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INFRARED SPECTROSCOPY FOR EVALUATING THE EFFECT OF ELECTRON BEAM STERILIZATION ON POLYETHYLENE TEREPHTHALATE MEDICAL TUBES

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The paper studies the effect of electron beam sterilization on the polyethylene terephthalate parts of blood sampling systems. The structural state and crystallinity degree of polyethylene terephthalate are estimated from the analysis of infrared spectra. Relative intensities are calculated by the reference band (overall intensity level) at 1410 cm^{-1}. The Gaussian intensities of the absorption bands for trans and gauche conformations with respect to reference band at 1505 cm^{-1} are calculated. The spectral coefficients D_{973}/D_{795}, D_{848}/D_{795}, D_{1042}/D_{795}, D_{895}/D_{795}, D_{1098}/D_{1370}, and D_{1255}/D_{1370} are determined. The dose of up to 25 kGy has no significant effect on either the ratio of integral intensities or the ratio of trans and gauche conformations.

Keywords: polymers, irradiation embrittlement, infrared (IR) spectroscopy

1. Introduction

It is known that medical blood collection systems contain parts made of polyethylene terephthalate (PET), and they are subject to sterilization. Ionizing radiation causes the formation of free radicals in the polymer. The evaluation of the degree of PET degradation in products during electron beam sterilization is of great interest.

PET can exist in both amorphous and crystalline states. PET in the amorphous state does not have the ordered structure of macromolecules; it is transparent and has a low degree of crystallinity (2.1–2.5%). PET macromolecules in the crystalline state form various ordered structures depending on temperature and crystallinity, namely spherulites, crystallites, lamellae, and meander structures [1, 2]. PET crystallinity increases after machining. However, the maximum degree of PET crystallinity is no more than 50–65% [3]. PET crystallinity and macromolecule orientation determine its mechanical properties. In this regard, the study of the structural features of PET under the action of electron beam sterilization is an important task.

The IR spectra of amorphous and crystalline PET are noticeably different, and this makes it possible to use this method to assess the structural state and changes of PET crystallinity.

It is known [4–6] that for the unit cell of PET, vibrations are possible due to both the phenylenecarbonyl and ethylene glycol bonds [7].

Rotation of the unit cell about the glycol bond causes the presence of two isomers of gauche and trans conformations. Unit cell transition to the trans conformation is a prerequisite for PET crystallization, while in the amorphous state, the macromolecules are in the gauche and trans conformations in dynamic equilibrium.

The absorption bands associated with a change in polyester chain configuration caused by CH_2 group vibrations, as well as with the presence of gauche and trans isomers and other possible absorption groups, are shown in Table 1 [2, 4–13].

Table 1

Absorption bands of IR spectra of PET [2, 4–13]

Wave number, cm^{-1}	The nature of vibrations	Conformation
848	Rocking vibrations of CH_2 in glycol	trans
895	Bending vibrations of CH_2 in glycol	gauche
962–975	Stretching vibrations of the C–O ester group	trans
1015	Plane bending vibrations of the C–H bond	gauche
1042	Bending vibrations of the C–O ester group	gauche
1255	Bending vibrations of the C–O ester group	trans
1340–1350	Wagging vibrations of CH_2	trans
1370–1375	Wagging vibrations of CH_2	gauche
1410	Ring in-plane vibrations	–
1460	Scissoring vibrations of CH_2	gauche
1470	Scissoring vibrations of CH_2	trans
1505	Ring in-plane vibrations	–
1712–1715	Bending vibrations of the C = O ester group	trans
1950	Vibrations of two adjacent aromatic H in p-substituted compounds and aromatic bands	–
2350	Axially symmetric deformation of CO_2	–
2853	Symmetric stretching of CH_2	–
2924	Asymmetric stretching of CH_2	–
2960	Asymmetric stretching of CH_3	–
3030–3150	Stretching vibration of CH	–
3150–3750	O–H group (hydroxyl)	–

The authors of [7] assessed the crystallinity of fine powders of recycled polyethylene terephthalate using IR spectroscopy. They revealed the structural features of fine PET powders with particle sizes from 5 to 70 μm, obtained from various PET polymer wastes (PET bottles, polyester fiber waste) by the solvent method. In this study, a similar approach is applied to PET products subjected to electron beam sterilization. It is of great interest to evaluate the possible degradation of PET using IR spectroscopy since e-beam irradiation may release free radicals, which can have a negative impact on the properties of both the PET test tube and the biomedical material stored in it.

