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Abstract

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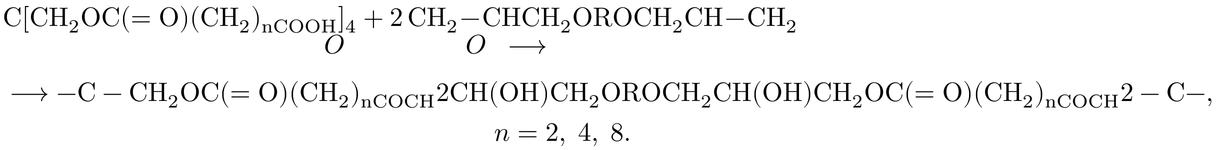
Synthesis and Physicomechanical Properties of Films of Polymers of Regular Structure

The aim of the present work was the synthesis and study of polyether-epoxy-acid and silicon-containing polyether-amide-epoxy polymers of regular cyclonetwork structure, suitable for coatings, electrical-insulation compounds, or binders for fiberglass-reinforced plastics.

The synthesis of polyether-epoxy-acid polymers was carried out according to the scheme:



$$\mathrm{C[CH_2OC(=O)(CH_2)_{nCOOH}]_4} + 2\,\mathrm{\underset{O}{CH_2-CH}CH_2OROCH_2\underset{O}{CH-CH_2}} \longrightarrow$$

$$\longrightarrow -\mathrm{C}-\mathrm{CH_2OC(=O)(CH_2)_{nCOCH}2CH(OH)CH_2OROCH_2CH(OH)CH_2OC(=O)(CH_2)_{nCOCH}2}-\mathrm{C}-,\quad n = 2,\ 4,\ 8.$$

As the diglycidyl component we used the diglycidyl ether of hydroquinone and the diglycidyl ether of diphenylolpropane. We found that, with an increase in the length of the branch in the ether-acid or in the distance between the epoxy groups in the diglycidyl compound, the reaction rate decreases. The extent of reaction by the time of gelation did not exceed 35–40%.

Silicon-containing polyether-amide-epoxy polymers of regular structure were obtained in two stages. In the first stage, pentaerythritol tetraadipate was condensed with bis-(phenylaminomethyl)-tetramethyldisiloxane according to the scheme:

$$\mathrm{C[CH_2OC(=O)(CH_2)_4COOH]_4} + 2\,\mathrm{HNC_6H_5CH_2Si(CH_3)_2OSi(CH_3)_2CH_2NHC_6H_5} \xrightarrow{-\mathrm{H_2O}}$$

$$\longrightarrow -\mathrm{C}-\mathrm{CH_2OC(=O)(CH_2)_4C(=O)N(C_6H_5)CH_2Si(CH_3)_2OSi(CH_3)_2CH_2N(C_6H_5)C(=O)(CH_2)_4COCH_2}$$

Before the gel point of the reaction mixture was reached, the extent of reaction with respect to the terminal groups was 40–45%. The resulting polymers, containing phenylaminomethylsilylene and carboxyl groups, were converted by interaction with diglycidyl ethers (the diglycidyl ethers of hydroquinone or diphenylolpropane) into copolymers with a regular distribution of carbon atoms in the network. The reactions were carried out in films on a metal surface. The physicomechanical properties of the resulting films were evaluated. To study the influence of the copolymer structure, experiments were conducted on three copolymers. Copolymers I and II

$$-C-CH_2OC(=O)(CH_2)_4COCH_2CH(OH)CH_2O{-}C_6H_4{-}C(CH_3)_2{-}C_6H_4{-}OCH_2CH(OH)CH_2OC(=O)(CH_2)_4$$

$$-C-CH_2OC(O)(CH_2)_4C(O)NCH_2Si(CH_3)_2OSi(CH_3)_2CH_2N-$$

$$-CH_2CH(OH)CH_2OC_6H_4C(CH_3)_2C_6H_4OCH_2CH(OH)CH_2OC(O)(CH_2)_4COCH_2-C- \qquad \text{II}$$

were obtained according to the reaction schemes given above. Copolymer III, obtained by condensation of pentaerythritol with adipic acid and the diglycidyl ether of diphenylolpropane with simultaneous charging of the components, was distinguished by irregularity of structure. To determine the influence of the composition and structure of the polymers on their properties, the mechanical and electrical properties of films of the copolymers obtained were studied.

