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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Influence of Zirconium Dioxide Nanopowders on Thermal Oxidative Degradation of an Epoxy Polymer

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Abstract—The influence of zirconium dioxide nanopowders on the thermal oxidative degradation of an amine-cured epoxy polymer was studied.

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Introduction into polymers of nanodispersed fillers is a simple and efficient method of controlling the mechanical and thermal properties of composite materials. Zirconium dioxide nanopowders are promising fillers for composite materials based on epoxy oligomers [1]. In epoxy polymers (EPs) containing such a filler, the mechanical properties vary with the ZrO_2 content in an unusual fashion depending on both the degree of dispersion of the ZrO_2 powder and its ability to form aggregates and agglomerates with different modes of particle binding [2].

At the same time, it is known that finely dispersed transition metal oxides are catalysts of various processes that can occur at elevated temperatures in polymeric and composite materials and can affect their heat resistance [3, 4]. In particular, transition metal oxides are catalysts of decomposition of hydroperoxides [5–7], which are initial stable products of high-temperature oxidation with oxygen of organic compounds, including polymers. Catalytic decomposition of hydroperoxides with a high yield of active radicals accelerates the thermal oxidative degradation of polymers. At a low yield of active radicals, the contribution of degenerate branching of oxidation kinetic chains in thermal oxidative degradation, the steady-state concentration of hydroperoxy groups, the oxidation autoacceleration factor, and the maximal oxidation rate decrease [8–10]. All the above factors substantially enhance the heat resistance of epoxy and other polymeric materials.

The mechanism of catalytic decomposition of hydroperoxides in the presence of transition metal compounds is not fully understood. In this study, we examined how the phase composition of zirconium dioxide powder, degree of its dispersion, and ability to form aggregates and agglomerates affect the thermal oxidative degradation of amine-cured EPs.

EXPERIMENTAL

Epoxy polymers and composites filled with ZrO_2 nanopowder were prepared from a mixture of diglycidyl ether of diphenylolpropane (DGDPP) and diglycidyl camphorate (DGC) and were cured with a stoichiometric amount of cyanoethylated diethylenetriamine UP-0633M. The curing of the compounds was performed at room temperature for 20 h with the subsequent heat treatment at 60°C for 2 h. Film samples 200 ± 5 μm thick were prepared on glass plates with a polysiloxane release coating. DGDPP samples were prepared by molecular distillation of ED-22 epoxy oligomer at a residual pressure of no more than 10 Pa. The melting point of crystalline DGDPP was 36.3°C; epoxy number 25.1. DGC [TU (Technical Specification) 88 Ukr. SSR 21 533-83; epoxy number 26.0, $n_D^{20} = 1.4832$; $\eta_{25} = 0.30 \pm 0.05$ Pa s) and UP-0633M (TU 6-05-1863–78; $d_4^{20} = 1.100 \times 10^6$ g m^{-3}; $n_D^{20} = 1.4822$; $\eta_{25} = 0.18$ Pa s) were used without additional purification.

Nanopowders of zirconium dioxide were prepared by physical impacts (UHF, pulsed magnetic field, ultrasound) after precipitation of zirconium oxynitrate (to obtain the monoclinic phase) and a mixture of zirconium oxynitrate and yttrium nitrate in a 0.97 : 0.03 molar ratio counting on ZrO_2 and Y_2O_3 (to obtain the tetragonal phase) with the subsequent filtration and drying.[1] Calcination of the powders provided conversion (with crystallization) of the hydroxide into oxide and growth of particles to required size controlled by the heat treatment temperature.

The calcination temperature T_c and particle size D_{CSR} found from the X-ray diffraction patterns (mean size of coherent scattering regions, CSR), considering nanoparticles as single crystals, are listed in Table 1, together with the BET specific surface area S_{BET} found from the nitrogen adsorption and the specific surface area S_{CSR} calculated assuming the powder to be a set of spherical particles of the size equal to CSR size. The fractional composition and morphology of ZrO_2 powder were studied by transmission electron microscopy. Preliminarily the powders were treated by a special procedure [11] with ultrasonic sputtering over a carbon support. The D_{CSR} value was calculated by the Selyakov–Scherrer formula from the halfwidth $B_{0.5}$ of (111) diffraction peaks.

