

MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Elastification of Heat-Resistant Epoxy Polymer Matrices

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Abstract—The behavior of fracture toughness parameters in comparison with other physicochemical parameters of failure was examined with the aim to evaluate the efficiency of modification (elastification) of heat-resistant binders, with four epoxy–amine compounds taken as examples.

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Polymeric composite materials (PCMs) used in aerospace industry should exhibit not only high elastic and strength characteristics but also high fracture toughness of both the polymer matrix (PM) and the PCM as a whole [1–3]. At the same time, these materials should exhibit high heat resistance determined by the glass transition point of PM. To meet these requirements, the PCM molding should be performed at elevated temperatures. This inevitably gives rise to residual internal stresses of thermal origin in PCMs, caused by the difference in the thermal expansion coefficients of the PM and reinforcing materials, particularly significant when using carbon fibers. To reduce to a minimum the residual internal stresses and enhance the fracture toughness, it is necessary to elastify the PM to an optimal extent. To monitor the PM elastification, it is important to choose an efficient procedure for measuring the fracture toughness. The fracture toughness as a dissipative parameter is identified with three parameters: (1) specific surface energy γ entering into the well-known Griffith's strength relationship [4]

$$\sigma_c = (2E\gamma/\pi I_c)^{1/2},$$

where E is the tensile Young's modulus and I_c , critical defect size. This formula was deduced using the energy approach to analysis of the failure process; (2) critical strain energy release rate G_{IC} entering into Irwin's equation

$$\sigma_c = (EG_{IC}/\pi \alpha_0)^{1/2},$$

where α_0 is the critical defect size. This equation was deduced on the basis of a force approach to failure analysis [5]; (3) critical stress intensity factor K_{IC} related to G_{IC} by

$$G_{IC} = K_{IC}^2(1 - \nu^2)/E,$$

where ν is the Poisson's coefficient [6].

Note that, in tensile tests, $G_{IC} = 2\gamma$. The above parameters are determined experimentally, though by different procedures and according to different standards.

The goal of this study was to examine the fracture toughness parameters (G_{IC} and K_{IC}) in comparison with other physicochemical parameters of failure with the aim to evaluate the efficiency of modification (elastification) of heat-resistant binders.

EXPERIMENTAL

Elastification experiments were performed with the following epoxy–amine compounds: no. 1, UP-610 + ED-22 + Eut with varied ratio of UP-610 and ED-22 epoxy resins; no. 2, UP-610 + EA + Eut with varied ratio of UP-610 and EA epoxy resins; no. 3, UP-610 + SKU-PFL-100 + Eut with varied content of SKU-PFL-100 polyurethane rubber; no. 4, UP-610 + Eut + MGF-9 + DCP with variable content of the diacrylate

oligomer (commercial grade MGF-9). Here UP-610 is a trifunctional epoxy resin based on *p*-aminophenol; ED-2 and EA are commercial-grade bifunctional epoxy-4,4'-isopropylidenediphenol and epoxy-aniline resins; Eut is an eutectic mixture of *m*-phenylenediamine and diaminodiphenylmethane (40 : 60 wt % weight ratio, UP-0638/1 commercial grade) used as curing agent; DCP is dicumyl peroxide (curing agent); SKU-PFL-100 is a commercial-grade rubber containing isocyanate groups at molecular chain termini; and MGF-9 is a commercial-grade dimethacrylate.

All the components of the binder were preliminarily mixed in a beaker at 80°C in an oven and transferred into a three-necked glass mixer equipped with a stirrer, a heated jacket, and a discharge stopcock and connected to a vacuum pump. The contents were stirred with a high-speed stirrer at 80°C with simultaneous degassing to a residual pressure of $\sim 10^{-2}$ torr. Then the binder was cast into metal and glass molds and was cured in a three-step temperature mode: 80°C, 1 h; 120°C, 2 h; and 165°C, 5 h.

Tensile tests were performed with a Zwick TC-FR 010 TH universal testing machine with bars of size $3 \times 5 \times 60$ mm, following ASTM D 882-95a standard, and with dumbbells according to GOST (State Standard) 11262-80. In so doing, we determined the tensile Young's modulus E_t (MPa), tensile strength σ_t (MPa), elongation at break ε_b (%), and total work of break W_b (kJ m^{-2}) evaluated as the integral area under the curves in the tensile strain-stress diagram.

