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PHYSICO-CHEMICAL PRINCIPLES OF MATERIALS DEVELOPMENT

Influence of Low-Temperature Plasma and γ Radiation on the Surface Properties of PET Track Membranes

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Abstract—Physical and chemical properties of the surfaces of polyethylene-terephthalate (PET) track membranes (TMs) exposed to low-temperature atmospheric plasma and to γ radiation produced by ^{60}Co isotopes are studied. It is established that the exposure to plasma leads to changes in the chemical composition of the surface and increases the number of polar (carbonyl and carboxyl) functional groups in a thin near-surface layer of a TM. The surface energy is also shown to grow owing to its polar component and surface reconstruction. The reconstruction consists in the growth of surface roughness owing to oxidation-reduction reactions, followed by the appearance of destructive areas. These changes promote a lyophilic behavior of the track-membrane surface. Subsequent γ irradiation of the surface is shown to reduce the plasma-modified TM undulation, while decreasing the number of destructive areas and bringing the material into a more equilibrium state.

Keywords: track membrane, polyethylene terephthalate, sterilization, contact angle, low-temperature atmospheric plasma

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INTRODUCTION

Polyethylene terephthalate (PET) is one of the most widely used polymers. The surface properties of PET such as wetting ability do not always meet the requirements because of a low surface energy (~32 mJ/m^2). This is especially important when PET is used for biomedical implants.

Exposure to low-temperature plasma is one of the most promising and up-to-date methods for modifying the surfaces of polymer materials; it makes it possible to vary the properties of polymer surface in rather broad ranges [2]. In addition, exposure to plasma has an antibacterial effect [3]. It is advantageous to use plasma, as it changes the properties of the material only in a thin near-surface layer of the membrane owing to low penetration depths of active plasma particles. The bulk properties of the material stay unchanged [4]; this is crucial from the viewpoint of retaining the mechanical and physicochemical properties of the implant.

A number of articles that are devoted to studying the effect of low-temperature plasma on polymers, including membranes, have recently appeared [5–8].

Golovyatinskij [9] studied the effect of pulsed atmospheric-pressure plasma on morphological and chemical properties of a number of polymer materials: polyoxymethylene copolymer, polycarbonate, polypropylene, low-density polyethylene, PET, polystyrene, and silastic. He showed that interaction of the surface with nitrogen or nitrogenated plasmas leads to the formation of nitrogen-bearing imide and urethane groups in a near-surface layer of the polymer; this improves the biocompatibility of the polymer owing to its enhanced wettability and adhesion to organic substances. Akishev et al. [10] studied the influence that low-temperature atmospheric-pressure plasma has on the surface properties of polypropylene and polyterephthalate films. Provotorova et al. [11] researched the effect of plasma on the properties of unsaturated rubbers. The data in [10, 11] indicate a significant hydrophilization of the polymer surface that persists for a long time (120 days). According to these works, the hydrophilization of the surface of a material after exposure to plasma is associated with changes in the chemical structure of the material and formation of a surplus surface charge on the surface itself and in a near-surface layer.

A lot of attention has recently been paid to using cold atmospheric-pressure plasma for these purposes. Such plasma is most effectively generated by a barrier discharge. In this case, no costly vacuum apparatus is required; this makes the treatment of the implant surface much cheaper. A drawback of barrier-discharge techniques is that a barrier discharge is inhomogeneous; this may damage the material if energy release at the locations of inhomogeneities is high. However, there are methods that make it possible to produce plasma with a highly homogeneous discharge. Cold

plasma allows one to measure the surface properties of materials without any significant heat load. Low-temperature atmospheric plasma is a source of active substances such as radicals, excited and charged particles, and photons. Therefore, one can expect the plasma to produce a sterilizing effect.

A sterilization procedure is mandatory for medical-purpose products in addition to plasma treatment. There are different sterilizing techniques, the exposure to ionizing radiation (γ radiation, in particular) being the most common. When exposed to γ radiation, the material may suffer radiation damage that entails changes in its surface and bulk properties.

All the research that has been carried out on ionizing-radiation treatment of materials can be divided into how irradiation affects the properties of films and how it affects membranes. Most works are devoted to studying the effect that irradiation has on the properties of films and PET, in particular [12]. Dae Hoon Jeon et al. [13] provided data on the effect that ^{60}Co γ irradiation has on the physical and chemical properties of PETs in a range of 0–200 kGy. They suggested a mechanism of how irradiation changes the structure of polymer chains. The mechanism involves intermolecular bonding with the subsequent formation of diglycol members in PET molecules. Undoubtedly, there is a difference between films and track membranes (TMs). Unlike in films, the material of a membrane gets subjected to significant preliminary treatments (irradiation with ions, UV irradiation with the goal to sensibilize the process of chemical etching of tracks, chemical etching itself) when being manufactured. In this connection, there appears the possibility for a synergetic effect of γ sterilization on TM characteristics.

Issues that are related to the radiation resistance of PET track membranes have been under scrutiny ever since the membranes were invented. Buczkowski et al. [14] studied the effect of electron irradiation with integral doses in a range of 30–990 kGy on the physical and chemical properties of PET track membranes. The ultimate tensile strength was shown to drop by approximately 30% for membranes that had been irradiated by a dose of 990 kGy.

Problems of sensibilizing and modifying the surfaces of PETs are also widely discussed today [15]. The effects of plasma of different composition and irradiation with Ar ions with energies of 0.2–1.4 keV on the PET surface properties were studied in [16–18] and in [19], respectively. Plasma and a beam of Ar ions affect PET properties in a similar way, increasing the wetting ability and decreasing the wetting contact angle. The chemical composition of the surface also undergoes changes. The number of hydrophobic groups (C–O, C=O) on the surface decreases and the number of hydrophilic groups increases; the surface free energy increases; the undulation develops catastrophically; and the parameter R_a grows almost tenfold from 5.8 to 49.7 nm.

