

Production of Nuclear-Track Etched Membranes

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ABSTRACT Track etched membranes were prepared in the laboratory by exposing commercially available polycarbonate sheets of 6 μm thickness to alpha particles emitted from nuclear reaction of (n, alpha) followed by chemical etching. A series of membranes were produced using different bombardment and etching periods and the hydraulic conductivity of the resulting porous membranes were measured for applied pressures from 10 kPa to 50 kPa. It was noted that at higher pressures the hydraulic conductivity declined with pressure, probably because the track etched pores, as evidenced by atomic force microscopy, were not normal to the membrane surface and this may have caused a partial collapse of the pores at higher pressures. It was found that a two hour (n, alpha) bombardment at $6.5 \times 10^8 \text{ neutron.m}^{-2}.\text{s}^{-1}$ flux together with a five minute etching in 6N NaOH at 85°C produced membranes with a hydraulic permeability for water of $158 \times 10^{-10} \text{ m}^3.\text{N}^{-1}.\text{s}^{-1}$, which is comparable with that of a commercial ("Millipore") MF membrane.

KEYWORDS: water flux, hydraulic permeability, track etched membrane.

INTRODUCTION

Membrane filtration technology has become increasingly important in the food processing, pharmaceutical and biotechnology industries as well as in the treatment of waste fluids and water purification. The latter is assuming a greater significance and will play a vital role in socio-economic development in the future. Membrane technology may be used to clarify water, to remove colour, KMnO_4 , iron, manganese and aluminium as well as heavy metals from water supplies.^{1,2}

Membranes used in these separation processes can be categorised into micro-filtration (MF), ultra-filtration (UF), nano-filtration (NF) and reverse osmosis (RO). These categories are based on the effective size of the membrane pores or the size of particles to which the membrane is impermeable. Thus MF membranes normally retain particles and living organisms of 0.02 - 10 μm whilst UF membranes retain particles in the range 0.001 - 0.02 μm .³ To remove ions such as Na^+ membranes are required with even smaller pore sizes; these are generally referred to as reverse osmosis (RO) membranes. To use RO membranes for desalination requires high pressures.

Commercially available membranes are costly and in order to promote both research and development

of applications of membrane technology in Thailand it is desirable therefore to establish methods for the low-cost, local, manufacture of membranes. Initially the requirement is for low volume production of membranes for use in research within academic institutions and later for larger manufacturing of membranes for applications in the field. The study described in this paper is a trial of bombardment and etching techniques to investigate the feasibility of meeting market requirements.

One method for the manufacture of porous membranes is to bombard polymer films with alpha particles emitted by nuclear reactions (n, alpha) followed by chemical etching of the track left by the nuclear particle.^{4,5} It is known that this technique produces very high quality membranes with relatively uniform pores. Making pores in polymer membranes, however, is dependent on the properties of the material used and some of the parameters need to be determined empirically. The pore size in this process of manufacture is controlled by the chemical etching period whilst the pore density is controlled by the exposure time to the nuclear radiation.

Here we describe the manufacture of symmetric "track-etched" membranes from polycarbonate films and characterisation of their hydraulic permeability compared to commercially available track-etched membranes made of the same material.

MATERIALS AND METHODS

Transparent sheets of polycarbonate films (Oxford, England), were bombarded with alpha particles and etched with 6 N NaOH at 85°C. The neutron flux used to produce alpha particles was $6.5 \times 10^8 \text{ m}^{-2} \cdot \text{s}^{-1}$ and the exposure time to the radiation as well as the etching time were varied to obtain, respectively, different pore densities and pore sizes.

To determine the hydraulic permeability of the membranes, the membranes were mounted in a "dead-end" pressure driven filtration chamber as shown in Fig 1. De-ionised water was used for the feed solution and flux measurements were made for applied pressures in the range 0-50 kPa; the pressure was applied via compressed nitrogen gas. The water permeate was collected in a collection vessel placed on a digital balance interfaced with a computer. This allowed direct calculation of fluxes from changes with time of the total permeate collected. Measurements were also made on a commercial MF track-etched membrane (Millipore 0.2 μm pore size). The hydraulic permeability coefficient (L_p) for each membrane was estimated from the slope of a plot of the water flux (ΔJ) as a function of pressure (ΔP). When the applied pressure was increased the volume flow rate was referred to as forward flux, and the reverse was reverse flux. The thickness of the nuclear-pore membranes produced was 6 mm whilst the Millipore membranes had a thickness of 10 mm. The thickness was measured using a micrometer. The area of all membranes used were $15.2 \times 10^{-4} \text{ m}^2$, limited by the geometry of the feed unit in Fig 1.

