The Change in the Hydrophobic Properties of Track Membranes as a Result of Directional Modification By a Low-Energy Ion Beam

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Abstract: We present the results of study of the influence of low-energy ion beam irradiation on the structure of the surface and hydrophobic properties of PET membranes. To perform it we characterized ultrastructure, filtering and mechanical properties of the pristine and irradiated samples. Irradiation with a low-energy C and H ions increases the hydrophobicity of membranes made from PET films, while a decrease in strength properties is insignificant.

Keywords: PET film, radiation modification, hydrophobicity, water purification.

1. Introduction

The problem of water purification technologies is important issue in modern industry since rapid growth of water consumption. In countries like Kazakhstan it is additionally challenging because of the limited water resources, that requires water recirculation and proper purification of water used in industry[1].Currently existing technologies of industrial filtration include large, cumbersome and expensive systems. The technologies of developing porous membranes for purification, concentration and sterilization of liquids and gases have been extensively developed since they are much more effective [2]-[4]. The method of membrane-based filtration solves many problems: membranes are easy to manufacture, membrane-based devices may be used to make cheap and portable filtration units for industry or domestic use, they are easier to utilize after use, etc. Filters based on porous membrane materials can be used to sterilize liquids and gases from various bacteria and removal of dust particles, to clean water from turbidity, pesticides, naphthalenes, heavy metals, iron, mercury, lead, aluminum, free chlorine, chlorine compounds [5]-[7] However still remain a problem of contamination of membranes in such units, which can happen due to the precipitation of particles of the solid phase, growth of microorganisms, and the chemical interaction between the membrane material and the medium. Most composite membranes used in such units are manufactured as multilayer composites, where the supporting layer is made of polysulphone

(polysulphone), and the filter layers are made of polyamide (polyamide) or another material with similar properties. The regeneration of such membranes during operation is a very sophisticated process. These materials also are highly adhesive to most organic substances that make it difficult to regenerate them[8], [9]. This problem can be solved by using a special type of membranes monolayer PET membranes with track pores obtained by irradiating PET films with high-energy heavy ions and subsequent chemical treatment. The main distinctive properties of membranes obtained this way are (i) low thickness, (ii) high selectivity of separation and (iii) relatively high regeneration efficiency. In contrast to composite membranes, track membranes are nanoporous material with through pores of a given size. Due to a number of aforementioned properties track membranes are highly promising substrates compared to other types of membranes. An important condition for the use of track membranes in the purification and separation processes is the ability to regulate (usually to increase) the degree of hydrophobicity of membranes. One of the promising ways of modifying the surface of track membranes in order to increase hydrophobicity is surface treatment by accelerated ions. To date, this method of modification is a poorly studied process, and therefore the consideration of this problem deserves special investigation and careful technological elaboration. In the current study, we present the results of an investigation of the effect of irradiation with a low-energy ion beam on the morphology of track membranes and the degree of hydrophobicity. The filtering characteristics of the pristine and modified samples were determined, as well as the effect of irradiation on the strength parameters.

2. Materials and Methods

2.1. Preparation of Membranes

As pristine samples, polymer films based on polyethylene terephthalate of the Hostaphan® type produced by Mitsubishi Polyester Film (Germany) with a thickness of 12 μm were used. Irradiation of the PET film was done at the accelerator DC-60 (Astana, Kazakhstan), using krypton ions with an energy of 1.75 MeV/nucleon with a fluence of 4.0E+07 ion/cm^2.After irradiation, the polymer films were subjected to double-sided chemical etching in a solution of 2M NaOH at a temperature of 85 0.1°C and subsequent treatment in neutralization solutions in a 1.0% solution of acetic acid and then in deionized water. Investigation of the surface, structure, quality of irradiation of TM and density calculation was carried out in the Marker-12 software, using for this purpose micrographs of films obtained with the scanning electron microscope JEOL-7500F. For reliability of the calculations, 5 control points were selected for counting the width of the film at intervals of 5 cm (three parallel measurements for the front and back sides) and at least 10 meters along the length. The selection of optimal etching conditions ensures the obtaining of isotropic (symmetric) pores over the entire thickness of the film, which in turn ensures high membrane productivity (by water and air), minimum dispersion of bubble point values diameter of the largest pore in the membrane) and effective pore diameter, important is the degree of hydrophilicity (i.e. wettability) when working with hydrophobic polymeric materials.