X-ray photoelectron spectroscopy data that are presented in [20] indicate that atmospheric plasma acts on the PET surface in a complex way. First, the number of C=C and C=O groups decreases. Second, the number of benzene groups decreases as a result of exposure to helium (He) plasma, which indicates a possible rupture of PET chains along the bonds of "hanging" aromatic hydrocarbons. And, finally, on the other hand, amine (C–N), carbonyl (C=N), and anhydride (O=C–O–C=O) hydrophilic functional groups as well as carbon–silicon (C–Si) complexes are formed on the surface under the action of plasma. Similar results are reported in [21, 22]. Plasma exposure results in the growth of surface energy, the wetting ability of PET surface, and undulation. Such effects are also typical of high-frequency and microwave discharges [21]. Aflori and Drobota [22] subjected PET to the action of a combined plasma (10% of nitrogen and 90% of helium) and UV. Effects typical of plasma action were observed; namely, the C–C/C–N bonds present in the polymer were broken and filled with oxygen and nitrogen from the atmosphere. As a result, C–C/C–H (1), C–O (2) and/or C–N, O=C–O (3), and/or N–CO–N groups were formed on the polymer surface. In addition, N–C=O groups were present too. The surface energy with a predominant polar component grows, and the wetting ability of the surface increases. Novak et al. [23] carried out a comparative study of how different plasmas, with the working gas being oxygen O_2 or nitrogen N_2, affect the properties of PET surface. IR spectroscopy was the main analytical tool. Exposure to plasma leads to changes in IR optical-absorption spectra; a widening of the band at 1710 nm that is due to stretching C=O vibrations is observed regardless of the plasma type.

Therefore, analysis of the literature proves that exposure to plasma is highly effective for altering the surface properties of PETs.

It should be noted that there are no data available on the surface properties of PET track membranes that were plasma-treated or sequentially subjected to low-temperature plasma and γ irradiation in sterilizing doses.

The goal of this work was to study how low-temperature atmospheric plasma affects the surface properties of a PET track membrane and find out how these properties further change after the membrane is exposed to ^{60}Co γ radiation in sterilizing doses of 1 and 10 kGy.

MATERIALS AND METHODS

PET track membranes were obtained by bombarding a polymer film with $^{40}Ar^{+8}$ ions with a maximum energy of 41 MeV and then etching the film chemically. Selective alkaline etching of the material in the area of a track allows one to produce a porous system of through cylindrical holes with a characteristic symmetrical structure in the original film. Prior to etch-

ing, the film was treated with ultraviolet for extra sensibilization. An aqueous NaOH solution with a concentration of 1.5 N was used for etching at temperatures in the range of 72–82°C.

TM surfaces were modified using a low-temperature atmospheric-plasma experimental installation at the Tomsk Polytechnic University. A barrier discharge was generated using a specially designed source of cold plasma. The dielectric was a 1-mm-thick glass. The voltage was 25 kV, and the frequency was 5 kHz. The power density was 2 W/cm^2. The temperature of a surface that was subjected to plasma did not exceed 40°C. The airflow rate was 1 L/min. The distance between the electrodes was 0.5 mm. The samples were preliminarily cleansed with alcohol in order to remove contamination.

The surface topography was studied with a Centaur HR complex correlator of optical, spectral, and topographical properties of surfaces of objects. The surface roughness was estimated using Gwyddion software from simple-mean and absolute values of profile departures (R_a).

The dimensions and surface density of pores in a track membrane were determined by scanning electron microscopy from membrane images that were obtained with a Hitachi S3400N Type II electron microscope. A AuGd film with a thickness of approximately 200 nm was sputtered on the sample surface for contrast enhancement.

Static ^{60}Co γ radiation was used for membrane sterilization. Irradiation was performed at an Issledovatel' installation that has a cylindrical working chamber. The dose rate inhomogeneity (dose field inhomogeneity) did not exceed 10% within the certified volume of the working chamber with a diameter of 150 mm and a height of 240 mm. The dose field was validated with respect to silicon by using a set of thermoluminescent dosimeters. The level of γ-radiation exposure was adjusted by varying the irradiation time and characterized by the exposure dose expressed in Gy (Si). Two γ-radiation exposure levels of 1 kGy (Si) and 10 kGy (Si) were used in this work. These levels correspond to the lower and upper limits of the range of doses that are commonly used for sterilization with ionizing radiation. In a series of experiments, irradiation was performed both before and after plasma treatment; this made it possible to assess the combined (time-separated) effect of these treatments on the changes in the properties of the main characteristics of the membranes.

The wetting angles of deionized water (θ_w°) and glycerine (θ_g°) were measured to an accuracy of ±0.1° by the sessile-drop method at the room temperature of 25 ± 2°C by means of a KRUSS Easy Drop DSA 20 device and dedicated software. Four drops of water, each with a volume of 3 μL, were put on a sample. Every measurement was carried out over a period of less than 5 min after the drop deposition. The wetting contact angle was measured on days 1, 3, 7, 14, and 21 after plasma treatment and (by the same schedule) γ sterilization of the modified samples.

Surface free energy is one of the characteristics of the surface properties of a material. The total surface energy (σ_s) was considered within the Owens–Wendt model [24] as a superposition of dispersion (σ_s^p) and polar (σ_s^d) components that were calculated by means of the Owens–Wendt–Rabel–Kaeble (OWRK) method:

$$\frac{\sigma_l(\cos\theta+1)}{2\sqrt{\sigma_l^d}} = \frac{\sqrt{\sigma_l^p}}{\sqrt{\sigma_l^d}}\sqrt{\sigma_s^p} + \sqrt{\sigma_s^d}, \quad (1)$$

where σ_l is the surface free energy and σ_l^p and σ_l^d are the polarization and dispersion components, respectively.

