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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Influence of the Molar Ratio of Tetraethoxysilane and Glycidoxypropyltriethoxysilane on the Properties of Anhydride-Cured Epoxy–Siloxane Composites

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Abstract—The topological structure of epoxy–siloxane composites prepared by anhydride curing was studied in relation to the molar ratio of glycidoxypropyltriethoxysilane and tetraethoxysilane and to the total content of siloxane components of the system. The optical characteristics, glass transition point, sol fraction yield, concentration of internodal chains, and maximal rate of oxygen uptake by the hybrid materials were determined.

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Much attention is given today to the use of glycidyl derivatives of alkoxysilanes as a base for epoxy–inorganic composites [1, 2]. Film coatings for polymers and metals with increased hardness and hydrophobicity and with high anticorrosion characteristics were prepared using glycidoxypropyltriethoxysilane. The diversity of properties of the resulting materials is due to wide possibilities of combining various epoxy resins and curing agents, and also to mutual effect of the epoxy and siloxane components on formation of the structure and hence on the properties of hybrid materials [3, 4].

One of the most widely used procedures for preparing epoxy–siloxane composites is sol–gel synthesis. Tri- and tetraalkoxysilane precursors are often used in classical sol–gel systems for forming polysiloxane particles. Acid hydrolysis of such alkoxysilanes allows preparation of transparent uniform composites with improved characteristics [5]. The formation conditions and properties of amine-cured epoxy–siloxane composites have been well studied by now [6, 7], but there are virtually no data on how the ratio and content of ethoxysilane precursors used for forming polysiloxane particles affect the structure and properties of anhydride-cured composites. At the same time, anhydride curing of epoxy resins allows preparation of materials with high levels of strength, heat resistance, and dielectric characteristics.

Matejka et al. [8] showed that acid-catalyzed hydrolysis of alkoxysilane precursors yields octamers and other relatively low-molecular-weight (oligomeric) products with distorted topological structure, containing functional groups that provide the possibility of cross-linking and coarsening of such structures. In the process, branched polysiloxane particles are formed with a high content of Si–OH groups even in late steps of the polycondensation. It should be expected that, if functionalized nanosized polysiloxane particles (with defective three-dimensional network) are formed in the system into which a large amount of an epoxy resin is additionally introduced, the subsequent polymerization (or polycondensation) of the system via epoxy groups will lead to formation of composite materials with the structure of grafted interpenetrating polymer networks (IPNs). This should provide high uniformity and transparency of the materials obtained, and also modification of their properties. At the same time, formation of topological "defects" in the structure of composites can negatively affect their resistance to external factors, in particular, the heat resistance.

In this study we examined how the total concentration of ethoxysilanes and the molar ratio of tetraethoxysilane (TEOS) and glycidoxypropyltriethoxysilane (ES-1) in the initial epoxy–ethoxysilane systems affects the optical uniformity of the anhydride-cured composites,

the parameters characterizing the topological structure of the polymeric matrix, and the resistance of the hybrids to thermal oxidative degradation.

EXPERIMENTAL

In the majority of published papers, nanoparticles prepared by the sol–gel method from alkoxysilanes are termed silica. However, as noted above, acid-catalyzed hydrolytic polycondensation of tetraalkoxysilanes and their glycidyl derivatives yields particles with a low concentration of tri- and tetrafunctional branching and cross-linking points, containing a large amount of hydroxy groups. Therefore, in what follows, we will term them polysiloxane particles (PSPs), but present their content in the system counting on silicon dioxide.

To form the organic component of hybrid composites, we used the triepoxide derived from 1,1-dimethylol-3-cyclohexene (UP-650T) (MW 360 g mol^{-1}, EN 37.4%), *iso*-methyltetrahydrophthalic anhydride (*iso*-MTHPA) [AN 662 (mg KOH) g^{-1}], and curing accelerator, 2,4,6-tris(*N,N*-dimethylaminomethyl)phenol (UP-606/2). For preparing polysiloxane particles we used tetraethoxysilane (TEOS, ρ 0.9334 g cm^{-3}, n_D^{20} 1.383) and glycidoxypropyltriethoxysilane (ES-1, ρ 1.000 g cm^{-3}, n_D^{20} 1.425).

