ORIGINAL ARTICLE

Nuclear track-etched pore membrane production using neutrons from the Thai research reactor TRR-1/M1

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Abstract

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Songklanakarin J. Sci. Technol., 2002, 24(Suppl.) : 863-870

This work presents the results of the nuclear pore membrane production using the neutrons from the Thai research reactor TRR-1/M1 for pore piercing process on the polycarbonate thin film. With our experimental design, the fast neutron provides better results in pore piercing comparing with thermal neutron bombardment. This can be explained by most of the latent tracks produced by thermal neutron bombardment not penetrating through the thin film. Chemical etching process using NaOH solution with appropriate time, concentration and temperature is employed to enlarge the latent tracks in the bombarded film. Fast neutron bombardment with 5, 10 and 20 minutes bombarding time successfully produces the nuclear track membrane. Pore size and pore density of the produced membranes examined by SEM are 0.24 – 1.01 μm and 4.7 – 245 × 10^6 pore/cm^2, respectively. Bubble point tests show the maximum pore diameter of the produced membrane ranged between 1.18 – 3.25 μm.

Key words : nuclear track-etched pore membrane, neutrons, Thai research reactor, TRR-1/M1

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Received, 25 February 2003 Accepted, 11 July 2003

Nuclear track etching technique has triggered polymer scientists to produce a wide range of porous membranes after Fleischer and coworkers (Fleischer *et.al*, 1975) reported a novel filter for biological materials in 1964. By the early 1970s the first set of nuclear track membranes made from polycarbonate (PC) was available commercially. Ten years later, a number of works have concentrated on ion beam energy for pore piercing of pore size varing from micro to nano scale, and on the development of characterization technique for determining membrane pore size and membrane porosity (Gopalani *et al.*, 2000; Ferain and Legras, 2001; Hernandez *et al.*, 1998; Yamazaki *et al.*, 1996; Tretyakoa, 1997). The membrane is widely used for many purposes such as sensor, virus detection, high-quality water production, and laboratory filtration. With these wide applications, searching for new polymers and new particle sources for nuclear bombardment is simultaneously enhanced. Some materials for producing nuclear porous membranes have been reported by Apel (2001).

On the particle sources, thermal neutrons produced from the fission reactions in a uranium compound were used (Yamazaki, *et al.*, 1996) in pore piercing process. Some other sources were, for example, high energy (1.0-5.6 MeV/amu) heavy ions from an ion accelerator (Ferain and Legras, 1997) while Gopalani and coworkers (2000) used the high energy ions of 120 MeV. Etching time with NaOH solution was varied according to the bombarding conditions and materials used. Ultraviolet light (UV) was also introduced to the etching process (Khayrat and Durrani, 1995). In our previous study (Wanichapichart *et al*, 2000) neutrons produced from a small Pu/Be source were utilized to bombard a boron-coated plastic sheet. Alpha particles produced from ^{10}B (n,α) ^{7}Li reaction penetrated a commercial PC film of 6 μm thick, which was placed in contact with the boron surface. A bombarding time over 2 hours was needed to achieve a high pore density when using this small neutron source of a flux of 6.5×10^4 n cm^{-2} s^{-1}. This means that the process is too slow for large scale production. To overcome the time constraint, a more intense neutron source is required, which is available at the nuclear research reactor of the Office of Atomic Energy for Peace (OAEP) in Bangkok.

Materials and Methods

A commercially available PC thin film of 6 μm thickness was used in this study. The source of neutron is a 2 MW TRIGA Mark III thermal research reactor at the OAEP, which provides fast neutron flux of about 8.7×10^{10} n cm^{-2} sec^{-1}. NaOH (Merck, Germany), water bath, UV lamp (09815 series 6 watts, France) were used during chemical pore enlarging process. A Scanning Electron Microscope (SEM, JSM – 5800 LV, JEOL) and Carnoy version 2.0 software (Schols, 2001) were used to determine the pore size and pore distribution. Bubble point test technique (Hernandez *et al.*, 1998: McGuire *et al.*, 1995; Le *et al.*, 1997; Piatkiewicz *et al.*, 1999) was used to determine the maximum pore size of the produced membrane in this study. A set of commercial membranes (Millipore, Ireland) with average pore diameter of 0.2 and 0.4 μm was used as the reference standard membrane for characterization in comparison with the produced membrane.