The OWRK method allows one to accurately estimate the value of the surface free energy of polymer materials [25]. Samples were stored in air after plasma treatment and put in special sterilization bags after γ irradiation.

The IR spectra of original, modified, and sterilized membranes were measured with a Nicolet 5700 IR Fourier spectrometer.

RESULTS AND DISCUSSION

Figure 1 shows a typical SEM image of an element on the membrane surface.

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.

No noticeable traces of the effect of plasma treatment or γ irradiation on the morphology of the TM surface were discovered on the SEM surface images (Fig. 1).

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. Figures 2 and 3 show 3D images of the membrane surface topography after plasma treatment and γ irradiation. It can be seen from the topographic images of the TM surface in Fig. 2a that the surface is fairly plane with pores and large irregularly shaped relief fragments that vary in size and are probably polymer globules. The effect of low-temperature atmospheric plasma leads to significant changes in the surface morphology (Figs. 2b–2d). Destructive areas start to appear on the TM surface and manifest themselves as numerous small irregularities that are chaotically distributed over the surface

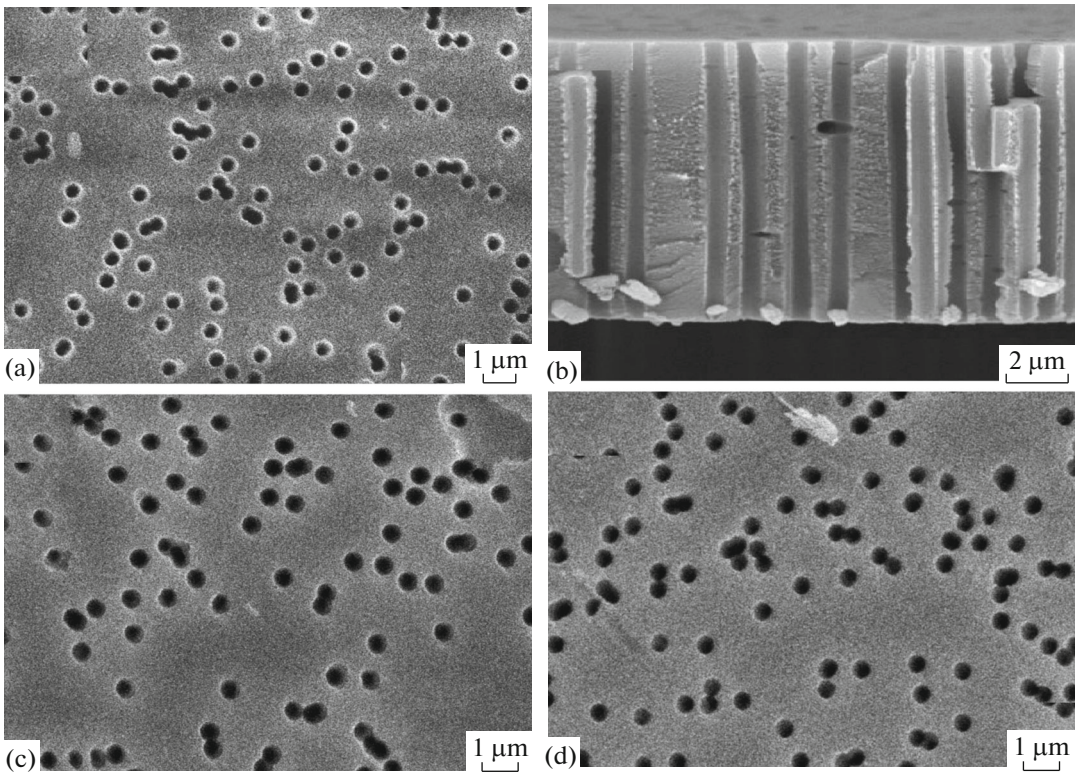

Fig. 1. SEM images of a TM: (a) the original sample; (b) the cross section of a membrane with through pores; (c) the sample after gamma sterilization; (d) the sample after exposure to plasma for 30 s.

and have a conical shape with a height of more than 100 nm. When the surface is exposed to plasma for 30 s, the density of these formations is as high as 2.43 peaks/μm^2, with the roughness increasing by approximately 15 times (see Fig. 4, curve *1*). The subsequent γ irradiation of the TM surface treated with plasma hardly changes the surface topography; however, extra large crateriform defects appear with a depth on the order of 4.25 μm and an average diameter of 0.5 μm (Fig. 3). Therefore, sterilizing doses of γ radiation lead to the appearance of surface-destruction elements, but the density of these flaws is small and reaches only 4×10^{-3} μm^2. The density of large crateriform defects grows as the plasma treatment time increases from 30 to 90 s.

Data on the values of surface roughness and on the effect of γ sterilization and plasma treatment are compiled in the table.

The results of measurements of the roughness parameter R_a vs. the duration of plasma treatment and subsequent γ irradiation are shown in Fig. 4. First of all, it should be noted that γ irradiation of the original TM samples has no significant effect on the roughness parameter of the TM surface (see table). As for plasma treatment, the data in Fig. 4 (curve *1*) show that it leads to a substantial (15 times) growth of the simple mean value of the R_a parameter for nonsterilized samples. Subsequent γ irradiation with the sterilizing doses of 1 and 10 kGy (Fig. 4, curves *2* and *3*) sharply decreases the surface roughness parameter R_a of the TM samples pretreated with plasma.

The wetting contact angle and surface free energy are important characteristics of the surface properties of a material. It is known that the wetting of a solid surface can be regulated with surfactants. In this article, we study the possibility and efficiency of influencing the wetting ability and surface free energy of TM samples by plasma treatment.

Measurements of the wetting contact angle showed that the initial surface of a PET track membrane has low wetting ability, with the average contact angle being $\theta = 72.0°$. Treatment with low-temperature atmospheric plasma leads to a sharp increase in the wetting ability of the surface; the interfacial angle decreases by 40°–43° (56%), with the average value becoming $\theta = 29°$.