A sol of polysiloxane particles was prepared by hydrolysis of ethoxysilanes at TEOS : ES-1 molar ratios of 1 : 0, 2 : 1, 1 : 1, 1 : 2, and 0 : 1. The hydrolysis was catalyzed by aqueous HNO_3 taken in an amount providing pH 1.5–2 at the ratios TEOS : H_2O = 1 : 2 and ES-1 : H_2O = 1 : 1.5. The sol was formed in the presence of UP-650T epoxy resin. The content of TEOS and ES-1 in the system, counting on SiO_2, was varied from 0.25 to 10 wt %. As solvent for performing the sol–gel process we used acetone. The sol was evacuated 24 h after the start of reaction to remove volatile components (nominal residual pressure 0.3 kPa), after which a stoichiometric amount of the curing agent (*iso*-MTHPA) and a curing accelerator (UP-606/2, 0.3 wt % based on the total amount of the anhydride and epoxy resin) was added. The curing was performed under the following conditions: 130°C, 2 h; 160°C, 4 h; and 180°C, 0.5 h. Samples were prepared as 200-μm-thick films. Block samples of composites were cylinders of the diameter and height of approximately 10 mm.

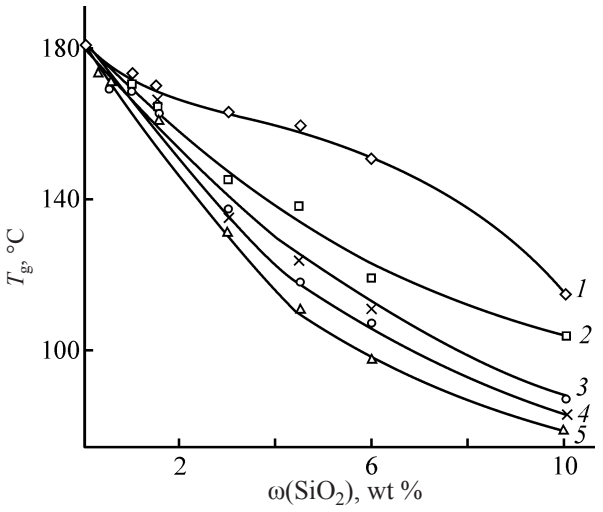

Fig. 1. Plot of T_g vs. material composition. [ω(SiO_2)] PSP content; the same for Figs. 2, 3, and 5. TEOS : ES-1: (*1*) 1 : 0, (*2*) 2 : 1, (*3*) 1 : 1, (*4*) 1 : 2, and (*5*) 0 : 1.

The light transmission coefficient of film samples was determined with a KFK-3 photocolorimeter at a wavelength of 540 nm. The glass transition point of the polymers was determined by the thermomechanical method. Measurements were performed on 25 × 6 × 0.2-mm film samples at a constant tensile stress of 2 MPa and a heating rate of 4 deg min^{-1}. The concentration of internodal chains and the rubbery modulus of block samples of the composites was determined by the thermomechanical method [9] at a load of 0.75 MPa and rate of cell heating of 4 deg min^{-1}.

Adhesion of the coatings was determined by grid notching according to GOST (State Standard) 15140–78. The yield of the sol fraction of the polymers and composites was determined from the change in the weight of the polymer films after extraction of low-molecular-weight products with methanol at 50°C for 3 days. The rate of the oxygen uptake by film samples (thickness 200 μm, weight 150–200 mg) was determined by gas volumetry at 200°C and a pressure of 0.1 MPa.

Thermogravimetric studies were performed with a Q-1500D derivatograph (MOM, Hungary) in the dynamic mode in the temperature range 20–850°C, at a heating rate of 10 deg min^{-1}.

