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Investigation of fullerene C_{60} effect on properties of polymethylmethacrylate exposed to ionizing radiation

K.B. Zhogova [a,*], I.A. Davydov [a], V.T. Punin [a], B.B. Troitskii [b], G.A. Domvachiev [b]

[a] *Russian Federal Nuclear Center—All Russia Scientific Research Institute of Experimental Physics, Mur Street 37, 607190 Sarov, Russia*
[b] *Rasuvaev Institute of Organometallic Chemistry, Russian Academy of Science, Nizhny Novgorod, Russia*

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Abstract

Effect of fullerene C_{60} was investigated on thermal, mechanical and optical properties of polymethylmethacrylate (PMMA) under ionizing radiation. It was stated that fullerene C_{60} behaves as an effective antirad with respect to PMMA. Fullerene C_{60} addition raises temperature of destruction for polymer subjected to electron radiation by 20–25 °C, lowers the rate from 4 to 4.5 times and increases the activation barrier for radiated PMMA destruction reaction. Fullerene C_{60} addition promotes improvement of strength properties of PMMA: for films containing C_{60} addition and else subjected to electron radiation treatment a decrease in rupture strength is 10–15%, for samples containing no fullerene it equals ~25%. Interaction of free radicals with fullerene at radiation treatment influences optical characteristics of PMMA films.

Keywords: Polymethylmethacrylate; Fullerene C_{60}; Thermal, mechanical and optical properties

1. Introduction

Lately interest of researchers engaged in different fields of knowledge is seen to be focused on determination of the action of nanomaterial addition, such as fullerene and nanotubes, on properties of polymers and their compositions. Incorporation of fullerene and nanotubes into chemical composition of polymers gives one more opportunities for their study and application as composite materials (films, fibres) serving different purposes. For all that properties of the above polymers can be substantially changed (strength, thermostability, gas-penetrability, electrical conduction).

This paper presents results of the investigation of thermal, mechanical and optical properties of polymethylmethacrylate (PMMA) films containing fullerene C_{60} after their radiation treatment. As it was stated before, fullerene C_{60} and C_{70} are proven to be inhibitors for thermal and thermoxidative destruction of PMMA and polystyrene [1–5]. It was evidenced that fullerene C_{60} also retained the properties of an effective high-temperature antioxidant applicable to PMMA after some ionizing radiation treatment and was a stabilizer for the molecular mass of polymer [6].

* Corresponding author. Tel.: +7 8313097224; fax: +7 8313045569.
E-mail address: zhogova@online.ru (K.B. Zhogova).

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2. Experimental procedure

The initial samples, prepared by the method described in the work [2], were polymer films of ~100 μm thick, which contained different concentrations of fullerene C_{60}. Fullerene C_{60} with purity 99.9% was used. Polymethylmethacrylate with an average-toughness molecular mass of 4×10^5 was received by the method of free-radical polymerization of monomer in balk under the temperature of 80 °C. In order to introduce C_{60} into PMMA, their solutions were mixed in such proportions, which allowed to reach fullerene concentration 2.6×10^{-3}–9.0×10^{-3} mol/kg (mole of fullerene C_{60} per kg of polymer). Samples were received by melding of films from the pointed solutions.

Analogous investigations were carried out for PMMA stabilized with NPDA (di(naphthalene-2)-phenylenediamine-1,4 being one of the most effective antirads [7]) for the efficiency of fullerene C_{60} action on radiation stability of polymer to be determined. Radiation treatment of the initial samples was carried out with the use of a linear electron accelerator of LU-10-20 type [8].

The amplifier has got following parameters of generating radiation:

capacity of the electron radiation dose per $S = 0.01$ m^2: 2 Mrad/s;
capacity of the brake radiation dose at the distance of 0.5 m per $S = 0.03$ m^2: 200 rad/s;
nominal energy: 7–9 MeV.