The dynamics of the interfacial angle versus the storage time at room temperatures shows (Fig. 5) a noticeable (~77%) increase in the contact angle over the first three days of storage. The contact angle undergoes virtually no changes (Fig. 5) during further storage; i.e., the wetting ability of the surface is preserved.

The results of studying the effect of plasma treatment and γ irradiation on the wetting ability of TMs are shown in Fig. 6. It can be seen from Fig. 6 (curve *1*)

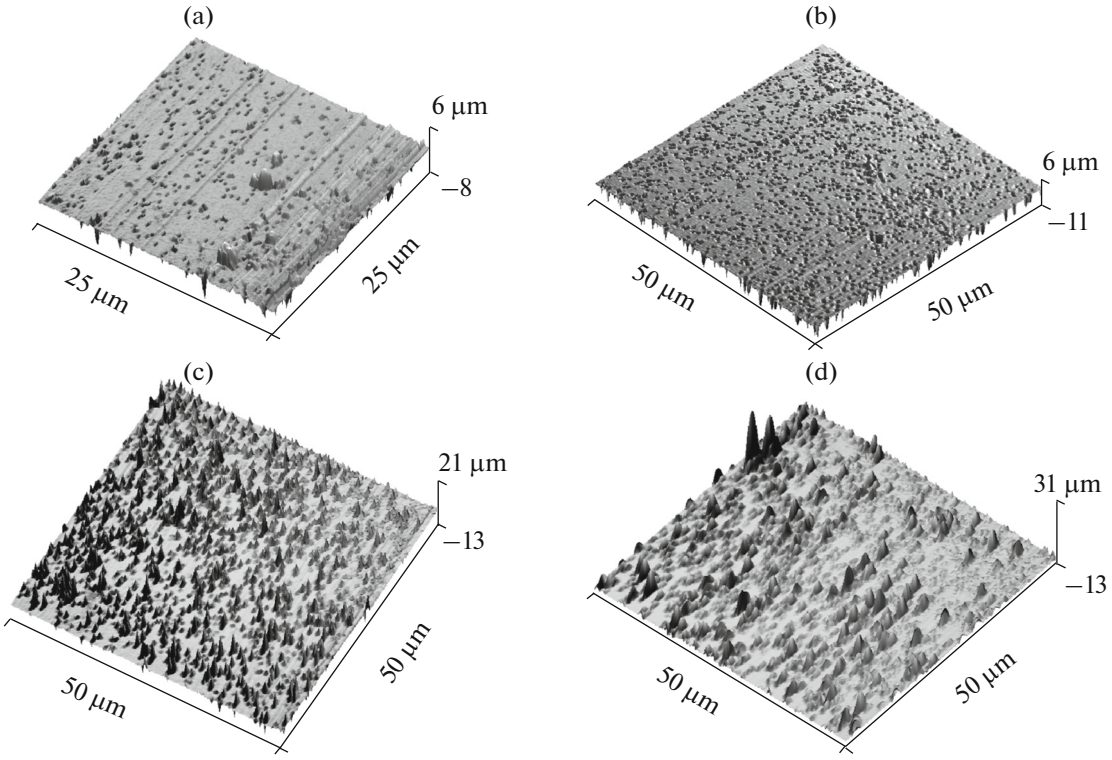

Fig. 2. Topography of the surface of original (a) and plasma-modified TMs with exposure times of 30 s (b), 60 s (c), and 90 s (d).

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 (Fig. 6, curve *1*) either. Sterilizing plasma-modified TM samples with γ radiation does not have any significant effect on the value of the contact angle (Fig. 6, curves *2* and *3*). The dynamics of changes in the wetting angle of consecutively plasma-modified and γ-sterilized TMs versus the storage time manifests a certain increase in the contact angle (by 10°–12°) to the value $\theta = 44.5°$ for a dose of 1 kGy over the first three days of storage (Fig. 6, curves *2* and 3). Further storage for 20 days does not lead to any noticeable changes in the wetting angle.

The above data indicate the significant effect that plasma treatment and subsequent γ irradiation have on the surface roughness and the contact angle of PET track membranes. First of all, this concerns the surface roughness parameter R_a, which determines the surface wetting properties. The available data [26] on the effect of plasma on the roughness and the wetting contact angle show that the roughness parameter R_a and the lyophily of the surface of PET films grow as the exposure time increases.

It was mentioned before that plasma oxidizes the surface of PET, which manifests itself in a decrease in the contact angle and hydrophilization of the surface [27]. The behavior of TMs with respect to plasma treatment is in many ways similar to that of a PET film, but the effects that are observed are more significant.

The table lists the values of the surface energy σ_s and its dispersion σ_s^d and polarization σ_s^p components for the original PET and TM. The data in the table indicate that PET belongs to the class of weakly polar polymers. The polarity of a PET film $p = \sigma_s/\sigma_s^p$, which is defined as the fraction of the polar component in the total surface energy, is 0.22, which is in good agreement with the data in [28]. The subsequent formation of a TM that involves ion irradiation and chemical etching of the surface only insignificantly affects (see table) the value of the surface energy σ_s, but dramatically (by more than 300%) increases the value of the polar component σ_s^p of the surface energy. Therefore, as opposed to PET films, the surface of a PET track membrane is strongly polar with a polarity of $p = 0.8$.

