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Influence of irradiation with accelerated electrons on the physical properties of polyethylene terephthalate

© V.A. Sharapova[1], I.S. Kamantsev[2], V.P. Shveikin[2], V.Yu. Ivanov[1], O.V. Ryaboukhin[1]

[1] Ural Federal University, Yekaterinburg, Russia
[2] Institute of Engineering Science, Ural Branch, Russian Academy of Sciences, Yekaterinburg, Russia
E-mail: v.a.sharapova@urfu.ru

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The influence of irradiation with accelerated electrons (energy 8.5 MeV, dose 5 kGy) on the physical properties of medical devices made of polyethylene terephthalate (PET) was studied by infrared (IR) spectroscopy. The revealed post−irradiation changes in the IR spectra can be used to justify the choice of the dose of irradiation of PET products with electrons during the radiation sterilization procedure.

Keywords: polyethylene terephthalate, irradiation with accelerated electrons.

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Implementation of radiation technologies in production and post−irradiation processing of polymer and plastic products makes quite topical the investigation of processes taking place in these materials under irradiation [1]. Polyethylene terephthalate (PET) is the most widely used material belonging to the sector of polyester fibers. At present, PET packaging extensively drives out of business such conventional materials for pharmaceutical, medical and laboratory packaging as glass and cardboard. However, because of their low heat resistance, PET medical devices need the so-called „cold" sterilization methods. Nowadays there exist techniques for gentle „cold" sterilization of medical devices with low−temperature atmospheric plasma [2] that ensures the necessary bactericidal effect with retaining the required physical/chemical properties of the medical devices. The industrial procedure allowing sterilization of medical devices directly in tightly sealed packages consists in processing with accelerated electrons with energies below the nuclear reaction threshold (typically of up to 10 MeV). This method allows short-term processing of large numbers of products without unsealing the manufacturer's packages. State standard GOST ISO 11137-1−2011 regulating the procedure of radiation sterilization in the Russian Federation specifies the sterilization dose range as 15−25 kGy. The dose will be selected from the specified range based first of all on the condition of meeting the established requirements for sterility. On the other hand, the radiation sterilization procedure should not significantly deteriorate the product's consumer properties [3]. Thus, it seems topical to search for sensitive methods for estimating the post−irradiation modification of PET product physical/chemical properties.

As a research material, we used specimens of medical PET test tubes for blood sampling produced by JSC „Zdravmed Tech-E". Modification of the test tube properties was assessed by IR spectroscopy methods [4]. The samples were irradiated with accelerated electrons at the Radiation Sterilization Innovation Center of the Ural Federal University. The dose was 5 kGy at the electron energy of 8.5 MeV (Table 1). In this work, the task of specifying the lower sterilization dose threshold was not assigned. The main goal of the study was assessment of the IR spectroscopy sensitivity to detecting initial stages of modification of the physical/chemical properties of the irradiated materials.

It is known [5] that ionizing irradiation indeed results in modification of physical/chemical properties of materials. Paper [6] has also reported that electron irradiation 1 MGy in dose reduces the material strength by 15−30%. Since the vibration and optical spectra also depend on the substance chemical composition and structure, it was decided to analyze the variation in the IR radiation transmission through the test tubes [7].

IR spectra were measured at laboratory „Complex investigation and expert assessment of organic materials" of the Common Use Center of the Ural Federal University by using an infrared Fourier spectrometer Bruker Alpha in the frequency range of 4000 to 500 cm^{-1} (with resolution of 1 cm^{-1}) using an accessory for single horizontal total internal reflection (Eco-ART) with a ZnSe crystal (with the transparent band of 0.5−20 μm and refractive index of $n = 2.42$). Mathematical processing of the results was performed using the Fityk software [8].

IR spectroscopy provides information on the presence of certain functional groups, their number, structure of molecules forming the matter, and on the types of intermolecular bonds. In the scope of this study, IR spectra allow revealing the fact of the radiation influence on the PET structure and composition. Fig. 1 presents the spectra after normalizing by the integral intensity of the 1410 cm^{-1} band, namely, „internal standard" [9]. The normalization procedure was as follows: (i) subtraction of the sloped linear background plotted through the absorption minima in the vicinity of the 1410 cm^{-1} band; (ii) determination

Table 1. Data on test tubes used for sampling

Test tube index	Trademark	Volume, ml	Irradiation dose, kGy
I_0 I_5	K2EDTA	5	0 5
II_0 II_5	Silica	9	0 5
III_0 III_5	K3EDTA	2	0 5

