Sterilization Influence on PET Track Membrane Properties

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Abstract. Polyethylene terephthalate (PET) track membrane (TM) has a great opportunity to use as a bio implant in ophthalmology's surgery due to its physical and chemical properties and biological comparability. Sterilization of medical implants can change its properties and can influence on regeneration process and success of surgical treatment. We researched influence on the PET track membrane of two sterilization methods wide used in medicine. The first sterilization method was steam sterilization. The second method was γ-irradiation of Co^{60} radionuclide sterilization. The sterilization processes influence on the track membrane properties was assessed by surface topography analysis, IR Fourier spectroscopy, wetting angle and surface energy of TM surface measurement.

INTRODUCTION

Polyethylene terephthalate (PET) is a thermoplastic of polyesters class wide used in different scientific and industrial areas: electronic, food industry, chemical and truck-mounted industry, cryogenic technique and medicine [1-6].

PET track membranes (TM) have a great opportunity to use in ophthalmology like corneal implant for bullous keratopathy due to the porous structure and its bio compatibility [3].

All medical implants need sterilize before operation. The polymer implants can be sterilized using only dry-heat sterilization, steam (moist heat) sterilization, ethylene oxide sterilization, low-temperature hydrogen peroxide with plasma, ozone sterilization and radiation sterilization.

The most acceptable methods sterilization for polyethylene terephthalate [7] are radiation, ethylene oxide, steam and dry-heat sterilization. There are wide spread sterilization methods like steam (moist heat) sterilization and γ-irradiation in Russian medicine practice.

The steam sterilization and γ-irradiation [8] can change physical and chemical properties of polymer implant causing could affect its functionality, toxicity and safety. The aim of this research is the study of sterilization influence on PET track membrane properties.

RESEARCH METHODS

Oriented PET films were irradiated with argon ion beam at the maximum ion energy of 41 MeV in a specially designed vacuum chamber with a tape drive to create track membranes. Ions passing through the film create an area of a high ionization density, the ion track. Selective alkaline etching of the material in the track resulted in the formation of a pore system with cylindrical through holes having a typical symmetric structure in the initial film. Before etching, the film was irradiated with ultraviolet light for additional sensitization. Etching was carried out in a 1.5 N Na. Researched samples were track membranes with a 7 µm of thickness, 0.5 µm of pore's diameter, 5×10^8 pores/sm^2 of pore density (Fig. 1).

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Pore density and pore's diameter were evaluated with Hitachi TM–1000 electron microscope. The surface topography analysis was researched using Centaur HR atomic force microscopy. The membrane thickness was measured by electronic thickness gauge Tesa Unit correct to ± 0.1 microns.

Wetting angle measurement and surface energy were performed by KRÜSS Easy Drop DSA 20 at room temperature 25 ± 2 °C. For wetting angle measurement we used deionized water and glycerol. On the each samples we dealt with four drops of 3 ml. The wetting angle and surface energy dynamics were analysed 1, 3, 7, 14, 21 days after sterilization.

The sterilization was carried out in two ways. The first: steam sterilization (temperature = 120 °C, pressure = 0.11 MPa). The second: γ-irradiation of Co^{60} radionuclide with 1 kGy dose using «Researcher» special devices for γ-irradiation of Tomsk Research Institute of Semiconductors.

The chemical analysis of track membrane after steam and γ-irradiation sterilization was carried out using Nicolet 5700 Fourier IR spectrometer.

RESULTS AND DISCUSSIONS

It can be seen from Fig. 1 that pores are rather uniformly distributed over the membrane surface. Calculations performed on the basis of the SEM data show that the average pore size is 0.5 μm and the surface density of pores is 5×10^8 pores/cm^2. The cross section of the membrane element is presented in Fig. 1b, from which the pores can be seen to have a cylindrical shape.