In using thermal neutron bombardment on an enriched boron-10 neutron converter attached to the PC film, the bombarding time was varied from 15 to 35 minutes. For fast neutron bombardment, a PC thin film was put into the core of the OAEP's reactor for the bombarding time of 5, 10 and 20 minutes. Before the chemical etching process, the bombarded films were exposed to UV light for two hours in order to enhance the etching process. All films were put into a NaOH solution with etching conditions of 5 - 300 minutes etching time, 0.75 - 3.25 N and 75 - 85 ^{0}C concentration and temperature of NaOH, respectively. Maximum pore size was determined by bubble point test technique and Cantor's equation (McGuire *et al.*, 1995; Lee *et al.*, 1997).

Results and Discussion

Thermal neutron bombardment

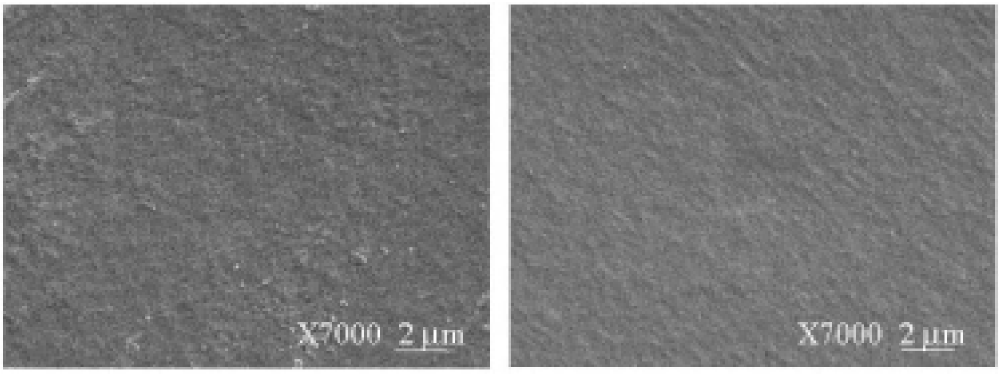
Figure 1 shows the SEM micrographs both front and rear sides of the original commercial PC thin film before bombardment with neutron and etching with NaOH solution. It can be seen that round or circular-curved tracks are present on either side of the PC film.

We can see that bombardment of the PC film with thermal neutrons from the OAEP's reactor has not been satisfactory since there are so many pores in the front side of the film only, but very few appearing on the rear side, as shown in Figure 2. We conclude therefore that thermal neutron bombardment cannot complete the pore piercing through the PC thin film.

Fast neutron bombardment

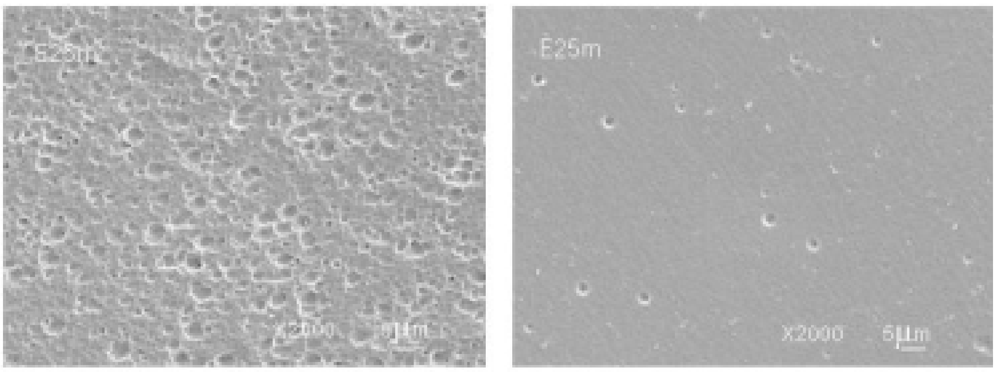
The produced membrane with fast neutron bombardment seems to be very satisfactory. The average pore diameter and pore density of the produced membrane is proportional to the fast neutron bombarding time and chemical etching conditions as shown in Table 1.