The kinetics of oxygen uptake was studied at a pressure of 0.1 MPa and a temperature of 200°C on a laboratory gas-volumetric device with an optoelectronic sensor whose sensitivity with respect to the rate of oxygen uptake by the polymers was 10^{-6} mol kg^{-1} s^{-1}. The rate of oxygen uptake was reduced to 1 kg of the organic component of the composite. The thermal gravimetric analysis (TGA) was performed on a Q-1500 derivatograph at a heating rate of 10 deg min^{-1} and free access of atmospheric oxygen. A 200-mg sample of a polymer film cut into 2 × 2-mm pieces was introduced into ceramic crucibles. Calcined aluminum oxide was the reference.

The study of the influence of the ZrO_2 concentration on the high-temperature autooxidation of EP showed that the oxidation of unfilled EP started after a relatively short (16–18 min) induction period (Fig. 1). Usually autooxidation of EP obtained by cationic polymerization proceeds without induction period [8–10]. Its appearance for amine-cured EP may be due to the inhibiting effect of unchanged amino groups of the curing agent. As known [12], at the stoichiometric ratio of the components of epoxy–amine systems, the polyaddition does not go to completion, and unchanged epoxy and amino groups inevitably remain in the polymer phase. In turn, amines are acceptors of peroxy radicals and exhibit antioxidative effect in motor fuel and polymers [13]. The thermal oxidative stability of hydrocarbons is substantially enhanced in the presence of not only aromatic but also aliphatic amines. Among the latter, secondary amines, including those obtained by polyaddition of epoxy compounds [14], are the most effective antioxidants.

Table 1. Characteristics of ZrO_2 powders

Powder no.	T_p, °C	Lattice type	D_{CSR}, nm	S_{CSR}	S_{BET}
				m^2 g^{-1}	
1	500	Monoclinic	16	65	65
2	700	Monoclinic	21	52	37
3	1000	Monoclinic	48	22	8.6
4	800	Tetragonal	22	44	30

After the induction period, the dependence of the oxygen uptake on time is typical of noninitiated oxidation of polymers, with a short period of autoacceleration and a fairly long period when the oxidation proceeds at a practically constant rate (maximal oxidation rate, or rate of developed oxidation). This is followed by a relative decrease in the oxidation rate associated with decreasing "concentration" of polymeric chain fragments that are

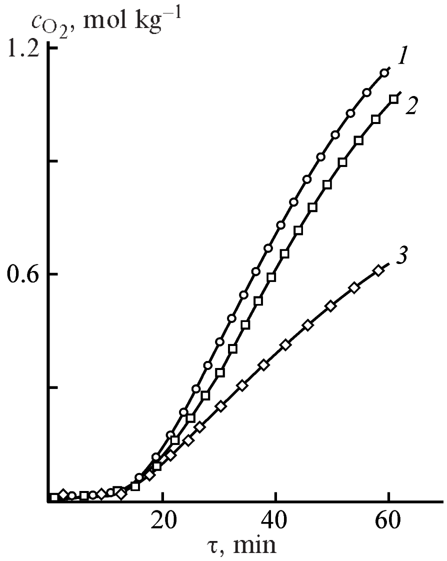

Fig. 1. Oxygen uptake c_{O_2} as a function of time τ for (*1*) EP and composites containing (*2*) 2 and (*3*) 10 wt % ZrO_2 nanopowder no. 2.

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[1] Nanopowders were prepared using the technology developed at the Donetsk Physicotechnical Institute, National Academy of Sciences of Ukraine.