2. Materials and Methods

Six series of six samples of PET test tubes for blood sampling served as the material for the study, with PET as the material of the cylindrical part of the tubes and polypropylene as the cap material. The samples were irradiated with accelerated electrons at the Innovation and Implementation Center for Radiation Sterilization affiliated to the Ural Federal University. The irradiation doses were 0, 5, 10, 15, 20, and 25 kGy at an electron energy of 8.5 MeV. The dose of 25 kGy is considered sufficient for sterilization by accelerated electrons according to the state standard [14].

The IR spectra were recorded from samples sized 10 × 10 mm on a Bruker Alpha IR Fourier spectrometer in the frequency range from 4000 to 500 cm^{-1} at a resolution of 1 cm^{-1}. A single horizontal external total internal reflection attachment (Eco-ART) with a ZnSe crystal (transparency range 0.5–20 μm, refractive index n = 2.42) was used. The results were mathematically processed by means of the Fityk software [15]. Two schemes for processing IR spectra were applied.

In order to assess the dependence of the IR spectra shape on the dose of electron beam sterilization in the first scheme, the integral intensities of the IR absorption bands in the wavenumber intervals 3030÷2830, 1772÷1662, 1330÷1185, 1110÷1050, and 750÷635 cm^{-1} were assigned to the integral intensity of the band in the range 1425÷1385 cm^{-1} [9, 16]. The obtained values are shown in Table 2.

According to the second scheme, the absorption bands 1490÷1425, 1425÷1350, 1350÷1330, 1330÷1160, 1160÷925, and 925÷760 cm^{-1} were selected. In each of them, the oblique linear background was subtracted from the levels of the minima surrounding the band. The obtained spectrum was automatically described in the Fityk program [17] using a certain number of Gaussian functions (Fig. 1). The number of functions was selected in such a way that the resulting curve coincided as closely as possible with the available IR spectrum of PET. The Gaussian intensities closest to the wavenumbers of interest were used to calculate the parameters given in Tables 3 and 4.

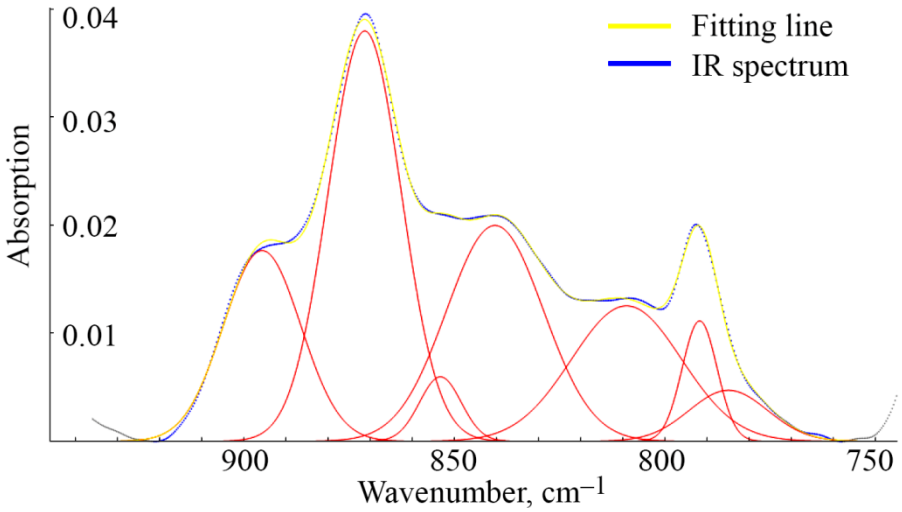

Fig. 1. An example of describing the IR spectrum of the resulting curve and the arrangement of Gaussians

Mechanical tests according to [18] in the form of uniaxial compression were carried out on 10 mm high samples cut from two test tubes: unsterilized and sterilized, with an irradiation dose of 25 kGy.

3. Results and discussion

From the analysis of the spectra normalized by the intensity of the 1410 cm^{-1} band (Fig. 2), we can make a preliminary conclusion that there are no significant changes in PET after exposure to radiation sterilization by accelerated electrons.

Table 2 shows the values of the relative intensities of the bands: stretching vibrations of the C–H bond group – 3000 cm^{-1}, the C=O carbonyl group – 1712 cm^{-1}, the ester group – 1234 cm^{-1}; the totality of methylene groups and C–O bonds of the ester group – 1084 cm^{-1}; interactions of polar groups with the benzene ring – 720 cm^{-1} [19].

