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Polyethersulfone Membrane Coated With Nanoporous Parylene for Ultrafiltration

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***Abstract*—In this letter, we describe the surface modification of a polyethersulfone (PES) membrane by deposition of a nanoporous parylene film. The glycerin vapor during parylene deposition prevented parylene from forming over the pores. Water contact angle measurements and diffusion measurements revealed that parylene could be coated onto the PES membrane while keeping some pores open when the amount of dimer was properly controlled. The parylene-coated membrane prepared by our modified deposition process gave higher diffusion values than that prepared conventionally. Moreover, the platelet activation and adhesion were suppressed after coating parylene; this result indicated that the parylene-coated PES membranes showed improved biocompatibility. This advancement has a potential benefit for ultrafiltration applications. [2012-0252]**

***Index Terms*—Nanoporous parylene, polyethersulfone (PES) membrane, surface modification, ultrafiltration.**

I. INTRODUCTION

Ultrafiltration technology is of great importance in biomedicine and other fields for its use in concentration, purification, and fractionation. Polyethersulfone (PES) is widely used as a membrane material for ultrafiltration due to its high mechanical, thermal, and chemical resistance [1]–[4]. However, the surface of a PES membrane is sensitive to many organic solvents and when they were used in blood-contact devices, platelet adhesion, and aggregation occurred [5]. Therefore, to reduce platelet adhesion, modification of the PES membrane is necessary. A number of efforts to modify the surface of PES membranes, such as surface grafting [6] and blending [7], have been attempted.

In this letter, we describe modifying the surface of a PES membrane by deposition of a parylene film. Parylene has been used on microfluidic devices because of its excellent biocompatibility and chemical inertness [8]. However, in previous reports, parylene was found to form nonporous transparent films that block the diffusion of gases or organic solvents [9], [10]. Hence, it is necessary to develop processes for parylene deposition that allow modification of a membrane surface while keeping the nanopores open. In our work, we investigated the optimum amount of parylene dimer for forming nanoporous parylene membranes. As shown in Fig. 1, our preparation uses the passage of glycerin vapor through the membrane pores during parylene deposition, which we consider aligns the pores of the PES membrane with those of the parylene film.

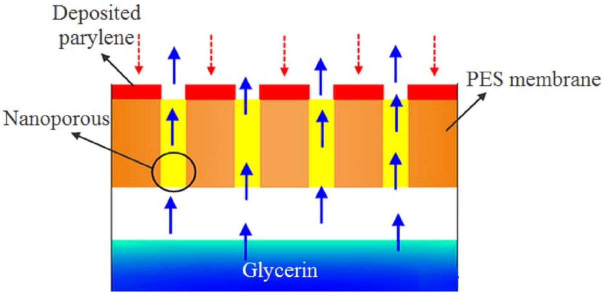

Fig. 1. Parylene deposition on PES membrane porous assisted by glycerin vapors.

Water contact angle measurements on the membrane surface were performed to validate the presence of the parylene film. To determine the permeability of the PES membrane before and after deposition, we measured the diffusion coefficients of NaCl in an aqueous solution. Moreover, platelet adhesion was also studied to investigate the biocompatibility of parylene coating on membranes.

II. MATERIALS AND METHODS

A. Materials

Flat-sheet PES membranes were prepared from PES (molecular weight: 4800, Sumitomo Chemical Company, Japan), polyvinylpyrrolidone (PVP) (molecular weight: 35 000, Wako Pure Chemical Industries, Ltd., Japan), and 1-methyl-2-pyrrolidone (NMP, Wako Pure Chemical Industries, Ltd., Japan), acting as the solute, the solvent, and the additive, respectively. The PES, PVP, and NMP were mixed at 20%, 20%, and 60% (wt.%), respectively, and kept at room temperature for about 48 h to form transparent casting solutions. Subsequently, the PES casting solution was poured onto a glass chip. The PES membrane was then prepared by spin coating at a spinning speed of 3500 r/min followed by direct immersion into distilled water. As soon as the glass chip sank into the distilled water, a thin layer of white membrane could be seen forming at the interface between the casting solution and the distilled water. The thus formed PES membranes were then stored for further use in distilled water at room temperature for more than 24 h to remove PVP.

