Properties of composite materials based on organosilicon lacquer KO-921 crosslinked with ED-20 epoxy resin

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Organosilicon coatings are widely used in electrical engineering due to their valuable properties, and in the anticorrosion protection of steel pipelines of different designation and metalwork [1–3]. They are noted for heat resistance, chemical stability, and high electrical insulation parameters with satisfactory physicomechanical properties. The given features of polyorganosiloxanes are due to thermodynamic stability of the silicon–oxygen bond.

It is well known that the introduction into organosilicon composites of an epoxy component increases their physicomechanical and technical and service parameters [1]. In the present work an investigation was made of the effect of ED-20 epoxy resin on the adhesion of coatings to a metal substrate and on the chemical and heat stability of organosilicon composite materials based on KO-921 lacquer.

Polymethylphenylsiloxane lacquer KO-921 of the Zaporozhye “Kremniipolimer” Works (GOST 16508–70) was used as the initial resin. To modify the organosilicon matrix, use was made of ED-20 epoxy resin (GOST 10587–84) in a quantity of 5 wt.% (1), 10 wt.% (2), 15 wt.% (3), 20 wt.% (4), and 25 wt.% (5) (the same numbering is used in all the figures) with curing agent diethylenetriamine (DETA). The initial composites were applied onto a metal or glass (to produce free films) substrate and cured at a temperature of 20 ± 5°C.

The degree of curing (crosslinking) of the composite materials was determined from the gel fraction content, extracting low molecular weight components with toluene in a Soxhlet apparatus. The adhesion was determined by direct pull and lattice notch methods (GOST 15140–78). The resistance of cured polymers to distilled water and to 5% solutions of NaOH and HCl was investigated by the gravimetric method according to GOST 12020–72. The heat resistance was studied by means of complex thermogravimetric analysis on a Paulik–Paulik–Erdei derivatograph in an air atmosphere. The heating rate was 10 K/min, the sensitivity was 500 units, and the range of investigated temperatures was 20–800°C. The effective activation energies of thermo-oxidative degradation were calculated by the Freeman–Carol method [4].

The effective concentration of curing agent DETA was selected by measuring the gel fraction content of a maximum modified composite (ED-20 content 25 wt.%). With increase in the DETA concentration from 1 to 2 wt.%, there is a sharp increase in the gel fraction content from 68 to 82 wt.%, which then slows down. Therefore, 2% curing agent can be considered to be the optimum quantity. The dependence of the gel fraction content on the amount of ED-20 is given in Table 1. All the composite materials produced are characterised by a high gel fraction content (83–86 wt.%), indicating effective combination of the organosilicon and epoxy components.

Experimental data from measuring adhesion by the direct pull method (see Table 1) showed that, with increase in the epoxide content to 20–25 wt.%c, the adhesion of coatings to the metal substrate increases to 8.8–9.0 MPa. The obtained effect is due to increase in the content of highly polar epoxy groups in the modified composite, on account of which there is an increase in the interaction of the coating and substrate. Adhesion measured by the lattice notch method for all organosilicon materials amounts to 1 rating, whereas for the organosilicon matrix (lacquer KO-921) this parameter does not exceed 2 ratings [2].

The introduction into the organosilicon matrix of an
epoxy modifier increases the water resistance of the system (Figure 1), and here sorption equilibrium of composites is achieved after 150–200 h exposure in distilled water. Reduction in the water diffusion coefficient through the coating (see Table 1) confirms the efficiency of crosslinking of organosilicon–epoxy materials with increase in the epoxide content.

The curves of change in the weight of organosilicon–epoxy composites in 5% aqueous solutions of NaOH and HCl (Figure 2) illustrate the chemical resistance of the materials investigated. With increase in the epoxy resin content, initially there is an increase in chemical stability (the minimum weight losses in both media — 2.5–3.0% — are possessed by a composite containing 10 wt.% ED-20), followed by a reduction in resistance (the maximum weight losses — 4.0–4.5% — are possessed by a composite containing 25 wt.% ED-20).

