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Effect of Fullerene C_{60} and Other Antioxidants on High-Temperature Oxidative Degradation of Poly(methyl methacrylate) and Methyl Methacrylate Copolymers with Methacrylic Acid

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Abstract — Fullerene C_{60} inhibits high-temperature oxitative degradation of poly(methyl methacrylate) and methyl methacrylate copolymers with methacrylic acid.

Methyl methacrylate copolymers with methacrylic acid are known [1] to be more thermally stable than poly(methyl methacrylate). It was shown in [1, 2] that thermal degradation of methyl methacrylate copolymers with methacrylic acid results in formation of six-membered anhydride rings in the macromolecules, which inhibit the depolymerization process.

We previously studied thermooxidative degradation of poly(methyl methacrylate) and methyl methacrylate copolymers containing 5, 10, and 15 mol % of methacrylic acid at 277°C [3]. The results showed that the rate of degradation of the copolymers, as compared to poly(methyl methacrylate), decreases with rise in the concentration of methacrylic acid units. After heating for 20 min, the IR spectra of samples of methyl methacrylate containing 15 mol % of methacrylic acid (weight loss 10%) lacked OH absorption (3100–3600 cm^{-1}), but bands assignable to six-membered anhydride ring appeared at 1800, 1750, and 1022 cm^{-1}. We anticipated that thermally stable six-membered anhydride rings formed in the copolymer macromolecules during thermolysis not only inhibit the depolymerization process [1, 2] but also catalyze decomposition of hydroperoxides (which are formed by oxidation of the polymer following the molecular mechanism involving no radical species), thus inhibiting the radical chain oxidation process.

We found in [3–7] that fullerenes C_{60} and C_{70} inhibit thermooxidative degradation of both poly(methyl methacrylate) and various methyl methacrylate copolymers and that the stabilizing effects of C_{60} and C_{70} are approximately similar. The inhibitory effect of fullerenes is explained by their reactions with macroradical species $R^{\cdot}$, $RO^{\cdot}$, and $RO_2^{\cdot}$, which give rise to thermally stable diamagnetic compounds.

Thermooxidative degradation of methyl methacrylate–methacrylic acid copolymers at 277°C in the presence of fullerene C_{60} [3] was characterized by very long induction period, and the rate of further degradation changed insignificantly. This made it difficult to determine the induction period for copolymers differing in the concentration of methacrylic acid. The dependence of the induction period on the fullerene concentration was not studied. Also, we thought it reasonable to examine the effect of commonly used antioxidants and their mixtures with fullerene C_{60} on thermooxidative degradation of the above copolymers.

In this work we studied thermooxidative degradation of poly(methyl methacrylate) and methyl methacrylate copolymers containing 15, 20, and 25 mol % of methacrylic acid at higher temperature, 304°C. The degradation rate was measured at various fullerene C_{60} concentrations. Some known antioxidants and their mixtures with C_{60} were tested as stabilizers for poly(methyl methacrylate) and methyl methacrylate–methacrylic acid copolymers. We have found that the conversion of poly(methyl methacrylate) at 304°C reaches 50% in 20 min (Fig. 1, *2*). In the presence of fullerene C_{60} (Fig. 1, *4*), after removal of volatile products and decomposition of unstable fragments of macromolecules (weight loss 7%), the sample weight remained constant over a period of 36 min; later on, the rate of weight loss increased, but it did not attain the value found for the degradation in the absence of fullerene C_{60}.

We previously showed [7] that commonly used antioxidants, such as sterically hindered amines and phenols and phosphorus- and sulfur-containing com-

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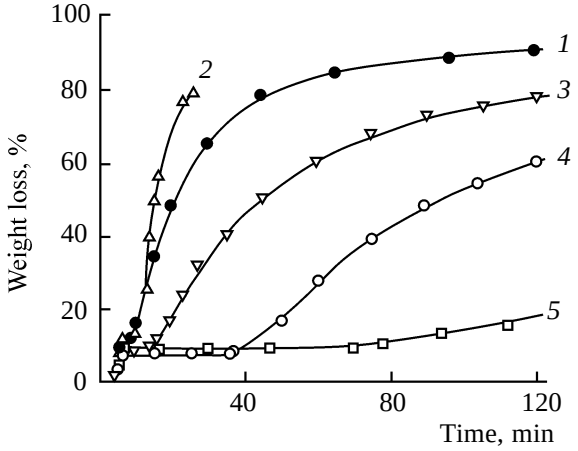

Fig. 1. Weight loss curves for thermooxidative degradation of poly(methyl methacrylate) (*1*) in the absence of additives and in the presence of (*2*) 9.7×10^{-3} mol/kg of 2,4,6-tri-*tert*-butylphenyl phosphite, (*3*) 20.2×10^{-3} mol/kg of triphenylantimony (**II**), (*4*) 9.2×10^{-3} mol/kg of fullerene C_{60}, and (*5*) 9.4×10^{-3} mol/kg of *N*,*N*'-di-β-naphthyl-*p*-phenylenediamine (**I**).