B. Membrane Modification

Surface modification of the PES membrane was carried out by deposition of parylene-C onto the membrane using a Labcoter 2 Parylene Deposition Unit (Specialty Coating Systems, Indianapolis, IN). During deposition, the parylene dimer charge was vaporized at 175 °C and 133.3 Pa, then decomposed to its monomer (paraxylylene) at 690 °C and 66.7 Pa, and finally condensed and polymerized onto the PES membrane at room temperature in a deposition chamber at 6.7 Pa. Parylene deposition by utilizing the passage of glycerin vapors through the membrane in order to create a nanoporous parylene film. The low vapor pressure of glycerin (0.2 Pa [11]) allows it to vaporize during the deposition process. As shown in Fig. 1, the glycerin vaporizes and passes through the membrane pores, preventing parylene deposition above the pores and subsequent blocking.

As a comparison, the glycerin was also placed aside the PES membrane during the parylene deposition. The thickness of the

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deposited parylene film was measured using a laser microscope (Keyence VX-1000); the result shows that the thickness of the parylene film produced was proportional to the parylene dimer used, and it can be determined based on the following equation:

$$y = 0.50x \tag{1}$$

where x is the parylene dimer used, and y is the thickness of the parylene film produced.

C. Contact Angle Measurements

In order to validate that parylene was deposited on the surface of the PES membrane, we performed water contact angle measurements on the modified surface. Pure water was used as the probe liquid, and images of water drops formed on the membrane were captured using a video microscope (Keyence VHX-V600). CAD software was used to calculate the contact angle of the water drop on the membrane. To minimize experimental error, the contact angle was measured in at least three random locations for each sample and the average calculated.

D. Diffusion Test Experiments

To examine whether the produced parylene film affects the membrane permeability, diffusion tests were conducted since nanoporous membrane evaluations using microscopic methods such as atomic force microscopic and scanning electron microscope (SEM) were reported to be so unreliable [12]. In the diffusion test, a NaCl aqueous solution was used as a representative sample for molecules smaller than 0.5 nm. The diffusivity measurements were performed in a diffusion chamber with the membrane clamped between the solution and pure water. The diffusion chamber was fabricated by bonding two pieces of polymethyl methacrylate (PMMA) chips and one piece of membrane. The chamber layers on PMMA chips were designed as a channel connection. The channel in the chamber layer was 14-mm long, 2.8-mm wide, and 200-μm deep.

The methodology for calculating the diffusion coefficient through a membrane has been previously described [13], [14]. In this letter, some modifications were made and the diffusion coefficient was determined based on the following equation:

$$D = \frac{Q \times H}{A} \times \ln\left[\frac{C_B - C_A}{C_{B'} - C_{A'}}\right] \tag{2}$$

where CA is the initial concentration of Na in solution A and CB is that in solution B, which is initially pure water $(CB = 0)$. H is the thickness of the membrane, and A is the diffusion area of the chamber. By feeding solution A and pure water into the dual inlets of the device, molecules smaller than the mean pore size of the membrane can diffuse through the membrane into the collected solution B (CB'). By measuring the concentration of the collected solution B and that of solution A (CA'), the diffusion of the solute through the membrane can be obtained. The experiments were conducted in three different samples, and the error bars are the standard deviations of the mean of the calculated diffusion coefficient from those three samples.

The platelet adhesion experiments were carried out by a diffusion test for 14 days using a blood and dialysate solution. A bare PES membrane and a membrane coated by 10 mg of parylene dimer were selected in this experiment. A SEM was used to observe the platelet adhesion on the membrane.

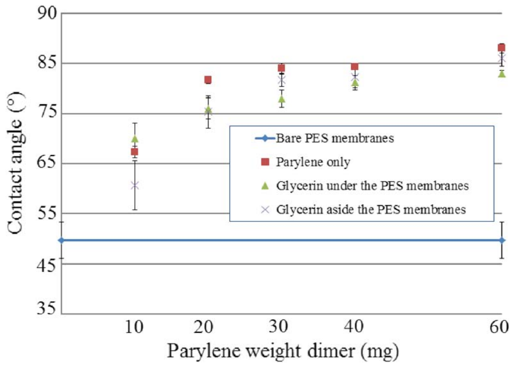

Fig. 2. Contact angle measurements of the membranes.