Amplifier has got a system of beam reamer and a transporting line. Transporting line moves being treated object through the influence region perpendicularly to the line of reamer. The rate of movement must provide the admission of required dose of absorption.

The values of radiation absorption were from ~5 Mrad to 30 Mrad (electron energy $\leqslant$ 9 MeV). The doses of radiation absorption for every process of radiation treatment were followed with a standard film dosimeter. The statistical error was 15%, the confidence level was 0.95.

2.1. Investigation of thermostability of PMMA films under the action of radiation

Physical transformations in PMMA stabilized with fullerene C_{60} have been investigated at the temperature interval of 20–520 °C by the differential thermal analysis method and thermogravimetry using linear heating-up in the air medium at a rate of 10 deg/min. Changes in the temperature and mass as well as the thermal effects were registered simultaneously while heating the samples. The determination error for the thermal effect temperatures was ±5 °C, sensitivity for the thermogravimetry determination 0.2 mg, the mass determination error at the given sensitivity ±0.5%. Table 1 and Fig. 1 present results of the investigations.

Intensity of effects, temperatures for peak maximum values (T_m) and destruction temperatures (T_d) undergo considerable changes when fullerene C_{60} is incorporated into PMMA. Introduction of C_{60} involves an increase in the temperature for endopeak maximum values by 20–55 °C, in the temperature of the initial destruction by 20–40 °C and yields a 2-fold decrease in loss of mass at 350 °C (Δm) for nonradiated samples as well as 1.2-fold decrease for samples after their radiation treatment with dose 10 Mrad. Intensity of exothermic effects involves in its turn a 5–10-fold increase at adding C_{60}.

Activation energy for polymer thermal destruction was estimated by Novikov–Pilojan method [9]: for nonradiated samples it was ~11.4 and 14.9 kcal/mol; and for radiated ones it was 11.2 and 11.5 kcal/mol for cases when C_{60} was absent and in its presence, respectively.

Addition of fullerene to polymer influences the rate of destruction as well. According to recent findings [6] fullerene had shown a 4–4.5-fold decrease in the rate

Table 1
DTA- and TGA data for thermal destruction of PMMA films

	Samples										
	PMMA		PMMA + C_{60} (5.3×10^{-3} mol/kg)			PMMA + C_{60} (7.4×10^{-3} mol/kg)			PMMA + NPDA (8.2×10^{-3} mol/kg)		
Dose (Mrad)	0	10	0	5	10	0	5	10	0	5	10
T_m (°C)											
Endothermic effect	305	250	360	295	273	355	297	270	340	308	295
	365	365	385	380	375	385	380	370	388	380	385
Exothermic effect		287		330	315		325	310		335	330
	415	402	420	420	410	420	410	410	495	510	510
T_d (°C)	260	250	290	287	280	300	285	270	320	305	290
Δm (%)	67.8	72.5	32.2	48.1	56.8	33.8	47.1	58.3	24.6	35.5	48.2

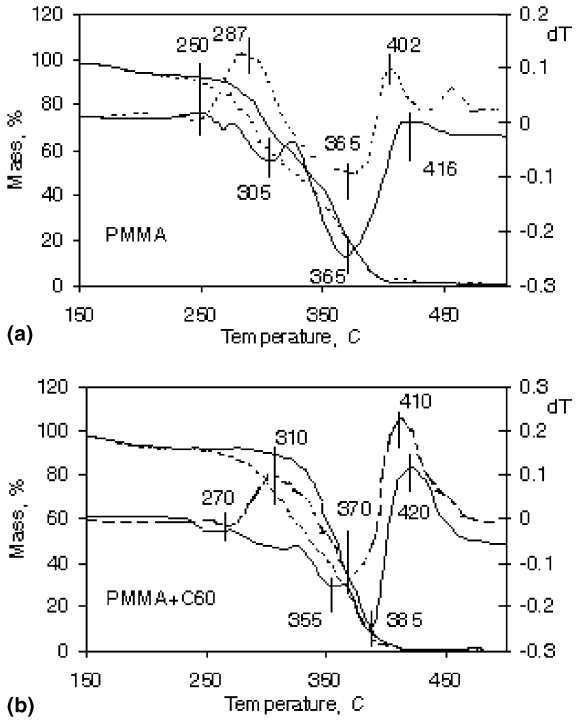

Fig. 1. Results of the investigations for thermoxidative destruction of PMMA films in the air medium: *solid line*—nonradiated samples; *dotted line*—samples after their radiation treatment with dose 10 Mrad; *numerical designation*—typical value of temperature.