Figures 3 - 5 show the SEM micrographs



(a) front side **(b) rear side**

Figure 1. SEM micrographs of polycarbonate thin film surface with X7,000 before exposed with neutron bombardment.



(a) front side **(b) rear side**

Figure 2. SEM micrographs of the PC thin film with thermal neutron bombardment for 20 minutes and etching with 6.25 N of NaOH at 85°C for 25 minutes.

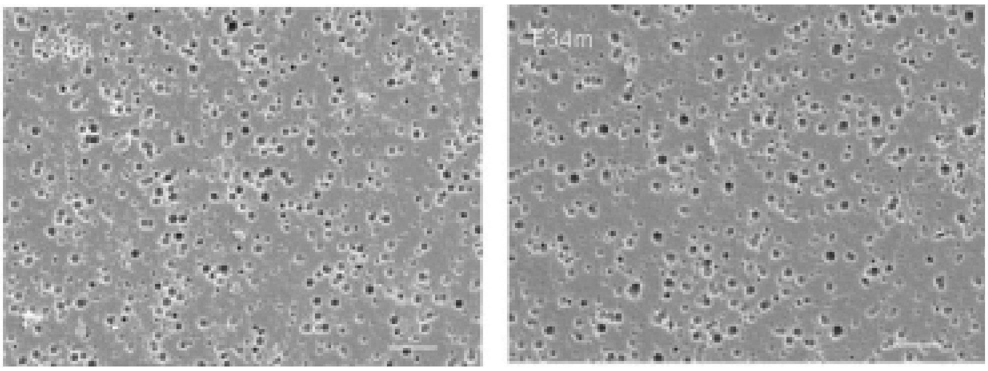
Table 1. Mean pore size (ϕ_{mean}) and pore density of the membrane produced with fast neutron at different bombarding time.

Bombarding time (min)	ϕ_{mean} (μm)	Pore density ($\times 10^6$ pore/cm^2)
5	1.0	1 – 6
10	0.4	54 - 239
20	0.3	57 – 337

of the produced membrane for both the front and rear sides with the fast neutron bombardment time of 5, 10 and 20 minutes, respectively. Similar micrographs taken with the commercial membrane (Millipore) are shown in Figure 6.

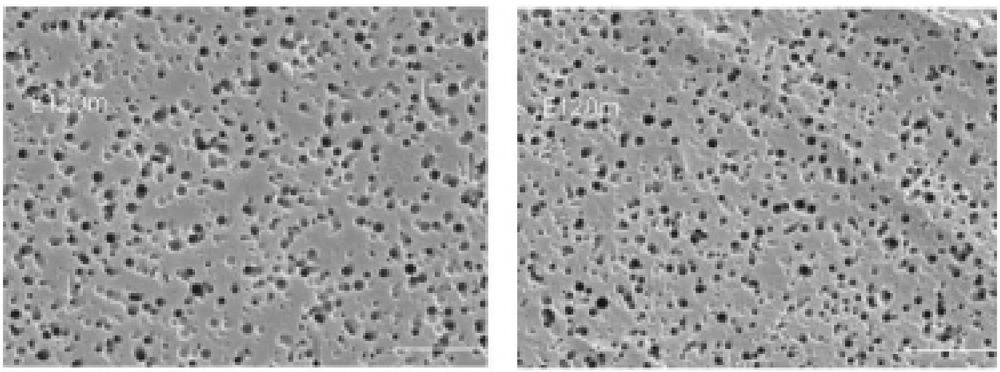
Determination of pore size distribution

In determination of mean pore size and pore size distribution using SEM image analysis and the Carnoy computer program, the result are presented in Figures 7-8 and Table 2. Figure 7 shows the histograms of pore size distribution both front and rear sides of the membrane produced by fast neutron at 20 minutes bombarding time. The mean pore size and pore density deter-



