# PRODUCTION AND PROPERTIES OF POLYPROPYLENE TRACK MEMBRANES

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Received July 30, 1996
Accepted November 29, 1996

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This paper describes results of the method of manufacturing the polypropylene track membranes produced by physicochemical treatment under irradiation of accelerated heavy ions of polymer films. The developed method allows to produce membranes with pores of 0.1–0.2 μm in diameter and more, with an improved structural and physicochemical properties. Polypropylene track membranes of a novel sample are characterized by high homogeneity of pore sizes in magnitude, considerable mechanical strength, advanced thermal stability and resistance to oxidation in aggressive media. It opens new fields for their usage.

**Key words:** Track membrane; Polypropylene; Accelerated heavy ions; Chemical etching; Sensitization.

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The track membranes (TM) obtained by irradiation of polymeric films with high energy heavy ions and their subsequent physicochemical treatment[1,2] are used for purification and separation of fluid and gaseous media in electronic engineering, medicine, and biotechnology. Their small thickness, high separation selectivity, and easy regeneration stand them out sharply against the filtering materials of other types. However, the track membranes produced by industry from poly(ethylene terephthalate) and polycarbonate are not applicable to active media with high values of pH and in concentrated mineral acids. To produce the TM possessing the high chemical resistance, polypropylene (PP) can be considered as a source polymer.

When producing the track membranes, main goals arise – to search for selected etchants compounds and to develop the track sensitization methods. A compound for the track etching in polypropylene (sulfuric acid saturated with potassium dichromate) was suggested for the first time in ref.[3]. The authors of ref.[4] obtained the polypropylene track membranes (PPTM) with conical pores in view of low etching selectivity (the ratio between longitudinal and radial rate of track etching). Up till now an objective regularity of the chemical etching of polypropylene[5] has been studied, and track sensitization methods increasing the etching selectivity have been developed[6,7]. They allow to produce PPTM with cylindrical pores of 0.4 μm in diameter and more. However, the restricted etch selectivity caused by using of the inefficient etchant results, first of all, in generating a heterogeneous pore size and, secondly, does not permit to produce PPTM with the cylindrical pores of a diameter of less than 0.4 μm. So the search for more affective etching compounds is of practical interest. Besides, the produced polypropylene membranes are of low mechanical strength and subject to damage. Even short exposure to light and heat causes a complete destruction of the membranes.

The purpose of the present investigation is the elaboration of polypropylene track membranes with an improved structural and physicochemical properties.

## EXPERIMENTAL

A biaxially oriented polypropylene film produced by Toray Co. (Japan) was used. The film was 10 μm thick and contained 0.50 ± 0.04% antioxidant Irganox 1010. The sample was irradiated by xenon ions (1 MeV/nucleon) or krypton ions (3 MeV/nucleon) from U-400 cyclotron in the JINR Laboratory of Nuclear Reactions. The sample was etched in chromium(VI) solutions. The etching conditions (reagents content temperature and time of etching) were varied. The longitudinal track etch rate ($v_t$) was determined by using a conductivity technique according to the time of generating the holes[8]. The radial track etch rate ($v_r$) as well as the pore diameter on the membrane surface were measured by the electron microscope JSM-840. The distribution on pore size has been measured with the help of the Coulter Porometer II (Coulter Electronic Ltd).

Mechanical strength of the membranes was determined by a pressure difference when the sample placed in the holder with a round hole of 1 $cm^2$ square is damaged. The membranes resistance to oxidation is estimated according to their mechanical resistance to light and heat[9]. The chromium impurity was determined after damage of an adsorbed chromocontaining layer by treating 30% aqueous solution of hydrogen peroxide while boiling by means of spectrophotometry of chromium(VI) concentration in the obtained solution. Spectrophotometer Specord M-40 was used. Determination response is $2 \,.\, 10^{-3}$%.

The results obtained were processed by standard methods of mathematical statistics. The confidence interval corresponds to the reliability index 0.95 (ref.[10]).

## RESULTS AND DISCUSSION

The investigation on etching polypropylene has allowed to see following general rules. While etching a PP-film in the chromium(VI) solution, the film is oxidized intensively, so on the membranes surface and on the pores walls a polymeric layer with a damaged structure is formed. Moreover, the depth of the layer depends on the etchant, temperature and time of etching[11]. In the process of oxidation the antioxidant serving as a radical acceptor, is depleted[12]. The formation of the damaged layer and the decrease of the antioxidant influence the membranes properties.