Table 2

Relative intensities of IR absorption bands in the unsterilized test tube samples (spectrum I) and in the test tube samples after electron beam sterilization: 5 kGy (II); 10 kGy (III); 15 kGy (IV); 20 kGy (V); 25 kGy (VI)

Wavenumber interval, cm^{-1}	Spectrum number						Average value	Standard deviation
	I	II	III	IV	V	VI		
3030÷2830	1.8	1.3	1.7	1.7	1.7	2.1	1.7	0.3
1772÷1662	9.1	9.2	9.1	9.2	8.9	8.9	9.07	0.14
1330÷1185	14	14	13	15	14	14	14.0	0.6
1110÷1050	2.2	2.2	2.1	2.4	2.1	2.2	2.20	0.11
750÷635	11	11	12	13	11	12	11.7	0.8

The comparison of the IR spectra in the fingerprint region (1500–700 cm^{-1}) makes it possible to establish conformational transitions proceeding from changes in the shape and intensity of the bands typical of trans and gauche conformations.

To quantify these changes, it is proposed to use the band of conjugated C=C bonds of the aromatic ring at 1505 cm^{-1} as a reference band. We use the 1410 cm^{-1} band.

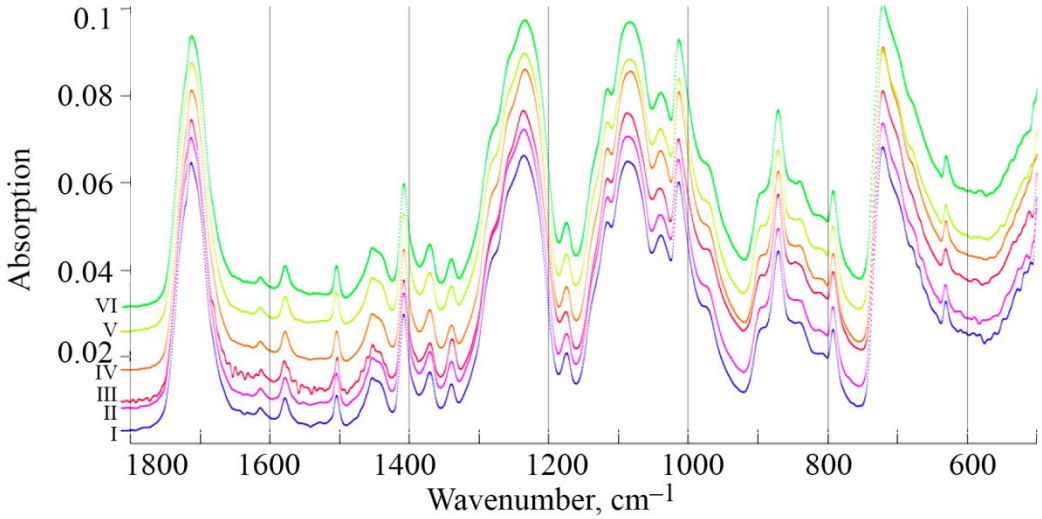

Fig. 2. IR absorption spectra of an unsterilized tube (spectrum I) and tubes after electron beam sterilization in a spectral region of 1800–500 cm^{-1}

The band at 1410 cm^{-1} related to the in-plane vibration of the benzene ring was mentioned in [20] in connection with its use as a reference band for the normalization of spectra. It is also sensitive to conformation [2, 21, 22]. However, the peak at 1505 cm^{-1}, also assigned to the in-plane ring vibration, behaves like a 1410 cm^{-1} band. Sometimes 1505 cm^{-1} is also used as a control band since its intensity is independent of the degree of crystallinity [23].

The relative intensities of the absorption bands typical of trans and gauche conformations were calculated for PET samples subjected to various doses of electron beam sterilization (Table 3). According to Table 3, both trans and gauche conformations are present in the PET samples. Electron beam sterilization in the PET tubes has no effect on the ratio of trans and gauche conformations in the samples at irradiation doses up to 25 kGy.

The authors of [24] attribute the increase in the intensity of trans-conformation vibrations in PET films to increased crystallinity. However, in the amorphous state, the trans and gauche conformations of PET exist in equilibrium, and it is impossible to evaluate the crystallinity of PET from changes in the vibration intensities of only trans conformations.