The fracture toughness parameters K_{IC} and G_{IC} were determined with flat samples of size $3 \times 6 \times 27$ mm with a triangular notch and a microcrack made with a knife edge at the notch apex, in accordance with ASTM D 5045-96 standard. From the test results, we calculated the strain energy release rate G_{IC} . The parameter $\alpha_0 = I_c$ was calculated from the relationship $\alpha_0 = EG_{IC}/\pi\pi_c^2$.

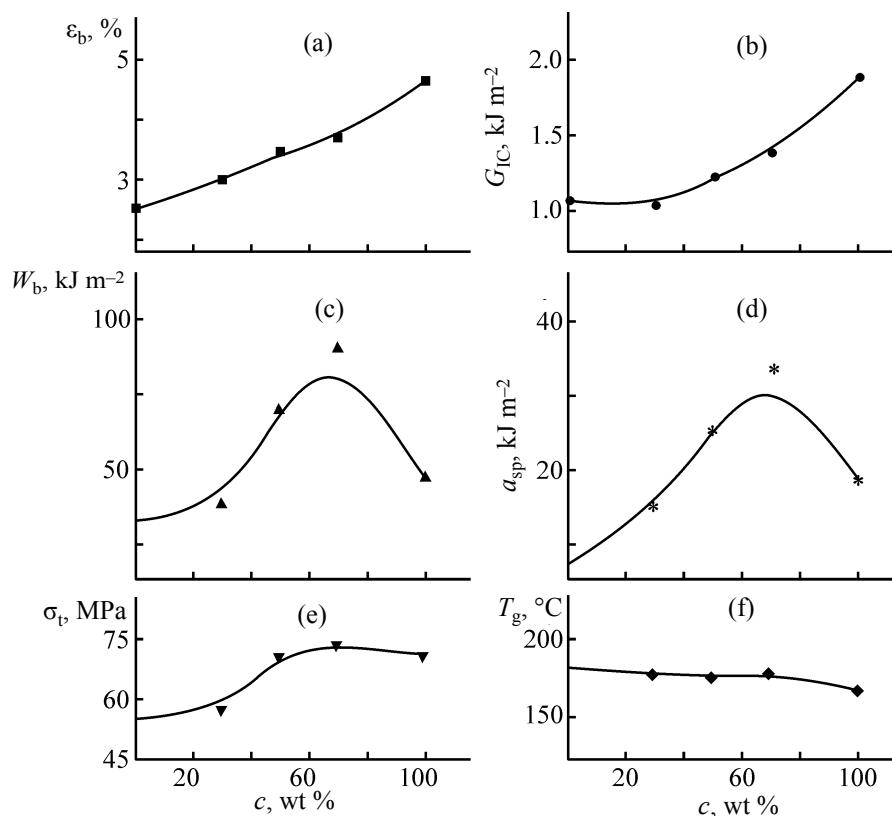
The segmental molecular mobility was monitored by determining the glass transition point T_g using a UIP-70 thermal analyzer. The Charpy toughness was determined with a Zwick testing impact machine.

It is known [7] that commercial brands of polymeric matrices under conditions of weak loading exhibit satisfactory cracking resistance with G_{IC} of about 0.25–0.35 kJ m^{-2} , and for structures operating under strong loads $G_{IC} \geq 1.0$ kJ m^{-2} is required. The maximum attained values of G_{IC} for binders based on epoxy-urethane heterophase dispersions reach 10.0 kJ m^{-2} [8].

It was found previously [9, 10] that, for a binder of commercial grade ENFB-2M, modification with polyether di(meth)acrylates allows the fracture toughness K_{IC} to be increased by 30% (from 1.85 to 2.43 $\text{MPa m}^{1/2}$). It was found that the other physico-mechanical properties of the modified binder, such as the tensile strength, elongation at break, and total work of break, increased to a considerably greater extent (by 100% and more). This result is in agreement with the fact [2] that modification of heat-resistant densely cross-linked binders with various rubbers led to a twofold increase in the fracture toughness, whereas for less cross-linked binders the increase in this parameter was tenfold. This result is attributed in [2] to a decrease in the contribution of the mechanism of plastic pore growth in the course of fracture energy dissipation. It follows from the aforesaid that elastification of heat-resistant binders can be monitored more efficiently (from the percentage viewpoint) using the parameters σ_t , ε_b , and W_b , which can be readily determined from the extension curves of samples fabricated in the form of dumbbells, blades, or bars.