Table I gives the parameters of the PPTM obtained under different etching conditions at 80 °C. The etching time is chosen in order to produce pores of 0.30 μm in diameter on the surface of the membranes. It can be seen that the membranes obtained by etching in sulfuric acid solution of potassium dichromate are of lowest mechanical strength. That can be explained a long etching time (70 min) required for the production. The prolonged etching caused by its low rate leads to forming a damaged layer of a considerable depth, and essential part of the membrane matrix is destructed, and its strength is decreasing. Besides, the prolonged etching results in full oxidant depleting. If the oxidant is absent, it is impossible to produce the oxidation-resistant membranes. Even a short exposure to light and heat causes a complete destruction of the membranes and shortens their useful life (Fig. 1, curves *1*).

The use of chromic anhydride ($CrO_3$) possessing better water solubility, if comparing to potassium dichromate, allows to increase chromium(VI) concentration in the solu-

TABLE I

Etching PP-films in different media at 80 °C. Films are exposed to xenon ions, pore density is $10^8$ $cm^{-2}$

| No. | Etching agent (solution) | Time, min | Pore diameter, μm | | $p_d$ $10^5$ Pa |
|---|---|---|---|---|---|
| | | | on surface | effective | |
| 1 | $H_2SO_4$ (ρ = 1.44 $g/cm^3$) + $K_2Cr_2O_7$ (50 g/l) | 70 | 0.30 | 0.10 | 0.95 |
| 2 | $H_2SO_4$ (ρ = 1.30 $g/cm^3$) + $CrO_3$ (250 g/l) | 15 | 0.30 | 0.25 | 1.90 |
| 3 | Aqueous $CrO_3$ (1 000 g/l) | 10 | 0.30 | 0.30 | 2.40 |
| 4 | Aqueous $CrO_3$ (1 000 g/l) | 4[a] | 0.30 | 0.30 | 2.85 |

[a] Etching at 80 °C till 0.10 μm pore diameter, then at 20 °C.

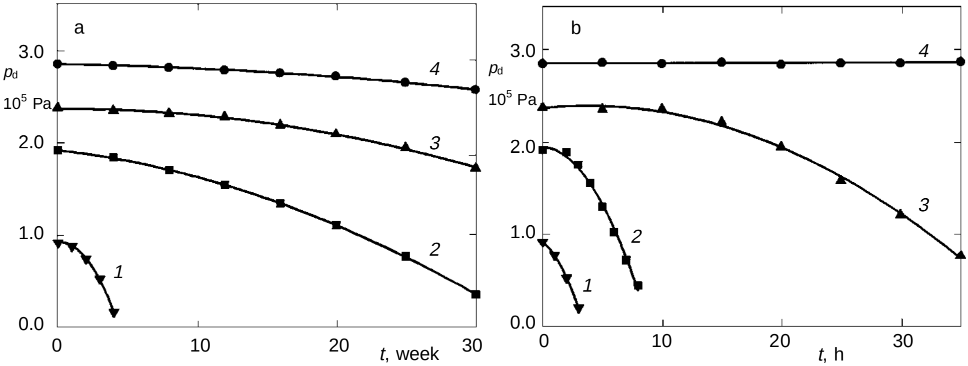

FIG. 1

Alteration of the mechanical strength of the PP track membranes produced by etching in various media (the numbers of the curves correspond to the numbers of the membranes in the Table I) at aging: a under the natural conditions in light; b in air at 140 °C tion that increases the rate by an order and shortens the etch time. That leads to increasing the mechanical strength of the membranes (Table I, No. 2) and their oxidation resistance – the time till the complete damage of the membranes (see Fig. 1, curves *2*). In this case a damaged layer of a lower depth is formed, and the membranes matrix contains some amount of antioxidant.

Decrease of sulfuric acid concentration in the solution leads to both increasing solubility of chromium anhydride and decreasing, as found in ref.[13], extent of polypropylene oxidation. The exclusion of the sulfuric acid etchant out of the compound decreases drastically the membrane oxidation extent leading to the additional increase of the mechanical strength (Table I, No. 3). However, such membranes are not oxidation-resistant enough (Fig. 1, curves *3*). The etch time seems to be much enough.

