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Track-Etch membranes: the Kazakh experience

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ABSTRACT

In 1972 track-etch membranes were first developed by General Electric Corporation. Initially used as a simple laboratory tool, track-etch processes have grown into an industrial method of considerable technological and commercial impact. For instance, track-etch membranes are widely utilized for liquid and gas purification, controlled drug delivery, cell culturing, and serve as supports or templates. Track-etch technology utilizes heavy ion accelerators meaning exploitation of such a technology is relatively inaccessible to most. The existence of a unique heavy ion accelerator in the Republic of Kazakhstan (RK) provides the country with an opportunity to manufacture domestically track-etch membranes. In this work fabrication of symmetrical polyethylene terephthalate (PET) track-etch membranes using a heavy ion accelerator located in the capital city of RK, Astana, is presented. The developed membranes have been examined using a scanning electron microscope (SEM), a goniometer, and mechanical and water permeability testers; the results obtained having been compared with characteristics of commercially available membranes.

Keywords: Track-etch; Symmetrical; Membrane; PET; Cylindrical pores; Kazakhstan

1. Introduction

Due to tremendous growth in human population, coupled with various other activities, water shortage has become a global problem. In many situations part of the available water supply is either not accessible or of low quality. The Republic of Kazakhstan (RK) is among those countries experiencing such issues. According to a recent RK report the country has the lowest total water availability in Eurasia. Low water availability is limiting development of natural and land resources. The situation in the region is critical because of the combination of water pollution and lack of supply. Disproportion between environmental resources and anthropogenic needs leads to ecology distress and full exhaustion of water sources. The current water demand exceeds average annual flow by fifty per cent. Hence, it is vitally important to find alternative water resources for further economical development and sustained environment [1]. As readily available water resources are utilized, competition for what remains between agriculture, industry and public water users arises. This competition leads to higher water prices, constricted economic development, and social problems in regions with limited water access. As a result, the general welfare of RK is threatened due to conditions arising from access to water.

Among commonly used water and wastewater treatment processes, membrane separation is presently the most efficient technology available [2]. Phase inversion is a common membrane fabrication technique. While phase inversion membranes are widely used in laboratories and industry, they possess several drawbacks. Pore size, geometry, density and pore size distribution of the phase inversion membranes cannot be produced in a controllable manner [3,4]. Earlier works have shown that only track-etch technology is able to overcome these difficulties [5–7]. The track-etch process involves polymer irradiation with high-energy ions followed by subsequent physical and chemical treatment (i.e. etching) [8].

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The application of membrane processes in Kazakhstan has the potential to solve the problem of water scarcity in the country. Capital and maintenance costs of membrane based facilities however are not cheap. For Kazakhstan this issue can be solved by developing a domestic membrane manufacturer for the local market. This work focuses on the development of polyethylene terephthalate (PET) microfiltration track-etch membranes by using a DC-60 heavy ion accelerator available at the Institute of Nuclear Physics, Astana. Main exploitation characteristics such as pore size, porosity, hydrophobicity, mechanical strength, and water productivity of the developed membranes have been measured and compared with those of commercially available membranes. The commercial membranes have been purchased from Reatrack, Nerox and It4ip manufactures. The selection of commercial samples is based on the fact that It4ip is one of the global leaders in track-etch membrane production, while Reatrack and Nerox represent another fast developing market of the region.

2. Materials and methods

2.1. Commercial track-etch membranes

Microfiltration track-etch membranes made of PET have been purchased from Reatrack (Russia), Nerox (Russia) and It4ip (Belgium).

2.2. Fabrication of track etch membranes

PET polymer (RNK 12.0 Hostaphan, Mitsubishi Polyester Film, Germany) of 12 μm thickness and 0.32 m width has been irradiated with krypton ions using a DC-60 ion accelerator. Ion energy, irradiation angle, and ion density consisted of 1.75 MeV/nucleon, 90°, and 10^8 cm^{-2}, respectively. The energy loss of the ions in PET was 5–6 MeV/μm. The film was then chemically etched using 2.2 M sodium hydroxide at a temperature of 85°C.

2.3. Membrane characterization

Membrane pore size was determined using a Scanning Electron Microscope (SEM) and the bubble point method. A JEOL-7500F SEM was used to characterize the membranes. The instrument had 2 nm resolution, an accelerating voltage range of 0.1–30 kV and a magnification from 25 to 100,000. SEM images also were used for membranes' porosity determination by taking into account membrane thickness, pore size and density.