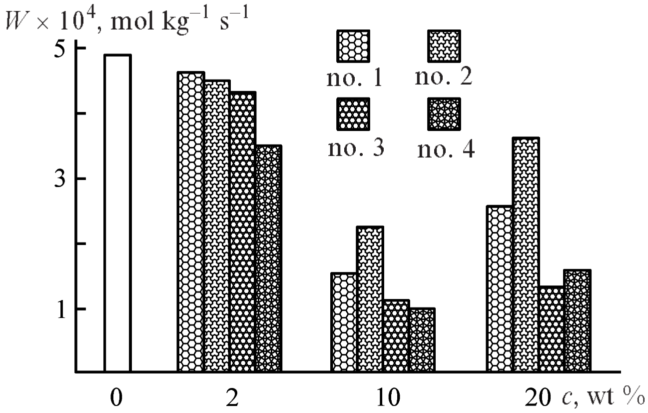

Fig. 2. Diagrams of the rate of developed oxidation W of EP and composites filled with ZrO_2 nanopowder nos. 1–4 at various filler concentrations c.

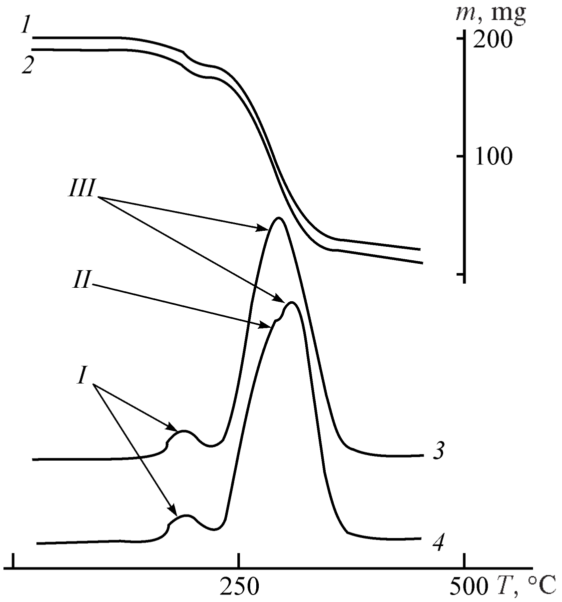

Fig. 3. Temperature dependences of the (*1, 2*) weight loss m and (*3, 4*) its temperature derivative for (*1, 3*) EP and (*2, 4*) composite filled with ZrO_2 nanopowder no. 4.

the most susceptible to oxidation. The rate of the developed oxidation for unfilled EP reaches 4.9×10^{-4} mol kg^{-1} s^{-1}.

Introduction into the polymeric matrix of ZrO_2 powder nos. 1–4 (2 wt %) does not noticeably affect the duration of the induction period (Fig. 1) and slightly decreases the rate of developed oxidation (Fig. 2). This rate decreases in the order 1 > 2 > 3 > 4 for the composites filled with powder nos. 1–4, respectively. The decrease in the maximal rate of polymer oxidation without a change in the induction period is observed, as a rule, in the case of suppression of degenerate branching of oxidation kinetic chains because of decomposition of hydroperoxides (primary stable oxidation products) by metal compounds including oxides [8–10].

In the presence of 2 wt % ZrO_2 in the polymeric matrix, the decrease in the oxidation rate is insignificant. However, at the filler content increased to 10 wt %, the rate of the polymer oxidation decreases by a factor of 1.3–3.6. The highest antioxidative activity is observed with filler nos. 3 and 4 (Fig. 2). Powder nos. 3 and 4 also decrease the maximal rate of EP oxidation, but their antioxidative power is substantially weaker. With an increase in the ZrO_2 content to 20 wt %, the stabilizing effect of the filler against thermal oxidative degradation tends to decrease, but the ratio of the rates of polymer oxidation with additives of various nanopowders remains similar: The rate of the developed oxidation for the composites filled with powder nos. 3 and 4 is lower than that for the composites filled with powder nos. 1 and 2.

The thermal gravimetric (TG) study of thermal and thermal oxidative degradation of the composite showed that introduction into the amine-cured polymer of 10 wt % ZrO_2 weakly affects the variation of its weight on heating. Typical TG and differential thermogravimetric (DTG) curves of the filled and unfilled EPs are shown in Fig. 3. The TG and DTG curves for the unfilled sample are typical of amine-cured EPs. Within the range 170–200°C, the weight loss is small and is associated with evaporation of low-molecular-weight impurities. Further heating leads to the main stage of the thermal and thermal oxidative degradation with a maximum of the weight loss rate at 300°C.