RESULTS AND DISCUSSION

Water fluxes

The permeate flux as a function of pressure difference for one of the nuclear-track etched membranes is shown in Fig 2 (a). It can be seen that the fluxes were close to linearly dependent on the applied pressures, as expected, over the pressure range between 10-60 kPa. There appeared to be a small difference between the forward and reverse hydraulic permeabilities, particularly for the membrane made with a 30 minute exposure to (n, alpha) nuclear reaction, as evidenced by the slight differences in the slopes of the plots. The membrane produced using a 60 minute bombardment time (06005) had a slightly higher hydraulic permeability than the 30 minute one. A stronger dependence on nuclear bombardment time was expected since the pore number density should have increased with bombardment time. The somewhat lower slope of the flux-pressure plots for the reverse fluxes for R06005 than R03005 might reflect asymmetries in the pores which led to an effective partial closure when the membrane is pressurised from the reverse side.

When the bombardment time was increased to 120 minutes (F12005), a further and much greater increase in permeability was obtained. The results for this membrane are shown in Fig 2b. The fluxes as function of pressure for this membrane were comparable to that of a 0.2 μm nominal pore size commercial track etched membrane (0.2 μm "Millipore"). When the membrane was dried out at room temperature and flux measurements repeated, similar results were obtained.

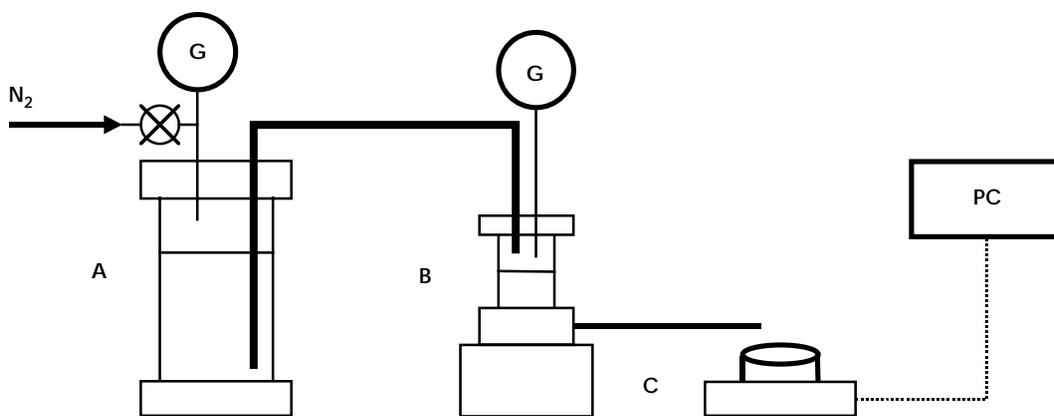


Fig 1. Schematic representation of experimental set up. A is the feed reservoir, B feed unit, C permeate container and electronic balance, G pressure gauge, PC computer, $\rightarrow \text{N}_2$ gas line and $--$ water lines.

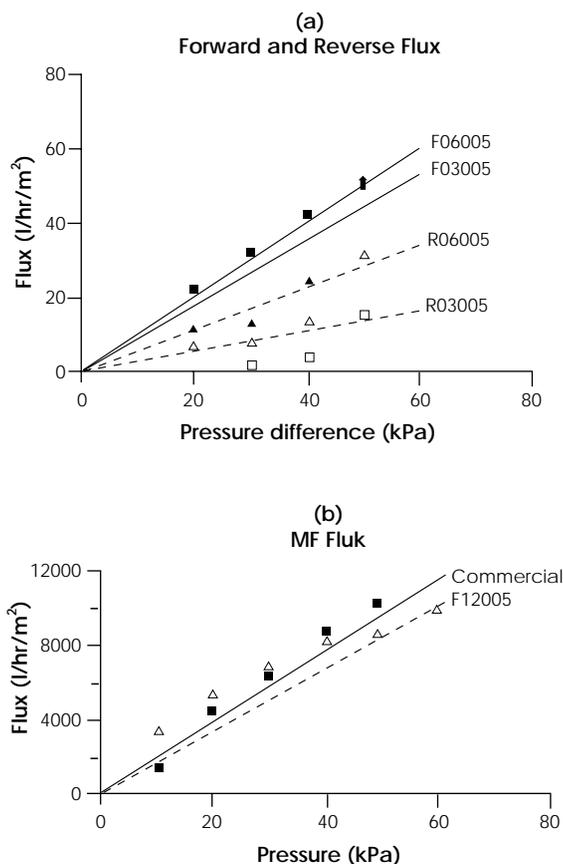


Fig 2. Water flux through membranes produced with different alpha particle radiation exposure periods. (a) Forward and reverse fluxes for membranes produced with 30 minute and 1 hour exposure and 5 minutes chemical etching. (b) Comparison between the forward flux through a membrane produced with 2 hour radiation exposure and 5 minute chemical etching (F12005) with a commercial MF membrane.

