การสร้างเมมเบรนพอลิเอทิลีนและพอลิคาร์บอเนตรูพรุนระดับนาโน โดยการกัดรอยอนุภาคแอลฟา : ศึกษาการควบคุมขนาดรูระดับนาโน

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บทคัดย่อ

งานวิจัยนี้ศึกษาการสร้างรูพรุนระดับนาโน บนแผ่นเมมเบรนพอลิเอทิลีนและพอลิคาร์บอเนต โดยการระดมยิงด้วยอนุภาคแอลฟา และกัดรอยด้วยสารเคมีภายใต้สภาวะที่แตกต่างกัน โดยมีประเด็นศึกษาเกี่ยวกับอิทธิพลของระยะเวลาในการระดมยิงด้วยอนุภาคแอลฟา ระยะเวลาในการกัดรอยด้วยสารเคมี และความเข้มข้นของสารเคมีที่ใช้ในการกัดรอย ที่มีผลต่อการสร้างรูพรุน ความหนาแน่นของจำนวนรู และขนาดของรูพรุน ข้อมูลของรูพรุนวิเคราะห์ด้วยเครื่องสแกนนิงอิเล็กตรอนไมโครสโกป (SEM) และเครื่องอะตอมิกฟอร์ซไมโครสโกป (AFM) ภาพถ่าย SEM และ AFM แสดงให้เห็นว่า รูพรุนที่เกิดขึ้นมีลักษณะกลม และความหนาแน่นของจำนวนรูเท่ากับ 3×10^5 รูต่อตารางเซนติเมตร เมื่อทำการระดมยิงเป็นระยะเวลา 120 ชั่วโมง สำหรับขนาดของรูพรุน พบว่ามีขนาดเล็กลงเมื่อลดระยะเวลาและความเข้มข้นของสารเคมีที่ใช้ในการกัดรอย โดยรูพรุนของแผ่นเมมเบรนพอลิเอทิลีนและพอลิคาร์บอเนต มีขนาดเฉลี่ยประมาณ 60 และ 300 นาโนเมตร ตามลำดับ เมื่อกัดรอยด้วยสารเคมี เป็นเวลา 10 นาที

คำสำคัญ : รูพรุนระดับนาโน พอลิเอทิลีน พอลิคาร์บอเนต อนุภาคแอลฟา

Fabrication of Polyethylene and Polycarbonate Nanoporous Membranes by Alpha Particle Track-Etching: Nanopore Size Controlled Study

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Abstract

Alpha particle irradiation and chemical etching were used to prepare two polymeric nanoporous membranes, i.e., polyethylene (PE) and polycarbonate (PC), under different conditions. The effects of activation times, etching times and chemical etching concentration on pore formation, pore density and pore size were investigated. The pore information was evaluated using scanning electron microscope (SEM) and atomic force microscope (AFM). The SEM and AFM images demonstrated the pore formation in round shape. The pore density was approximately 3×10^5 pore/cm^2 after 120 h of activation. The pore sizes were reduced by decreasing the etching time and etching concentration. The pore sizes of PE and PC can be created with the average diameter of approximately 60 and 300 nm after etching for 10 min, respectively.

Keywords: nano-porous, polyethylene, polycarbonate, alpha particle

1. Introduction

Nanotechnology is one of the fastest growing areas in science. This technology is associated with dimension in the range of 0.1-100 nm[1]. In recent years, nanoporous membranes have been developed for use in many purposes such as sensor[2], virus detection[3], gas separation[4] and laboratory filtration[5]. Polymeric membranes such as polycarbonate (PC)[6], polyethylene terephthalate (PET)[7], polypropylene (PP)[8] and polyvinylidene fluoride (PVF)[9] are widely used for fabrication of nanoporous membrane with nuclear track-etching technique[10]. The advantages of nuclear track-etching technique include efficiency, lack of radioactive contamination and environmental friendliness. A number of researches reported the fabrication of nanoporous membrane by track-etching using heavy ion[11,12] and neutron[13]. Their pore size, shape and density can be varied in a controllable manner, therefore the required pore qualities of the membrane can be achieved. In the present work, the conditions for fabrication of PE and PC nanoporous membranes using alpha particle from radioisotope source and chemical etching technique were studied. PE was used as an alkaline and inorganic resistant material for aggressive environment. On the other hand, PC was studied as an acid and organic resistant, biological inert and mechanically strong material.