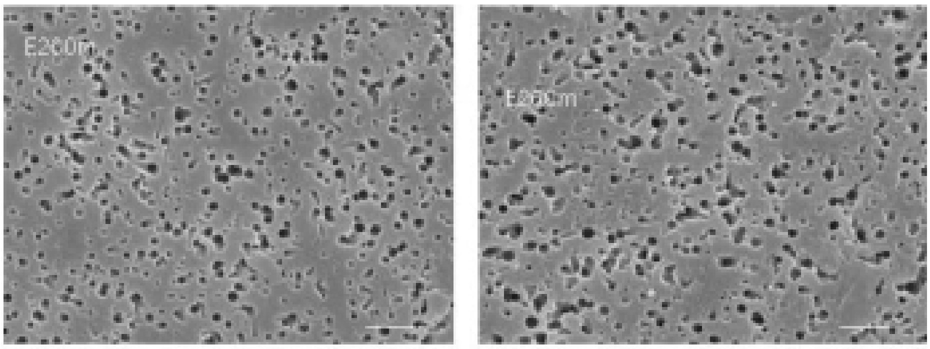
a) front side **b) rear side**

Figure 3. SEM micrographs at X2000 of the produced membrane with 5 minutes fast neutrons bombarding time.



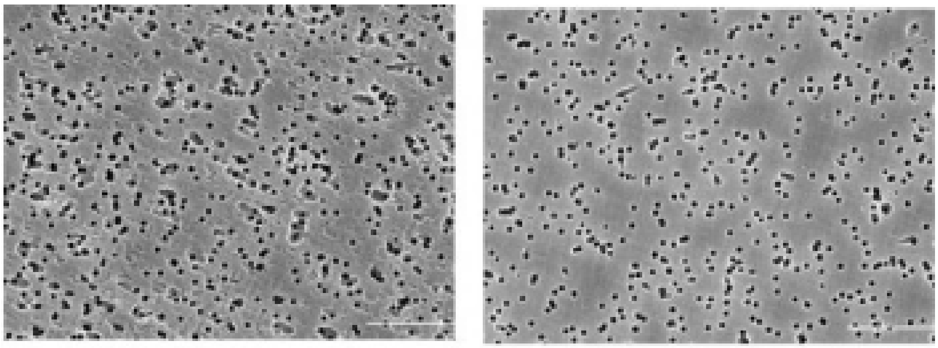
a) front side **b) rear side**

Figure 4. SEM micrographs at X5000 of the produced membrane with 10 minutes fast neutrons bombarding time.