Fig. 1. Kinetics of the buildup and relaxation of internal stresses during curing of films 600 μ thick at 160° based on epoxy resin ED-5 and polyethylene polyamine (*1*), copolymer I (*3*), copolymer II (*4*), and copolymer III (*2*).

Internal stresses and the magnitude of film adhesion were studied by the methods described in ([1], [2]). Hardness was determined on an ME-3 pendulum instrument with automatic readout. Figure 1 presents data on the kinetics of the buildup and relaxation of internal stresses for copolymer films. As can be seen from the figure, the internal stresses in films of regular structure are 2–3 times smaller than in films of irregular structure (cf. curves *3* and *4* with curve *2*). From the data obtained it follows that, with increasing orderliness of the structure, the internal stresses in the films decrease. The curing process of the films ends with a monotonic increase in internal stresses to a certain constant value. When the films are stored under room conditions, some relaxation of the internal stresses is observed.

Data on the kinetics of the increase in the modulus of elasticity during formation of films from copolymers I, II, and III are presented in Fig. 2. From the data given it follows that the modulus of elasticity reaches its limiting value after 10–15 h of formation. The most rapid curing is observed for films of copolymer II (cf. curve *1* with *2* and *3*). The greatest hardness value is observed for films of copolymer I (Fig. 2, curve *4*).

The adhesion of the copolymers to a glass substrate was also investigated. Figure 3 presents the dependence of the limiting internal stresses on film thickness.

Fig. 2. Kinetic data on the change in elastic modulus during curing of films at 160° for copolymers: II (1), I (2), and III (3), and changes in hardness for copolymers: I (4), II (5), and III (6)

Figure 1: Fig. 2. Kinetic data on the change in elastic modulus during curing of films at 160° for copolymers: II (1), I (2), and III (3), and changes in hardness for copolymers: I (4), II (5), and III (6)

Fig. 3. Dependence of limiting internal stresses on the thickness of coatings made from ED-5 resin and polyethylene polyamine (1), and copolymers: III (2), I (3), and II (4)

Figure 2: Fig. 3. Dependence of limiting internal stresses on the thickness of coatings made from ED-5 resin and polyethylene polyamine (1), and copolymers: III (2), I (3), and II (4)

With increasing film thickness, the internal stresses increase least of all for copolymer II (curve *4*) and most of all for the copolymer of irregular structure (curve *2*). As can be seen, in copolymer films of regular structure the internal stresses increase less with increasing film thickness. Along with low internal stresses, copolymer films of regular structure have good adhesion properties.

The test results for the synthesized copolymers were compared with data for diglycidyl ethers (ED-5), cured with polyethylene-polyamine, recommended for industrial use. Comparing curves 1, 3, and 4 in Fig. 1 shows that the internal stresses in films of copolymers I and II are 4–10 times lower than in a film of epoxy resin cured with polyethylene polyamine. It also follows from Fig. 3 that, if the epoxy coatings now in use, made from ED-5 resin cured with polyethylene polyamine, delaminate at a thickness of 400 μ (curve 1), then films of polymer I delaminate at the same value of internal stresses, but at thicknesses > 2500 μ. Thus, copolymers of regular structure have a considerably greater reserve of adhesive strength.

Fig. 2. Kinetic data on the change in elastic modulus during curing of films at 160° for copolymers: II (1), I (2), and III (3), and changes in hardness for copolymers: I (4), II (5), and III (6)

Fig. 3. Dependence of limiting internal stresses on the thickness of coatings made from ED-5 resin and polyethylene polyamine (1), and copolymers: III (2), I (3), and II (4)

Table 1 gives comparative data on the physicomechanical properties of films of copolymers I, II, and III, as well as films of epoxy resin ED-5 cured with polyethylene polyamine.