In this study we made a comparative evaluation of the dependences of K_{IC} , G_{IC} , σ_t , ε_b , E_t , and W_b and of the specific impact fracture toughness a_{sp} on the composition of the four epoxy-amine compounds chosen. It should be noted that, in contrast to K_{IC} values having the dimension of $\text{MPa m}^{1/2}$, incommensurate with the dimensions of the other parameters, the dimension of G_{IC} (kJ m^{-2}) allows its comparison with the W_b and a_{sp} values, also expressed in kJ m^{-2} . This fact allows comparison of the dissipated energy levels evaluated by each of the above procedures.

Table 1 and the figure show the results of determining all the above physico-mechanical parameters for epoxy-amine compound no. 1 with varied ratio of the resin components UP-610 and ED-22. We expected that an increase in the content of ED-22 bifunctional resin and a decrease in the content of UP-610 trifunctional resin should lead to elastification of the compound and, correspondingly, to an increase in the toughness parameters K_{IC} and G_{IC} . However, as seen from Table 1, K_{IC} is virtually insensitive to structural changes caused by variations in the ratio of the resin components. At the same time, the dissipative parameter G_{IC} continuously increases with an increase in the ED-22 content. At 100% ED-22 content, it exceeds the initial value by 80%. Hence, ε_b and G_{IC} show practically additive



(a) Elongation at break ε_b , (b) fracture toughness G_{IC} , (c) work of break W_b , (d) impact toughness a_{sp} , (e) tensile strength σ_t , and (f) glass transition point T_g as functions of the content of ED-22 bifunctional resin in compound no. 1 (wt %).

Table 1. Physico-mechanical properties of epoxy-amine compound no. 1 at varied content of UP-610 and ED-22

| Binder composition, % | σ_t , MPa | E_t , MPa | ε_b , % | W_b , kJ m ⁻² | a_{sp} , kJ m ⁻² | K_{IC} , MPa m ^{1/2} | G_{IC} , kJ m ⁻² | T_g , °C |
|----------------------------------|------------------|-------------|---------------------|----------------------------|-------------------------------|---------------------------------|-------------------------------|------------|
| UP -610 (100) + Eut | 55.1 ± 3.6 | 2256 ± 236 | 2.5 | 32.7 ± 0.1 | 7.3 ± 1.5 | 1.07 ± 0.19 | 1.06 ± 0.21 | 182 |
| UP -610 (70) + ED -22 (30) + Eut | 57.9 ± 3.0 | 2231 ± 260 | 2.97 | 38.1 ± 7.6 | 15.2 ± 2.1 | 1.04 ± 0.21 | 1.03 ± 0.24 | 179 |
| UP -610 (50) + ED -22 (50) + Eut | 71.2 ± 3.0 | 2289 ± 190 | 3.45 | 70.3 ± 5.3 | 25.7 ± 3.0 | 0.97 ± 0.20 | 1.23 ± 0.23 | 176 |
| UP -610 (30) + ED -22 (70) + Eut | 74.4 ± 3.5 | 2338 ± 200 | 3.70 | 90.7 ± 14 | 33.9 ± 4 | 1.03 ± 0.13 | 1.39 ± 0.19 | 179 |
| ED-22 (100) + Eut | 71.7 ± 3.8 | 1650 ± 170 | 4.65 | 47.4 ± 7.0 | 19.0 ± 3.3 | 1.06 ± 0.20 | 1.90 ± 0.27 | 168 |

dependence on the composition of the epoxy compound. Table 1 shows that the tensile Young's modulus does not vary significantly, whereas the tensile strength reaches a limit, exceeding the initial value by 38%, at 30 wt % content of ED-22. At the same time, the parameters W_b and a_{sp} pass through a maximum at 70% content of ED-22, exceeding in the maximum the initial values by 177 and 364%, respectively, i.e., these parameters are highly sensitive to the elastification. The observed maximum indicates that elastification of epoxy-amine compound no. 1 is characterized by a synergistic effect of structural

fragments of the network epoxy polymer on these parameters.