Table 3

Relative absorption band intensities (normalized to peak 1505 cm^{-1}) in the unsterilized test tube samples (spectrum I) and in the test tube samples after electron beam sterilization: 5 kGy (II); 10 kGy (III); 15 kGy (IV); 20 kGy (V); 25 kGy (VI)

D_x/D_{1505}	I	II	III	IV	V	VI
Relative absorption bands (trans conformation)						
848	2.25	1.95	1.81	2.37	2.08	2.27
975	2.76	2.63	2.53	3.25	2.90	3.01
1255	2.66	2.45	2.02	2.71	3.06	2.49
1348	0.75	0.75	0.99	0.70	0.70	0.72
1470	0.37	0.39	0.42	0.36	0.32	0.40
Relative absorption bands (gauche conformation)						
1015	1.93	1.89	2.35	2.16	1.75	1.94
1042	3.04	3.14	2.99	3.45	2.95	3.06
1375	1.02	0.89	0.72	1.01	0.90	0.95
1460	0.43	0.27	0.71	0.28	0.14	0.33

In this regard, as a criterion for assessing the change in the degree of crystallinity, it is proposed to use the ratio of the intensities of various absorption bands (trans conformations, 973 and 848 cm^{-1}; gauche conformations, 1042 and 895 cm^{-1}) with respect to the intensity of the 795 cm^{-1} absorption band, which changes only slightly upon transition from one conformation to the other [4, 5].

P. G. Schmidt [4] showed that the D_{973}/D_{795} ratio correlates well with X-ray phase analysis data and, in combination with density data, provides information on the ratio of PET trans conformations in the amorphous and crystalline phases. The ratio of the absorption bands at 1098 cm^{-1} (stretching vibrations of C–O–C) and 1255 cm^{-1} (bending vibrations of C–O–C), typical of PET trans conformation, to the absorption band of wagging vibrations of methylene groups at 1370–1375 cm^{-1} can also be used to evaluate crystallinity [25]. The ratios were calculated from the IR spectra of the PET samples (Table 4).

Table 4

Spectral coefficients showing the variation of PET crystallinity in the unsterilized test tube samples (spectrum I) and in the test tube samples after electron beam sterilization: 5 kGy (II); 10 kGy (III); 15 kGy (IV); 20 kGy (V); 25 kGy (VI)

D_x/D_{1505}	I	II	III	IV	V	VI	Average value	Standard deviation
D_{973}/D_{795}	1.92	1.88	2.21	2.08	1.98	1.99	2.01	0.12
D_{848}/D_{795}	1.57	1.39	1.58	1.51	1.42	1.50	1.50	0.08
D_{1042}/D_{795}	2.11	2.24	2.61	2.21	2.01	2.03	2.20	0.22
D_{895}/D_{795}	1.61	1.56	1.56	1.55	1.57	1.52	1.56	0.03
D_{1098}/D_{1370}	8.01	8.41	9.55	8.79	8.73	8.43	8.7	0.5
D_{1255}/D_{1370}	2.62	2.74	2.79	2.69	3.39	2.63	2.81	0.29

It follows from the data in the rows of Table 4 that the spectral coefficients are independent of the irradiation dose. The observed changes in the parameters can be caused by the heterogeneity of the material itself subjected to radiation sterilization or by errors introduced by the peculiarities of the sterilization process and measurement of spectra. It seems possible to assume that the parameters under consideration, which reflect the state of crystallinity of the material, remain unchanged after sterilization. However, further research will be required to verify this reliably.

The application of the band intensity ratio correlates with the results of testing the mechanical properties. The results in Fig. 3 demonstrate the absence of a critical difference in the ability of the sample to take up load depending on the use of radiation sterilization. The ratio of the compressive force of the unsterilized sample to that of the sterilized sample at 25 kGy stabilizes after passing through a deformational displacement of 0.5 mm and does not exceed 5%.