In composites, particles prepared by the sol–gel method have a nanometric size, which provides high optical transparency of such systems. Therefore, such materials are often used as optical adhesives and coatings [10, 11]. The anhydride-cured epoxy–siloxane hybrid composites obtained are also characterized by uniformity and fairly high optical characteristics. In the concentration intervale

Table 1. Influence of the composition of epoxy–siloxane composites on thermomechanical properties of block samples

$\omega(SiO_2)$, wt %	r, °C			ΔT, °C		
	TEOS : ES-1 ratio					
	1:0	1:1	0:1	1:0	1:1	0:1
0		210			18	
0.25	211	203	208	19	21	13
0.5	208	198	204	18	18	15
1.0	206	196	196	20	18	17
1.5	202	189	185	20	18	19
3.0	198	170	154	19	17	20
4.5	194	156	123	18	20	18
6.0	193	147	117	18	19	20
10	157	120	97	20	20	19

0.25–1.5 wt % SiO_2, the light transmission coefficient at a wavelength of 540 nm (T_{540}) is 99.9–98.5%. With an increase in the fraction of the siloxane component in the system to 10 wt %, the light transmission coefficient decreases to 96% for all the concentrations and ratios of ethoxysilanes. A sharp decrease in the light transmission coefficient is observed only for samples with 10 wt % SiO_2 at a TEOS : ES-1 ratio of 1 : 0 (2 h after mixing all the components, the sol becomes opaque: rapid particle aggregation starts, and the system becomes turbid); for a film sample of this composition T_{540} is 84.5%.

On introducing into epoxy compounds sols prepared by hydrolytic polycondensation of tetraethoxysilanes (without glycidyl derivatives of alkoxysilanes), polysiloxane particles become uniformly dispersed in the epoxy matrix and do not interact chemically with it. In the process, so-called particulate composites are formed [12, 13]. Therefore, apparently, in the systems under consideration the presence of polysiloxane particles in the epoxy matrix relatively weakly affects the properties of the composites, which depend on the topological structure of the network polymers. The glass transition point T_g appreciably decreases with an increase in the content of the polysiloxane component to 10 wt % (Fig. 1). The rubbery transition point T_r corresponding to completion of the transition to the rubbery state varies similarly. The temperature interval ΔT of the α-relaxation transition does not change noticeably and is 18–20°C (Table 1).

With an increase in the PSP fraction in the composites, the sol fraction yield W_s increases (Fig. 2), suggesting distortion of the topological structure of the epoxy matrix. The influence of the concentration of polysiloxane particles on W_s is the stronger, the higher the ES-1 content in the initial composite. The amount of extractable low-molecular-weight substances is the largest in composites based on sols prepared by hydrolytic polycondensation of ES-1 without TEOS.

A decrease in T_g and an increase in W_s can be attributed to the mutual effect of the epoxy and siloxane components on the structure formation. Davis et al. [14] showed that the formation of the organic and inorganic networks is not independent and that the degree of cross-linking of the organic network directly affects the formation of the inorganic network, and vice versa. In the process, formation of IPN-type structures is possible [15].

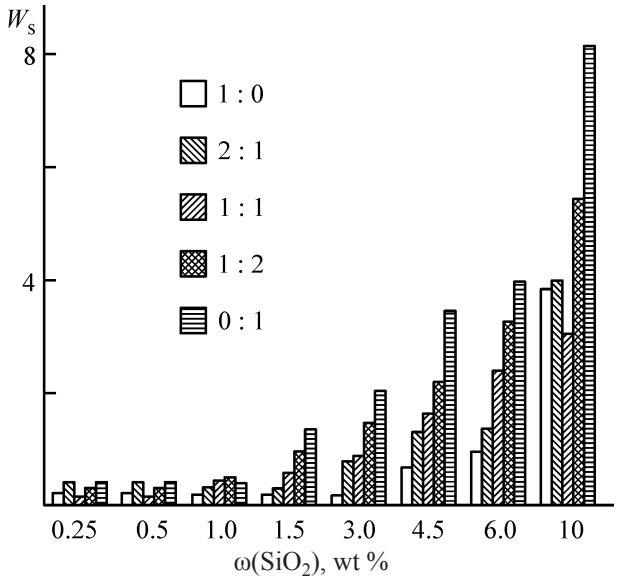

Fig. 2. Yield of sol fraction of film samples of composites W_s as a function of composition.

Formation of IPNs with incomplete phase segregation of the components is accompanied by formation of topological defects of the three-dimensional polymer network and of structural fragments with increased molecular mobility and by mutual plasticization of the system components [16–18]. Distortion of the topological structure in the previously studied epoxy–allyl IPNs is manifested in nonadditive monotonic and significant decrease in the effective concentration of internodal chains of the polymer network.

