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BRIEF COMMUNICATIONS

Features of High-Temperature Thermal Oxidative Degradation of Organic-Inorganic Compositions Based on Poly(methyl methacrylate) with Tetrabutoxytitanium

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Abstract—Thermal oxidative degradation of organic-inorganic compositions based on poly(methyl methacrylate) and the methyl methacrylate–methyl acrylate copolymer with tetrabutoxytitanium was studied by thermo-gravimetric methods.

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It has been shown earlier [1–8] that C_{60} and C_{70} fullerenes are effective inhibitors of high-temperature (≥300°C) thermal-oxidative degradation (TOD) of poly(methyl methacrylate) (PMMA) and its copolymers. Temperature and concentration limits of the inhibition of the disintegration of polymers by fullerenes were determined. It was found that their small concentrations (10^{-4}–10^{-3} mol kg^{-1}) effectively decelerate TOD of PMMA and MMA copolymers at temperatures up to 340°C. Organic antioxidants (branched phenols, amines, sulfur- and phosphorus-containing compounds) traditionally applied in practice of the polymer stabilization lose antioxidative properties at temperatures higher than 270°C [4]. However a high cost of fullerenes hampers their practical use.

It was found [9, 10] that organic-inorganic PMMA compositions with hydrolysates of various alkoxysilanes: tetraethoxysilane, phenyltrimethoxysilane, aminopropyltriethoxysilane are more thermally stable than PMMA at a high-temperature TOD. The greatest stabilizing effect was observed for aminopropyltriethoxysilane, its additions shift the maximum of the thermal-oxidative degradation rate to the high temperature by 60–65°C. Unlike PMMA compositions (MMA copolymers) with fullerenes, which have clearly pronounced induction periods at high-tempera-ture TOD, the hydrolysates of alkoxysilanes reduce the TOD rate of polymers without an induction period.

The aim of the present work was to study high-temperature oxidative decomposition of organic-inorganic compositions obtained on the basis of PMMA and the copolymer of MMA and methacrylic acid (MAA) with tetrabuthoxytitanium (TBOT).

EXPERIMENTAL

Tetrabuthoxytitanium was purified by vacuum distillation.

Poly(methyl methacrylate) was obtained according to the ordinary procedure [1] in sealed ampoules by MMA batch polymerization in the presence of 0.4% of dinitrile of azoisobutyric acid (AIBN) as the initiator. Before polymerization MMA was purified by vacuum distillation and deoxygenated by triple freezing a reaction mixture in a vacuum by liquid nitrogen. Ampoules were heated up at 70 (3 h), 90 (4 h), and 120°C (2.5 h). Samples of the MMA copolymer with 15 mol % of MAA were obtained in a similar way.

The MMA polymerization and MMA copolymerization with MAA were carried out with adding various amounts (from 0.5 up to 20 wt %) of TBOT to a reaction mixture. To remove monomer residuels, the