Thus, bifunctional epoxy resin ED-22 chosen for the elastification, when taken in an optimal combination with UP-610 trifunctional resin, ensures considerable enhancement of the dissipative properties of the epoxy-amine compound. The presence of ED-22 resin does not lead to a significant decrease in the glass transition point (Fig. 1) and hence in the heat resistance.

It was interesting to compare the modifying effects of two different bifunctional resins: ED-22 and EA.

Table 2. Physicomechanical properties of epoxy–amine compound no. 2 at varied content of UP-610 and EA

| Binder composition, % | σ_t , MPa | E_t , MPa | ε_b , % | W_b , kJ m ⁻² | a_{sp} , kJ m ⁻² | K_{IC} , MPa m ^{1/2} | G_{IC} , kJ m ⁻² | T_g , °C |
|-----------------------------|------------------|-------------|---------------------|----------------------------|-------------------------------|---------------------------------|-------------------------------|------------|
| UP-610 (100) + Eut | 55.1 ± 3.6 | 2256 ± 236 | 2.86 | 32.7 ± 0.1 | 7.3 ± 1.5 | 1.07 ± 0.19 | 1.06 ± 0.21 | 182 |
| UP-610 (75) + EA (25) + Eut | 65.8 ± 4.0 | 2240 ± 265 | 2.1 | 32.0 ± 2.9 | 10.4 ± 2.5 | 1.02 ± 0.17 | 0.69 ± 0.13 | 179 |
| UP-610 (50) + EA (50) + Eut | 70.0 ± 3.3 | 2558 ± 300 | 2.3 | 42.0 ± 8 | 8.4 ± 2.9 | 0.82 ± 0.15 | 0.35 ± 0.10 | 166 |
| EA (100) + Eut | 60.0 ± 2.9 | 2312 ± 230 | 2.1 | 24.4 ± 2 | 6.3 ± 1.4 | 0.86 ± 0.17 | 0.38 ± 0.08 | 132 |

A technological advantage of EA is low viscosity. The physicomechanical parameters of epoxy–amine compound no. 2 with varied content of the modifying resin EA are given in Table 2. As can be seen, the parameter K_{IC} for this compound does not change up to 50 wt % EA content, after which it slightly (by 23%) decreases. At the same time, the parameter G_{IC} drastically decreases (by a factor of 3 at 50 wt % EA content). The parameters ε_b and E_t vary insignificantly. At the same time, σ_t , W_b , and a_{sp} pass through a weakly pronounced maximum at 50 wt % EA. The maximum values of these parameters exceed the initial values by 27, 41, and 42%, respectively.

These results indicate that introduction of up to 50 wt % modifying resin EA leads to considerable embrittlement, rather than to elastification, of the compound. To understand this effect, let us consider the following facts. Epoxy–aniline resin EA is characterized by significantly higher content of epoxy groups than epoxy–4,4'-isopropylidenediphenol resin ED-22 (epoxy numbers 33 and 22%, respectively) [11]. In addition, its chemical structure should ensure shorter distance between the network points in the cross-linked structure formed [12]. Hence, the use of this resin should lead to higher cross-linking density and hence to higher glass transition point, compared to the use of ED-22 resin. However, upon curing with an eutectic mixture of amines, T_g appeared to be 168°C with ED-22 and only 132°C with EA. This result can be attributed to the fact that the steric structure of EA resin (with two epoxy groups linked to one nitrogen atom) is favorable for cyclization in the course of curing. The cyclization should lead to lower cross-linking density and hence to decreased glass transition point of the compound. A decrease in T_g , in turn, should lead to an increase in the α -relaxation properties of the epoxy compound (owing to an increase in the molecular mobility) and, simultaneously, to a decrease in the dissipative properties of the compound (owing to a decrease in the effective volume of the kinetic unit of the α -relaxation

process) [3]. The latter fact causes a significant decrease in the fracture toughness parameter G_{IC} .