In the bubble point method, the pressure of nitrogen on one side of the membrane was slowly increased until gas bubbles were observed on the other side of it. The pressure at which bubbles appear is known as the so-called bubble point [9]. The pore diameter, d, was calculated using:

$$d = \frac{4\gamma}{P}\cos\theta \quad (1)$$

where γ is the surface tension of the liquid, θ the contact angle of the liquid on the pore wall, while P is the bubble pressure.

To determine the hydrophobic/hydrophilic properties of the membrane the contact angle of the polymers was measured. The measurements were performed at room temperature using the sessile drop method of water on dry membranes.

Tensile strength test was carried out by applying pressure to the membrane and gradually increasing it up to the point of failure in the sample. Tensile stress when it failed was measured to indicate the mechanical strength of the membrane and the degree of deformation that could be expected under a given load.

The filtration area of the tested samples in the membrane holder was 2.54 cm^2. The water flux of the membrane was determined by testing samples in a pressurized dead-end filtration cell. The water permeability was obtained by applying deionized water to the membrane at 0.15 atm pressure. To calculate the water flux of the membrane, J

$$J = \frac{m}{t\rho A} \quad (2)$$

was used; here m is a permeate weight, ρ the density of the permeate filtered through the membrane, t the time interval used, while A is the cross-sectional area of filtration.

3. Results and discussion

By using the bubble point method pore size of the polymers etched for different times has been determined (Fig. 1).

As can be seen from the figure, the pore size gradually increased with etching time magnification. For example, etching times of 180, 210, 240, 270 resulted in 185, 292, 393, 425 nm membrane pore size, respectively. Hence, the membrane pore size is a linear function of the etching time with the coefficient of determination equal to 0.95.

SEM images of the membranes etched for 180, 210, 240 and 270 s are depicted in Fig. 2.

The SEM micrographs show that the membranes possess homogeneous morphology and have cylindrical, 90° aligned pores (tortuosity equal to 1) with no intercross. It also can be seen that membrane pore sizes measured with the help of a SEM are in full agreement with results obtained by the bubble point method. For instance, 181 nm (for 180 s

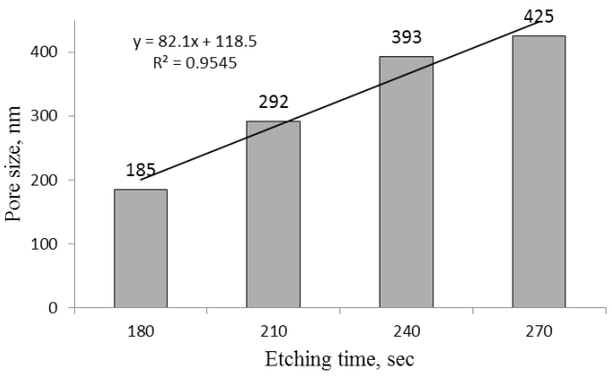

Fig. 1. Membrane pore size as a function of etching time obtained using the bubble point method.