of thermoxidative destruction for radiated PMMA samples under the action of ionizing radiation treatment.

2.2. Investigation of rupture strength of fullerene C_{60} stabilized PMMA films

Rupture strength of PMMA films before their electron radiation treatment and after it was investigated with the use of a strength testing machine of 2038P-0.05 model. The test temperature was 16 °C, the rate of motion of the machine-moving clamp was 5 mm/min. It was the effect of fullerene C_{60} on the level of PMMA breaking stress that was studied.

The results of the investigations show that nonradiated PMMA films containing fullerene C_{60} from 0 to 8.5×10^{-3} mol/kg do not suffer any considerable change in their rupture strength. As for the films with C_{60} addition subjected to electron radiation treatment (dose 5 and 10 Mrad), they had a decrease of 10–15% in their rupture strength. The decrease in the rupture strength for samples containing no fullerene was ~25%, opposed to the above-mentioned finding. Fig. 2 presents mean values and the confidence interval for rupture strength of the films considered.

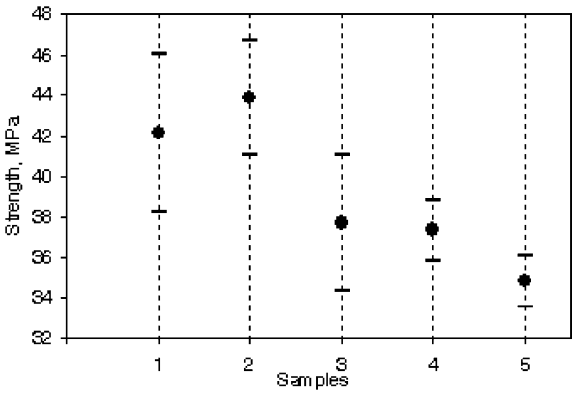

Fig. 2. Rupture strength of the examined PMMA films containing no addition agent 0 Mrad (1), 10 Mrad (5); PMMA containing C_{60} (8.5×10^{-3} mol/kg) 0 Mrad (2), 5 Mrad (3), 10 Mrad (4).

2.3. Investigation of optical properties of PMMA before the ionizing radiation treatment and after it

Optical characteristics of the films were measured in order to determine fullerene influence on the properties of polymer.

Transmission spectra for PMMA films in the wavelength range 190–3500 nm were obtained by UV-, visual and IR-spectrometry before they were exposed to electron radiation and after the treatment (dose 10 and 30 Mrad).

Irrespective of the addition agent, all the samples had background transmission from 85% to 90% for spectral range 1000–2500 nm, and one could observe actually the whole coincidence of the spectra in this range up to 3500 nm. Within UV- and visual range it was possible to notice significant difference in the spectra for the samples containing C_{60} as an addition agent, NPDA and C_{60} + NPDA. For the samples containing C_{60} in the range 200–400 nm one could observe band broadening for the $\pi \rightarrow \pi^*$ transition due to the formation of double bond group with different surroundings and chromophore chains consisting of coupled C=bonds as well as a sharp absorption band at 405 nm, which could be attributed to fullerene C_{60} not bound with polymer. The broadening for the samples subjected to radiation is so substantial that the shoulder of the above stated band reaches 700 nm, the latter evidence gives an explanation to the occurrence of dark-brown colour of the sample after its radiation treatment (Fig. 3). The absorption band at 405 nm in turn is absent. This fact speaks about the bond of free C_{60} and polymer with the further formation of fullerene-containing polymers.