It should be noted that, in modification (pseudo-elastification) of epoxy–amine compound no. 2, the sensitivity of G_{IC} is higher compared to K_{IC} and even to W_b and a_{sp} .

It was interesting to evaluate the efficiency of the procedures used as applied to modification of epoxy–amine compound no. 3 with varied additions of SKU-PFL-100 rubber containing isocyanate groups at molecular chain termini. It could be expected a priori that an increase in the rubber content should be accompanied by elastification of the epoxy–amine compound and hence an increase in the dissipative parameters K_{IC} and G_{IC} .

However, as seen from Table 3, K_{IC} , on the contrary, decreases with an increase in the rubber content (by 27% in the minimum point corresponding to 5 wt % rubber), and G_{IC} passes through an even more pronounced minimum (decrease by 61% at 4 wt % rubber). The parameters σ_t , E_t , and W_b do not change noticeably, whereas ε_b passes through a weakly pronounced minimum at 54 wt % rubber. At the same time, the parameter a_{sp} passes through a weakly pronounced maximum at 4–5 wt % rubber, exceeding in the maximum point the initial value by 57%.

The minimum observed with both dissipative parameters, as in the case of epoxy–amine compound no. 2, indicates that the network structure becomes more rigid under the action of the rubber. This is also confirmed by the observed increase in the glass transition point, with the maximum observed at 5 wt % rubber. From the chemical viewpoint, this result may be due to reaction of isocyanate groups of the rubber with hydroxy groups of the initial epoxy resin UP-610. This should lead to an increase in the effective functionality of the resin [13] and, correspondingly, to thicker cross-linking. At 5 wt % rubber, apparently, the stoichiometric ratio of the isocyanate and hydroxy groups is attained, and, correspondingly, T_g passes through a maximum.

Table 3. Physicomechanical properties of epoxy–amine compound no. 3 at varied content of the modifying rubber SKU-PFL-100

| Binder composition, % | σ_t , MPa | E_t , MPa | ε_b , % | W_b , kJ m ⁻² | a_{sp} , kJ m ⁻² | K_{IC} , MPa m ^{1/2} | G_{IC} , kJ m ⁻² | T_g , °C |
|--------------------------------|------------------|-------------|---------------------|----------------------------|-------------------------------|---------------------------------|-------------------------------|------------|
| UP-610 + Eut | 55.1 ± 3.6 | 2256 ± 236 | 2.86 | 37.2 ± 2.5 | 7.3 ± 1.5 | 1.07 ± 0.19 | 1.06 ± 0.21 | 182 |
| UP-610 +Eut + SKU-PFL -100 (3) | 60.7 ± 4.1 | 2380 ± 240 | 2.5 | 40.9 ± 3.0 | 10.5 ± 1.4 | 0.98 ± 0.18 | 0.90 ± 0.24 | 187 |
| UP-610+ Eut + SKU-PFL -100 (4) | 53.0 ± 3.1 | 2850 ± 270 | 2.19 | 38.1 ± 4.1 | 11.5 ± 1.8 | 0.88 ± 0.15 | 0.41 ± 0.075 | 191 |
| UP-610 +Eut + SKU-PFL (5) | 61.5 ± 3.8 | 2684 ± 280 | 3.05 | 34.3 ± 3.5 | 6.7 ± 1.4 | 0.78 ± 0.14 | 0.75 ± 0.16 | 193 |
| UP-610+ Eut + SKU-PFL (7) | 55.0 ± 3.5 | 2387 ± 245 | 3.2 | 24.6 ± 2.5 | 8.8 ± 2.2 | 1.05 ± 0.19 | 1.18 ± 0.25 | 176 |