2. Experimental

2.1 Materials

PC pellet (TRIREX® 3025IR) was purchased from Watwalth, Thailand. A commercially available high density polyethylene (HDPE) film, with the thickness of 9 µm, MFR of 0.004g/10 min and impact strength of 139 kJ/m^2, was used for fabrication of nanoporous membrane. Dichloromethane (CH_2Cl_2) and sulfuric acid (H_2SO_4) were purchased from JT Baker, USA. Sodium hydroxide (NaOH) was from Carlo Erba Reagents, Italy. Potassium dichromate ($K_2Cr_2O_7$) was obtained from Ajax Finechem Pty Ltd, Australia.

2.2 Equipment and instruments

A plate of plutonium-239 (10×10 cm^2) was used as an alpha particle source (5.15 MeV, 1743 Bq, $t_{1/2} = 2.4 \times 10^4$ years). It was provided by the Office of Atoms for Peace (OAP), Ministry of Science and Technology (MOST), Thailand. SEM images were taken using a JEOL JSM-5410LV. A Nano world NCHR-50 with MFP-3D™ AFM software was used to confirm the pore formation and size.

2.3 Activation setting

The setting of alpha activation process is shown in Figure 1. The polymer membrane in the frame-holder was located between alpha source and basement supporter. The bottom area provides the cavity for alpha particle movement after passing through the membrane.

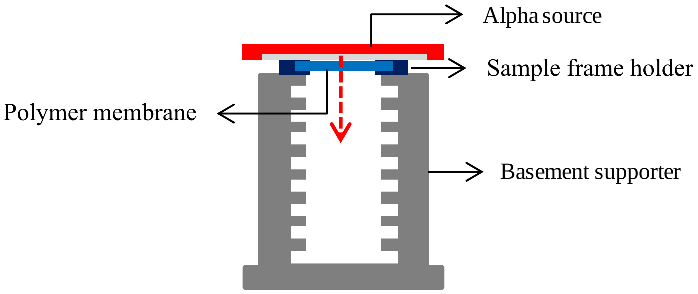

Fig. 1 Alpha particle activation setting.

2.4 Preparation of polymeric nano-porous membrane

PC membranes with the thickness of 20 µm were prepared by using solution cast method. Dichloromethane (CH_2Cl_2) was used as a solvent. For PE, the commercially available film with the thickness of 9 µm was used. The membrane was cut into 5×5 cm^2. The polymer membranes were activated with 5.15 MeV alpha particles from Pu-239 radioisotope source for 48, 72, and 120 h. The activated membranes were immersed into chemical etching solutions of 10% w/v $K_2Cr_2O_7$ in 30% v/v H_2SO_4 for PE and 3N and 6N NaOH for PC. The etching time and the temperature were also varied for 10, 20, 30 and 60 min and for 25, 40, 60, 70 and 80°C, respectively.

3. Results and Discussions

Nuclear track-etching technique can be used to fabricate polymeric nanoporous. The latent tracks formed on materials caused by ionization of charged particles can be revealed by chemically etching to form cylindrical pores[14]. In this work, Pu-239 radioisotope was use as a source for alpha particles. The alpha particles moved through the membrane and transferred their energy along the distance. The particles stopped when they lost all of their energy. The distance that they moved before they stopped is called a range of particle. Therefore, the polymeric membranes were fabricated with the thickness less than the range of alpha particle, depending on polymer types.