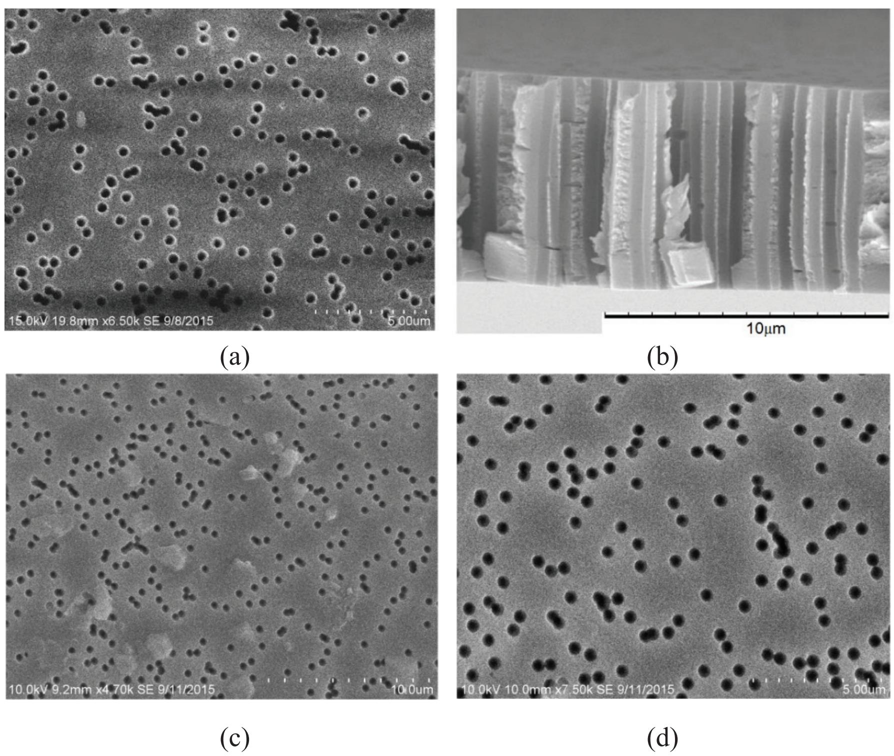

FIGURE 1. SEM image surface of the PET TM, pore's diameter 0.4 μm:
a) virgin; b) spalling; c) sream sterilisation; d) γ-irradiation.

A better idea of the surface structure can be obtained by atomic force spectroscopy (AFS), which is a highly informative technique that is widely used for collecting data on surface topography. Figure 2 shows 3D images of the membrane surface topography before and after sterilization.

The table 1 illustrates results of surface roughness, wetting angle and surface energy measurement.

The Figure 3 illustrates the results of texture changes and peak count in the horizontal section, which is formed on the sample center.

The results show that sterilization has a different effect on the surface topography PET track membrane. The TM surface before sterilization is smooth (Ra = 0.23 μm) but there is local ups and downs with peaks high of 0.5 μm. Obtained peaks are the result of mechanical action on the material during the preparation of the starting membrane film.

TABLE 1. Surface properties of the PET TM before and after sterilization

Sample	Ra (μm)	Rms (μm)	Wetting angle (θ°)	Surface energy (mJ/m^2)		
				dispersing	polarizing	full
Virgin 0.4 μm pore's diameter	0.23	0.49	72.6	5.97	23.98	29.95
Steam sterilization 120°C	0.39	0.72	81.4	1.7	29.78	41.48
Sterilization γ-irradiation 1 kGy	0.26	0.45	68.7	0.3	43.43	43.73