In the examined systems, appreciable decrease in the concentration of internodal chains n_c is observed already at a PSP content of 0.25–0.5 wt % (Fig. 3). However, in the plot of the internodal chain concentration vs. concentration of siloxane component, an increase in n_c (by approximately 20%) is observed at 1–1.5 wt %, after which the internodal chain concentration again decreases to the initial level. As seen from Fig. 3, in the range of polysiloxane particle concentrations of 1–1.5 wt %, a pronounced increase in E_∞ is also observed. A jumpwise increase in the rubbery modulus at a monotonic decrease in the glass transition point is due to an increase in the concentration of internodal chains.

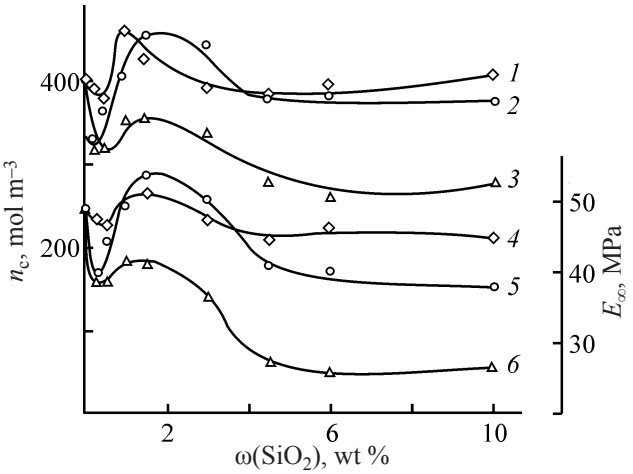

Fig. 3. (*1–3*) Concentration of internodal chains n_c and (*4–6*) rubbery modulus E_∞ of epoxy–siloxane composites as functions of their composition. TEOS : ES-1: (*1, 4*) 1 : 0, (*2, 5*) 1 : 1, and (*3, 6*) 0 : 1.

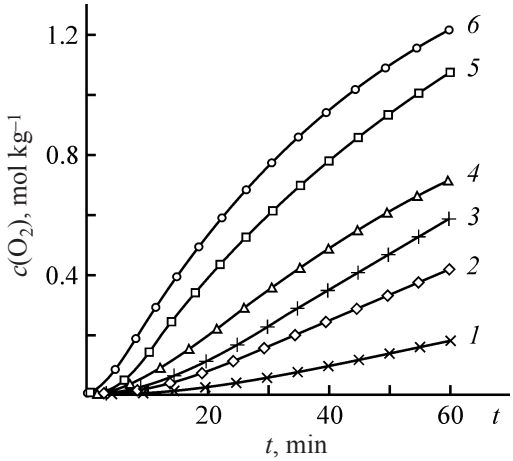

Fig. 4. Typical curves of oxygen uptake by film samples of epoxy–siloxane composites. [$c(O_2)$] O_2 concentration and (t) exposure time. TEOS : ES-1 = 0 : 1, 200°C. ω(SiO_2), wt %: (*1*) 0, (*2*) 1, (*3*) 1.5, (*4*) 3, (*5*) 6, and (*6*) 10.

The peaks in the concentration dependences of n_c and E_∞ may be due to attainment of the percolation threshold at a PSP content of 1–1.5 wt %. It is known that, for systems containing nanoparticles, the percolation threshold can be observed already at very low "filler" concentrations (≥0.2%) [19–21]. The superposition of two opposite trends, distortion of the topological structure of the epoxy polymer and its plasticization, on the one hand, and formation of a continuous cluster of polysiloxane particles, on the other hand, leads to a complex nonmonotonic shape of the concentration dependences of the rubbery modulus and internodal chain concentration.

An increase in the rubbery modulus is manifested more clearly on introduction into the system of sols prepared from an equimolar mixture of tetraethoxysilane and ES-1. In this case, a jumpwise increase in the concentration of internodal chains reaches 35–40% relative to the unmodified polymer and occurs at a polysiloxane particle concentration of 0.5–1.5 wt %. Apparently, an increase in the peak amplitude is due to formation of covalent bonds between the polysiloxane particles and polymeric (epoxy) matrix as a result of copolycondensation of the anhydride curing agent with epoxy groups of both the epoxy resin and the polysiloxane particles.