Table 1

Physicomechanical properties of films

Film-forming material	Tensile strength, kg/cm^2	Elastic modulus, kg/cm^2	Internal stress, kg/cm^2	Adhesion, kg/cm^2
Copolymer I	252	15	14	150
Copolymer II	343	24	7	150
Copolymer III	215	12	22	–
Epoxy resin ED-5 and PPA	600	24	70	130

It is seen that the tensile strength of polymers of regular structure is 20-50% higher than that of the copolymer of irregular structure, but 1.5-2 times lower than the strength of the epoxy resins in use. However, the internal stresses in coatings made from the new film-forming materials of regular structure are considerably lower. From the data presented it follows that films of copolymer II possess the best physicomechanical properties. They have the highest curing rate, the lowest internal stresses, and high strength and adhesion properties.

Films of polymers of regular structure are resistant to the action of moisture. When kept in a 3% aqueous NaCl solution for 10 days with po-

with subsequent drying of the films at 160°, the physicomechanical properties do not change.

Thermal stability of copolymer I during thermal aging at 200°:

Test duration, h	24	100	500	900	1500
Weight loss, %	0.76	0.95	3.60	4.20	6.32

Table 2 gives the dielectric characteristics of copolymer I during thermal aging at 200°.

Table 2

Dielectric loss tangent, specific volume resistivity, and dielectric permittivity of a compound based on copolymer I during thermal aging at 200°

After 24 h: test temperature, °C	After 24 h: ρ_v	After 24 h: tg δ	After 24 h: ε	After 500 h: test temperature, °C	After 500 h: ρ_v	After 500 h: tg δ
20	$2.4 \cdot 10^{15}$	0.002	5.2	20	$3.2 \cdot 10^{15}$	0.010
50	$5.0 \cdot 10^{14}$	0.011	5.4	50	—	—
100	$1.1 \cdot 10^{12}$	0.013	7.3	100	$6.0 \cdot 10^{12}$	0.170
150	$2.6 \cdot 10^{10}$	0.313	8.4	150	$6.8 \cdot 10^{11}$	—
200	$3.3 \cdot 10^{9}$	> 1	—	200	$2.0 \cdot 10^{11}$	0.360

Dielectric properties were also investigated for glass-reinforced laminate 0.88—0.95 mm thick based on copolymer I. The flexible glass-reinforced laminate obtained had the following characteristics: tg δ 1.6%, ε 5.64 (at 50 Hz), ρ_v 10^{14}. After heating for 6 h at 150°, 12 h at 180°, and 6 h at 200°, the glass-reinforced laminate had tg δ 0.22—0.35%, ε 4.95.

Copolymer I was obtained by reacting 15.79 g (0.024 mol) of pentaerythritol tetraadipate (acid number 345 mg KOH per 1 g, ester number 346 mg KOH per 1 g) with 16.57 g (0.048 mol) of diphenylolpropane diglycidyl ether (b.p. 220°/2 mm) in a stream of nitrogen with stirring at 160°. On the eve of the gel point of the polymers, the degree of completion of the reaction, according to acid and ester numbers, was 37%; the intrinsic viscosity (1% solutions in an alcohol—toluene 1:1 mixture), compared with the initial value, had increased twofold. To prepare films, 60% solutions of the resulting copolymer in an alcohol—benzene mixture were used. The procedure for obtaining and testing the films was described in ([1],[2]). The films were cured at 160° (Fig. 1 and Table 1).

Copolymer II was obtained by condensation of 11.43 g (0.017 mol) of pentaerythritol tetraadipate with 12.12 g (0.035 mol) of bis-(phenylaminomethyl)-tetramethyldisiloxane. The reaction was carried out and monitored analogously. Before the polymer gel point was reached (degree of completion of the condensation by terminal groups 45%), the reaction was interrupted. A 60% solution of the polymer was mixed with a 60% solution of diphenylolpropane diglycidyl ether (12.0 g, 0.035 mol). Curing and testing of the films were carried out analogously to the preceding case.

Copolymer III was obtained by condensation of 10.96 g (0.08 mol) of pentaerythritol with 47.0 g (0.32 mol) of adipic acid and 54.7 g (0.16 mol) of diphenylolpropane diglycidyl ether with simultaneous charging of the components. The reaction was carried out and monitored analogously.

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Note: Figure translations are in progress. See original paper for figures.