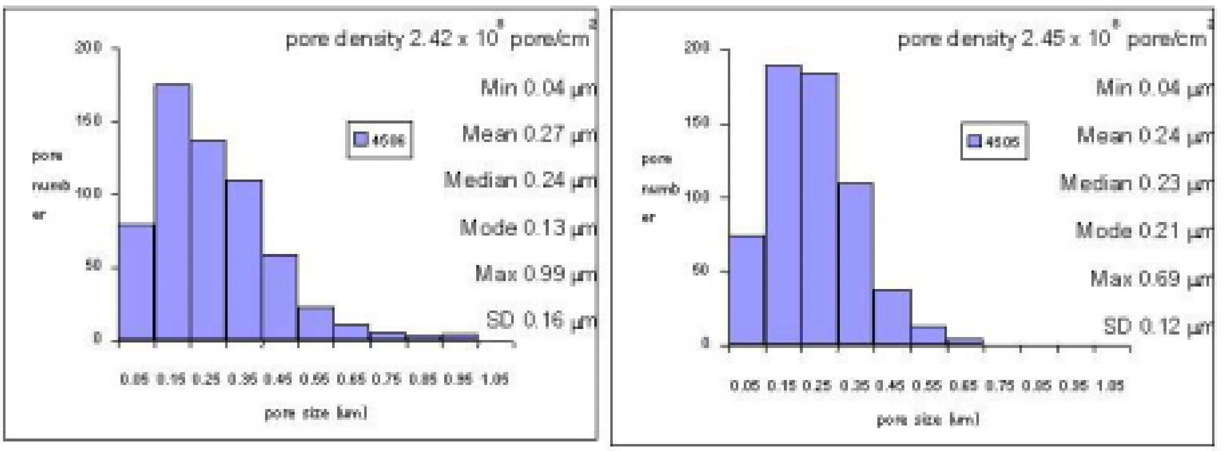
a) front side **b) rear side**

Figure 5. SEM micrographs at X7000 of the produced membrane with 20 minutes fast neutrons bombarding time.



a) front side **b) rear side**

Figure 6. SEM micrographs at X5000 of commercial membrane (0.4 mm pore diameter)



front side **rear side**

Figure 7. Pore size distribution and pore density of the produced membrane with 20 minutes fast neutrons bombarding time estimated by Carnoy program.

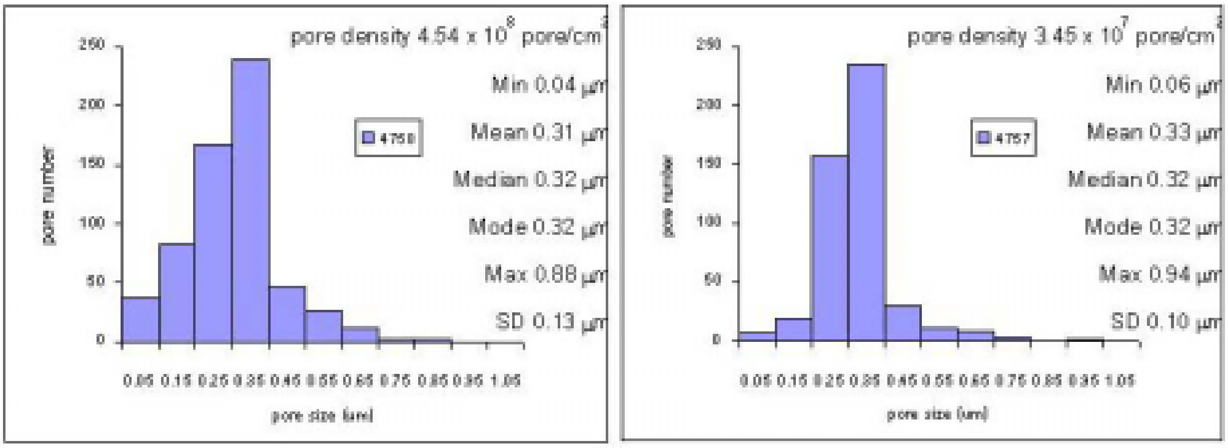


Figure 8. Pore size distribution and pore density of the commercial membrane with the certified pore diameter of 0.4 µm estimated by Carnoy program

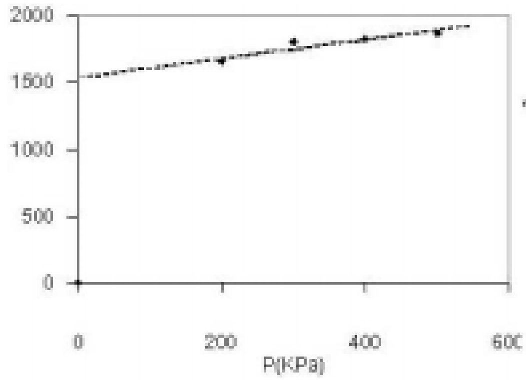
Table 2. Results of the analyses for ϕ_{mean} , pore density, standard deviation (SD), and f_{max}, by SEM, Carnoy program and by bubble point test.

