Properties of epoxy polymers modified with polydimethylsiloxane rubber

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The modification of epoxy polymers with liquid rubbers is widely used for increasing their crack resistance, their impact and vibration strength, and also their static and dynamic adhesive strength [1–3]. In this respect, it is of interest to use organosilicon rubber as the modifier, distinguishing features of which are a low glass transition temperature \(T_g\) and also high heat resistance and heat stability, which is due to the high Si–O bond energy [4].

In the available literature, an extremely limited number of publications on the combination of epoxy resins with organosilicon compounds has been found. According to [5], organosilicon liquids and rubbers are used in the adhesive formulations in very small quantities (~0.1%). Here, their function is insufficiently clear. It is evident that, in such small quantities, they are unable to have a substantial effect on the main physicomechanical and adhesive properties of the composites. This appears to be a matter of controlling the processing characteristics. Li and Nevill [5] have also shown that the modification of organosilicon adhesives with 10–40% bisphenol A diglycidyl ether leads to an improvement in the strength in simple shear, while dicyclopentadiene dioxide is added to the organosilicon vulcanisate to improve its adhesion to metal and to prevent cracking of the vulcanisate under the action of an atmosphere containing sulphur gases.

In connection with the above, the aim of the present work was to investigate the effect of modifying additions of organosilicon rubber on the mechanical and adhesive properties of epoxy polymers.

Industrial bisphenol A resin ED-20 with properties in accordance with GOST 10587–72 was used as the epoxy oligomer. The modifier used was oligodimethylsiloxane rubber SKTN (grade A) with end hydroxyl groups and properties corresponding to GOST 13835–73. The combination of resin with rubber was carried out by heating the mixture to 60°C and thorough stirring. The amount of rubber was varied from 0 to 15 parts per 100 parts epoxy oligomer. The composites were cured with a stoichiometric amount of aminophenol UP-583T by schedule I (20°C, 240 h) and schedule II (20°C, 240 h + 100°C, 3 h).

The limiting mechanical properties under uniaxial elongation (the stress causing failure \(\sigma_t\) and the tensile strain \(\varepsilon_b\)) were determined on a Polyani-type instrument with a rigid dynamometer and automatic recording of the quantities being measured [6]. The deformation rate amounted to \(3.83 \times 10^{-5} \text{ m/s}\). On the same instrument, a study was made of the process of stress relaxation at a constant elongation rate. The elastic modulus \(E\) was calculated from the slope of the initial section of the elongation curve. The area beneath the \(\sigma-\varepsilon\) curve was used as a measure of the work of failure \(A_f\).

The glass transition temperature \(T_g\) was determined on a unit [7] ensuring the maintenance of a constant tension. The magnitude of the applied stress when the thermomechanical curves were recorded was 1 MPa.

The crosslink density of the chemical network \(n_c\) was calculated from the magnitude of equilibrium creep \(\varepsilon_o\) measured at a temperature \(T = T_g + 50^\circ\text{C}\) by means of the formula \(n_c = \sigma_o / 3RT\varepsilon_o\).

The investigation was conducted on films of 100–150 \(\mu\text{m}\) thickness, produced by curing polymer composites between the two polarised surfaces of metal plates coated with a layer of antiadhesive.

The dynamic mechanical properties (the tangent of the angle of mechanical losses \(tg\delta\) and the dynamic shear modulus \(G\)) were studied on an MK-1 torsion pendulum on specimens measuring \(75 \times 10 \times 0.5 \text{ mm}\) at a vibration...
frequency of 1 Hz. Electron microscope investigations were carried out on a UEMB-100K electron microscope by the method of two-step replicas with brittle spalling.

The adhesive strength in shear $\tau_B$ and the resistance to uniform direct pull $\sigma_{dp}$ were determined in accordance with GOST 14759–69 and 14760–69. The surfaces for bonding together were treated on a polishing plate with abrasive material, after which they were degreased with acetone.

As can be seen from Table 1, the stress causing failure $\sigma_t$ decreases extremely rapidly with increase in the rubber concentration $C$. A similar trend is observed for the dependence of the elastic modulus $E$, although a decrease in $E$ with increase in the SKTN content occurs at a lower rate than in the case of the dependence $\sigma_t$–$C$.

