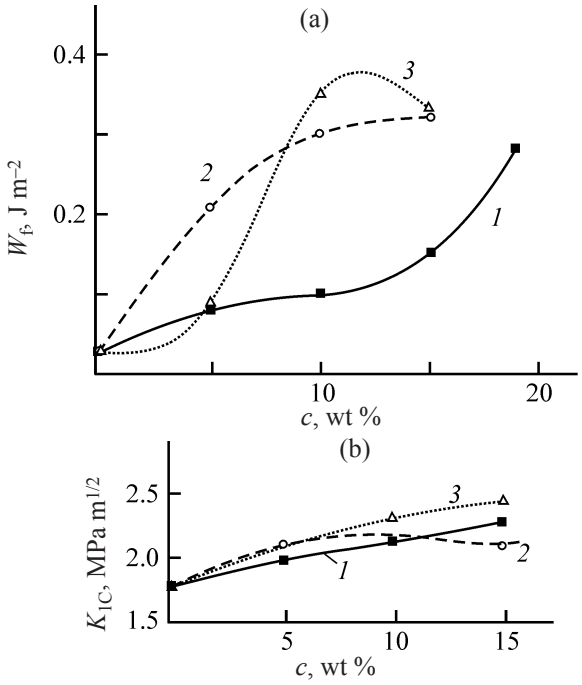


Fig. 2. (a) Fracture energy W_f and (b) crack resistance K_{1C} as functions of the modifier concentration c: (*1*) PEDA, (*2*) adduct 1, and (*3*) adduct 2.

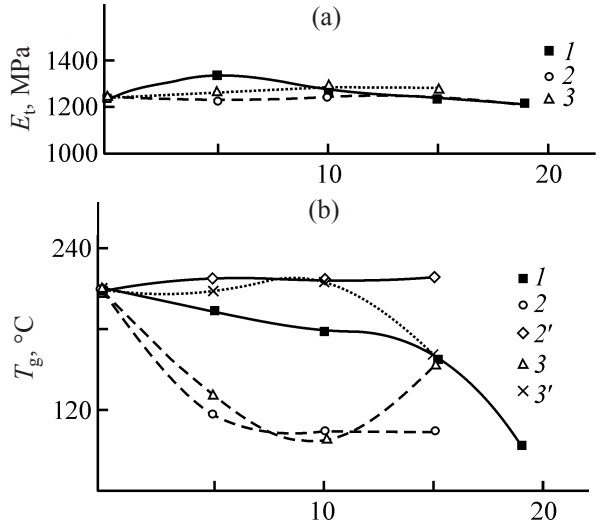


Fig. 3. (a) Tensile elastic modulus E_t and (b) glass transition point T_g of (*2, 3*) epoxy and (*2*', *3*') acrylate networks as functions of the modifier concentration c: (*1*) PEDA, (*2, 2*') adduct 1, and (*3, 3*') adduct 2.

of up to 19%, and at higher concentrations it even somewhat increases, whereas with adduct 2 T_g noticeably decreases. Particularly strong decrease in T_g is observed with PEDA additives. In the latter case, a fully transparent modified polymer is formed. This fact indicates that the acrylate network acts as a typical plasticizer. With

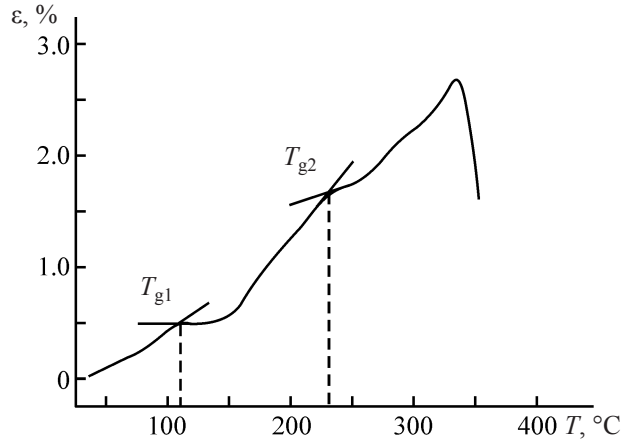


Fig. 4. Typical thermomechanical curve for modified binder in the presence of adduct 1. (ε) Elongation at break and (*T*) temperature.

piperazine adducts of PEDA as modifiers, slightly opalescent polymers are obtained. This fact indicates that curing is accompanied by phase segregation of the modifying additive in the epoxy matrix. This conclusion is unambiguously confirmed by the presence of two glass transition points in the thermomechanical curves (Fig. 4), caused by high-temperature α-relaxation of the epoxy matrix (T_{g2}) and low-temperature α-relaxation of the modifying additive (T_{g1}).

CONCLUSIONS

(1) The phase segregation effect manifested when piperazine adducts of diacrylates are taken as modifiers is a significant factor influencing the modifying effect of the additives.

(2) The use of such modifiers allows the plasticity, fracture energy, and crack resistance to be considerably enhanced, without a decrease in the elastic characteristics and heat resistance of the modified epoxy matrix.

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