Zirconium dioxide does not noticeably affect the evaporation of low-molecular-weight impurities, and at the same time the position of maximum *I* in the DTG curves remains unchanged (Table 2). The maximum corresponding to the main stage of the degradation splits in two components: *II* and *III* (Fig. 3). The similar effect was observed in [15] for a system consisting of epoxy–novolac block copolymer and amorphous boron. This splitting is due to the effect of the filler surface on the structure of the boundary layers of the polymeric matrix. On introduction of ZrO_2 into the polymer, in most cases, the temperatures of 5% and 10% weight loss (T_5, T_{10}), temperatures of the onset of the main degradation stage T_O, and temperatures of DTG maxima T_M vary within the limits of the measurement accuracy (Table 2). Only for the composite containing ZrO_2 powder no. 4 (it exhibits the most pronounced

Table 2. Thermal characteristics* of degradation of epoxy compounds containing 10 wt % ZrO_2.

Powder no.	T_5	T_{10}	T_H	T_I	T_{II}	T_{III}	T_{50}
	°C						
Without filler	175	230	270	185	–	300	340
1	170	235	275	185	–	305	340
2	170	215	270	190	290	310	340
3	170	230	270	185	290	305	350
4	175	235	270	190	295	305	350

* T_5, T_{10}, and T_{50} are temperatures of 5, 10, and 50% weight loss, respectively; T_I, T_{II}, and T_{III}, temperatures of maxima in the DTG curve.

antioxidant properties), the temperatures characterizing thermal and thermal oxidative degradation slightly increase.

The difference in the effects exerted by ZrO_2 on the rate of oxidation of the amine-cured polymer and on its weight loss during a thermal gravimetric experiment can be attributed to the fact that the oxidation processes in thickly cross-linked EPs are accompanied by formation of additional cross-links hindering evaporation of the decomposition products [16]. Therefore, the data of derivatography and gas volumetry do not always quantitatively correlate with each other. In addition, gas-volumetric data characterize the stability of polymers with respect to thermal oxidative degradation in the initial stages of the process at relatively low temperatures, whereas derivatography gives the corresponding information for high temperatures, when pyrolytic degradation of the polymer makes a substantial contribution to the total degradation process.

It follows from the above data that the antioxidative performance of zirconium dioxide, on the whole, increases with the temperature of the ZrO_2 thermal treatment. The temperature of calcination of ZrO_2 powders substantially affects the degree of their dispersion and the ability to form aggregates. We found that, with increasing T_c from 500 to 1000°C, the mean size of the powder particles of the monoclinic modification increases from 16.5 to 48.2 nm, and their specific surface area decreases by a factor of 7 (Table 1). In the process, the particles of powder no. 1 form planar aggregates of the size exveeding 2000 nm (Fig. 4a). The fact that interparticle gaps are observed suggests that these nanoparticles are weakly bound with each other. Powder no. 2 prepared at 700°C is also characterized by relatively low degree of binding and aggregation of particles (Fig. 4b). At 1000°C, powder no. 3 is formed, which is characterized by high degree of aggregation and forms agglomerates including strongly bound particles (Fig. 4c). Such bonding is provided by diffusion processes of agglomeration type and gives polycrystalline aggregates. Powder no. 4 doped with 3 mol % Y_2O_3 has a tetragonal lattice and is characterized by small degree of particle aggregation (Fig. 4d).

The observed trends in variation of antioxidative properties of the composites, caused by the influence of ZrO_2 nanopowders, are hardly associated with differences in the specific surface area of the filler and, the more so, with the degree of their aggregation. Variation of the surface properties of the filler is apparently a more significant factor.

It is known that metal oxide nanopowders are characterized by the high degree of defectiveness of the surface, mainly associated with the oxygen nonstoichiometry. The defects give rise to excess charge and enhance the interaction with the polymeric matrix, which leads to hydroperoxide decomposition due to acceleration of the catalytic reactions. The differences in the degree of defectiveness of nanopowders are determined by conditions of their preparation, in particular, by T_p. This factor may be responsible for quantitatively different effects of powder nos. 1–3, although they all have a monoclinic lattice.