Properties	Commercial membrane				Produced membrane by fast neutron bombarding time (min)					
	ϕ = 0.2 mm		ϕ = 0.4 mm		5		10		20	
	front	rear	front	rear	front	rear	front	rear	front	rear
ϕ_{mean} (µm) by SEM	0.17	0.22	0.33	0.31	1.00	1.01	0.38	0.34	0.24	0.27
Pore density by SEM ($\times 10^6$ pore/cm^2)	337	370	34.5	45.4	4.67	5.43	136	140	245	242
SD	0.05	0.13	0.10	0.13	0.36	0.40	0.19	0.16	0.12	0.16
ϕ_{max} (µm) by SEM	0.49	1.10	0.10	1.05	2.77	2.54	1.68	1.08	0.69	0.99
ϕ_{max} (µm) by bubble point	0.76		0.92		3.25		2.53		1.18	

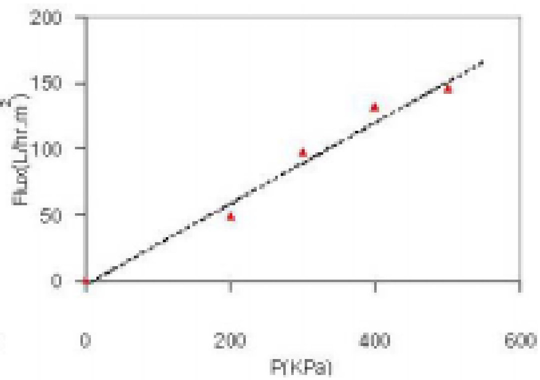
mined by Carnoy program are 0.24 – 0.27 µm and 2.42×10^8 – 2.45×10^8 pores/cm^2, respectively (Table 2). Examination of the commercial track etched membrane (Millipore, pore size 0.4 µm) by the same procedures, indicates the mean pore size and pore density of 0.31 – 0.33 µm and 3.45×10^7 - 4.54×10^8 pores/cm^2, respectively. These results are comparable with the certified values (Table 2).

Pure water flux tests

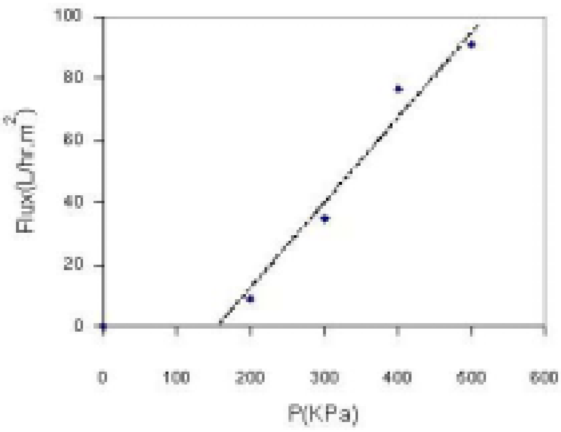
The result of pure water flux tests of the produced membrane with different operating pressures up to 500 kPa is presented in Figure 9. Three different patterns can be classified by this test. Figure 9a indicates an incomplete penetration of pore in membrane when the bombarding time with fast neutron is 5 minute, which is probably too short. The nuclear energy deposited in the PC film is not enough to completely penetrate



(a) 5 min.



(b) 10 min.



(c) 20 min.

Figure 9. Three different types of the pure waterflux versus pressure graphs of the produced membrane with the fast neutron bombarding time of (a) 5 min, (b) 10 min and (c) 20 min, respectively.

the film. An anomalously high flux at pressure above 200 kPa in Figure 9a indicates the membrane rupture when an applied pressure reaches 200 kPa. Figure 9b shows a good complete pore piercing produced membrane, which exhibits a theoretical flux–pressure relationship. This membrane is produced using the fast neutron bombarding time of 10 minutes. Figure 9c indicates another type of incomplete pore piercing membrane. However, after a high pressure is applied to this type of membrane, the pore penetration is proper, for example, a pressure of 150 kPa is needed for the produced membrane in Figure 9c.