2.2. Membrane Efficiency Measurements

The productivity of membranes by air was determined at a pressure drop of 0.02 MPa, passing gas through a membrane with an area of 1 cm^2 [9]. The effective pore diameter was calculated from the value of gas permeability, according to the (1):

$$r^3 = Q \cdot 3l \left(\sqrt{\frac{2\pi}{R \cdot T \cdot M}} \cdot \Delta p \cdot 4n \right)^{-1} \quad (1)$$

where r is the radius of the pore, Q is the air capacity, l is the film thickness, Δp is the applied pressure, R is the universal gas constant, M is the molar mass of the air, n is the irradiation density, and T is the temperature. The productivity of membranes in water in units of $l/m^2 \cdot h$ was determined on samples measuring 2.54 cm^2, passing deionized water (18 M Ω) through a sample of TM at a pressure difference of 0.08 and 0.15 MPa. The productivity Q was estimated using (2):

$$Q = \frac{n \cdot \pi \cdot r^2}{8\mu \cdot l} \cdot \Delta p \quad (2)$$

where r is the radius of the pore, l is the thickness of the film, Δp is the applied pressure, n is the irradiation density, and μ is the dynamic viscosity of the liquid. The degree of hydrophilicity of the track membranes was determined by measuring the wetting contact angle (θ) by the drop drop method. To do this, a drop of working fluid of the order of 15 μl was applied from the microsyringe to the surface of the samples. The contact angle of wetting was determined by the goniometric method, proceeding from the basic dimensions of the drop and the condition that θ<90° according to the (3):

$$tg\Theta = \frac{2h \cdot r}{r^2 - h^2} \quad (3)$$

where, θ is the wetting contact angle, r is the radius of the contact area of the drop with the surface, and h is the height of the drop. To study the degree of purification, the following solutions were used: 10 mM NaCl (filtered solution) and 5 M NaCl (extract solution). The rate of liquid pumping in the system was 23 cm/s. The flow of liquid that passed through the membrane was calculated from (4):

$$J_w = \frac{\Delta V}{\Delta t} \cdot A^{-1} \quad (4)$$

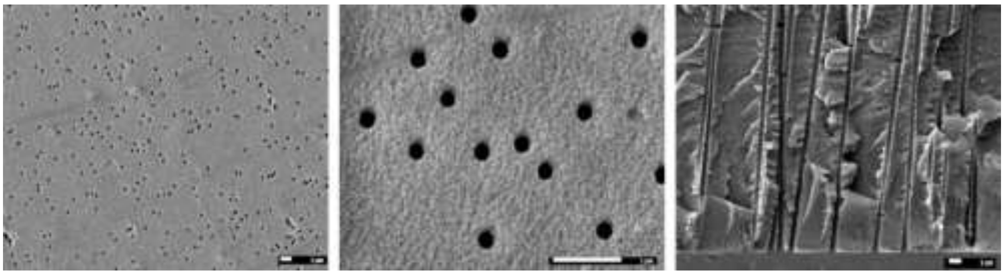
where ΔV is the volume of liquid passed through the membrane, Δ is the time, and A is the area of the membrane, which is 0.003034 m^2. Tensile strength test was carriedout by applying pressure to the membrane and gradually increasing it to the point of failure in the sample. Tensile stress, when it broke out, was measured to indicate the mechanical strength of the membrane and the degree of deformation.

2.3. Surface Modification of Membranes

For directional modification of the surface of track membranes in order to change the hydrophobic properties, the track membranes were exposed to a pulse ion accelerator TEMP using beam consisting of 70% C^+ ions and 30% of H^+ of 30% ion with ions energy of 200 keV. Pulse duration was 100 ns, beam current: I <10 kA. The radiation doses were 1·1011 ion/ cm^2, 2·1011 ion/cm^2, 3·1011 ion/ cm^2.