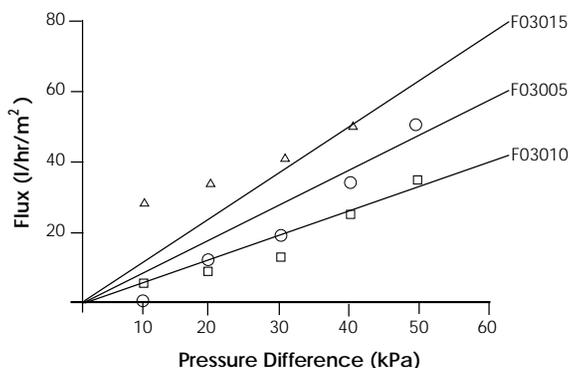


Fig 3. Water flux through a track etched membrane produced with 30 minute exposure to alpha radiation bombardment membranes, with chemical etch times of 5 minutes (F03005), 10 minutes (F03010) and 15 minutes (F03015).

There was some indication that the fluxes at higher pressures increased less than linearly with pressure. One explanation for this is that the pore sizes decrease as the pressure increases. This could occur, for instance, if the pores are not normal to the surface. Atomic Force Microscopy (AFM) of the membrane surfaces provided evidence that this indeed was the case. Fig 4 shows AFM images of the surfaces of a F03005 membrane and a commercial membrane. As can be seen, the pores in the locally track etched membrane are not normal to the membrane surface.

Hydraulic Conductivity

Table 1 shows estimations of hydraulic permeability coefficient (L_p) of the membranes, calculated from the slope of graphs. The L_p for 30 minute bombardment membranes was between 2.0×10^{-10} and $3.9 \times 10^{-10} \text{ m}^3 \cdot \text{N}^{-1} \cdot \text{s}^{-1}$, depending on the etching time. The unexpected smaller L_p of the membrane chemically etched for 10 minutes would indicate variability of some parameter such as uniformity of the polycarbonate films and orientation between the neutron source and the polycarbonate film. This variability was also evident in the dependence on nuclear bombardment time where it would have been expected that the hydraulic permeability of the membrane bombarded for 60 minutes (F06005) should have been much higher than the membrane exposed for only 30 minutes (F03005). One explanation may lie in the fact that alpha particles have a very short range (1 cm in air for 1 MeV) and the energy for alpha particles produced from the (n, alpha) reaction was about 2-3 MeV, adequate to penetrate the thin film completely. However, some longer distances may have been involved when the bombardment was not in a perpendicular manner to the membrane. Only completely penetrating tracks will produce pores after chemical etching. This could lead to variations in the number of pores in the membranes.

However, when the bombardment period was increased to 120 minutes, the hydraulic permeability increased dramatically to $158 \times 10^{-10} \text{ m}^3 \cdot \text{N}^{-1} \cdot \text{s}^{-1}$ (Fig 2b), only slightly smaller than that of the commercial MF membranes ($166 \times 10^{-10} \text{ m}^3 \cdot \text{N}^{-1} \cdot \text{s}^{-1}$). It should be noted here that the thickness of F12005 membrane was half of the commercial one and the hydraulic permeability would be expected to decrease as the membrane thickness is increased. A micrograph of the 03005 membrane obtained using Atomic Force Microscopy (AFM) is shown in Image1 and shows that pores piercing the membrane were not normal