The loosening effect of polysiloxane particles on the topological structure of the epoxy network is well manifested on introduction of sols prepared from ES-1 without TEOS. In this case, relative increase in n_c in the region of polysiloxane particle concentrations of 0.5–1.5 wt % is less pronounced, and at a PSP concentration exceeding 3 wt % the concentration of internodal chains becomes 25–35% lower than for the unmodified epoxy polymer.

A decrease in the concentration of internodal chains and the presence of increasing amount of low-molecular-weight substances in the composites leads to plasticization of the polymeric (epoxy) matrix. The plasticization phenomenon can also be associated with the formation

Table 2. Influence of the composition of epoxy–siloxane composites on adhesion of coatings to the surface of aluminum supports

$\omega(SiO_2)$, wt %	Adhesion, points, at indicated TEOS : ES-1 ratio		
	1:0	1:1	0:1
0	2	2	2
0.5	2	2	2
3.0	1	1	1
10	1	1	1

of –Si–O–Si– bonds with a low potential barrier to rotation in the course of polycondensation of hydrolyzed alkoxysilane precursors. However, an important and probably decisive role of the distortion of the topological structure in the change of the glass transition point is confirmed by the fact that a good correlation is observed between the sol fraction content and T_g of the composite. For example, for the composite based on the sol prepared by hydrolytic polycondensation of TEOS, the pair linear correlation coefficient between W_s and T_g is 0.991.

It is known that unmodified anydride-cured thick-network epoxy polymers are very brittle and show poor adhesion strength [22]. It was shown previously that, on introducing the siloxane component into an epoxy–anhydride matrix, the spreadability of the composite over the substrate surface (preliminarily degreased with acetone) substantially increases, and, in going from 0 to 30 vol % ethoxysilane precursors, adhesion of the coatings is enhanced from five points to one point, respectively [23]. An increase in the adhesion is due to plasticizing effect of the polymer and formation of covalent bonds between the surface of the aluminum substrate and polysiloxane particles of the composite. In this step of our study we found that chemical activation of the surface of aluminum supports by the procedure described in [24] leads to good spreadability of the composites, with the adhesion of 1–2 points irrespective of the material composition and component ratio. The adhesion indices for the composites containing 0.5, 3 and 10 wt % PSPs are given in Table 2. Similar values of adhesion are observed at intermediate PSP concentrations.

To elucidate the effect of formation of a defective topological structure on the heat resistance, we examined how the material composition affects high-temperature oxidation of film samples with molecular oxygen. Curing accelerator UP-606/2, being a sterically hindered phenol,

Table 3. Influence of the composition of epoxy–siloxane composites on the induction period in oxidation of samples in molecular oxygen atmosphere at 200°C

$\omega(SiO_2)$, wt %	τ, min, at indicated TEOS : ES-1 ratio		
	1:0	1:1	0:1
0	19	19	19
0.25	18	18	17
0.5	18	15	17
1.0	16	13	11
1.5	13	14	10
3.0	12	7	8
4.5	10	6	7
6.0	8	7	4
10	7	5	3

has antioxidant properties [25]. Therefore, the kinetic curves of the oxygen uptake at 200°C for the unmodified polymer and composites have a form typical of the inhibited autioxidation of polymers (Fig. 4). Oxidation starts after the completion of the induction period τ of various lengths. Introduction into the composites of an increasing amount of polysiloxane particles leads to a monotonic decrease in the duration of the induction period (Table 3). The most pronounced decrease in τ is observed with sols based on "pure" ES-1. Taking into account the diffuse character of oxidation of epoxy network polymers [26], the observed decrease in the induction period may be due to an increase in the concentration of low-molecular-weight products in composites and