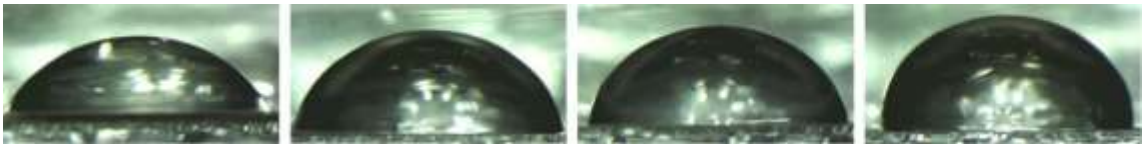
3. Results and Discussion

To study the effect of irradiation of C^+ and H^+ ions by low-energy beams on the morphological and hydrophobic properties of track membranes, the samples obtained were exposed to irradiation with a pulsed TEMP ion accelerator as described. Fig. 1 shows SEM images of the surface and lateral fractures of the track membranes after irradiation and chemical etching. The pore diameter after NaOH etching were measured on images obtained by the SEM. To determine the average pore size, 100 pores from the front and the rear sides of film were measured. There was insignificant (~5%) difference of pore size on both PET surfaces: pore size at front side was 202±10 nm and 193±10 nm on the rear side. SEM study shows that the tracks formed by accelerated particles in membranes are cylindrical, arranged uniformly and there is no overlapping section. To assess the effect of ion irradiation on the surface properties of track membranes, we measured the contact angle of wetting and determine the degree of roughness. In addition we determined the strength and filter characteristics. Fig. 2 shows the image of drop of distilled water on surface of film before and after irradiation and chemical etching. It was used to measure the contact angle of wetting the samples too. An increase in the contact angle with increasing irradiation dose is observed, which may be due to a change in the surface of the track membranes as a result of interaction with the ion beam.



(a) SEM of film surface (b) SEM of film surface (c) SEM of film side cut

Fig. 1. Scanning electron microscopy of film surface after treatment, the image a and b represent front surface of film pierced by accelerated article.

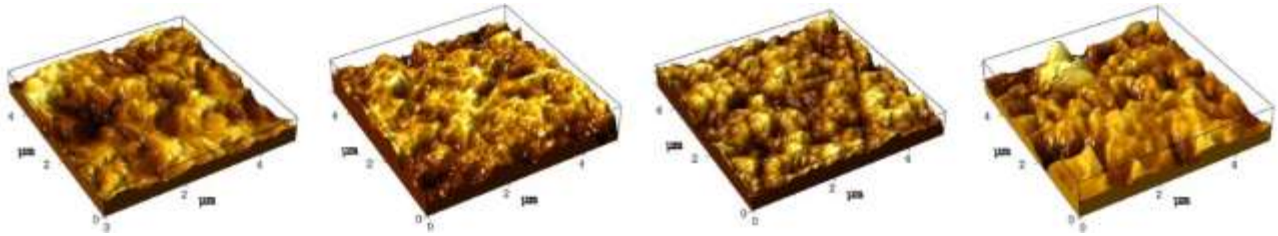


(a) Pristine (b) 1 1011 ion/cm^2 dose (c) 2 1011 ion/cm^2 dose (d) 3 1011 ion/cm^2 dose

Fig. 2. Images of change of the contact angle of wetting a and b represent front surface of film pierced by accelerated particle.

Table 1 shows the results of changing the wetting contact angle from the front side. At beam energies of C^+ ions of 300 keV, the maximum penetration depth in polymer films is 1232 Å, according to the calculations of the SRIM Pro 2013. As a result, when ions interact with the surface of the membrane, the main ions retard and transfer their energy to a shallow near-surface layer of the membrane. At large beam densities and radiation doses, a huge amount of energy accumulates in the surface layer of the membrane, which can lead to a change in the molecular structure of the surface of the membrane. This was analyzed using the atomic force microscopy technique. Topographical study of the surfaces of irradiated samples was carried out on an atomic force microscope (AFM) of the STSM SmartSPM, AIST- NTLtd. Fig. 3 presents 3D images of the surface of track membranes before and after irradiation with different doses. As can be seen from the pictures, with an increase in the irradiation dose, a change in the morphology of the track membrane surface become more obvious, which confirms the earlier assumption about a change in the near-surface layer of the membrane during irradiation.

When the low-energy beam of C and H ions is irradiated on the surface, formation of hilacs is observed, with increasing radiation dose, a change in the shape and size of hilaks happens, which may be due to thermal effects occurring in the material during irradiation. The degree of roughness of the surface of membranes increases along with irradiation dose (Table 1). By irradiation with low-energy ions, a change in morphology and structure lead to a deterioration in the strength properties of the film. The effect of irradiation on the strength characteristics of membranes, was examined by the rupture method. The results of measurements are shown in Table1. There is direct ration between effective pore diameter measurement determined by gas permeability and permeability techniques and the apparent pore diameter determined by scanning electron microscopy.



(a) Film surface before irradiation | (b) Film surface after 1·1011 ion/ cm² dose | (c) Film surface after 2·1011 ion/ cm² dose | (d) Film surface after 3·1011 ion/ cm² dose

Fig. 3. Atomic force microscopy of the surface of track membranes before and after irradiationa and b represent front surface of film pierced by accelerated article.