The absorption band broadening for the samples containing NPDA as a filler is not so considerable. For the samples containing C_{60} or NPDA filler an increase in the exposure dose from 10 to 30 Mrad is

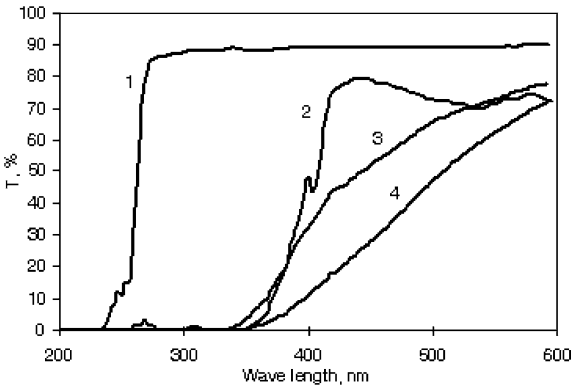

Fig. 3. Transmission spectra for PMMA samples in UV- and visual ranges: without an addition agent 0 Mrad (1); PMMA containing fullerene C_{60} (9×10^{-3} mol/kg) 0 Mrad (2), 10 Mrad (3), 30 Mrad (4).

accompanied by an increase in the absorbing ability. Contrary to the above finding, one could notice a decrease in the degree of transmission for the visual range under conditions of increased exposure dose for the samples containing both C_{60} and NPDA as an addition agent.

3. Discussion of the results

Being used in this work method of samples preparation, from our point of view, determines the character of C_{60} dispersion in the polymer matrix. Fullerene was introduced into PMMA in small concentrations in a way of mixing of polymer and fullerene solutions in one the same dissolver. Because of this in the received samples C_{60} can present, probably, in a molecular form. We hold microscopic investigations of the received polymer films and their X-ray analyses. The investigations by the method of atomic force microscopy with using of AFM model SOLVER P-47 of the firm NT-MDT showed, that there was no significant difference in the topography of PMMA films surface with fullerene presence and without it (Fig. 4).

Permission of having used electronic scanning microscope (~50 nm) did not allow us to fix the fullerene distribution in the polymeric matrix. X-ray analysis of the films did not determine the crystal lattice of fullerene C_{60}. Thus presence of clusters or crystallites of fullerene C_{60} in the polymeric matrix are not fixed. This fact approves the proposal concerning molecular character of fullerene dispersion in the investigated samples.

The results of the investigations of thermal and mechanical properties of polymer films as well as the data for changes of polymer molecular mass show improvement of the system stability owing to adding fullerene. The obtained results together with the data for changes in optical characteristics of the films allow one to bring to light the nature of fullerene C_{60} action on polymer properties. Inhibiting action of C_{60} on radiated and nonradiated PMMA films to all appearance comes mainly to formation of fullerene-containing polymers and inhibition of chain reactions of polymer decomposition in the process of radiation, heating and mechanical destruction.

This is approved by the data of spectrometric investigations, which showed that clear absorption band at 405 nm (Fig. 3), which we ought to ascribe to fullerene C_{60}, unconnected with the polymer, disappears with the increasing of the absorbed doze of radiation. After the irradiation one can see the formation of fullerene-containing polymers. This fact is approved by the following methods: methods of Size Exclusion Chromatography (SEC) [11,12] and EPR [13,14]. It is also shown that in the case of C_{60} presence during radical polymerization of polymers occurs active interaction between fullerenes and macroradicals.