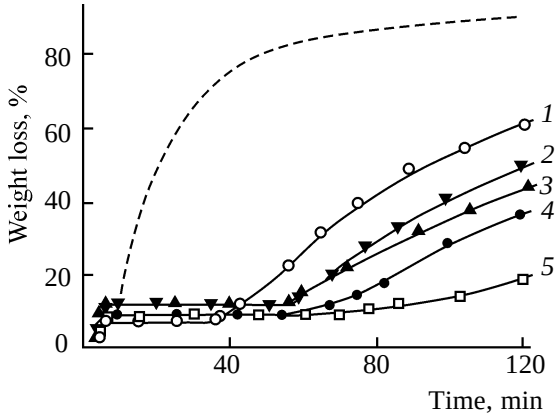

Fig. 2. Effect of fullerene C_{60} and *N*,*N*'-di-β-naphthyl-*p*-phenylenediamine (**I**) mixtures on thermooxidative degradation of poly(methyl methacrylate): (*1*) 9.2×10^{-3} mol/kg of fullerene C_{60}, (*2*) 2.0×10^{-3} mol/kg of **I** and 9.0×10^{-3} mol/kg of fullerene C_{60}, (*3*) 7.1×10^{-3} mol/kg of **I** and 4.7×10^{-3} mol/kg of fullerene C_{60}, (*4*) 9.4×10^{-3} mol/kg of **I** and 2.3×10^{-3} mol/kg of fullerene C_{60}, and (*5*) 12.0×10^{-3} mol/kg of **I**; dashed curve corresponds to degradation of poly(methyl methacrylate) in the absence of additives.

pounds, at about 300°C no longer inhibit thermooxidative degradation of poly(methyl methacrylate) and polystyrene. According to our present results, among numerous compounds belonging to various classes of antioxidants, only *N*,*N*'-di-β-naphthyl-*p*-phenylenediamine (**I**) effectively inhibits degradation of poly(methyl methacrylate) at 304°C (Fig. 1). Its mixtures with C_{60} (Fig. 2) exhibit no synergistic effect in this process.

The kinetic curves of weight loss for methyl methacrylate copolymers with 15, 20, and 25 mol % of methacrylic acid (Fig. 3, curves *1*–*3*) clearly show an induction period of 15 to 40 min. After the induction period, the degradation rate decreases in going to copolymers with a larger fraction of methacrylic acid. These data support the scheme proposed previously [3] for inhibition of thermooxidative degradation of methyl methacrylate–methacrylic acid copolymers via formation of six-membered anhydride rings in the macromolecules. The kinetic curves for degradation of the copolymers in the presence of fullerene C_{60} (Fig. 3, curves *1*'–*3*') are characterized by an iduction period of 55–60 min even at such a high temperature. The subsequent rate of weight loss is very small, 0.1–0.2%/min. As follows from the weight loss curves for methyl methacrylate–methacrylic acid copolymer containing 15 mol % of the latter, a C_{60} concentration of $(3–4)\times10^{-3}$ mol/kg is sufficient to achieve optimal results (Fig. 4a).

We also examined the effect of some antioxidants, namely, 2,4,6-tri-*tert*-butylphenyl phosphite (Fig. 4b, curve *1*), compound **I** (Fig. 4b, curve *2*), and triphenylantimony (Fig 4b, curve *3*) on thermooxidative degradation of methyl methacrylate–methacrylic acid (15 mol %) copolymer. All these compounds inhibit the degradation process but are inferior to fullerene C_{60} (Fig. 4b, *4*) in the stabilizing effect. A weak synergistic effect was observed for a mixture of triphenylantimony (**II**) with C_{60}. After the induction period (65–70 min), the rate of degradation in the presence of C_{60}–**II** mixtures (Fig. 4c, curves *3*, *4*) was slightly lower than in the presence of fullerene (Fig. 4c,

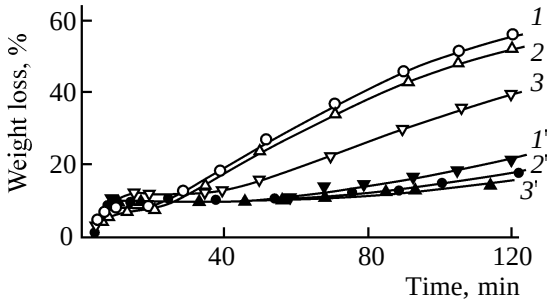

Fig. 3. Weight loss curves for thermooxidative degradation of methyl methacrylate–methacrylic acid copolymers containing (*1*, *1*') 15, (*2*, *2*') 20, and (*3*, *3*') 25 mol % of the latter (*1*–*3*) in the absence of additives and in the presence of (*1*') 9.2×10^{-3}, (*2*') 5.4×10^{-3}, and (*3*') 10.9×10^{-3} mol/kg of fullerene C_{60}.