Table 1. The Results of Changing the Contact Angle of Wetting and Strength Properties

Dose, ion/ cm²	Marginal angle of wetting	Maximum pressurea, Mpa	Roughness, m
Pristine	66.6 ± 1.2	0.34 ± 0.03	0.127 ± 0.005
1·1011	85.9 ± 1.3	0.34 ± 0.04	0.209 ± 0.008
2·1011	87.5 ± 1.1	0.33 ± 0.02	0.247 ± 0.006
3·1011	89.6 ± 1.2	0.32 ± 0.03	0.309 ± 0.002

a The maximum value of pressure at which the membrane retains its strength properties

Table 2 shows the results of measuring the productivity and degree of purification. It can be seen that with an increase of the irradiation dose results in insignificant decrease in the strength properties that is within the error margin. This observation confirms that the structural properties of the membrane changes only in the near-surface layer without destroying the membrane structures over all thicknesses. The efficiency of these changes increase with dose of irradiation. Another parameter studied was efficient pore diameter measured by determining gas and water permeability along with direct measurement of pore diameter by SEM. The results are presented in Table 2 and on Fig. 4. The correspondence in the sizes of pores established by different methods confirms that the pores have a cylindrical shape across the membrane.

Table 2. PET Membranes Efficiency Measurements

Dose, ion/ cm²	Air efficiency, ml/min	Water efficiency, L/m²-h	NaCL purification, %
Pristine	179,31	9,23	45
1·1011	184,3	9,86	57
2·1011	191,15	10,11	59
3·1011	197,26	10,56	61

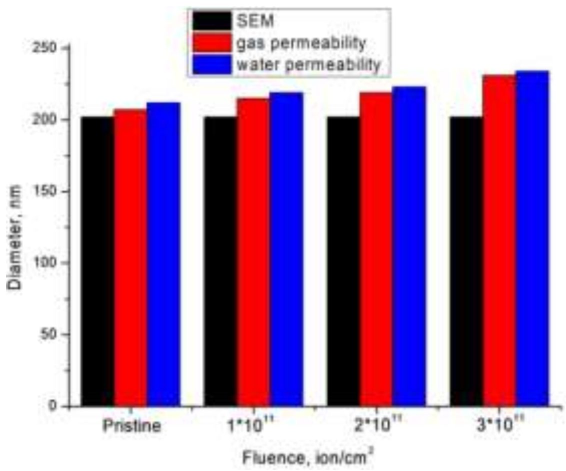


Fig. 4. Comparison of pore diameter and measured gas and liquid permeability of membranes.

The increase in the effective pore diameter for gas and water permeability can be explained by the increased roughness of the surface layer of track membranes. At the same time, as a result of irradiation, a change in the productivity of water and air filtration with an increase in the radiation dose is observed, as well as an increase in the degree of purification of filtered substances by approximately 30%.

4. Conclusion

Our results of using radiation modification of the surface of track membranes for the purpose of increasing hydrophobic properties are highly positive. During the tests, the filtering characteristics of the pristine and modified samples were determined, as well as the effect of irradiation on the strength parameters of track membranes. It is shown that irradiation with a low-energy C+ and H+ beam leads to an increase in the degree of hydrophobicity of track membranes, while a decrease in strength properties is insignificant. At the same time, as a result of irradiation, a change in the productivity of water and air filtration with an increase in the radiation dose is observed, as well as an increase in the degree of purification.

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References

[1] UNDP Kazakhstan. (2004). Water Resources of Kazakhstan in the New Millennium. Almaty, Republic of Kazakhstan: UNDP Publication in Kazakhstan.

[2] Oganessian, Y., Dmitriev, S., & Penionzhkevich, Y. (1997). *Track-Etched Membranes in Biomedical and Biotechnological Processes*. Russian Federation: Institute for Nuclear Research.

[3] Patent RU 2335328 C1, IPC B01D 2948, published 10.10.2008 (In Russian).

[4] Shtondina, V., & Baranova, L. (1990). *Cleaning Oily Water Electronics Industry*. Russian: Moscow Institute VODGEO.

[5] Patent RU 38503, IPC F28G 1/12, published 20.06.2004 (In Russian).

[6] Zhukov, A., Mangayt, I., & Radziller, I. D. (1977). *Techniques for Treating Industrial Wastewater*. Moscow: Stroyizdat.

[7] Geoffrey, D., Jennifer, K., & Kenneth, S. (2013). Counting viruses using polycarbonate Track Etch membrane filters as an alternative to Anodisc membrane filters. *Pdx Edu.* from http://web.pdx.edu/kstedman/PCTE_virus_counting_protocol.pdf.

[8] Henri, H. (2007). Use of High-Technology Track-Etched Polymer Membranes in a Wide Range of Industries. *American Biotechnology Laboratory, 8*, 24-26.

[9] Shao, P., Huang, R. Y. M., Feng, X., Anderson, W., Pal, R., & Burns, C. M. (2005). Composite membranes with an integrated skin layer: Preparation, structural characteristics and pervaporation performance. *Journal of Membrane Science, 254 (1-2)*, 1-11.

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