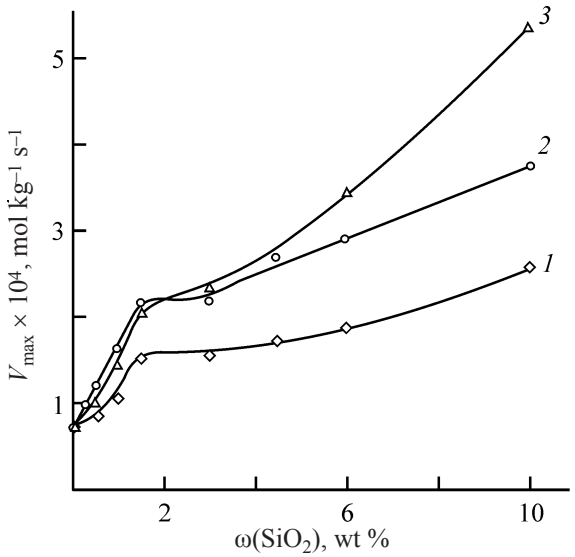

Fig. 5. Maximal rate of oxygen uptake V_{max} as a function of the material composition. TEOS : ES-1: (*1*) 1 : 0, (*2*) 1 : 1, and (*3*) 0 : 1.

Table 4. Influence of the composition of epoxy–siloxane composites on the thermal degradation parameters (TEOS : ES-1 = 1 : 0)

$\omega(SiO_2)$, wt %	τ, min, at indicated TEOS : ES-1 ratio		
	1:0	1:1	0:1
0	19	19	19
0.25	18	18	17
0.5	18	15	17
1.0	16	13	11
1.5	13	14	10
3.0	12	7	8
4.5	10	6	7
6.0	8	7	4
10	7	5	3

to their counter diffusion into surface layers of film samples. For the same reason, with an increase in the PSP concentration in the composites the maximal rate of the oxygen uptake increases. In this case, the rate of oxidation of the composites containing polysiloxane particles derived from ES-1 also increases to the largest extent. The dependence of the oxidation rate on the PSP concentration has a well-defined break in the region of the suggested percolation threshold, and at the PSP concentration in the composites exceeding 1.5 wt % the oxygen uptake decelerates (Fig. 5). This shape of the curves may be due to the fact that formation of an infinite polysiloxane cluster prevents the diffusion of oxygen and low-molecular-weight substances into surface layers of polymer films.

As the composites based on tetraethoxysilane are characterized by the lowest rate of oxygen uptake, for such systems we examined the influence of the PSP concentration on the resistance to thermal oxidative degradation. Fast degradation of the composites starts at 280–290 and is complete at 340–350°C. These temperatures decrease by 15°C in going to samples containing 4.5 and 6 wt % PSPs. Similar trend is observed for the temperatures of 5 and 10% weight loss and also for the temperature of the maximal degradation rate (Table 4). The composites containing up to 3 wt % PSPs have the same heat resistance as the straight epoxy compound.

CONCLUSIONS

(1) Variation of the ratio of ethoxysilanes used for the formation of polysiloxane particles in a sol–gel process strongly affects the structure of the hybrids obtained: from particulate composites to grafted interpenetrating polymer networks, which is reflected in the properties of the systems studied.

(2) An increase in the content of polysiloxane particles in the composites and in the fraction of glycidoxypropyltriethoxysilane leads to distortion of the topological structure of the epoxy network, which is manifested in a decrease in the concentration of internodal chains and an increase in the sol fraction yield. The plasticizing effect of polysiloxane particles on the polymeric matrix favors an increase in the adhesion of the composite to the surface of aluminum substrates, but is accompanied by an increase in the rate of the oxygen uptake in the course of high-temperature oxidation of the composites.

(3) For preparing composites with an optimal combination of properties, it is appropriate to use systems containing 1.5–3.0 wt % polysiloxane particles (counting on SiO_2).