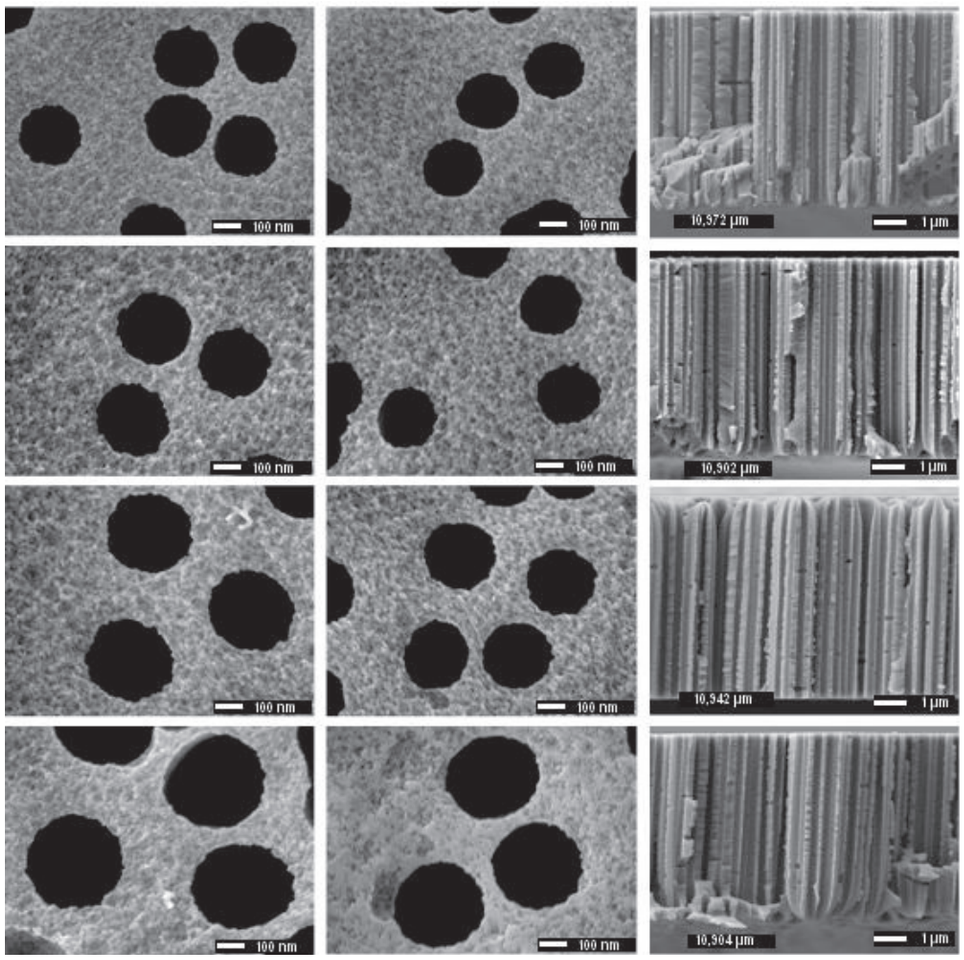

Fig. 2. SEM images of the polymer etched for 180 s (first row), 210 s (second row), 240 s (third row), 270 s (fourth row). Left column represents the front face side, middle column the reverse side, right column gives the cross section.

etching), 290 nm (for 210 s etching), 380 nm (for 240 s etching) and 421 nm (for 270 s etching) have been observed from SEM images.

Fig. 3 illustrates the tensile strength at break as function of etching time.

With an increase in the etching time from 180 to 270 s, the tensile strength at breaking point of the membrane gradually decreased from 0.22 to 0.05 MPa. Such a trend can be explained by an increase in the porosity resulting from the prolonged etching time (Fig. 4).

For example, when the etching time was 180 s, membrane porosity was 5.7 %. Increasing the etching time to 210, 240, and 270 s led to membrane porosities of 12.28, 18.05, and 23.3%, respectively.

The hydrophilicity of the membrane was also studied (Fig. 5).

The figure shows when etching times are prolonged there is a slight increase in the hydrophilicity of the samples. For example, incrementing the etching time by 90 s (from 180 to 270 s) diminished the membrane contact angle by 5° (from 65 to 60°).

After the characterization of the developed samples, comparison with the commercially available membranes

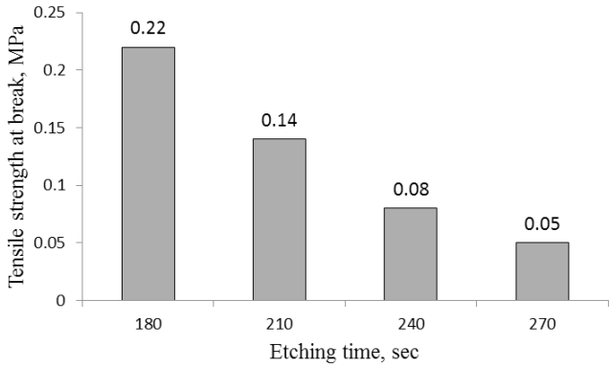

Fig. 3. Impact of etching time on membrane tensile strength at breaking point.

was undertaken. Table 1 shows the pore size, pore density, porosity, tensile strength at breaking point, and contact angle of Reatrack, Nerox, and It4ip samples.

The membrane pore size measurements represented in the Table 1 are based on SEM analysis (Fig. 6).