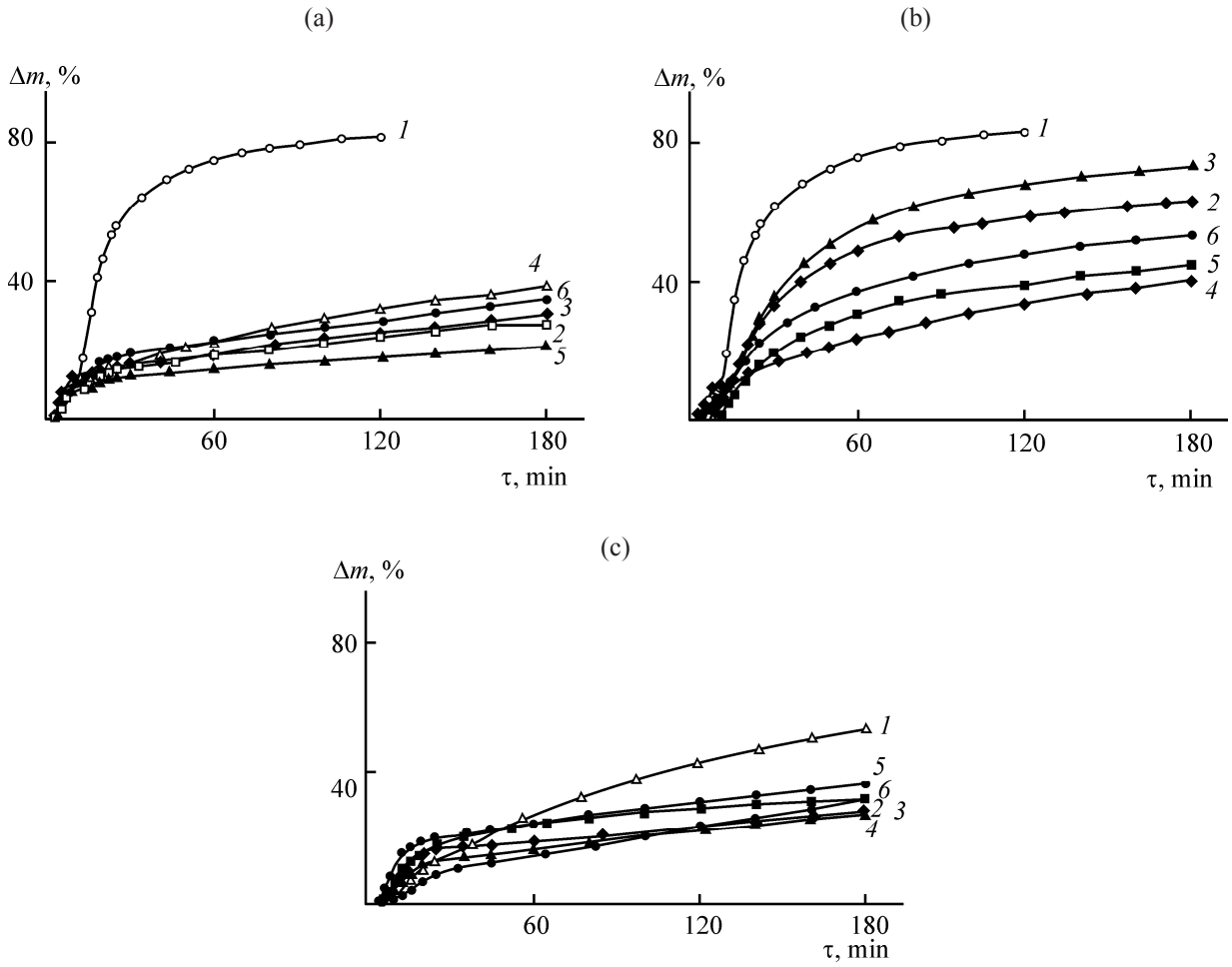


Fig. 1. Dependence of weight loss Δm on time τ at the thermal oxidative degradation of composites with TBOT additions. T = 302°C, $P(O_2)$ = 200 mm Hg. (a) PMMA mixture with TBOT; (b) composite obtained by joint MMA and TBOT polymerization; (c) MMA–MAA copolymer (15%) with TBOT. TBOT content (wt %): (*1*) 0, (*2*) 0.5, (*3*) 1.0, (*4*) 5.0, (*5*) 10.0, and (*6*) 20.0.

composites obtained by joint polymerization were held several hours in vacuum at 60–80°C.

To obtain organic-inorganic mixtures, a PMMA solution in methylene chloride was mixed with tetrabuthoxytitanium. From thus prepared solutions we obtained transparent films and dried them in a vacuum drying cabinet at 60–80°C. The width of films was about 100 μm. We failed to prepare mixtures from MMA–MAA copolymer owing to TBOT hydrolysis in the course of mixing with the copolymer.

The rate of the thermal-oxidative degradation at a constant temperature (302°C) was determined from the sample weight loss on a thermogravimetric installation with a McBain balance under an oxygen pressure of 200 mm Hg.

The thermogravimetry of samples was studied in a dynamic mode in air flow on a Perkin-Elmer Pyris 6 TGA device at a heating rate of 5 deg min^{-1} in the temperature range 40–490°C.

Volatile products of the decomposition of composites were analyzed on a POLARIS Q/TRACE GC ULTRA chromato-mass-spectrometer, using a TR 35 MS capillary column of length 60 m and diameter 0.25 mm.

