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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Modification of Epoxy–Anhydride Polymers with Aluminum Oxide

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Abstract—The effect of the heat treatment of aluminum hydroxide on the heat resistance and mechanical strength of composite materials based on ED-20 epoxy oligomer cured with isomethyltetrahydrophthalic anhydride was studied.

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Polymeric compounds based on the system ED-20 epoxy–4,4'-isopropylidenediphenol oligomer–isomethyltetrahydrophthalic anhydride (iso-MTHPA) are widely used as structural and functional materials owing to the developed production basis and long-term operation experience. ED-20–iso-MTHPA formulations have low viscosity which changes insignificantly during a period of several hours. The properties of finished materials can be controlled by using various modifiers of epoxy systems. The most widely used method is introduction into polymers of small amounts of active fillers [1]. Fillers with active surface can affect certain properties of polymeric materials, in particular, enhance the heat resistance and improve the physicomechanical characteristics [2]. Metal oxides are widely used as fillers of thermoplastics and thermosetting plastics.

In this study we chose as modifying filler aluminum oxide whose surface chemistry has been extensively and comprehensively studied [3–7]. The improvement of properties of polymeric materials on adding active fillers is due to various kinds of interaction of the filler surface with the matrix and to a change in the mobility of macromolecules on the phase boundary. The chemical composition and specific surface area of aluminum oxide are also important [8, 9].

The goal of this study was the development of anydride-curable epoxy compounds with a high level of process and service characteristics using active fillers-modifiers.

EXPERIMENTAL

As starting materials we used the following substances. Components of the polymeric compound: ED-20 epoxy–4,4'-isopropylidenediphenol oligomer [GOST (State Standard) 1587–84], iso-MTHPA [TU (Technical Specification) 6-08-3321–73]; 2,4,6-tris-(dimethylaminoethyl)phenol (Alkofen, TU 22-362–95); modifiers of the epoxy–anhydride polymer: γ-AlO(OH) (S_{sp} = 20–30 $m^2 g^{-1}$), Al_2O_3 (S_{sp} = 20–30 $m^2 g^{-1}$), and α-Al_2O_3 (S_{sp} = 15–25 $m^2 g^{-1}$).

As starting compound for preparing aluminum oxide we used aluminum hydroxide precipitated from a concentrated solution of aluminum nitrate with ammonium hydroxide. The physicochemical properties occurring in aluminum hydroxide under thermal action were studied by derivatography (Fig. 1; MOM Q-1500D derivatograph, heating rate

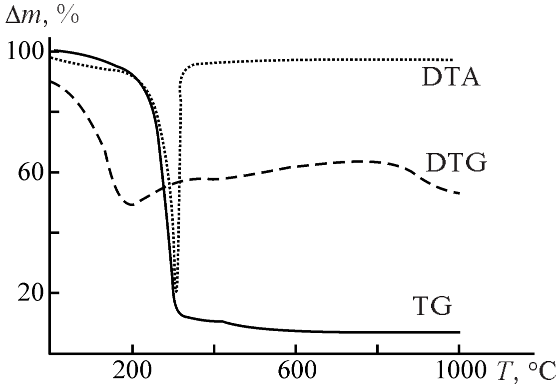

Fig. 1. Derivatograms of aluminum hydroxide powder: (Δm) weight loss and (T) temperature.

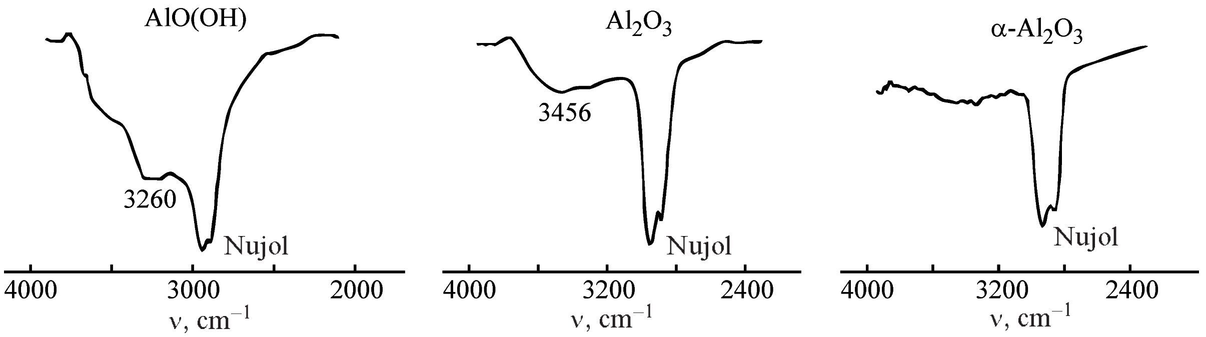

Fig. 2. Fragments of the IR spectra of products formed by thermal decomposition of aluminum hydroxide. (ν) Wavenumber.