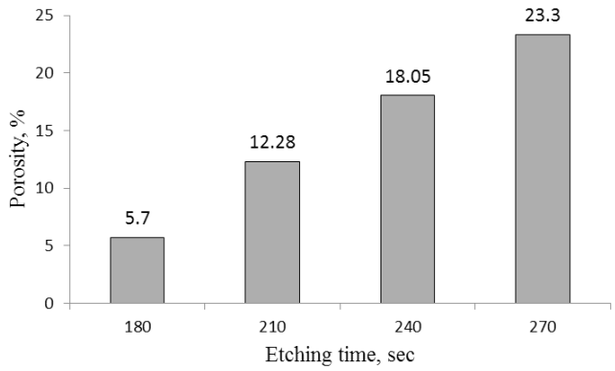

Fig. 4. Membrane porosity as a function of etching time.

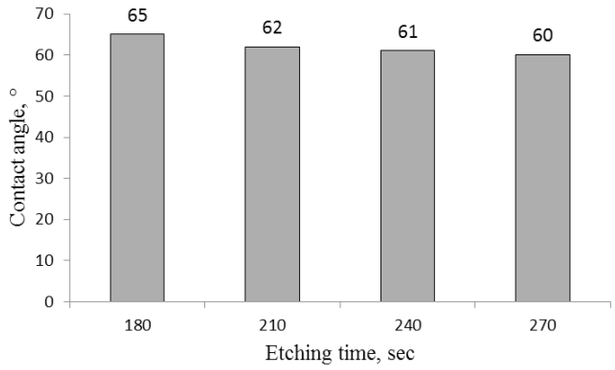

Fig. 5. Influence of etching time on membrane contact angle.

Table 1
Characteristics for the commercial membranes

Membrane	Pore density, cm^{-2}	Pore size, nm face/ back (from SEM analysis)	Porosity, %	Tensile strength at break, MPa	Contact angle, °
Reatrack	$2.66 \times 10^{8*}$	392/378	28	0.031	53
Nerox	$1.8 \times 10^{8*}$	373/367	26	0.037	57
It4ip	$1.22 \times 10^{8*}$	372/366	25	0.04	57

*Provided by manufacturer.

The water fluxes of all four membranes are depicted in Fig. 7.

From a consideration of the data, it can be seen all commercial membranes have similar characteristics. For example, porosity of all three samples lies in 25–28% range; mechanical strength and contact angle are between 0.031–0.04 MPa and 53–57°, respectively. Comparison with those parameters for the developed membranes (etched for 270 s) it can be seen that the developed membranes possess higher mechanical strength (0.05 MPa versus 0.031–0.04 MPa), while porosity and hydrophilicity are close to the commercial samples. On the other hand, microscopic analysis shows the commercial membranes and those developed in this work do have some morphological differences. For instance, the developed, Nerox, and It4ip membranes have parallel cylindrical pores (tortuosity equal to 1). In contrast, the Reatrack membranes possess tortuosities greater than one since irradiation has not been conducted at 90°. From the SEM images it can also be seen that polymer from which the It4ip sample is made is softer than other membranes.

The membranes developed in this study and the commercially available membranes were all found to have similar pore sizes (396.5 ± 24.5 nm for the face side and 383 ± 17 nm for the reverse side) and pore densities (10^8 cm^{-2}) while the water flux for the developed membranes were higher than the water flux for the Reatrack and It4ip membranes by amounts equal to 2.2 and 1.6 times, respectively. On the other hand, the water flux for the Nerox membranes was 6.8–3.1 times higher than the water flux for Reatrack, It4ip, and the membrane developed in this study. For example, water fluxes for Reatrack, Nerox, It4ip and the developed membrane were 19.3, 131.2, 26.4 and 42.8 ml/cm^2-min, respectively. From the table it also can be seen that the pore size on the face side is slightly larger than the pore size on the reverse side. This was observed for all membranes. For instance, the face side pore size for the developed membranes was 21 nm larger than the reverse side pore size (421 versus 400 nm). The commercial membranes demonstrated 6 (Nerox and It4ip) and 14 nm (Reatrack) differences. Non-ideal cylindrical shape of pores was reported earlier by other researchers. For example, [10–12] relate this observation to accelerated ion energy onto the membrane surface. When surfactant is applied along with the etchant, it can be explained by the hindered diffusion of surfactants into the nanochannels [13]. Since in the current study surfactant was not used, the latter explanation can be discounted.