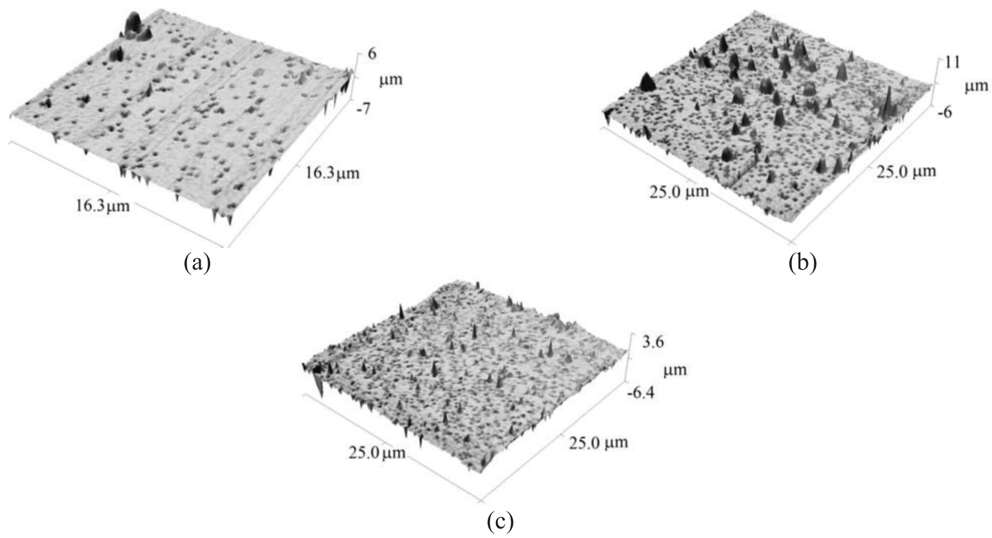

FIGURE 2. AFM 3D-images of the PET TM: a) virgin PET TM, b) PET TM after steam sterilization, c) PET TM after γ-irradiation.

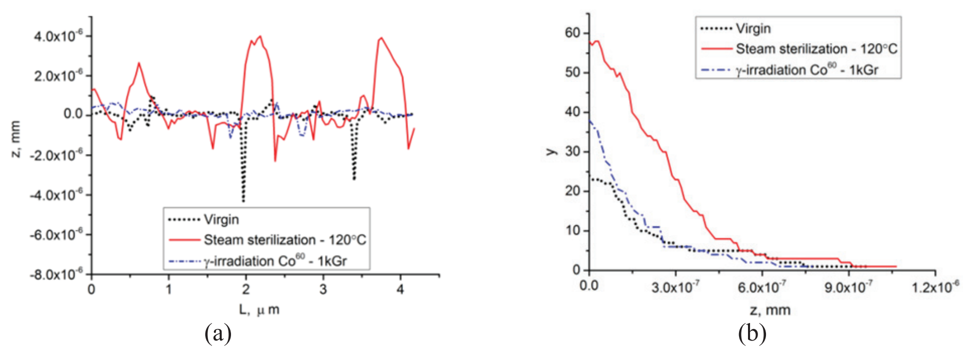

FIGURE 3. Surface texture (a) and peak count (b) of the PET TM before and after sterilization.

As a result of steam sterilization at 120 ° C for 20 minutes domed peaks of up to 0.6 μm height form on the TM surface. The surface roughness increase to 0.39 μm (Ra parameter) due to TM texture changes and surface peak counters increases (table 1, figure 3a). The wetting angle increases to 8.8° which is a negative effect for the ophthalmology's implants. The full surface energy decreases twice.

The γ-irradiation sterilization has a less significant effect on TM texture compared with steam sterilization. The surface roughness and TM texture measurements have similar values in comparison with the virgin. Measured peaks number (fig. 3b) increases slightly on the surface. The wetting angle values after γ-irradiation decrease to 4.1°. The full energy values increase to 13.68 mJ/m^2.

The figure 4 illustrates IR spectrum of the PET TM before and after sterilization. The graphic shows the main for TM absorption peak.