10 deg min^{-1}). As seen from Fig. 1, the weight loss associated with the removal of adsorbed water and hydroxy groups is observed in the temperature range 150–600°C. Above 600°C, the weight does not change noticeably. Taking these data into account, to prepare modifiers with different content of surface hydroxy groups, we heated aluminum hydroxide to constant weight at 200, 600, and 1200°C. The sample of aluminum oxide prepared by isothermal heating at 200°C was identified by IR spectroscopy (IR Prestige 21) and chemical analysis as γ-AlO(OH) [10]. The sample of aluminum oxide (Al_2O_3) prepared at 600°C is X-ray amorphous. Calcination of aluminum hydroxide at 1200°C, according to X-ray phase analysis (Shimadzu XRD-6000), yields α-Al_2O_3 (corundum).

The obtained polymorphous modifications of aluminum oxide contain various amounts of hydroxy groups. An IR study showed (Fig. 2) that the intensity of the peak at 3400–3200 cm^{-1} originating from stretching vibrations of the hydroxy groups noticeably changes depending on the polymorphous modification of aluminum oxide, which indicates that different modifications contain different amounts of hydroxy groups: γ-AlO(OH) contains more OH groups and adsorbed moisture than does X-ray amorphous Al_2O_3, and α-Al_2O_3 contains no OH groups.

By differential scanning calorimetry (Shimadzu DSC-60 calorimeter) we studied the thermal effects of the polycondensation of the epoxy oligomer with the anhydride in the presence of active additives, aluminum oxides of various polymorphous modifications (Fig. 3). It can be seen that additions of γ-AlO(OH) and α-Al_2O_3 shift the exothermic peak toward higher temperatures by 15–20°C, whereas Al_2O_3 prepared at 600°C decreases the reaction onset temperature by 20°C. In the γ-AlO(OH)–oligomer–anhydride system, there is the second exothermic peak of curing at 170°C, suggesting that the oligomer/curing agent stoichiometry is disturbed by the large amount of OH groups present on the filler surface. Thus, Al_2O_3 prepared at 600°C exhibits the properties of active filler-modifier of the epoxy system: It reacts with the system components and decreases the onset temperature of the polycondensation of the epoxy oligomer with the anhydride.

The chemical reaction of the surface hydroxy groups with the epoxy groups was proved experimentally (GOST 12497–78) by the example of the model system phenyl glycidyl ether (PGE) : aluminum oxide (600°C) = 50 : 50. The results of determining the amount of epoxy groups in relation to the treatment temperature and time are given in Table 1.

It can be seen that the chemical reaction of the

Table 1. Concentration of epoxy groups X after curing in the PGE–Al_2O_3 system

T, °C	X, %, at indicated curing time, min					
	5	10	30	60	90	120
20	28.3±0.2	28.2±0.2	28.0±0.1	27.8±0.1	26.9±0.2	26.3±0.2
80	26.1±0.3	27.2±0.1	23.0±0.2	17.0±0.2	13.5±02	10.1±0.1
100	23.1±0.2	18.2±0.3	14.5±0.1	10.2±0.1	8.5±0.2	6.0±0.2
120	19.2±0.2	9.9±0.1	5.3±0.1	4.0±0.1	3.1±0.1	2.6±0.1
160	8.1±0.3	5.3±0.3	3.0±0.2	1.4±0.2	0.9±0.1	0.2±0.1

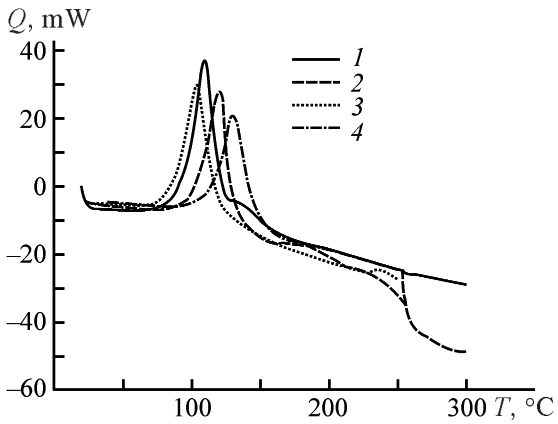

Fig. 3. Thermal effects Q of polycondensation of ED-20 with iso-MTHPA in the presence of modifiers. (T) Temperature. Modifier: (*1*) none, (*2*) γ-AlO(OH), (*3*) Al_2O_3, and (*4*) α-Al_2O_3.

hydroxy and epoxy groups with opening of the epoxy ring occus even at 20°C and becomes considerably faster at elevated temperatures; at 160°C, the epoxy groups disappeare virtually completely in 2 h.