In the case of nanopowder no. 4 doped with Y_2O_3 (it has a tetragonal lattice), there is one more factor. When ZrO_2 powder is doped with Y_2O_3, replacement of one Zr(IV) atom by one Y(III) atom is accompanied by formation of two oxygen vacancies. As a result, the surface, which is neutral in monoclinic particles, becomes positively

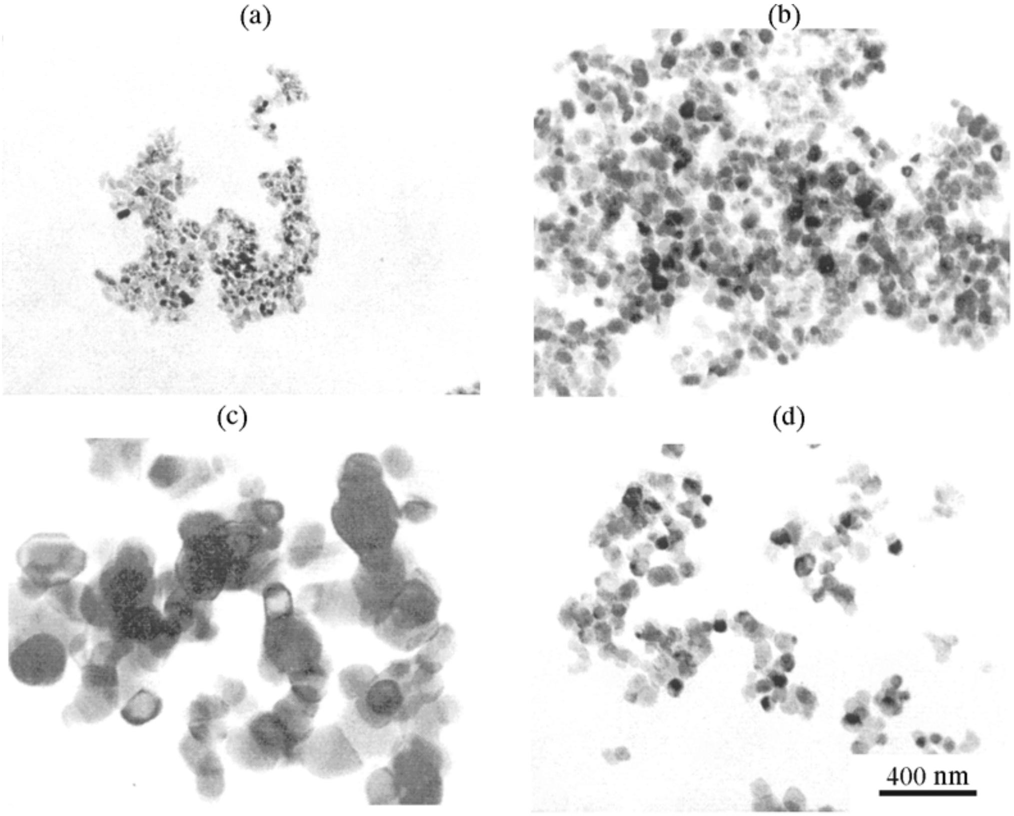

Fig. 4. Electron micrographs of ZrO_2 nanopowder nos. (a) 1, (b) 2, (c) 3, and (d) 4.

charged. This factor can favor catalysis of the hydroperoxide decomposition with a low yield of active radicals, suppression of the degenerate branching of oxidation kinetic chains, and decrease in the rate of thermal oxidative degradation.

Gas-volumetric study confirms this assumption. As seen from Fig. 2, composites containing 2 and 10 wt % powder no. 4 are characterized by the lowest oxidation rate. For such nanocomposites, the temperatures of the maxima in the DTG curves and the temperature of completion of thermal oxidative degradation are the highest.

CONCLUSIONS

(1) ZrO_2 nanopowders exhibit high antioxidative activity in amine-cured epoxy polymers, which is caused by the high defectiveness of the nanoparticle surface.

(2) The value of the antioxidant effect depends on conditions of nanopowder preparation (T_p, doping) and filler concentration.

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