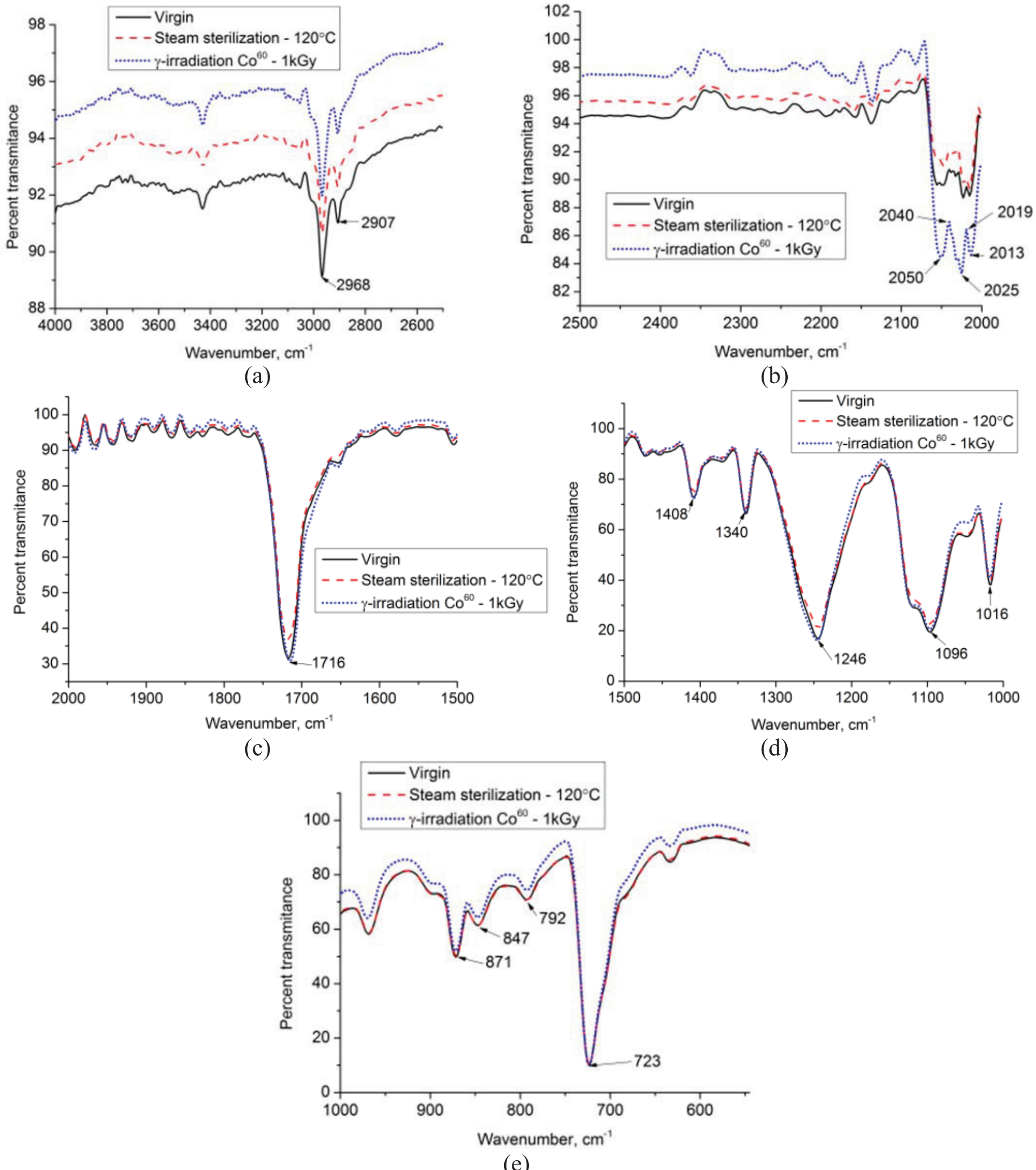

FIGURE 4. IR spectrum of the PET TM before and after sterilization. Wavenumbers are 4000-2500 cm $^{-1}$ (a), 2500-2000 cm $^{-1}$ (b), 2000-1500 cm $^{-1}$ (c), 1500-1000 cm $^{-1}$ (d), 1000-500 cm $^{-1}$ (e)

The table 2 shows the results of the accessory definition to the characteristic absorption peak groups and references.

The greatest interest are the 723, 1246, 1716 absorption peaks and 2000-2070 peaks group (tabl. 2). The 723 peak of methylene CH_2 rocking band is useful as four or more CH_2 groups are required in a chain to produce a distinct [9, 10]. Therefore all samples have adding CH_2 groups. 1246 peak and 1716 peak evidence of impact on the bond C = O, leading to delocalization and its transition to the C = C bond. Fluctuations in 2000-2070 according to [10] include atmospheric carbon dioxide (CO_2), which leads to the generation of a pseudo signal in this area.

The wetting contact angle and surface free energy are important characteristics of the surface properties of a material. The figure 5 illustrates the graphic of contact angle changes during 21 days after steam sterilization and γ-irradiation Co^{60} sterilization. It can be seen from Fig. 5 that sterilization of a TM by ^{60}Co γ radiation only insignificantly affects the wetting angle of the original TM, and the storage of the samples for 22 days does not bring any noticeable changes in the contact angle either. The contact angle changes after sterilization are insignificant which indicates the long-term stability properties of the sterilized sample.