The heat resistance after Martens for samples with various filler contents was determined according to GOST 21341. As seen from Table 2, addition of Al_2O_3 (600°C) increased the heat resistance relative to the unfilled polymer by approximately 15°C. In the polycondensation of the epoxy oligomer with the anhydride, aluminum oxide particles form additional network points and react with the epoxy matrix, which increases the adhesion of the polymer to the filler.

Table 2. Characteristics of polymeric composites prepared

Modifier, wt %	Heat resistance after Martens, °C	Strength, MPa	
		tensile	bending
–	110±2	44±4	110±3
γ-AlO(OH):			
0.25	109±3	21±4	100±5
0.5	106±3	24±2	63±3
1.0	111±3	20±1	62±3
1.5	101±3	24±2	63±2
5.0	105±1	22±4	62±6
Al_2O_3:			
0.25	116±3	31±2	105±3
0.5	115±2	34±1	107±4
1.0	123±2	38±2	125±4
1.5	122±1	35±5	130±4
5.0	125±2	27±4	82±3
α-Al_2O_3:			
0.25	110±2	27±3	67±5
0.5	114±3	25±1	70±4
1.0	110±2	25±5	65±4
1.5	114±2	24±4	60±2
5.0	115±3	33±1	72±4

Physicomechanical characteristics of the filled epoxy composites were determined with an IR 5057-50 testing machine (Table 2). The polymers modified with X-ray amorphous Al_2O_3 showed satisfactory mechanical strength. The tensile strength varied insignificantly, and the bending strength increased by approximately 15% with an increase in the modifier content by 1–1.5 wt %.

Thus, our results show that aluminum oxide prepared at 600°C exhibits properties of an active filler of epoxy–anhydride polymers. In the course of polycondensation of epoxy oligomer with the anhydride, aluminum oxide particles are incorporated in a polymeric matrix with the formation of chemical bonds between the polymer and filler, enhancing the heat resistance and mechanical strength of the material.

CONCLUSIONS

(1) The occurrence of a chemical reaction of active centers on the aluminum oxide surface with epoxy groups was proved by the example of a model system phenyl glycidyl ether–aluminum oxide.

(2) Al_2O_3 prepared at 600°C decreases the onset temperature of the polycondensation by 20°C.

(3) The highest heat resistance, increased by 15°C, is attained with X-ray amorphous Al_2O_3 used as modifier.

(4) On introducing 1–1.5 wt % X-ray amorphous Al_2O_3, the bending strength increases by approximately 15%.

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REFERENCES

1. Khozin, V.G., *Usilenie epoksidnykh polimerov* (Reinforcement of Epoxy Polymers), Kazan: Dom Pechati, 2004.
2. Mezhikovskii, S.M., *Fizikokhimiya reaktsionnosposobnykh oligomerov* (Physical Chemistry of Reactive Oligomers), Moscow: Nauka, 1998.
3. Ryazanov, M.A. and Dudkin, B.N., *Kolloidn. Zh.*, 2003, vol. 65, no. 6, pp. 831–836.
4. Ryazanov, M.A. and Dudkin, B.N., *Kolloidn. Zh.*, 2004, vol. 66, no. 6, pp. 807–810.
5. *Khimiya privitykh poverkhnostnykh soedinenii* (Chemistry of Grafted Surface Compounds), Lisichkin, G.V., Ed., Moscow: Fizmatlit, 2003.
6. Tsyganenko, A.A. and Mardilovich, P.P., *J. Chem. Soc., Faraday Trans.*, 1996, vol. 92, pp. 4843–4847.
7. Morterra, C. and Magnacca, G., *J. Chem. Soc., Faraday Trans.*, 1996, vol. 92, pp. 5111–5116.
8. Paukshtis, E.A. and Yurchenko, E.N., *Usp. Khim.*, 1983, vol. 52, no. 3, pp. 426–443.
9. Gregg, S.J. and Sing, K.S.W., *Adsorption, Surface Area, and Porosity*, New York: Academic, 1982, 2nd ed.
10. Lazarev, A.I., *Kolebatel'nye spektry i stroenie silikatov* (Vibration Spectra and Structure of Silicates), Leningrad: Nauka, 1968.