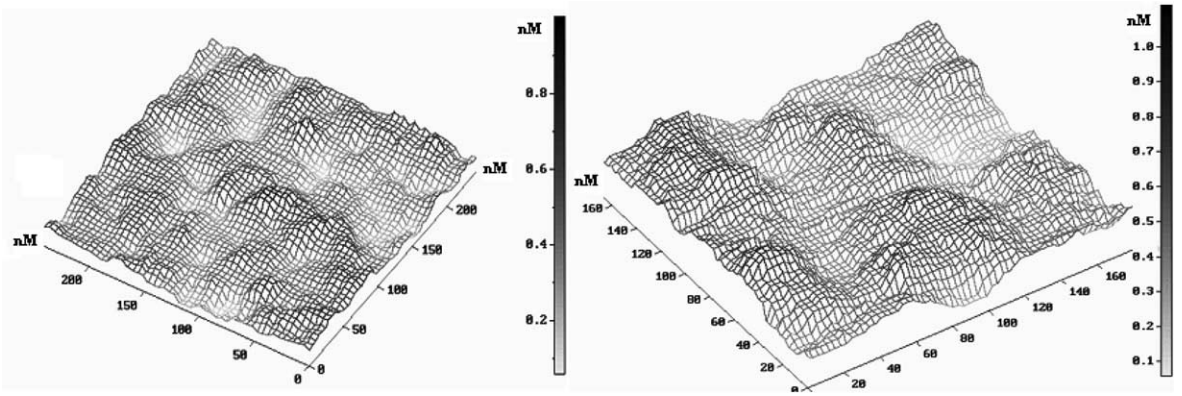

Fig. 4. Topography of PMMA films surface with fullerene presence and without it.

Investigation of the ultimate strength at the extension of PMMA films showed that under the influence of radiation pure PMMA films lost strength more than the samples containing C_{60} (Fig. 2). By present time the author's possibilities, concerning investigations of mechanical properties, are limited. They can only determine tensile strength of the samples. Investigations of the elastic-plastic properties of PMMA, modified by polymer C_{60} and subjected to influence of various factors, are in the field of our interest.

Numeral estimates show that concentration limit of C_{60} is sufficiently high to bind all the radicals formed both during thermodestruction and at mechanical loading. One cannot exclude potential action of fullerene addition agents (especially at high concentrations) both on the degree of crystallinity and on the form and size of polymer crystallites because C_{60} molecule possesses substantial Van-der-Waals volume in comparison to the volume of structure groups for majority of polymers. On the basis of the data of gravimetric analysis one can also assume an increase both in rupture strength and durability of PMMA when fullerene C_{60} is added. Because of some dependence between durability of material, mechanical stress and absolute temperature [10]:

$$\tau = \tau_0 e^{\frac{U_0 - \gamma\sigma}{kT}},$$

where τ_0—parameter concerning frequency of thermal vibrations of atoms; γ—structure sensitive parameter; σ—stress, kT—mean value of energy for thermal vibrations, U_0—initial potential or activation barrier governing a rate of solid polymer destruction. Numerous investigations revealed that the value of activation barrier U_0 obtained thanks to the study of durability is commensurable with the activation energy value for thermal destruction processes of polymer [8]. Hence increase of the activation barrier for PMMA destruction reactions ought to increase its durability.

Comparison of characteristics of PMMA films stabilized with fullerene C_{60} and NPDA reveals that efficiency of fullerene C_{60} addition competes with that of NPDA. Thus fullerene C_{60} is connected with PMMA not only as an effective antioxidant but also as an effective antirad.

4. Conclusion

1. Fullerene C_{60} behaves as an effective antirad with respect to PMMA.
2. Fullerene C_{60} addition raises temperature of destruction for polymer subjected to electron radiation by 20–25 °C, lowers the rate from 4 to 4.5 times and increases the activation barrier for radiated PMMA destruction reaction.
3. Fullerene C_{60} addition promotes stabilization of strength properties of PMMA: For films containing C_{60} addition and subjected to electron radiation treatment a decrease in rupture strength during extension is 10–15%, for samples containing no fullerene it is ~25%.
4. Fullerene C_{60} exerts influence on the optical characteristics of PMMA films when radiation processing. Meantime one can govern changes in the degree of transmission for PMMA under the action of ionizing radiation within visual range while using some other stabilizing fillers together with fullerene.

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