Plasma treatment significantly, by more than 4 times, increases the surface energy of a TM, the increase being associated with the growth of the polar component σ_s^p of the total energy (table). It should be noted that the contribution of the dispersion component σ_s^d to the total surface energy does not exceed 7% (table). Subsequent γ irradiation with a dose of 1 and 10 kGy slightly decreases the surface energy σ_s. Therefore, the

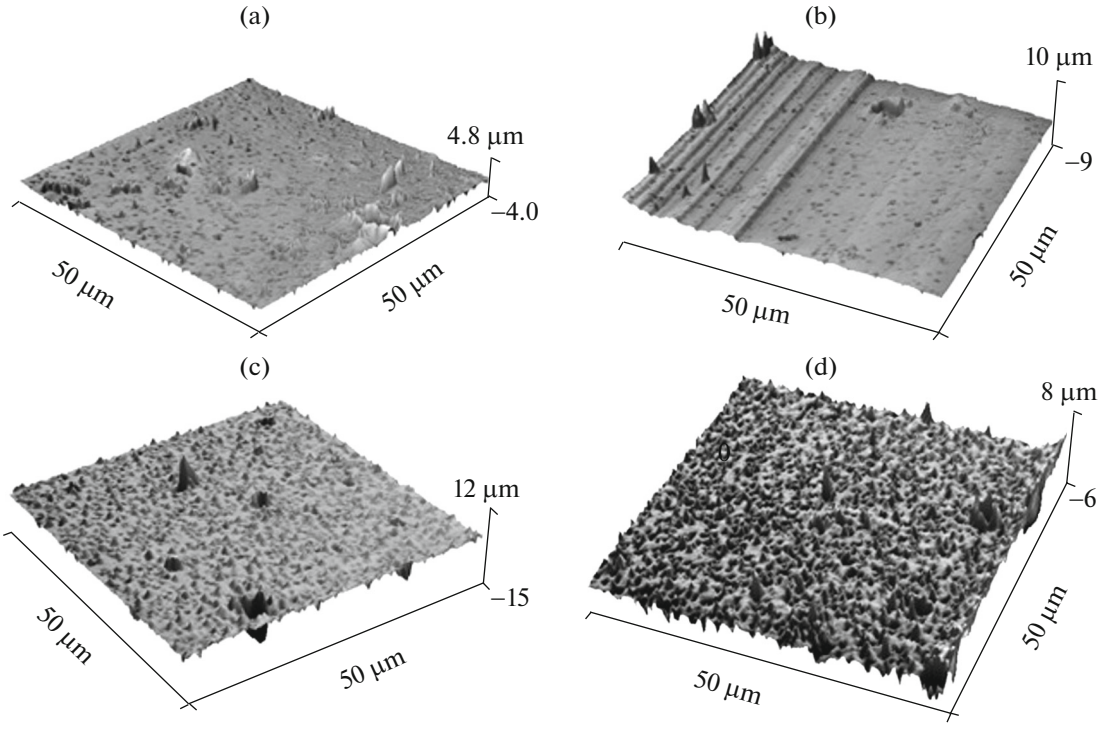

Fig. 3. Topography of the surface of sterilized (1 kGy) original (a) and plasma-modified track membranes with exposure times of 30 s (b), 60 s (c), and 90 s (d).

surface energy of a PET track membrane is of a predominantly 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.

Changes in the chemical composition of the TM surface were studied by infrared spectroscopy. IR optical-absorption spectra are shown in Fig. 7. A classical set of absorption lines typical of PET films can be seen in the IR spectra.

The absorption line at 723 cm^{-1} is ascribed [29, 30] to the twist mode of vibrations of the methylene (CH_2) group and the one at 792 cm^{-1} corresponds to vibrations of the carbonyl γ(C=O) + δ(COO) groups [31]. The absorption line at 850 cm^{-1} is due to vibrations of the methylene (CH_2) group, and the one at 872 cm^{-1} refers to vibrations of the phenyl γ(CH) ring. Absorption at 1016 cm^{-1} is due to (–C–C–) valence vibra-

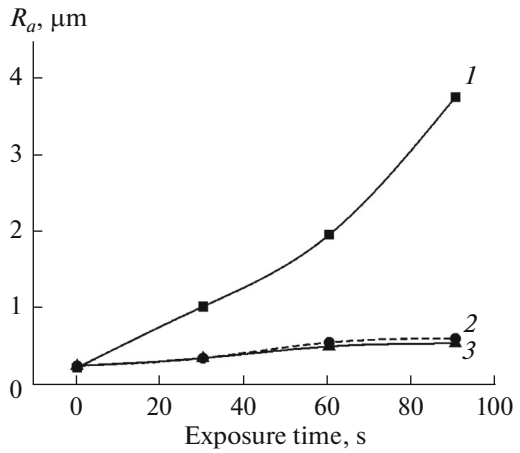

Fig. 4. Dependence of the roughness parameter R_a on the time of exposure to low-temperature atmospheric plasma.

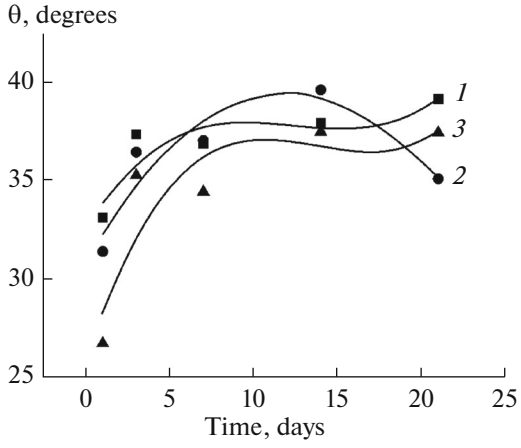

Fig. 5. Dependence of the interfacial angle of a plasma-modified TM with exposure times of 30 s (*1*), 60 s (*2*), and 90 s (*3*) on the storage time.

tions and to vibrations of (C–H) groups of the benzene ring in the bonding plane [31]. The absorption lines at 1093 and 1241 cm^{-1} correspond to vibrations of nonpolar (C=C, C=O) functional groups, and the line at 1340 cm^{-1} reflects vibrations of methylene ($=CH_2$) groups [32]. Absorption at 1407 cm^{-1} is treated as deviations of (C–C) groups. The absorption band at 1712 cm^{-1} is due to valence vibrations of (C=C) and (C=O) groups [31, 32].