The effect of TBOT additions on the thermal properties of the composites was studied by the TG method in the isothermal mode in the oxygen atmosphere. Compared to the initial polymer without additions, an essential decrease was observed in the degradation degree of the compositions obtained by

Results of the thermogravimetric analysis in an air flow

Sample	TBOT amount, wt %	Temperature of the weight loss maximum, °C	Weight loss rate, % min^{-1}	Weight loss, %
Mixture of PMMA with TBOT	0.0	331	5.3	98.6
	0.5	366	6.3	98.1
	1.0	372	7.0	97.3
	5.0	390	5.7	97.7
	10.0	386	5.5	95.3
	20.0	382	5.5	94.1
Polymer[a] of PMMA with TBOT	0.0	331	5.3	98.6
	0.5	320	6.8	98.0
	1.0	330	5.7	95.7
	5.0	361	6.9	97.2
	10.0	363	6.5	95.0
	20.0	350	4.9	88.2
Polymer[a] of MMA–MAA with TBOT	0.0	360	6.0	98.6
	0.5	393	6.9	95.3
	1.0	379	8.4	91.8
	5.0	397	7.6	88.2
	10.0	397	4.8	79.5
	20.0	383	4.2	77.3

[a] Joint polymer.

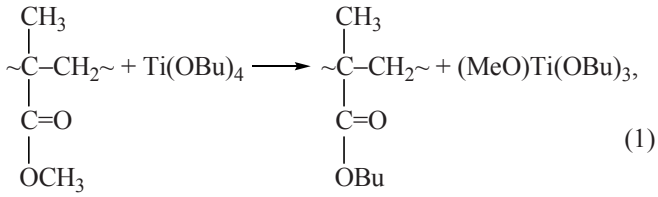
mixing TBOT with a PMMA solution (Fig. 1a) and by the joint polymerization of MMA (Fig. 1b) and MMA–MAA (Fig. 1c) with TBOT.

Especially strong deceleration of the weight loss occurs in the composites obtained by mixing TBOT with a PMMA solution (Fig. 1a). It is interesting to note that the decomposition rate only slightly depends on the TBOT amount in the composition, which was varied from 0.5 up to 20%.

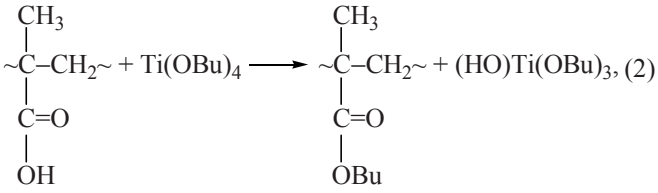
In the compositions obtained by MMA polymerization in the presence of TBOT (Fig. 1b) the thermal-oxidative degradation proceeds faster than in mixtures, but slower than in PMMA without additions.

In the case of thermal-oxidative degradation of TBOT composites with MMA–MAA (copolymerization) with a high TBOT concentration (Fig. 1c, curves *5* and *6*) in the beginning of the process a greater weight loss (up to 20%) with a higher rate is observed as compared to the copolymer without additions. Obviously, the reaction of TBOT with carboxyl groups of the copolymer with the evolution of great amounts of volatile products manifests itself in this case. In the following the decomposition rate decreases, and the weight loss occurs more slowly than in the copolymer without additions. It is known [6–8] that copolymers of MMA with MAA are much more resistant to the oxidative decomposition than PMMA.

The DTG study of the degradation of the composites has shown (see the table) that the main peak in the range 200–400°C corresponds to the depolymerization process initiated by the random bond breaking in macromolecules [10]. The maximal decay rate of PMMA compositions was observed at 360–380°C as unlike 320–330°C for the initial polymeric compound without additions. The maximum of the



(1)



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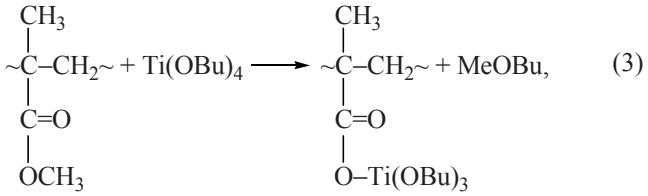

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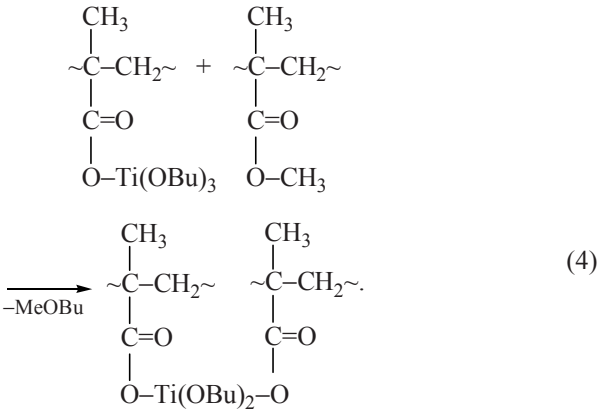

(4)

decay rate of the MMA–MAA copolymer compositions is at 380–400°C (364°C for the copolymer without TBOT, see the table).