Evidently, to improve the operating features of the membranes, the etch time at elevated temperature should be shortened. For this purpose we used a two-stage etching procedure. At the first stage the short-term etching at 80 °C makes holes with a possibly small pore diameter in the irradiated film. The subsequent etching at room temperature (15–30 °C), *i.e.* at lower thermooxidation destruction rate, makes the pores of a given size[14]. The use of the suggested procedure of the track etching allows to produce PPTM which are not inferior in the strength to the well-known poly(ethylene terephthalate) track membranes (Fig. 2) and resistant to oxidation (Fig. 1, curves 4). Decrease of the etching procedure at elevated temperature allows to relieve oxidizing and to preserve the content of antioxidant at the considerable level 0.42 ± 0.04%. The second-stage etching does not cause additional oxidation and leads to etching the oxidized surface layer developed at the first stage. Evidently, the duration of the second stage should be enough to remove the oxidized layer. The absence of the surface damaged layer and the membranes with a high content of antioxidant provide a higher strength and oxidation resistance. The membranes developed under the mentioned conditions are taking some more features, *e.g.*, the maximal working temperature is increasing up to 140 °C. So their sterilization by aqueous vapor is getting possible. Their stability in aggressive

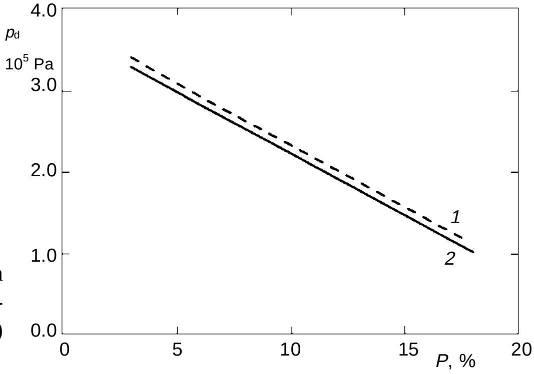

FIG. 2
Dependence of the mechanical strength upon the porosity of the track membranes produced out of poly(ethylene terephthalate) (*1*) and polypropylene (*2*)

media is increasing. For instance, the long-time effect (30 days) at room temperature to the concentrated solutions of mineral acids and sodium hydroxide does not change practically such membranes's features as gas permeability and the burst strength (Table II).

The production of PPTM with the improved characteristics can be reached only if all stages of the chemical etching are executed in the mentioned sequence. A change of this order does not lead to the desired result because etching at elevated temperature on the second stage causes increasing the destructed layer and, therefore, inflicting the quality of the membranes. Etching at elevated temperature is necessary to develop the holes of cylindrical shape. Etching should be performed at 60–100 °C. This temperature interval is characterized by most track etch selectivity. At a temperature lower than 60 °C and more than 100 °C the selectivity is reduced, as shown in ref.[6]. This leads to changing the structural characteristics of the PPTM, *i.e.* the pores get a conical shape. Therefore, etching should be performed at possibly low temperature on the second stage. It should be noted that there is a little point in second etching at temperature lower than 10 °C, since in doing so the etching time is increasing drastically and the whole process is not effective.

The coincidence of the effective pore diameter and the surface pore diameter for the membranes No. 3 and 4 (etching in chromic anhydride, 1 000 g $l^{-1}$) points at forming the cylindrical pores. Therefore, this etchant is most selective, if comparing to the other ones presented in Table I. However, even the use of this etchant does not allow producing the PPTM with cylindrical pores of less than 0.2 μm in diameter. To produce them, the etch selectivity should be improved. This can be reached by applying a sensitization consisting in strengthening the track destruction processes. When applying the sensitization method suggested in ref.[6], *i.e.* the PP-film exposed to accelerated ions are heat treated in air at temperature 80–105 °C, the etching selectivity increases as much as twice (Table III). In case of etching in a water solution of chromic anhydride, the obtained value $v_t/v_r = 600$ provides both the formation of cylindrical pores of less than 0.2 μm in diameter and the decrease of the variations in pore sizes (Fig. 3), *i.e.* provides

TABLE II
Chemical resistance of PPTM ($d_p = 0.25$ μm, pore density is $2 \cdot 10^8$ $cm^{-2}$). Exposure to aggressive media is 30 days

| Parameters | Media, mass % | | | | | |
|---|---|---|---|---|---|---|
| | None | NaOH, 20 | $H_2SO_4$, 96 | $HNO_3$, 56 | HCl, 35 | HF, 35 |
| Air flow rate[a], l/h $cm^2$ | 230 | 235 | 245 | 240 | 235 | 240 |
| Burst strength, $10^5$ Pa | 2.75 | 2.65 | 2.55 | 2.50 | 2.70 | 2.65 |

[a] Measured at the pressure of $10^5$ Pa.

the membranes of homogeneous structure. Besides, the sensitization provides a way for using the ion beams of less atomic mass for irradiation. For instance, etching the krypton ion trucks, $v_t/v_r = 340$, allows to develop top-quality PPTM.