The effect of plasma on the TM surface leads to a certain decrease in absorption at 1712, 1241, and 1093 cm^{-1}, which is associated with nonpolar (C=C, C=O) functional groups in a thin near-surface layer. The data that we obtained are in good agreement with the results in [19–21], where X-ray photoelectron spectroscopy data are provided that indicate a decrease in the number of nonpolar (hydrophobic) C=C and C=O functional groups. The broken bonds are filled with atmospheric oxygen and nitrogen. This results in the formation of C–C/C–H, C–O, and/or C–N, O=C–O, and/or N–CO–N groups on the polymer surface. One can also observe N–C=O groups; i.e., the number of polar (hydrophilic) functional groups grows [19–21].

Therefore, plasma treatment destroys polymer chains on the surface predominantly in an amorphous phase that is prone to oxidation. Kravec et al. [15] believe that ruptures of the C–O bond (binding energy of 376 kJ/mol) and the C–C bond (binding energy of 335 kJ/mol) are most likely to occur. For example, the following chemical reaction is possible:

$$-OOC-C_6H_4-COO-CH_2-CH_2-$$
$$\rightarrow -OOC-C_6H_4-COO- + -CH_2-CH_2-$$
$$\rightarrow -OOC-C_6H_4-COOH + CH_2=CH-.$$

Carboxyl groups that appear at the locations of rupture of chemical bonds determine the hydrophilization of the membrane surface. Radicals that are thus formed are unstable, and, for example, terminal carboxyl groups are formed as a result of secondary reactions. All these changes are associated with a plasma-induced reorganization of polymer chains that results from the rupture of chemical bonds in the chains with subsequent joining and formation of new bonds on the TM surface [33]. Morphological changes in the sample surface that are caused by low-temperature atmospheric plasma lead to a reconstruction of the TM surface that manifests itself via formation of numerous craters, namely, destructive areas that increase the lyophily of the surface.

The typical value of the surface roughness parameter R_a for a PET film is R_a = 2–6 nm [20, 21]. Plasma exposure significantly increases the PET undulation to values of R_a in a range of 10–20 nm, that is, 2–5 times greater [20, 21]. The process of creation of a TM promotes significant, approximately by a factor of 10, growth of the roughness (R_a = 0.2 μm). Subsequent plasma treatment increases the roughness further to R_a = 3.3 μm. Therefore, reconstruction of the TM surface under atmospheric-plasma treatment significantly alters the surface topography.

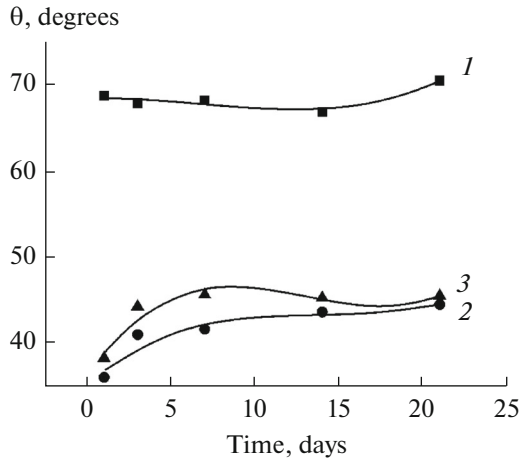

Fig. 6. Dependence of the interfacial angle of a plasma-modified and γ-sterilized (1 kGy) TM on the storage time: (*1*) without plasma treatment (γ sterilization); (*2*) plasma treatment for 30 s + γ sterilization; (*3*) plasma treatment for 60 s + γ sterilization.

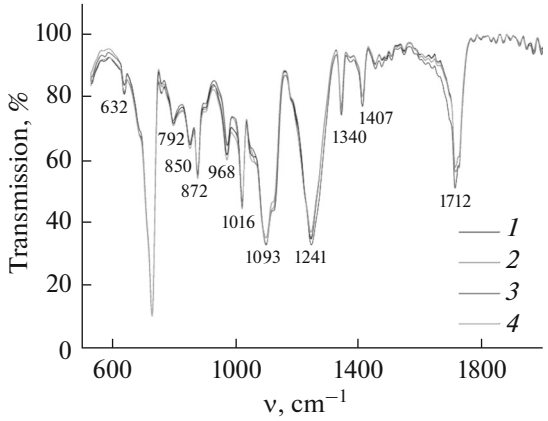

Fig. 7. IR optical-absorption spectra of original (*1*) and plasma-modified TM with exposure times of 30 s (*2*), 60 s (*3*), and 90 s (*4*).

Sterilization of plasma-modified 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. 7). 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 (sterilization of modified samples led to an interfacial angle increase of 3°–5°). Effects of hard UV radiation from a λ = 172 nm eximer lamp on PET films (growth of the surface energy, dissociation of chemical bonds) [34] are similar to the effect from γ irradiation observed in this work.

Mean values of the parameters of TM surface: roughness R_a, surface energy σ_s, dispersion σ_s^d, and polarization σ_s^p components of the surface energy and the wetting angles for water θ_w° and glycerine θ_g°

TM	R_a	σ_s	σ_s^d	σ_s^p	Polarity	θ_w°	θ_g°
PET film	–	36.76	29.15	7.61	0.2	61.1	76.5
PET film	0.231	29.95	5.97	23.98	0.8	72.8	74.8
TM + γ 1 kGy	0.265	43.73	0.30	43.43	0.99	68.7	77.2
TM + γ 10 kGy	–	37	0.9	36.34	0.98	72.3	80.9
TM + pl 30	1.03	131.53	7.33	124.21	0.94	33.0	73.3
TM + pl 60	1.97	146.04	9.91	136.13	0.93	31.2	73.3
TM + pl 90	3.77	129.64	7.46	122.18	0.94	26.6	74.5
TM + pl 30 + γ 1 kGy	0.357	110.3	3.1	107.2	0.97	36.0	70.5
TM + pl 60 + γ 1 kGy	0.55	108.56	2.68	105.88	0.98	38.1	69.3
TM + pl 90 + γ 1 kGy	0.6	107.1	2.43	104.67	0.98	36.1	71.1
TM + pl 30 + γ 10 kGy	0.345	120.1	7.08	113.02	0.94	39.1	76.9
TM + pl 60 + γ 10 kGy	0.497	123.07	8.15	114.91	0.93	41.4	79.1
TM + pl 90 + γ 10 kGy	0.54	128.13	9.6	118.53	0.93	38.3	78.6

TM + pl is plasma-treated TM; + γ is γ irradiation; the dimensions of the roughness parameter, the surface energy, and the contact angle are μm, mJ/m^2, and degrees (θ°), respectively.