Since the heat resistance of polyepoxides (the temperature of the start of thermo-oxidative degradation (5% weight loss) amounts to 130–180 °C) is considerably lower than that of polyorganosiloxanes (350–400 °C) [5], a considerable reduction would be expected in the heat stability of the modified composites. However, data of thermogravimetric analysis (Figure 3) indicate the high heat stability of the materials investigated, although, with increase in the ED-20 content, the temperature of the start of thermal degradation is lowered from 360 to 305 °C (see Table 1). For unmodified lacquer KO-921 it is equal to 385 °C.

A correlation is observed between experimental results and values theoretically calculated by Lyapishev et al. [6] for the temperatures of the start of thermal degradation of the characteristic areas of the structure of organosilicon–epoxy materials, amounting to 350–360 °C. The composites obtained by the present authors are more heat resistant than materials based on modified lacquer KO-945 (a block copolymer of polymethylphenylsiloxane and ED-20 epoxy resin), the temperature of the start of thermal degradation of which amounts to 270 °C [6]. This is additional confirmation of the high efficiency of “cold” (temperature 20 ± 5 °C) crosslinking of organosilicon–epoxy materials and the formation of crosslinked composites.

<table>
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<tr>
<th>ED-20, wt.%</th>
<th>Gel fraction, wt.%</th>
<th>Adhesion, MPa</th>
<th>K_{diff} \times 10^{-4}, mm^2/s</th>
<th>T_{35%}, °C</th>
<th>T_{25%}, °C</th>
<th>Oxygen number, %</th>
<th>E_a, kJ/mol</th>
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</table>

**Figure 1** Dependence of water absorption Δm/m (%) of organosilicon–epoxy composites on time τ (h)

**Figure 2** Dependence of weight loss Δm/m (%) of organosilicon–epoxy composites on time τ (h) in 5% aqueous solutions of NaOH (a) and HCl (b)
With increase in the epoxy resin content, two maxima are observed on the differential thermogravimetric (DTG) curves (Figure 3b): the first in the region 300–400 °C (degradation of the epoxy component predominates), and the second in the range 450–550 °C (degradation of the organic radicals of the organosilicon matrix). In this case there is a regular reduction in the coke number of the modified composites with increase in the ED-20 content (see Table 1), since, under such conditions, epoxy polymers degrade entirely (the coke number of material based on ED-20 after heating to 800 °C according to [6] amounts to 0.1 wt.%).

The curves of differential thermal analysis (DTA) illustrate the processes occurring during thermo-oxidative degradation (Figure 4). All organosilicon–epoxy composites, besides material with 5 wt.% ED-20, are characterised by an endothermic effect in the region 80–150 °C, most likely indicating partial melting. Exothermic peaks in the temperature range 280–400 °C relate to thermo-oxidative degradation of the epoxy component. This conclusion is confirmed by increase in the intensity of extrema with increase in the amount of ED-20 in the materials investigated and by the simultaneous increase in the rate of weight loss of the specimens (Figure 3b). The exothermic effects in the region above 500 °C, as on DTG curves, are due to oxidation and degradation of the organic framing of polymethylphenylsiloxane.

Regular reduction in the effective activation energies of thermo-oxidative degradation (see Table 1) confirms the reduction in the thermal stability of the modified composites with increase in the content of the epoxy component.

Thus, it has been established in experiments that modification of organosilicon lacquer KO-921 with ED-20 epoxy resin in a quantity of 20–25 wt.% makes it possible to increase the adhesion of coatings to a metal substrate by a factor of 2–3. The composites obtained have high water and chemical stability, and also have considerably higher heat resistance compared with epoxy materials, which enables them to be used as high molecular weight binders of heat-resistant anticorrosion coatings.

REFERENCES

5. V. V. Korshak, Chemical structure and temperature characteristics of polymers, Nauka, Moscow, 1970, 419 pp.

(No date given)