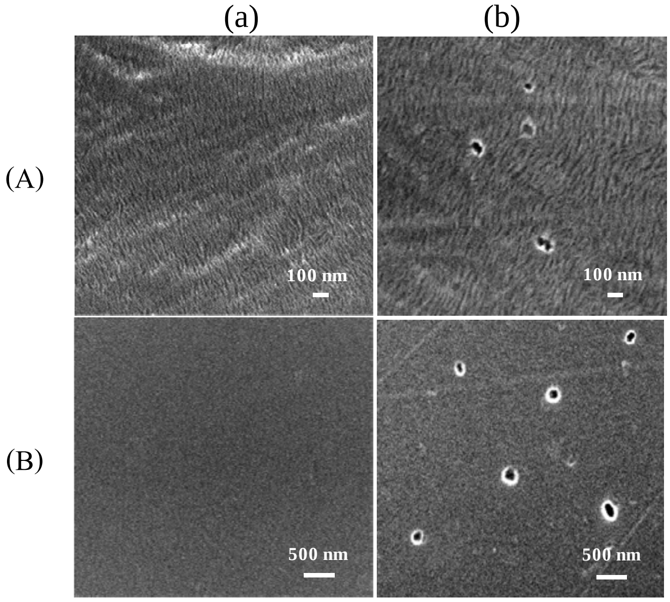

Fig. 2 SEM micrograph of PE (A) and PC (B) membranes, before (a) and after (b) alpha particles activation for 48 h and chemical etched for 30 min

SEM images in Figure 2 show that alpha particle track-etching resulted in round-shape pores in both PE (Fig 2A) and PC (Fig 2B) membranes. AFM images in Figure 3 also confirmed the pore formation. The dark spots indicated the position of the pores.

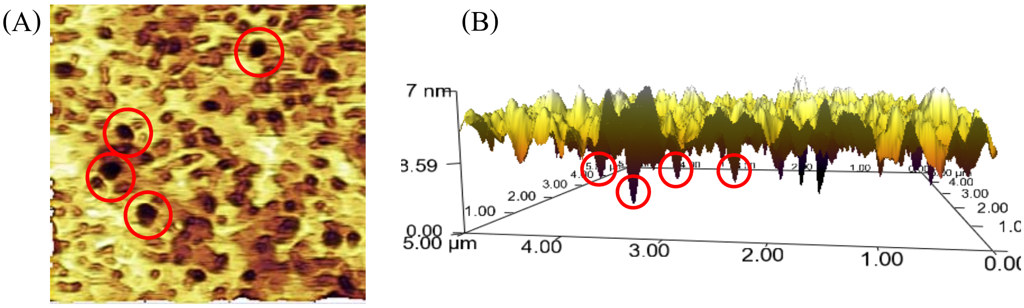

Fig. 3 (A) AFM micrograph of porous PC membrane and (B) AFM depth profile of (A).

3.1 Effect of activation time on pore density and pore size of the polymer membranes

To observe how activation time affects the pore density and pore size of the polymer membranes, the membranes were activated at different activation time (48, 72, and 120 h) and etched using appropriate chemical solutions for 30 min. The results presented in Table 1 indicated that the pore density on the polymer membrane depended on the activation time. The pore density increased with activation time due to the increase of radiation flux for both types of polymer. It was also found that, at the same activation time, PE and PC membranes showed similar pore density.

Table 1 Pore density of PE and PC at various activation times and etched for 30 min

Polymer	Activation time (h)	Pore density (pore/cm^2)	Pore size (nm)
PE	48	203136 ± 41900	101 ± 36
	72	259826 ± 52036	144 ± 46
	120	297619 ± 47241	154 ± 43
PC	48	207860 ± 15428	662 ± 125
	72	297619 ± 56426	717 ± 309
	120	325963 ± 38956	556 ± 202