At the same time, the concentration dependences of the tensile strain $\varepsilon_b$ and the glass transition temperature $T_g$ have an extremal nature, with the formation of a maximum at $C \sim 7$ parts. Because of the rapid decrease in $\sigma_t$, even in spite of the increase in $\varepsilon_b$ (at low rubber additions), the work of failure $A_f$, determined by the area beneath the elongation curve (in a first approximation, $A_f = \sigma_t \varepsilon_b/2$), hardly increases at a low (up to 7 parts) content of elastomer and decreases in the range 7 < $C$ < 15 parts. Since the quantity $A_f$ correlates well with the impact strength [3], it can be stated that the introduction of polydimethylsiloxane rubber does not lead to any increase in the impact strength of the epoxide. This fact is further borne out by data obtained by dynamic mechanical spectroscopy. It can be seen (Figure 1) that the introduction of SKTN results in a very small increase in the intensity of $\beta$-transition observed in epoxy polymers at roughly $-60^\circ$C and connected with energy absorption through short-time relaxation processes. As is known [8, 9], the magnitude of this transition correlates fairly well with the impact strength.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Rubber content, parts</th>
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<tbody>
<tr>
<td>1. Tensile strength, MPa</td>
<td>0  2  5  7  10  15</td>
</tr>
<tr>
<td>2. Breaking elongation, %</td>
<td>5.3 4.9 4.2 3.8 3.6 3.4</td>
</tr>
<tr>
<td>3. Elastic modulus $E$</td>
<td>1.38 1.37 1.34 1.30 1.23 1.08</td>
</tr>
<tr>
<td>4. Work of failure, kJ/m²</td>
<td>2.65 2.68 2.65 2.60 2.27 1.51</td>
</tr>
<tr>
<td>5. Glass transition temperature, °C</td>
<td>65  66  65  64  63  57</td>
</tr>
<tr>
<td>6. Adhesive strength in shear of adhesive joints, MPa:</td>
<td>at 20°C  19.1 22.5 23.7 23.4 22.0 21.6</td>
</tr>
<tr>
<td>7. Adhesive strength in uniform direct pull of adhesive joints, MPa:</td>
<td>at 150°C  2.2 4.3 7.3 8.3 6.5 4.6</td>
</tr>
<tr>
<td>8. Adhesive strength in uniform direct pull of adhesive joints, MPa:</td>
<td>at 20°C  41.0 41.9 43.4 44.3 45.6 45.9</td>
</tr>
<tr>
<td>9. Adhesive strength in uniform direct pull of adhesive joints, MPa:</td>
<td>at 150°C  2.7 3.5 4.8 5.3 5.8 4.7</td>
</tr>
</tbody>
</table>

* Numerators – specimens cured by regime I; denominators – specimens cured by regime II.

![Figure 1. Temperature dependences of $\tan \delta$ (1, 2) and $G''$ (1, 2) for initial epoxy polymer (1, 1) and for epoxy polymer modified with 10 parts SKTN rubber (2, 2)](image-url)
Here, as shown by the results of electron microscope studies, the very structure of the modified polymer is two-phase. Particles of a second phase, combined with the rubber component, appear clearly on micrographs. These particles have a size of 0.1–0.5 μm and are distributed fairly uniformly in the matrix of the epoxy polymer.

Thus, the formation of a two-phase structure is not a sufficient condition for increase in impact strength. Adhesion between the molecules of the rubber and epoxide is still necessary.

As follows from data in Table 1, mixing of the epoxy polymer with SKTN rubber promotes an increase in adhesive strength. Here, the dependence $\tau_B$–$C$ determined at 20°C has an extremal nature with a maximum at $C = 5$ parts. At the same time, the parameter $\sigma_{dp}$ increases monotonically with increase in the amount of modifier. In addition, the relative increase in $\tau_B$ at the maximum point amounts to ~25%, and for $\sigma_{dp}$ at $C = 15$ parts the magnitude of the parameter increases only by 12%.

At elevated test temperature (150°C), the dependences both of $\tau_B$ and of $\sigma_{dp}$ on concentration are extremal in nature, and here the maximum properties are observed with different rubber contents. The effect of strengthening itself differs both in absolute magnitude and in relative magnitude. It is more pronounced for the parameter $\tau_B$. The effect of strengthening at elevated temperature may be connected both with an increase in the content of the more heat-resistant organosilicon component and with an increase in the crosslink density $n_c$ (from 0.86 kmol/m$^3$ for the initial epoxy polymer to 1.28 kmol/m$^3$ for an epoxy polymer modified with 10 parts siloxane rubber). On the strength of this it is possible to explain the increase in $T_g$ when the liquid elastomer is introduced (Table 1), and also the increase in the level of the relaxing stress retained in the specimen (Figure 2).

Note also (Table 1) that, in the entire investigated range of SKTN concentrations, the adhesive strength of the modified specimens both at room temperature and at elevated test temperature is greater than that of the initial epoxide.

At the same time, blends of epoxy polymer with organosilicon rubber in the region of reduced (to −125°C) and moderately elevated (to ~100°C) temperatures are substantially inferior, as follows from Figure 3, to the initial epoxy polymer in terms of strength and rigidity, and also in terms of the work of failure. Only at temperatures above 100°C do the modified specimens have higher mechanical properties than the initial epoxy polymer.

Thus, the results of the investigation indicate a comparatively low effect of modification of the epoxy polymers with polydimethylsiloxane rubber in terms of improving the mechanical and adhesion properties.

REFERENCES