Unlike UV exposure, γ irradiation significantly influences the surface roughness. The action of γ radiation on plasma-modified TM samples led to significant changes in the surface morphology. The surface roughness considerably declined as compared to nonsterilized TM samples. The roughness parameter R_a for TMs that were treated with plasma for 60 s decreased from 1.97 to 0.55 μm for a γ-radiation dose of 1 kGy and to 0.497 μm for a dose of 10 kGy; for treatment for 90 s, it decreased from 3.77 to 0.6 μm (1 kGy) and to 0.54 μm (10 kGy) (see Fig. 4 and table).

Therefore, small (1–10 kGy) doses of γ radiation decrease the dimensions of destructive areas, i.e., smoothen the surface, which is the reason for a certain growth of the interfacial angle (table). We believe that the observed effect of TM surface reconstruction after small doses of γ radiation is of the same nature as the effect of small doses of ionizing radiation [35]; a weak action of ionizing radiation causes a reconstruction of the structure of the material that takes place during irradiation.

CONCLUSIONS

Exposure of PET track membranes to low-temperature atmospheric plasma and ^{60}Co γ radiation leads to considerable changes in the surface properties of the membranes:

(1) A reconstruction of the TM surface occurs. It consists in a sharp (15 times) increase in the surface roughness and the formation of destructive areas in the form of numerous irregularities that are chaotically distributed over the surface.

(2) The reconstruction of the TM surface is due to redox chemical reactions that occur as a result of plasma action and alter the chemical composition of the surface: nonpolar functional groups decrease and polar ones increase in number in a thin near-surface TM layer.

(3) Plasma-induced changes of the chemical composition of the TM surface and further surface reconstruction lead to a more than fourfold increase in the surface energy owing to the growth of its polar component, which leads to the growth of the surface lyophily.

(4) Small doses of ^{60}Co γ radiation decrease the surface roughness, reduce the number of destructive areas, and bring the material into a state that is more equilibrium than the initial state.

REFERENCES

1. Mironyuk, A.V., Pridatko, A.V., Sivolapov, P.V., and Sviderskii, V.A., The features of polymer's wettability, *Vost.-Evrop. Zh. Peredovykh Tekhnol.*, 2014, nos. 1/6, pp. 23–26.
2. *Entsiklopediya nizkotemperaturnoi plazmy* (Encyclopedia of Low-Temperature Plasma), Fortov, V.E., Ed., Moscow: Nauka, 2000, vol. 4.
3. Aleinik, A.N., Baykov, A.N., Dambaev, G.Ts., and Semichev, E.V., Application of cold atmospheric pressure plasmas for biological tissue treatment, *Adv. Mater. Res.*, 2005, vol. 1084, pp. 602–605.
4. Dmitriev, S.N., Kravets, L.I., and Sleptsov, V.V., Modification of track membrane structure by plasma etching, *Nucl. Instrum. Methods Phys. Res.*, 1998, vol. 142, pp. 43–49.