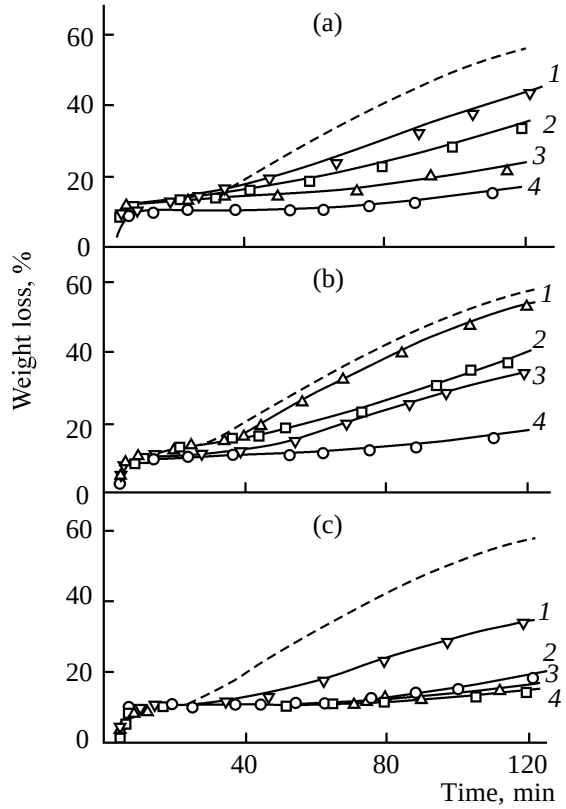

Fig. 4. Thermooxidative degradation of methyl methacrylate copolymer with 15 mol % of methacrylic acid (a) in the presence of fullerene C_{60}, mol/kg: (*1*) 0.4×10^{-3}, (*2*) 1.1×10^{-3}, (*3*) 2.2×10^{-3}, and (*4*) 4.3×10^{-3}; (b) in the presence of (*1*) 10.1×10^{-3} mol/kg of 2,4,6-tri-*tert*-butylphenyl phosphite, (*2*) 7.8×10^{-3} mol/kg of compound **I**, (*3*), 9.7×10^{-3} mol/kg of **II**, and (*4*) 4.3×10^{-3} mol/kg of fullerene C_{60}; (c) in the presence of fullerene C_{60} and compound **II**: (*1*) 9.7×10^{-3} mol/kg of **II**, (*2*) 4.3×10^{-3} mol/kg of fullerene C_{60}, (*3*) 3.8×10^{-3} mol/kg of fullerene-C_{60} and 5.8×10^{-3} mol/kg of **II**, and (*4*) 8.9×10^{-3} mol/kg of fullerene C_{60} and 2.1×10^{-3} mol/kg of **II**; dashed curves correspond to the degradation in the absence of additives.

curve *2*) or compound **II** (Fig. 4c, curve *1*) taken alone.

Thus, the thermooxidative degradation of poly(methyl methacrylate) at 304°C occurs at a very high rate. Addition of fullerene C_{60} inhibits the process. An induction period is observed, followed by much slower degradation than in the absence of C_{60}. This effect may be explained in terms of successive reactions of fullerene C_{60} with two macroradicals $R^{\cdot}$ and $RO^{\cdot}$ to afford diamagnetic molecules which are stable at the given temperature. The products are capable of taking up one more couple of macroradicals, thus inhibiting the degradation after the induction period. Among numerous known antioxidants, only diamine **I** was found to inhibit the thermooxidative degradation of poly(methyl methacrylate) more efficiently than does fullerene C_{60}. The latter is superior to the other examined antioxidants, including compound **I**, in the stabilizing effect on heat-resistant methyl methacrylate–methacrylic acid copolymers.

EXPERIMENTAL

Fullerene C_{60} was prepared and purified by the procedures reported previously [8, 9]. Its purity was no less than 99.9%. The monomers used were freed from inhibitors by known procedures and were distilled under reduced pressure. Their purity was checked by comparing their refractive indices with published data. Methyl methacrylate copolymers were obtained in a way similar to polymerization of methyl methacrylate described in [10]. Thermooxidative degradation of methyl methacrylate copolymers was studied by thermogravimetry at 304 ± 1°C; oxygen pressure 200 mm; film thickness ~100 μm.

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