4. Conclusions

This work focused on the development of microfiltration track-etch membranes and the comparison of their operating parameters with those of commercially available samples. The experimental data demonstrated that the developed membranes possess higher water flux and mechanical strength compared to commercial membranes. It has also been shown that the equipment and methods used in this research can be used to develop ultrafiltration track-etch membranes of between 25 to 100 nm pore sizes (not shown). Furthermore, it should be mentioned that the selling price of the developed membranes is in the range of the commercial samples (~20 USD/m^2), which is much lower than track-etch membranes produced by other membrane manufacturers. The data obtained in this study confirms our belief that Kazakhstan has the capacity of developing into a track-etch membrane manufacturing country enabling it to solve locally many of the problems which it now faces as a result of issues associated with clean water demand.

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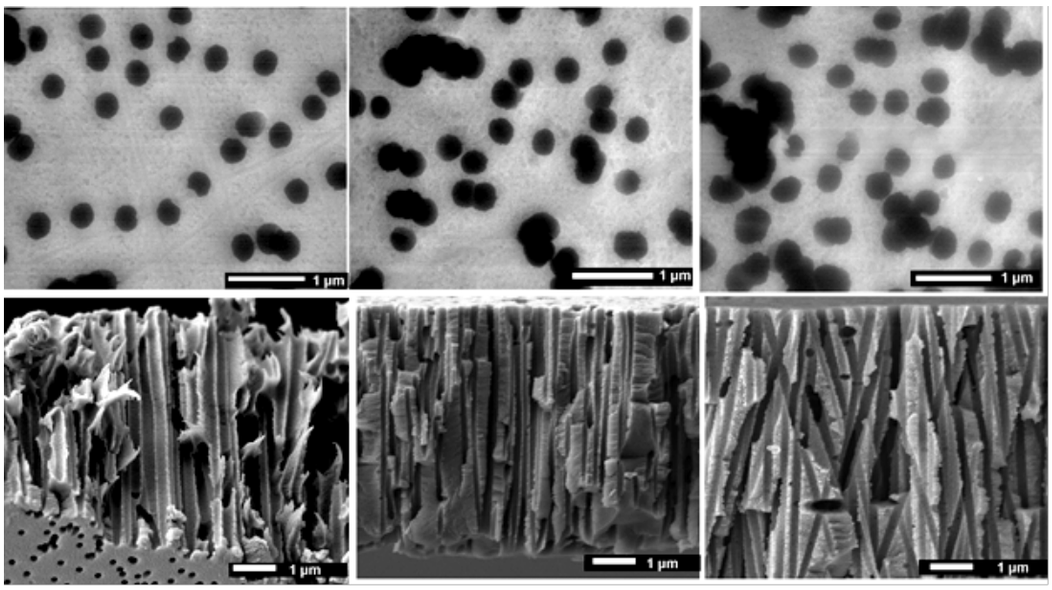

Fig. 6. SEM images of commercial available membranes: It4ip (left column), Nerox (middle column), Reatrack (right column). Top row shows the front face side of the membranes, bottom row gives the cross section.

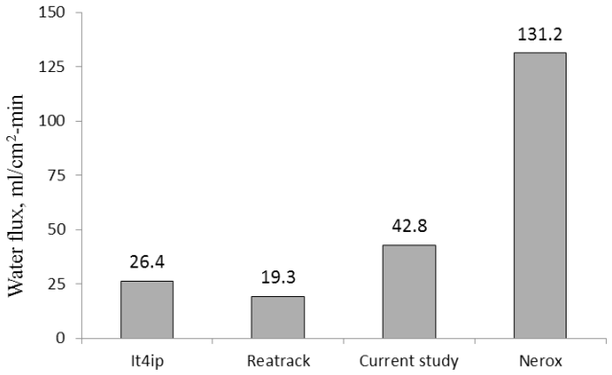

Fig. 7. Water flux of membranes developed in this study (270 s etching) compared to the commercial samples.

Symbols

- A — Area of filtration
- d — Pore diameter
- J — Water flux
- m — Weight of collected permeate
- P — Bubble pressure
- t — Time interval
- γ — Liquid surface tension
- θ — Contact angle of liquid on the pore wall
- ρ — Density of permeate filtrated through the membrane

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