5. Yu, H.-Y., He, X.-Ch., Liu, L.-Q., Gu, J.-Sh., and Wei, X.-W., Surface modification of poly(propylene) microporous membrane to improve its antifouling characteristics in an SMBR: O_2 plasma treatment plasma process, *Polymer*, 2008, vol. 5, no. 1, pp. 84–91.
6. Zhou, J., Li, W., Gu, J.-Sh., and Yu, H.-Y., Surface modification of polypropylene membrane to improve antifouling characteristics in a submerged membrane-bioreactor: Ar plasma treatment, *Membr. Water Treat.*, 2010, vol. 1, no. 1, pp. 83–92.
7. Slepicka, P., Vasina, A., Kolska, Z., Luxdacher, T., Malinsky, P., Mackova, A., and Svorcik, V., Argon plasma irradiation of polypropylene, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2010, vol. 268, nos. 11–12, pp. 2111–2114.
8. Kravets, L.I., Dmitriev, S.N., Sleptsov, V.V., and Elinson, V.M., Production of asymmetric track membranes by gas-discharge method, *Surf. Coat. Technol.*, 2003, vols. 174–175, p. 821.
9. Golovyatinskii, S.A., Modification of polymer's surface by atmospheric plasma, *Vestn. Khark. Gos. Univ.*, 2004, no. 628, pp. 80–86.
10. Akishev, Yu.S., Experimental and theoretical research of low-temperature plasma influence on polymer films surface, *Mater. 5-go mezhd. simp. po teoreticheskoi i prikladnoi plazmokhimii, Ivanovo, 3–8 sentyabrya 2008* (Proc. Fifth Int. Symp. on Theoretical and Applied Plasma Chemistry, Ivanovo, September 3–8, 2008), Ivanovo, 2008, pp. 360–363.
11. Provotorova, D.A., Kablov, V.F., Ozerin, A.N., Gilman, A.B., Yablokov, M.Yu., Aksenov, V.I., and Keybal, N.A. Modification of unsaturated rubbers in low-temperature plasma as a method to improve their adhesion properties, *Polym. Sci. Ser. D*, 2014, vol. 7, no. 2, pp. 99–101.
12. Mizani, M., Sheikh, N., Ebrahimi, S.N., Gerami, A., and Tavakoli, F.A., Effect of gamma irradiation on physico-mechanical properties of spice packaging films, *Radiat. Phys. Chem.*, 2009, no. 78, pp. 806–809.
13. Jeon, D.H., Lee, K.H., and Park, H.J., The effects of irradiation on physicochemical characteristics of PET packaging film, *Radiat. Phys. Chem.*, 2004, no. 71, pp. 1059–1064.
14. Buczkowski, M., Sartowska, B., Wawszczak, D., and Starosta, W., Radiation resistance of track etched membranes, *Radiat. Meas.*, 2001, no. 34, pp. 597–599.
15. Kravets, L.I., Dmitriev, S.N., and Gil'man, A.B., Modification of properties of polymer membranes by low-temperature plasma treatment, *High Energy Chem.*, 2009, vol. 43, no. 3, pp. 181–188.
16. Papakonstantinou, D., Amanatides, E., Mataras, D., Ioannidis, V., and Nikolopoulos, P., Improved surface energy analysis for plasma treated PET films, *Plasma Surf. Eng.*, 2006, vol. 4, suppl. 1, pp. 1057–1062.
17. Pelagade, S.M., Singh, N.L., Anjum Qureshi, Rane, R.S., Mukherjee, S., Deshpande, U.P., Ganesan, V., and Shripathi, T., Investigation of surface properties of Ar-plasma treated polyethylene terephthalate (PET) films, *Nucl. Instrum. Methods Phys. Res., Sect. B*, 2012, vol. 289, pp. 34–38.
18. Kim, M.M., Kim, H.S., and Lim, J.Y., A study on the effect of plasma treatment for waste wood biocomposites, *J. Nanomater.*, 2013, pp. 2–6.
19. Choi, K.-H. and Kim, H.-K., Effect of Ar ion beam pre-treatment of polyethylene terephthalate substrate on the mechanical and electrical stability of flexible InSnO films grown by roll-to-roll sputtering system, *Jpn. J. Appl. Phys.*, 2013, vol. 52, pp. 10–14.
20. Dowling, D.P., Tynan, J., Ward, P., Hynes, A.M., and Cullen, J., Atmospheric pressure plasma treatment of amorphous polyethylene terephthalate for enhanced heat sealing properties, *Int. J. Adhes. Adhes.*, 2013, vol. 35, pp. 1–8.
21. Navaneetha Pandiyaraj, K., Selvarajan, V., Deshmukh, R.R., and Changyou, G., Adhesive properties of polypropylene (PP) and polyethylene-terephthalate (PET) film surfaces treated by DC glow discharge plasma, *Vacuum*, 2009, vol. 83, pp. 332–339.
22. Aflori, M. and Drobota, M., Combined treatments for the improving of the PET surfaces hydrophilicity, *Digest J. Nanomater. Biostruct.*, 2015, vol. 10, no. 2, pp. 587–593.
23. Novak, I., Chodak, I., Sedlia, J., et al., Investigation of poly(ethylene terephthalate) treated by low-temperature plasma, *Ann. Wars. Univ. Life Sci.–SGGW For. Wood Technol.*, 2010, no. 72, pp. 83–89.
24. Owens, D., Estimation of the surface free energy of polymers, *Appl. Polym. Sci.*, 1969, no. 13, pp. 1741–1747.
25. Carre, A., Polar interactions at liquid/polymer interfaces, *Adhes. Sci. Technol.*, 2007, vol. 21, no. 10, pp. 961–981.
26. Nastuta, A.V., Rusu, G.B., Topala, I., Chiper, A.S., and Popa, G., Surface modifications of polymer induced by atmospheric DBD plasma in different configurations, *J. Optoelectron. Adv. Mater.*, 2008, vol. 10, no. 8, pp. 2038–2042.
27. Nastuta, A.V., Rusu, G.B., Topala, I., Chiper, A.S, and Popa, G., Surface modifications of polymer induced by atmospheric DBD plasma in different configurations, *J. Optoelectron. Adv. Mater.*, 2008, vol. 10, no. 8, pp. 2038–2042.
28. Guzhova, A.A., Temnov, D.E., and Galikhanov, M.F., The electret effects influence on surface and electricity properties of polyethylene terephthalate, *Izv. Ross. Gos. Pedagog. Univ. im. A.I. Gertsena*, 2013, no. 157, pp. 55–60.
29. Stuart, B.H., *Infrared Spectroscopy Fundamentals and Application*, New York: Wiley, 2004.
30. Larkin, P.J., *Infrared and Raman Spectroscopy. Principles and Spectral Interpretation*, Amsterdam: Elsevier, 2011.
31. Liang, C.Y. and Krimm, S., Infrared spectra of high polymers. Part IX. Polyethylene terephthalate, *J. Mol. Spectrosc.*, 1959, no. 3, pp. 554–574.
32. Prasad, S.G., De, A., and De, U., Structural and optical investigations of radiation damage in transparent PET polymer films, *Int. J. Spectrosc.*, 2011, vol. 2, pp. 7–14.
33. Chiper, A., Apetroaiei, N., and Popa, G., Correlation between surface modifications induced on PET/TiO_2 sample by DBD plasma produced in He/N_2 gas mixture and plasma parameters, *Optoelectron. Adv. Mater.*, 2005, vol. 7, no. 5, pp. 2561–2570.
34. Kasahara, T., Shoji, S., and Mizuno, J., Surface modification of polyethylen-terephthalat (PET) by 172-nm eximer lamp, *Trans. Jpn. Inst. Electron. Pack.*, 2012, vol. 5, no. 1, pp. 47–54.
35. Mamontov, A.P. and Chernov, I.P., *Effekt malykh doz ioniziruyushchego izlucheniya* (The Effect of Low Doses of Ionizing Radiation), Tomsk: Del'toplan, 2009.

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