Table 4. Physicomechanical properties of epoxy–amine compound no. 4 at varied content of diacrylate MGF-9

| Binder composition, % | σ_t , MPa | E_t , MPa | ε_b , % | W_b , kJ m ⁻² | a_{sp} , kJ m ⁻² | K_{IC} , MPa m ^{1/2} | G_{IC} , kJ m ⁻² | T_g , °C |
|----------------------------|------------------|-------------|---------------------|----------------------------|-------------------------------|---------------------------------|-------------------------------|------------|
| UP-610 + Eut | 57.9 ± 3.4 | 2250 ± 210 | 2.86 | 34.0 ± 4 | 8.7 ± 3.7 | 0.87 ± 0.11 | 0.78 ± 0.24 | 193 |
| UP-610 + Eut + MGF -9 (5) | 55.7 ± 3.7 | 2410 ± 220 | 1.86 | 26.5 ± 2.6 | 5.71 ± 2.6 | 1.07 ± 0.12 | 1.25 ± 0.35 | 170 |
| UP-610 + Eut + MGF -9 (10) | 88.9 ± 4.1 | 2520 ± 240 | 2.18 | 59.1 ± 2.5 | 7.4 ± 4 | 1.00 ± 0.17 | 1.4 ± 0.35 | 140 |
| UP-610 + Eut + MGF -9 (15) | 77.5 ± 3.8 | 2740 ± 280 | 2.55 | 50.4 ± 2.5 | 7.3 ± 3 | 0.83 ± 0.15 | 0.70 ± 0.13 | 94 |
| UP-610 + Eut + MGF -9 (20) | 66.9 ± 4 | 2660 ± 245 | 2.26 | 36.4 ± 5.1 | 6.0 ± 0.8 | 0.83 ± 0.17 | 0.53 ± 0.14 | 95 |

The physicomechanical characteristics of epoxy–amine compound no. 4 with varied content of MGF-9 are given in Table 4. As can be seen, in this case also K_{IC} does not noticeably vary with an increase in the content of the modifying additive MGF-9, whereas G_{IC} passes through a maximum at 10 wt % content of MGF-9, exceeding the initial value by 80%. The maxima of σ_t and W_b are also observed at this modifier concentration, with the initial values exceeded by 54 and 70%, respectively. At the same time, E_t , ε_b , and a_{sp} do not vary noticeably.

This pattern of variation of the physicomechanical properties in the case of epoxy–amine compound no. 4 is apparently due to the following facts. Curing of this compound can involve several different processes of three-dimensional cross-linking. The main process is formation of the epoxy network structure by polycondensation of epoxy and amino groups.

The second process is formation of a polyacrylate network by radical polymerization of dimethacrylate MGF-9 under the action of dicumyl peroxide. These two major cross-linking processes leading to the formation of interpenetrating networks can be accompanied by side reactions of amino groups with double bonds (Michael reaction) [9, 14]. Calorimetric studies show

that, with aromatic amino groups, this reaction becomes noticeable at temperatures exceeding 100°C. At three-step curing mode (80, 120, 165°C), the contribution of this reaction can become noticeable in later steps (at higher temperatures).

In addition, in this compound the reaction between amino and peroxy groups can occur already at room temperature [15]. Joint occurrence of the above reactions complicates designing heat-resistant elastified epoxy binders.

Thus, our comprehensive study of physicomechanical parameters of modified epoxy–amine compounds revealed their relative sensitivity to structural changes and allowed us to elucidate the nature of processes occurring in the course of modification of epoxy–amine compounds.

Differences in the scale of energy consumption for the most sensitive parameters should be noted. In particular, G_{IC} varied from 0.35 to 1.9; a_{sp} , from 5.3 to 36; and W_b , from 24 to 90 kJ m⁻². This means that the parameter G_{IC} reflects mainly local energy consumption for viscous failure near the apex of the growing crack, whereas the parameters W_b and a_{sp} involve energy consumption for elastic and plastic macrodeformation and failure. Therefore, to obtain a complete pattern

of elastification of heat-resistant epoxy binders, it is necessary to consider these parameters in combination.

CONCLUSIONS

(1) The strain energy release rate coefficient G_{IC} is considerably more sensitive to structural changes in the course of modification of heat-resistant binders, compared to the stress intensity factor for the crack opening. Therefore, it is not necessary to use the latter parameter for evaluating the fracture toughness of these materials.

(2) In the case of true elastification of rigid-chain epoxy compounds, the total work of fracture and impact toughness are the most sensitive to structural changes. In the case of embrittlement, G_{IC} is the most sensitive.

(3) Difference between the energy consumption for local and macroviscoelastic failure was evaluated.

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