3.2 Effect of etching time on pore size

Kinetic curve in Fig 5(a) indicated that the pore size increased with etching time. For PE, it was found that the pore sizes were smaller than 100 nm when the membranes were etched less than 20 min. The pore sizes were 59 ± 20 and 71 ± 19 nm when etching for 10 and 20 min. In the case of PC under our studied etching time and etching chemical concentration of 3N and 6N NaOH, the pore sizes were observed to be larger than 100 nm. The pore size of PC were approximately 166 ±

39 and 304 ± 134 nm after etching for 10 min under 3N and 6N NaOH, respectively. It is suggested that decreasing the etchant concentration as well as the etching time would bring the pore size in nanoscale range. The pore size increased with etching time because of the chemical etching solution destroys the polymer structure; therefore the increasing of etching time could enlarge the diameter pore. One can be seen that the pore size of PE were less than that of PC. This may be the result of different chemical structure of PE and PC. It was hypothesized that the bulky structure of PC, which contains benzene ring, obstructed alpha particle movement in the membrane. The energy transfer per target depth to the membrane should be high. Therefore, the polymer destruction severely occurred in PC than PE. Fig 5(b) shows the effect of etching temperature on the pore size. It was clearly observed that the increase of temperature could enlarge the pore size for both PC and PE membranes.

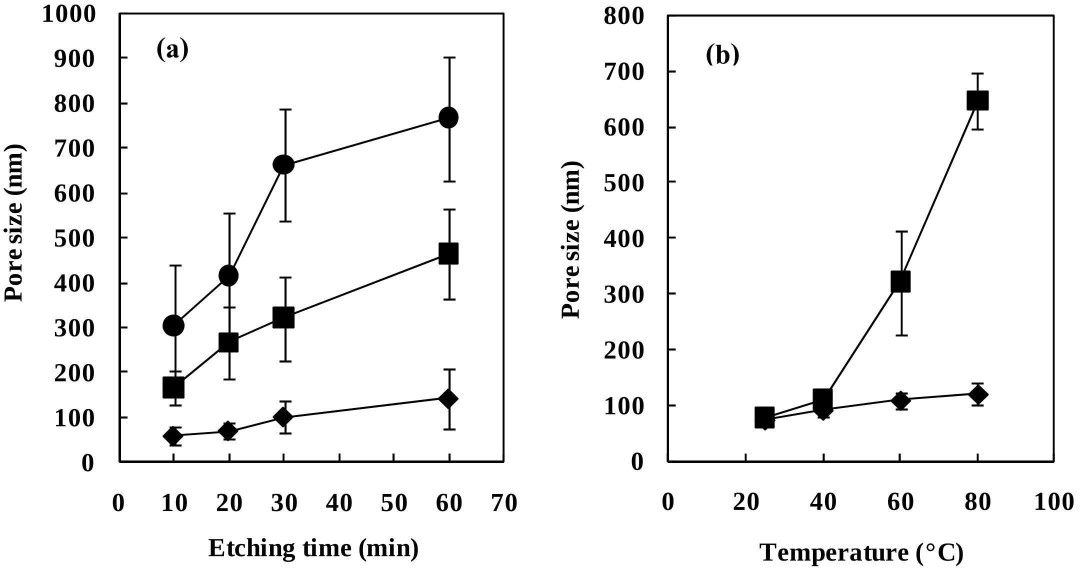

Fig. 5 Effect of (a) etching time and (b) etching temperature on pore size of polymeric membrane with activation time for 48 h and etched in 10% w/v $K_2Cr_2O_7$ in 30% v/v H_2SO_4 for PE (◆) and 3N NaOH, (■) and 6N NaOH, (●) for PC.

4. Summary

Nanoscale-pore size membranes were fabricated and investigated by alpha particle track-etching technique. The pore density and pore size can be controlled by activation time and chemical etching condition, i.e. etching time and temperature. Nanoscale pore diameter in the range of 10-100 nm could be achieved in the case of PE. For PC, the pore sizes were larger than 100 nm. For PC, It is suggested that the decreasing of etching time less than 10 min would reduce the pore diameter in nanoscale.

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