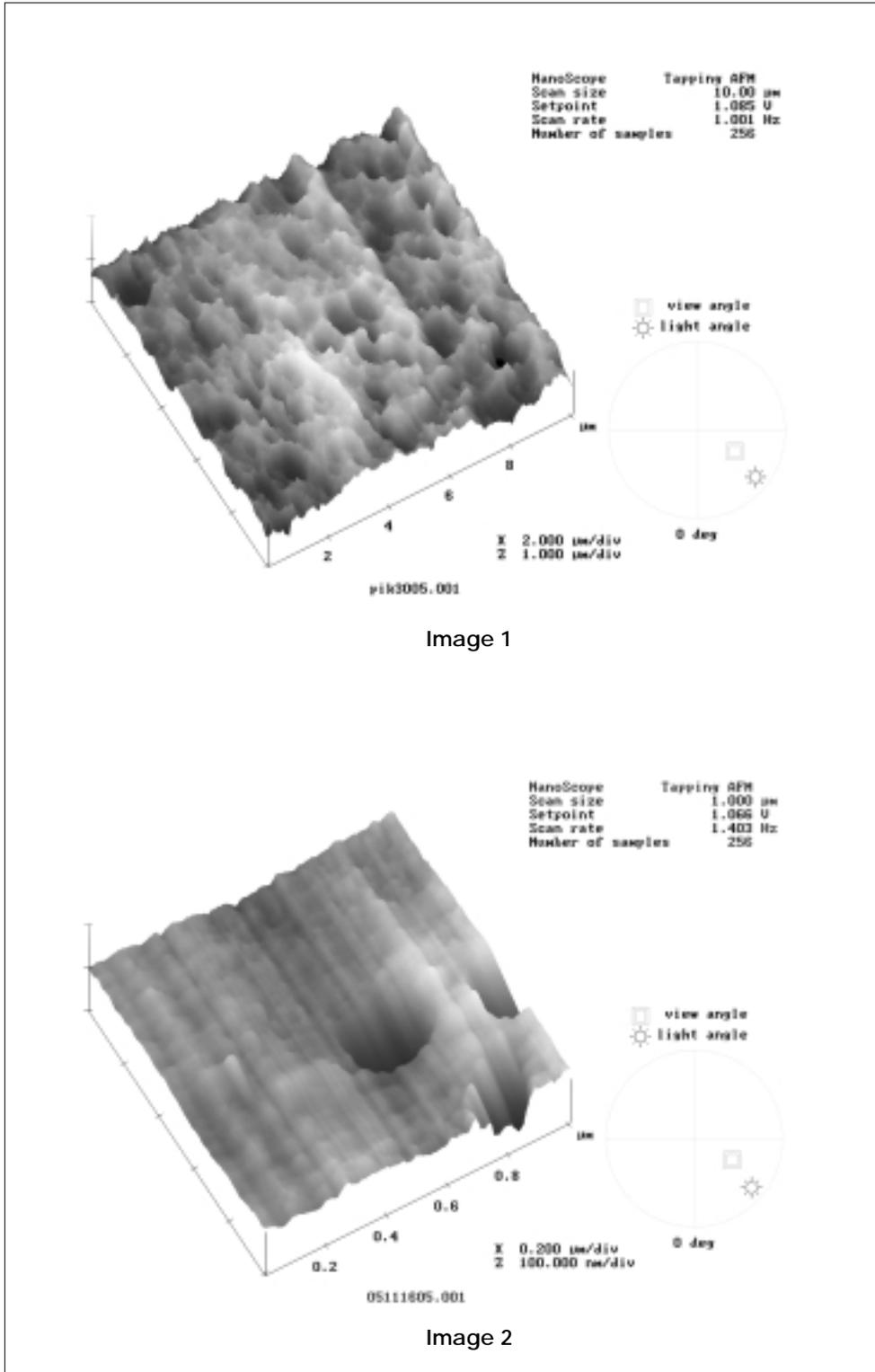


Fig 4. AFM micrographs of a locally produced track etched membrane on a polycarbonate sheet, F03005 (Image 1), and of a commercial ("Millipore") 0.2 μm membrane (Image 2)

Table 1. Estimations of hydraulic permeability coefficient (L_p) of the membranes.

Alpha Bombardment Time (minutes)	Chemical Etch Time (minutes)	Designation	L_p ($m^3N^{-1}s^{-1}$) $\times 10^{-10}$
Series 1			
30	5	F03005	3.1
60	5	F06005	3.3
120	5	F12005	158
		commercial	166
Series 2			
30	5	F03005	2.9
30	10	F03010	2.0
30	15	F03015	3.9

to the membrane surface. It is possible that at higher pressures this might cause the pores to partially collapse and this would cause a reduction in the hydraulic permeability. There is some evidence that this occurred; for instance the flux as a function of pressure rolled off (below the initial more linear relationship) in the results shown in Fig 2b for the F12005 membrane.

CONCLUSION

Measurements of water permeabilities have shown that bombardment of polycarbonate films with (n, alpha) nuclear reaction of $6.5 \times 10^8 \text{ m}^{-2} \cdot \text{s}^{-1}$ neutron flux for 120 minutes, followed by chemical etching in 6N NaOH at 85°C for 5 minutes produced membranes with water flux comparable to that of commercial Micro Filtration membranes. Etching time could be increased to obtain larger pores sizes (and hence higher hydraulic permeabilities), if required. It may be possible to produce membranes in the Ultra Filtration range by reducing the chemical etching time or altering the concentration and temperature of the NaOH. Some consideration should be given to ensure that the alpha particles strike the film normal to the surface so that the pores produced are not angled to the normal of the membranes. Further experiments are needed to explore the effect of the thickness of the polycarbonate films on the permeability of the membranes produced. For some applications the membranes need to work with large pressures and this imposes conditions on the mechanical strength of the membranes which is also related to their thickness.

It is encouraging that polycarbonate nuclear-track etched membranes comparable to commercial membranes can be readily made in the laboratory and this suggests that the application of membrane technology for waste water treatment and production of water for human consumption in Thailand might be not have to rely on costly imports.

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