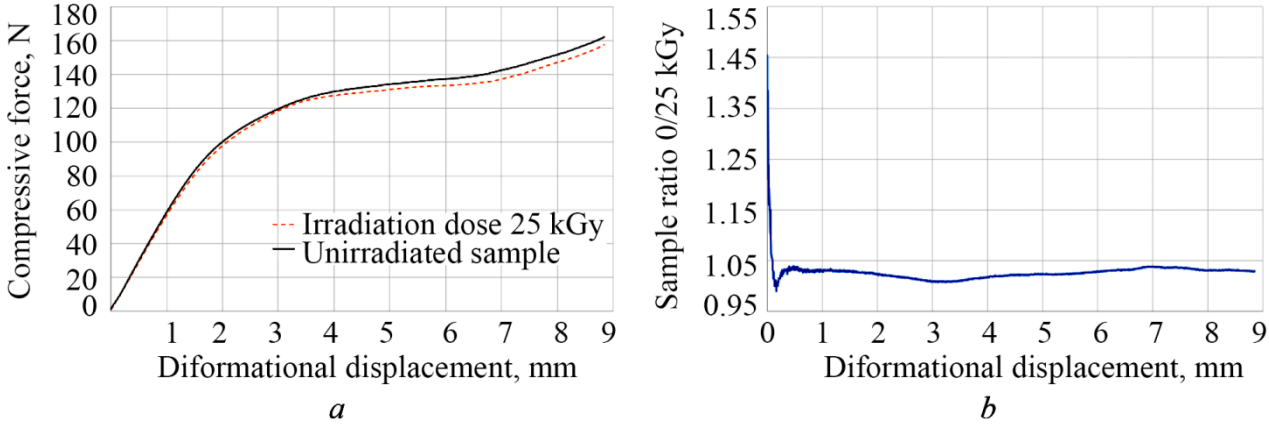

Fig. 3. Compressive force as dependent on the displacement of the walking beam of the testing machine (*a*); variation of the ratio of the compressive force for the unsterilized samples to that for the samples sterilized at 25 kGy (*b*)

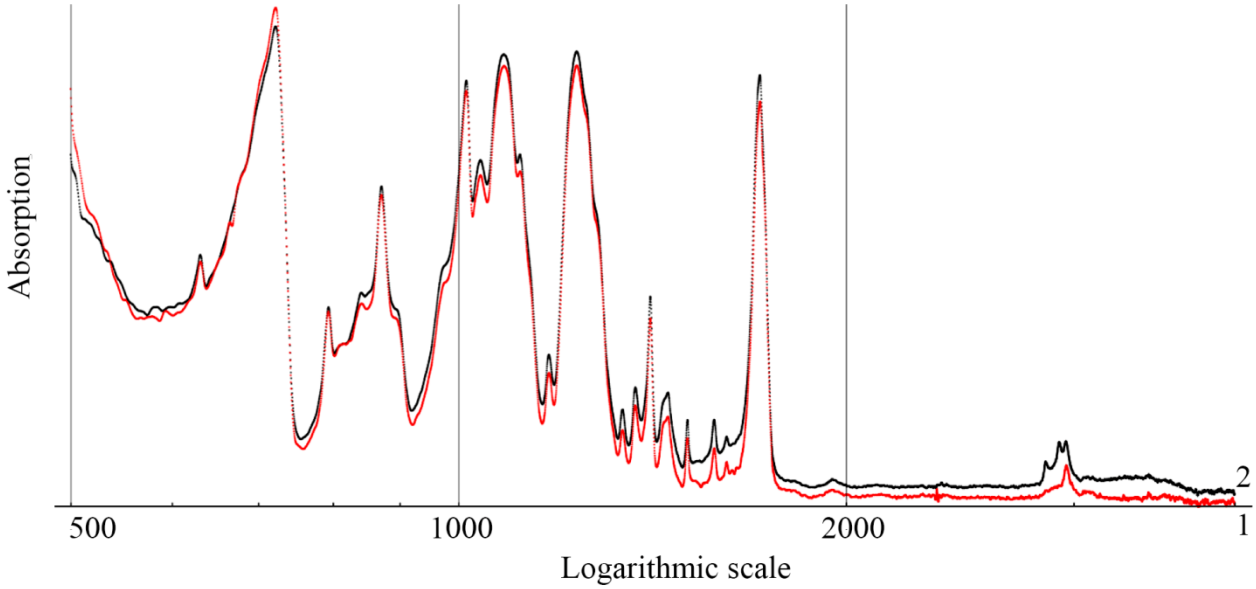

Fig. 4. Infrared spectra of initial PET (1) and after irradiation with 25 kGy (2), normalized to the absorption band at 1410 cm^{-1} and shifted along the vertical axis

It follows from the analysis of the average values (Table 2) and Fig. 4 that there is a tendency towards an increase in the relative intensity of the IR absorption bands with frequencies of 3750–3100, 3030–2820, 1712, and 1084 cm^{-1}. This result may indicate a possible increase in the number

of O–H, C–H bond groups, C=O carbonyl groups, and the combination of methylene groups and C–O bonds of the ester group. Thus, it can be concluded that the molecular chains of the PET near-surface layer are destroyed [26]. However, the point scatter of single values over the entire set of samples raises doubts on the significance of these processes. In addition, mechanical compression testing of a test tube sample before sterilization and after 25 kGy irradiation shows no cracks on the surface of the product. For further analysis of the risk of free radical release, it is planned to use the method of electron paramagnetic resonance.

4. Conclusion

The IR spectroscopic study of the structural features of PET blood collection tubes under electron beam sterilization has revealed that an irradiation dose of up to 25 kGy does not affect either the ratio of the crystalline and amorphous phases in PET or the ratio of the integrated intensities of the considered IR absorption bands.

According to the results of flattening tests, radiation sterilization with accelerated electrons in doses up to 25 kGy does not significantly impair the mechanical properties of the tube material.

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