TABLE 2. FTIR spectra of the PET TM

Wavenumber (cm^{-1})	Suggested bond configuration (Absorbing group)	Reference
723	Methylene CH_2 rocking band.	[9] p.72 and [10] p.75
792	γ(C=O)+δ(COO)	[11] p.4
847	γ(CH_2)	[11] p.4
871	Phenyl γ(CH)	[12]
1016	H vibration attached to phenyl ring-δ(CH)	[12]
1096	Aliphatic ethers C-O-C	[13]
1246	C=C stretch of phenyl ring	[12]
1340	C–C Alkane, $=CH_2$	[12]
1408	C–C deviation	[12]
1716	Aliphatic ketones C=O stretch [4] or C=C band	[12] or [9] p.76-77
from 2000 to 2070	Triple Bonds and Cumulated Double Bonds area	[10] p.126
2907	Aliphatic Groups C–H stretching vibrations	[10] p.125
2968	Symmetric C–H stretching occurs at 2960 cm^{-1}	[9] p.72

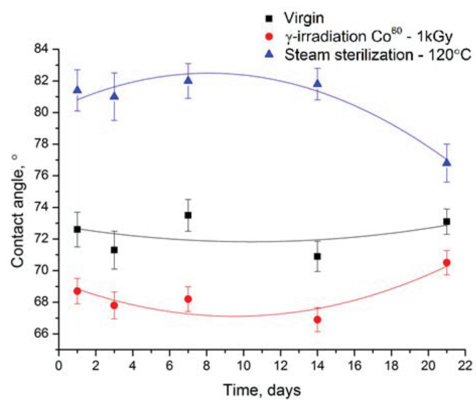

FIGURE 5. Contact angle of the PET TM before and after sterilization.

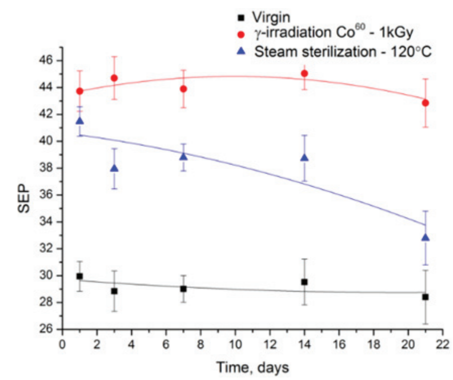

FIGURE 6. Full surface energy of the PET TM before and after sterilization procedure.

The figure 6 illustrates the graphic of full surface energy changes during 21 days after steam sterilization and γ-irradiation Co^{60} sterilization. γ irradiation with a dose of 1 kGy slightly increases the surface energy σ_s. Therefore, the surface energy of a PET track membrane is of a pre dominantly polar type, which is related to a decrease in the number of nonpolar groups and an increase in the number of polar groups on the TM surface.

The surface energy of PET TM remains unchanged during 21 days after γ-irradiation sterilization. The surface energy of PET TM increases after steam sterilisation (fig. 6).

Sterilization of TM samples by ^{60}Co γ radiation results in an insignificant decrease in the intensity of the 1716 cm^{-1} absorption band in IR optical-absorption spectra (Fig. 4). This result points to a decrease in the number of polar functional groups and, as a consequence, a certain reduction in the wettability of the surface. Effects of hard UV radiation from a λ = 172 nm eximer lamp on PET films (growth of the surface energy, dissociation of chemical bonds) [14] are similar to the effect from γ irradiation observed in this work.

CONCLUSION

Therefore we studied two ways of sterilization (steam sterilization and γ-irradiation of Co^{60}) influence on the polyethylene terephthalate track membranes.

1. The positive effects of γ-irradiation is increasing of hydrophilic surface properties and unchanged its during 21 days.
2. Sterilization doesn't change a chemical composition of track membrane polymer chain.
3. Both sterilization methods lead to a change of surface topography. The degree of influence on the relief membrane surface is less after γ-irradiation sterilization than steam sterilization.
4. Thus, the γ-irradiation sterilization is preferred over steam sterilization in an autoclave.

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