Apparently, when the compositions are heated, tetrabuthoxytitanium reacts with ester and carboxy groups in macromolecules to form cross-linked structures analogous to those described earlier [10, 11].

Such structures interrupt the chain process of depolymerization of macromolecules and reduce the degree of the polymer weight loss in the thermal-oxidative degradation. It can explain the rise in the thermal stability of the studied compositions. As a result of the specified reactions methyl butyl ether and butyl methacrylate should be formed as the products of exchange reactions between the methoxy group of the methyl methacrylate unit and the TBOT buthoxy group.

In the present work, using chromato-mass-spectrometry, we studied the composition of liquid volatile products formed on heating the compositions up to 300°C in the oxygen atmosphere for 20 min and have detected butyl methacrylate and methyl butyl ether that confirms schemes (1)–(4).

As it was noted, films of PMMA–TBOT mixtures are more heat-resistant than the compositions obtained by the joint polymerization. Probably, the difference is caused by the fact that in the case of the polymerization in the TBOT presence the interaction of the components occurs already on heating the polymerized compositions to give butylmethacrylate entering in polymer chains and reducing their resistance to thermal oxidation.

CONCLUSIONS

(1) It was shown that the high-temperature thermal-oxidative degradation of composites of poly(methyl methacrylate) and the copolymer of methyl methacrylate-methacrle with tetrabutoxytitanium under isothermal conditions at 302°C proceeds more slowly than in the case of polymers without additions.

(2) The maximum of the decay rate is displaced to higher temperatures by 30–50°C.

(3) For composites of the copolymer methyl methacrylate-methacrylic acid the temperature of the maximal depolymerization rate increases from 360 to 380–400°C.

(4) At the thermal-oxidative degradation of organic-inorganic compositions of the studied polymers with tetrabuthoxytitanium methyl metacrylate, butyl metacrylate, and methyl butyl ether are evolved.

REFERENCES

1. Troitskii, B.B., Troitskaya, L.S., Yakhnov, A.S., et al., *Eur. Polym. J.*, 1997, vol. 33, nos. 10–12, p. 1587.
2. Troitskii, B.B., Troitskaya, L.S., Yakhnov, A.S., et al., *Dokl. Akad. Nauk*, 1998, vol. 363, no. 1, p. 79.
3. Troitskii, B.B., Troitskaya, L.S., Dmitriev, A.A., Yakhnov, A.S., et al., *Eur. Polym. J.*, 2000, vol. 36, no. 7, p. 1073.
4. Troitskii, B.B., Troitskaya, L.S., Yakhnov, A.S., et al., *Intern. J. Polym. Mater.*, 2000, vol. 46, nos. 1–2, p. 315.

5. Troitskii, B.B., Domrachev, G.A., Khokhlova, L.V., and Anikina, L.I., *Vysokomolekulyarnye Soed*. *A*, 2001, vol. 43, no. 9, p. 1540.

6. Troitskii, B.B., Domrachev, G.A., Semchikov, Yu.D., et al., *Vestn. Nizhegorod. Univ. im. N.I.Lobachevskogo. Khimiya*, 2001, no. 1 (3), p. 60.

7. Troitskii, B.B., Khokhlova, L.V., Konev A.N., et al., *Vysokomolekulyarnye Soed*. *A*, 2004, vol. 46, no. 9, p. 1.

8. Troitskii, B.B., Khokhlova, L.V., Konev A.N., et al., *Zh. Prikl. Khim*., 2004, vol. 77, no. 12, p. 2047.

9. Troitskii, B.B., Khokhlova, L.V., Denisova, V.N., et al., *Zh. Prikl. Khim*., 2007, vol. 80, no. 9, p. 1543.

10. Troitskii, B.B., Khokhlova, L.V., Denisova, V.N., et al., *Zh. Prikl. Khim.*, 2008, vol. 81, no. 7, p. 1171.

11. Markin, A.V., Yakimovich, N.O., Smirnova, L.A., and Smirnova, N.N., *Vysokomolekulyarnye Soed*. *B*, 2008, vol. 50, no. 5, p. 933.