Conclusion

With the objective to produce the nuclear track-etched pore membranes by using neutrons from the TRR-1/M1 research reactor at the OAEP, it has been found that high thermal neutrons fluxes seem impractical for pore forming even though the enriched Boron-10 neutron converter and the direct electric field are also employed. This is probably because most of the tracks have not pierced through the film. While the high flux fast neutron from the core of the OAEP's nuclear reactor perform quite well in pore piercing through the thin film polycarbonate. The tiny latent tracks in the films were enlarging by chemical etching process using NaOH. The produced track-etch membranes with the pore size diameter in the range of 0.2 – 1.0 µm correspond with the fast neutron bombarding time in the range of 5 – 20 minutes. The pore density of 10^7 – 10^8 pore/cm^2 is obtained by using the Carnoy program, while the maximum pore size diameter of each produced membrane is analyzed by the bubble point technique. The pure water flux tests reveal three types of the produced membrane. First type is an incomplete pore piercing through membrane, which will rupture when a pressure applied. Second type is a good and complete pore piercing membrane, which exhibits a theoretical flux-pressure relationship. Third type is an incomplete pore piercing membrane, which can be completely pore-piercing using an applied pressure. Overall, the physical characteristics of the home-made nuclear pore membranes produced by fast neutrons of the OAEP's nuclear research reactor provide a good product similar to the commercial membrane.

References

Apel, A. 2001. Track etching technique in membrane technology. Radiation Measurement, 34 : 559-566.

Gopalani, D., Kuner, S., Jodha, A.S., Rita, S., Khatri, P.K., and Gopal, R. 2000. A novel for production of polyester films–based nuclear track microfilters. J. Membrane Sci., 178: 93 – 98.

Ferain, E., and Legras, R. 2001. Efficient production of nanoporous particle track etched membrane with control properties. Radiation Measurement, 34 : 585 – 588.

Ferain, E., and Legras, R. 1997. Characterization of nanoporous particle track etched membrane. Nuclear Instruments and Methods in Physics Research B, 131 : 97 – 102.

Ferain, E., and Legras, R. 2001. Pore shape control in nanoporous particle track etched membrane. Nuclear Instruments and Methods in Physics Research B, 174 : 116 – 122.

Fleischer, R.L., Price, P.B., and Walker, R.M. 1975. Nuclear in Solid : Principles and Application. University of California Press, Berkeley.

Hernandez, A., Calvo, J.I., Pradanos, P., and Trjerina, F. 1998. Pore size distribution in micro-porous membrane. Artificial analysis of the bubble point extended method, 112 : 1 – 12.

Khayrat, A.H. and Durrani, S.A. 1995. The effect of UV exposure on the track and bulk etching rates in different CR-39 plastics, Radiation Measurement, 25 : 163 – 164.

Schols, P. 2001. Carnoy 2.0. Laboratory of plant systematics. Katholieke Universiteit Leuven. Flanders, Belgium. **Http://www.kuleuven.ac.be/bio/sys/carnoy**

Yamazaki, I.M., Paterson, R., and Geraldo, L.P. 1996. A new generation of track etched membrane for microfiltration and ultrafiltration, Part I : Preparation and characterization. J. Membrane Sci., 118 : 239 – 245.

McGuire, K.S., Lawson, K.W., and Lloyd, D.R. 1995. Pore size distribution determination from liquid permeation through microporous membrane. J. Membrane Sci., 99 : 127 – 137.

Lee, Y., Jeong, J., Youn, J., and Lee, W.H. 1997. Modified liquid displacement method for determination of pore size distribution in porous membrane. J. Membrane Sci., 112 : 149 – 156.

Piatkiewicz, W., Rosinski, S., Lewinska, D., Bukowski, J., and Judycki, W. 1999. Determination of pore size distribution in hollow fibre membrane. J. Membrane Sci., 112 : 91 – 102.

Wanichapichart, P., Chittrakarn, T., Sujaritturakarn, W., and Coster, H.G.L. 2000. Production of nuclear track-etched membranes. Science Asia, 26 : 175 – 179.

Tretyakoa, S.V.V. 1997. Physical and chemical basis for the manufacturing of fluorpolymer track membrane. Radiation Measurement, 28 : 791 – 798.