When etching a polypropylene film in chromium(VI) solution, chromocontaining compounds not removed by running water completely, are formed on the surface of the membranes, as the microelement test shows. As a result, the membrane matrix is contaminated and is not purified fully from etching tracks. For instance, if filtering aggressive liquids destroying the adsorbed chromic compounds, the filtrate is contamined. Besides, the chromium impurity accelerates the oxidizing destruction processes leading to the drastically of membranes quality[15]. In order to destroy the adsorbed chromocontaining layer, the membranes were treated by concentrated solutions of mineral acids at 70 °C, that decreased the pollution of their surface[1] (Table IV, No. 2). However, the use of the mineral acids, *i.e.* nitric and sulfuric acids which are strong oxidizers, leads to a

Table III
Influence of the sensitization of ion track on the etch selectivity ($v_t/v_r$) of PP at 80 °C. The films were exposed to xenon ions (No. 1–3) or krypton ions (No. 4)

| No. | Etching agent (solution) | $v_r$ μm/min | Without sensitization | | With senzitization | |
|---|---|---|---|---|---|---|
| | | | $v_t$, μm/min | $v_t/v_r$ | $v_t$, μm/min | $v_t/v_r$ |
| 1 | $H_2SO_4$ ($\rho = 1.44$ g/cm$^3$) + $K_2Cr_2O_7$ (50 g/l) | 0.0022 | 0.085 | 40 | 0.16 | 70 |
| 2 | $H_2SO_4$ ($\rho = 1.30$ g/cm$^3$) + $CrO_3$ (250 g/l) | 0.012 | 1.45 | 120 | 3.35 | 290 |
| 3 | Aqueous $CrO_3$ (1 000 g/l) | 0.015 | 4.25 | 285 | 9.0 | 600 |
| 4 | Aqueous $CrO_3$ (1 000 g/l) | 0.015 | 2.50 | 165 | 4.50 | 340 |

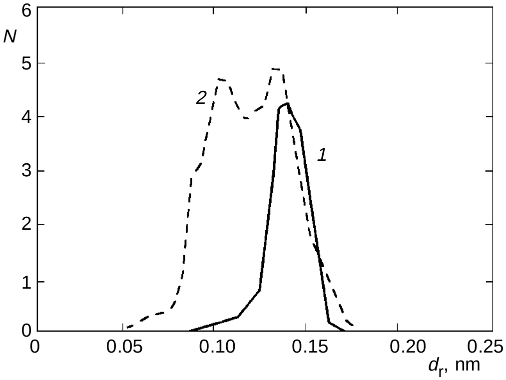

Fig. 3
Pore distribution curves over the pore diameters: *1* the sensitized PPTM, $v_t/v_r = 600$, *2* the non-sensitized PPTM, $v_t/v_r = 40$

polymer macromolecules destruction. Thus, the mechanical strength of the membranes is decreasing. Clearly, in order to keep the PPTM properties and to remove the chromium compounds, a reagent should be used that does not initiate oxidizing polypropylene. The use of hydroxide solution of the chromocontaining compounds takes place as a result of hydrolysis. The chromic compounds are removed from the membranes surface with running water. This technique does not reduce the strength of the membranes and at the same time drastically reduces the chromium content in them (Table IV, No. 3).

The use of the aqueous alkaline solutions possessing a high value surface tension does not permit a deep purification of the surface of PPTM with a small pore diameter. For example, while treating the membranes of the pore diameter of ≈0.3 μm by aqueous sodium hydroxide solution, the pores surface is not moistened, and the removal of the chromium compounds takes place only from the external membranes surface, because the PPTM are characterized by hydrophobic features (the value of the water contact angle is 115°). The introduction of alcohol into the alkali aqueous solution (or else the use of alkali aqueous solution) reduces the surface tension of the solutions. This leads to penetration of the hydrolyzing agent (ions $OH^-$) into the tracks and full cleaning the PPTM matrix of the chromium impurities (Table IV, No. 4 and 5). The problem can also be saved be means of the realization of this phase by sequential treatment in alcohol and aqueous solution of hydroxides of alkali metals (Table IV, No. 6).