REFERENCES

1. Robertson, M.A., Rudkin, R.A., Parsonage, D., and Atkinson, A., *J. Sol–Gel Sci. Technol*., 2003, vol. 26, nos. 1–3, pp. 291–295.
2. Weng, W.-H., Chang, Ch.-Ch., and Chen, H., *Compos. Interfaces*, 2005, vol. 11, nos. 8–9, pp. 631–641.
3. Voigt, A., Heinrich, M., Martin, C., et al., *Microel. Eng*., 2007, vol. 84, no. 5, pp. 1075–1079.
4. Mascia, L. and Tang, T., *J. Mater. Chem*., 1998, vol. 8, no. 11, pp. 2417–2421.
5. Farhadyar, N., Rahimi, A., and Langroudi, A.E., *Iran. Polym. J.,* 2005, vol. 14, no. 2, pp. 155–162.
6. Innocenzi, P., Kidchob, T., and Yoko, T., *J. Sol–Gel Sci. Technol*., 2005, vol. 35, pp. 225–235.
7. Yuan, J., Zhou, Sh., Gu, G., and Wu, L., *J. Mater. Sci*., 2005, vol. 40, pp. 3927–3932.
8. Matejka, L., Dukh, O., Brus, J., et al., *J. Non-Cryst. Solids*, 2000, vol. 270, pp. 34–47.
9. Paramonov, Yu.M., Artemov, V.N., and Klebanov, M.S., in *Sbornik nauchykh trudov "Reaktsionnosposobnye oligomery, polimery i materialy na ikh osnove"* (Coll. of Scientific Works "Reactive Oligomers, Polymers, and Materials Based on Them"), 1976, issue 3, pp. 81–86.
10. Lu, Sh.-R., Zhang, H.-L., Zhao, C.-X., and Wang, X.-Y., *J. Mater. Sci.,* 2005, vol. 40, pp. 1079–1085.
11. Castelvetro, V. and De Vita, C., *Adv. Colloid Interface Sci.,* 2004, vols. 108–109, pp. 167–185.

12. Mascia, L., Prezzi, L., and Haworth, B., *J. Mater. Sci.,* 2006, vol. 41, no. 4, pp. 1145–1155.

13. Ragosta, G., Abbate, M., Musto, P., et al*., Polymer*, 2005, vol. 46, pp. 10506–10516.

14. Davis, S.R., Brough, A.R., and Atkinson, A., *J. Non-Cryst. Solids*, 2003, vol. 315, pp. 197–205.

15. Bauer, B.J., Liu, D.-W., Jackson, C.L., and Barnes, J.D., *Polym. Adv. Technol*., 1995, vol. 7, pp. 333–339.

16. Stroganov, V.F., Mikhal'chuk, V.M., Zaitsev, Yu.S., et al., *Dokl. Akad. Nauk SSSR*, 1987, vol. 292, no. 3, pp. 670–673.

17. Mikhal'chuk, V.M., Lipatov, Yu.S., Nikolaevskii, A.N., and Maklakov, L.I., *Polymer*, 2001, vol. 42, pp. 1691–1695.

18. Mikhal'chuk, V.M., Lipatov, Y.S., and Stroganov, V.F., Polym. Networks Blends, 1996, vol. 6, no. 3, pp. 135–139.

19. Poetschke, P., Dudkin, S.M., and Alig, I., *Polymer,* 2003, vol. 44, no. 17, pp. 5023–5030.

20. Trakhtenberg, L.I., Gerasimov, G.N., Potapov, V.K., et al., *Vestn. Mosk. Gos. Univ*., Ser. 2: Khimiya, 2001, vol. 42, no. 5, pp. 325–331.

21. Hubert, T., Shimamura, A., and Klyszcz, A., *Mater. Sci. (Poland*), 2005, vol. 23, no. 1, pp. 61–68.

22. Zaitsev, Yu.S., Kochergin, Yu.S., Pakter, M.K., and Kucher, R.V., *Epoksidnye oligomery i kleevye kompozitsii* (Epoxy Oligomers and Adhesive Formulations), Kiev: Naukova Dumka, 1990.

23. Zhil'tsova, S.V., Mikhal'chuk, V.M., Petrova, E.M., et al., *Zh. Prikl. Khim*., 2007, vol. 80, no. 3, pp. 479–483.

24. Zandi, Z.R., Langroudi, A.E., and Rahimi, A., *Iran. Polym. J*., 2005, vol. 14, no. 4, pp. 371–377.

25. Ershov, V.V., Nikiforov, G.A., and Volod'kin, A.A., *Prostranstvenno-zatrudnennye fenoly* (Sterically Hindered Phenols), Moscow: Khimiya, 1972.

26. Kryuk, T.V., Mikhal'chuk, V.M., Filippenko, T.A., and Nikolaevskii, A.N., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol*., 2000, vol. 41, no. 6, pp. 142–145.