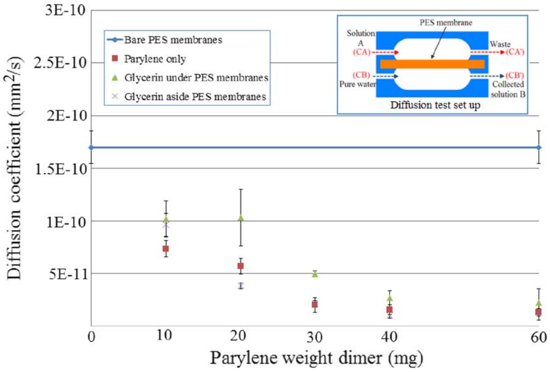

Fig. 3. Diffusion coefficients for transport through the membranes.

III. RESULTS AND DISCUSSION

A. Water Contact Angle of the PES Membrane

As shown in Fig. 2, the water contact angle of the bare PES membrane was 49.6°, which indicates that the surface of the PES membrane is moderately hydrophilic. The contact angle of the membranes after parylene coating increased to 67°–88° for the conventional parylene coating and 70°–83° for the modified parylene coating, which indicated that the surface became moderately hydrophobic.

The value of 67° obtained for the 10-mg parylene dimer in the conventional parylene coating, which was below the reference values of 82°–91° [15], [16], was considered to be an underestimation as a result of discontinuous formation of the parylene film on the membrane. When 20–60 mg of parylene dimer was used, the water contact angle increased to 82°–88°. Hence, it is not surprising that the modified parylene coating was less hydrophobic than the conventional parylene coating. This is attributed to the use of glycerin during the deposition process, whereby the parylene is not completely deposited over the membrane pores.

B. Diffusion of the Electrolytes

Fig. 3 shows the diffusion coefficients of NaCl molecules for three samples: the bare PES membrane, the PES membrane coated with parylene by a conventional process, and the PES membrane with parylene by our modified process. The weights of the parylene dimer used ranged from 10 to 60 mg.

As expected, the bare membrane gave the highest diffusivity among the membranes due to lack of any surface coating.

When the amount of parylene dimer used is reduced to the submilligram range, the parylene film becomes semipermeable and microporous [17]. In the conventional parylene deposition process, parylene is randomly deposited on the surface. This random deposition may block some of the membrane pores and prevent permeation, resulting

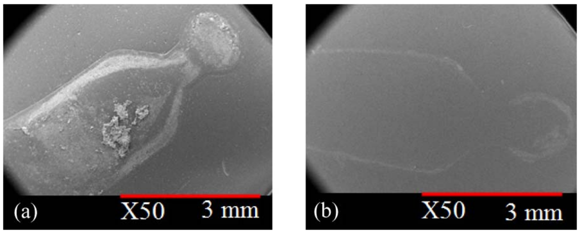

Fig. 4. SEM images of platelets adhering on diffusion channel. (a) PES membrane. (b) PES membrane coated with parylene.

in a lower diffusion coefficient. In contrast, the PES membrane coated using our modified deposition process had a higher diffusion coefficient. We believe this is due to the glycerin vapor during parylene deposition that prevented parylene from forming over the pores. When a sufficiently large amount of dimer (greater than 30 mg) was used, the parylene formed over the pores of the PES membrane even during glycerin vaporization and the resulting diffusion coefficients were low.

The result also shows that when using 10 mg of parylene dimer, the diffusion coefficient of the membrane coated with glycerin aside has a slight difference than having the glycerin under the membrane, but we found many junks on the membrane surface by this approach. Moreover, when higher parylene dimer (20–60 mg) was used, the diffusion coefficients of the coated membrane are significantly decreasing even below the value of the membrane coated by normal parylene deposition.

In this letter, platelet adhesion on the membrane surface has been investigated. Fig. 4 shows the SEM images of the platelets adhering to the membrane surfaces. It could be observed that numerous platelets aggregated and accumulated on the surface of the PES membrane, and the platelets spread into irregular shapes. However, for the parylene coating on the PES membrane, very sparse platelets were observed. This should be attributed to the biocompatible parylene coating on the PES membrane surface.

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