Thus, the suggested procedure includes the following stages: (i) irradiation of the polypropylene film by high energy heavy ions; (ii) sensitization of particle tracks by burn in air; (iii) track etching in aqueous solution of chromium anhydride with concentration of 1 000 g/l at the temperature 60–100 °C till formation of holes of small size;

TABLE IV
Cleaning the PPTM ($d_p$ = 0.3 μm) of chromium impurity ($c_i$)

| No. | Reagent (aq. solution, mass %) | Treatment condotions | | $c_i$ mass % | $p_d$ $10^5$ Pa |
|---|---|---|---|---|---|
| | | °C | min | | |
| 1 | None | – | – | 0.054 | 2.95 |
| 2 | 50% $HNO_3$ | 70 | 30 | 0.016 | 1.55 |
| 3 | 5% NaOH | 50 | 10 | 0.007 | 2.80 |
| 4 | $C_2H_5OH$ + 2% KOH[a] | 40 | 15 | not detected | 2.85 |
| 5 | 20% $C_2H_5OH$ + 4% NaOH[a] | 40 | 15 | not detected | 2.80 |
| 6 | Isopropyl alcohol;<br>10% NaOH[b] | 25<br>40 | 5<br>10 | not detected | 2.75 |

[a] A mixture was used. [b] Sequential treatment.

(iv) etching in aqueous solution of chromium anhydride with the same concentration at room temperature till forming the pores of given size; (v) removal of the chromium compounds adsorbed on the membrane surface during the etching. Our etching method differs from the traditional one. It consists of two stages and improves a number of important membranes features. The introduction of the extra stage for removing the adsorbed chromic compounds improves the PPTM characteristics.

In Fig. 4 are shown microphotographs of the surface and cross-section of PPTM with pore size of 0.30 μm in diameter. In view of the fact that the pores in PPTM are cylindrical channels, cross-sections of which are independent of the depth. The polypropylene track membranes have a smooth surface. Their advantage is in small adsorption of the dissolved substances. The PPTM can also be successfully applied to cleaning gaseous media of moisture. High chemical resistance allows one to use PPTM in microfiltration processes on purification and analysis of aggressive media. The possibility of sterilization makes them attractive for medical purposes. At present the JINR produces the PPTM with the parameters given in ref.[16].

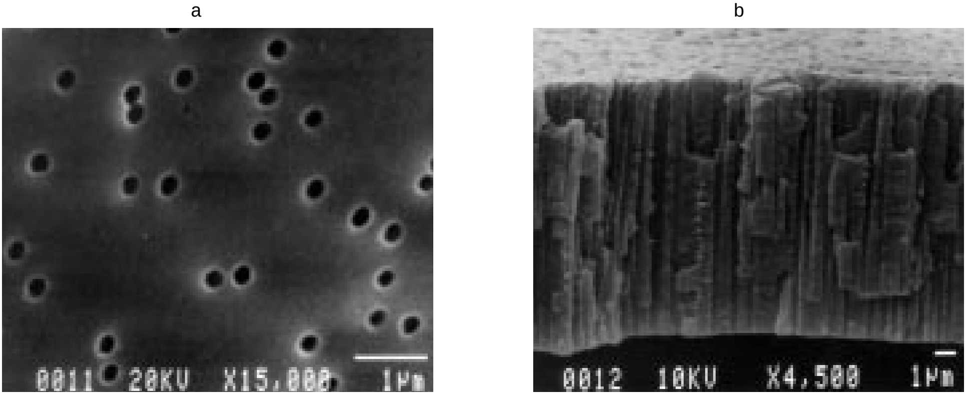

FIG. 4
Microphotographs of the surface (a) and of the cross-section (b) of a PPTM with the pore size of 0.30 μm in diameter

## SYMBOLS

| | |
|---|---|
| $d_p$ | pore diameter, μm |
| $N$ | number of pores, arbitrary units |
| $P$ | porosity, % |
| $p_d$ | burst strength, Pa |
| $v_t$ | longitudinal track etch rate, μm/min |
| $v_r$ | radial track etch rate, μm/min |
| $\rho$ | density of solution, g/cm$^3$ |

*The authors are very grateful to O. L. Orelovich for his help in performing the electron-microscopic measurements.*

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