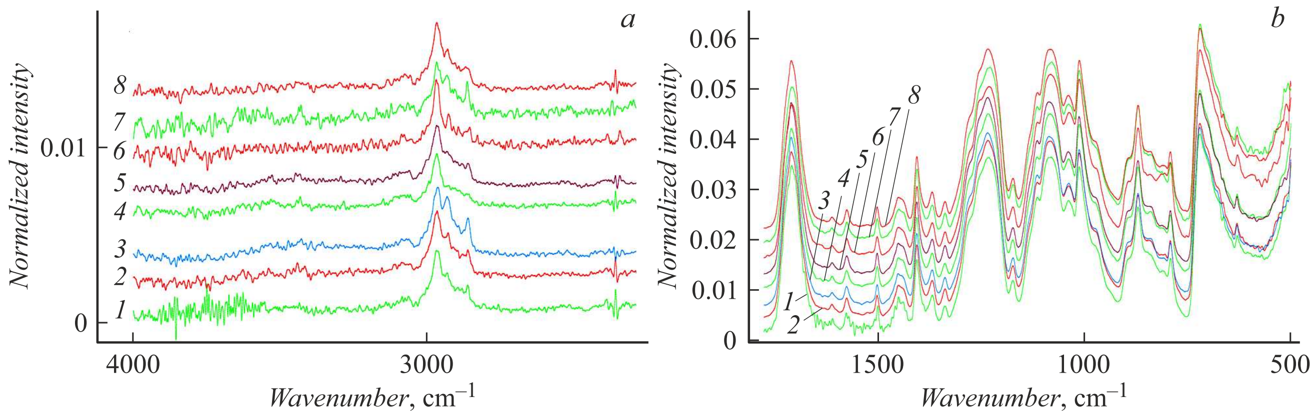

Figure 1. IR spectra of initial test tubes (*1* — I_0; *3*, *4* — II_0; *7* — III_0) and irradiated test tubes (*2* — I_5; *5*, *6* — II_5; *8* — III_5). Spectra *1*, *4*, *7* and *2*, *6*, *8* were obtained on intact test tubes, spectra *3* and *5* were measured on slides cut of the „Silica“ test tubes (Table 1). *a* spectral range of 4000–1800 cm^{-1}, *b* spectral range of 1800–500 cm^{-1}.

of area of the 1410 cm^{-1} absorption peak; (iii) calculation of the ratios between the maximal area and remaining ones; (iv) multiplication of each IR spectrum by the ratio obtained for this spectrum.

Table 2 presents relative intensities of the following bands: valence vibration of the C=O carbonyl group — 1712 cm^{-1}; etheric group — 1234 cm^{-1}; combination of methylene groups and etheric group C–O bonds — 1084 cm^{-1}; interaction of polar groups with benzene ring — 720 cm^{-1} [10]. First the spectra were measured on the side surface of intact test tubes (spectra *1*, *2*, *4*, *6*–*8*); then the measurements were performed on two stripes 40 mm long and 7 mm wide cut from test tubes „Silica“ (spectra *3*, *5*) (see Table 1).

Table 2 shows that relative intensities are independent of the radiation impact on the samples, however, there should be noticed a significant post–irradiation increase in parameters given in the columns for 1712, 1234, 1084 cm^{-1} (see the lines presenting the mean values). However, spectra *3* and *5* (given separately in Fig. 2) show that the range of valence vibrations of $C-H_2$ bonds changes after irradiation. The last evidences for a decrease in the number of $C-H_2$ bonds manifesting themselves at wavenumbers of 2854.6 and 2925.6 cm^{-1}.

In addition, Fig. 2 demonstrates a post–irradiation increase in intensities of absorption bands at 1712, 1234, 1084, and 720 cm^{-1}. As mentioned above, the spectrum processing comprised normalization by the integral intensity of the 1410 cm^{-1} absorption peak. If the assumption on destructive effect of irradiation on the test tube material is true (see the above mentioned decrease in the intensity of bonds $C-H_2$ absorption), then the enhancement of

Table 2. Relative intensities of the 1712, 1234, 1084, 720 cm^{-1} bands.

Spectrum No.	Test tube index	Wavenumber, cm^{-1}			
		1712	1234	1084	720
1	I_0	2.68	2.46	2.36	2.84
2	I_5	2.65	2.48	2.38	2.73
3	II_0	2.57	2.45	2.33	2.58
4	II_0	2.60	2.52	2.43	2.82
5	II_5	2.63	2.49	2.37	2.59
6	II_5	2.51	2.44	2.53	2.97
7	III_0	2.47	2.41	2.35	3.00
8	III_5	2.73	2.55	2.44	2.84
Mean values		2.60	2.48	2.40	2.80
Dispersions		0.007	0.002	0.004	0.024
Mean values for non-irradiated test tubes		2.58	2.46	2.37	2.81
Mean values for irradiated test tubes		2.63	2.49	2.43	2.78

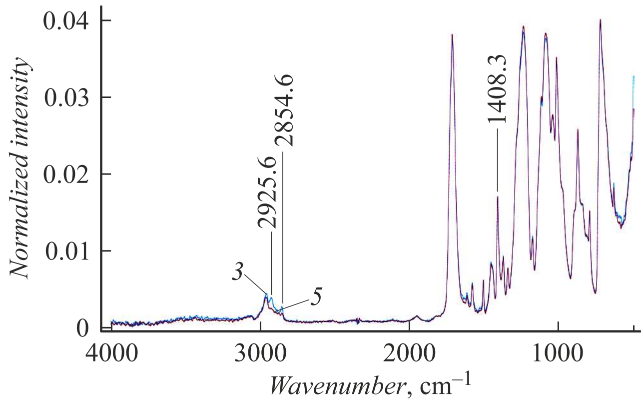

Figure 2. IR spectra *3* and *5*. The spectra are numbered in the same way as in Fig. 1.

absorption in the specified bands may be explained by the decrease in the internal standard area. An effort was also undertaken to normalize the spectra by the integral intensity of the entire spectrum in the 4000–500 cm^{-1} range. The result was similar to that when the absorption peak at 1410 cm^{-1} was used for normalization.

The results of this study show that irradiation of PET samples with accelerated electrons (8.5 MeV in energy, 5 kGy in dose) induces modification of IR spectra caused by a decrease in the number of C–H bonds due to the material dehydration. Thus, analysis of IR spectra of PET products may be used for express assessment of post–irradiation degradation of the medical device parameters and also for selecting the optimal sterilization dose.

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Conflict of interests

The authors declare that they have no conflict of interests.

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