



Control of nanoporous polymer matrix by an ionic liquid and water pressure for applications to water-treatment and separator



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HIGHLIGHTS

- Preparation of porous cellulose acetate polymer matrix by utilizing ionic liquid and water-pressure.
- The pore-generation of average 10 nm in cellulose acetate.
- The control of pore size with water-pressure.

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ABSTRACT

A novel, simple, low-cost, energy-efficient, and environment-friendly method for generating pores in a polymer matrix was developed using a combination of an ionic liquid and water pressure treatment. A porous cellulose acetate (CA) matrix was successfully prepared using the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄) and subsequent water pressure treatment. Pores were generated in the CA polymer matrix when the CA/ionic liquid composite was subjected to water pressure. The characteristics of the thus-generated porous polymer matrix were evaluated using porosimetry and scanning electron microscopy. The pore sizes were ranged from less than 10 nm to over 10 μm, with an average value of 10 nm. Fourier transform infrared spectra and thermogravimetric analysis showed that when the CA polymer was subjected to water pressure, most of the BMIM-BF₄ incorporated in the polymer during its preparation was removed, thereby generating the observed pores. In addition, it was observed that the flux was varied with water pressure, indicating that the pore size was controllable.

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1. Introduction

Nanoporous polymer matrix membranes have been used to separate mixtures of CO₂, N₂, and proteins [1]. A porous aramid-g-poly(ethylene oxide) (PEO) copolymer ultra-filtration (UF) membrane prepared by the phase inversion method was used to separate an aqueous solution containing solutes in the 20,000–400,000 Da range [2]. Porous polymer matrices have commonly been used in applications such as water treatment and purification [3,4]. Furthermore, porous polymer matrices have been shown to facilitate electrolyte uptake. Porous membranes based on the poly(vinylidene fluoride-co-hexafluoropropylene)(PVDF-HFP)/poly(ethyleneoxide-co polypropylene oxide (P123) matrix have been used as electrolyte membranes. These membranes were presented by photocurrent–voltage (I–V) characteristics. As a result, porous PVDF-HFP and P123 showed the improved the ionic conductivity as electrolyte [5].

Another approach for fabricating pores and controlling pore size is the track-etching method, which is utilized for fabricating pores in PET matrices via multi-step etching and track annealing [6–8]. To introduce porosity into the polymer matrix, PET was irradiated with Bi ions at room temperature under vacuum. Then, the irradiated PET matrix was etched in methanol-free. Finally, funnel- and pencil-shaped pores were fabricated in the PET matrix.

Another method involving the use of pore-forming agents has attracted much interest. For example, the amphiphilic copolymer Pluronic F127 was used as an additive for polyethersulfone (PES). PES and Pluronic F127 were dissolved in DMF and cooled to room temperature. Then, the solutions were cast on a glass plate using a casting knife and the polymer matrix was immersed in de-ionized water. The modified membranes showed the improved anti-fouling performance. Furthermore, it was found that membrane pore size increased with increasing Pluronic F127 content [9].

In other studies, thermally induced phase separation has been suggested for controlling porosity and pore size in polymeric matrices [10–15]. For example, polyethylene (PE) membranes were used in microfiltration and separation, and phthalates (as diluents)

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were used to fabricate pores in the polymer matrix [16–20]. However, the use of phthalates has been limited because of their toxic characteristics, and since then, non-toxic diluents such as triethylpropane tris(2-ethylhexanoate) (TEPTEH) have been evaluated. Upper critical solution temperature, (UCST)-type phase behavior was observed in the PE/TEPTEH blends. As the PE content was increased, the phase separation temperature decreased. Furthermore, mixtures of TEPTEH containing paraffin oil (PO) as the diluent were tested to control porosity and pore size. At fixed PE content, it was observed that the phase separation temperature decreased with increasing PO content. When the TEPTEH content in the diluent was increased, the average pore size as well as porosity increased. It was evident that the properties of the membrane were controlled by their PE, PO, and TEPTEH contents [21].

In another study, porosity in a polyacrylonitrile (PAN) matrix was controlled using a combination of phase inversion and different organic acid additives, including glacial acetic acid (GA), fumaric acid (FA), and citric acid (CA). After GA, FA, or CA was added to DMF, PAN was added to the mixture. After polymer solution was cast, those were immersed in a de-ionized water coagulation bath [22,23]. It was observed that membrane water flux decreased with increasing PAN concentration. The average pore size in the fabricated membrane was 0.1–0.17 μm . The porosity of the polymer matrix utilizing GA was higher than that of the matrices with FA and CA [24]. In addition to these researches, many studies for nanoporous materials have been recently investigated [25–30].

In the present study, we have developed a simple, low-cost, energy-efficient, and environment-friendly method for fabricating pores in a polymer matrix using a combination of an ionic liquid and low water pressure to control pore size.

2. Experimental

2.1. Materials

A 15% (w/w) solution of cellulose acetate (CA) was obtained by dissolving CA in acetone. Then, the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄) was added to this solution in various ratios. The final mixture was stirred for 12 h at room temperature. Subsequently, the solutions were casted to form a freestanding film on a glass plate and dried in a fume hood for 24 h. The dried polymer matrix containing BMIM-BF₄ was washed in distilled water. These polymer films were subjected to water pressures ranging from 1 to 10 bar. Water flux of the films with varying porosity was measured and expressed as L/m² h.

2.2. Characterization

The pore sizes of the PAN free-standing films dipped into the DMAc was examined using mercury porosimeter (Autopore IV9500, Micromeritics). The cross-section morphology of the films was shown by a scanning electron microscope (SEM) (JSM-5600LV, JEOL). Fourier-transform infrared (FT-IR) spectroscopy (VERTEX 70/70V FT-IR spectrometers, Bruker Optics) and thermogravimetric analysis (TGA) (Universal V4.5A, TA instruments) were conducted to investigate the structural changes and thermal stability of the film.

3. Results and discussion

The flux through porous CA membranes containing different ratios of BMIM-BF₄ was shown in Fig. 1. Up to a pressure of 2 bar, there was no significant water flux at any mole ratio. Unexpectedly, at pressures above 2 bar, the water flux gradually increased for all mole ratios of the polymer composite. The

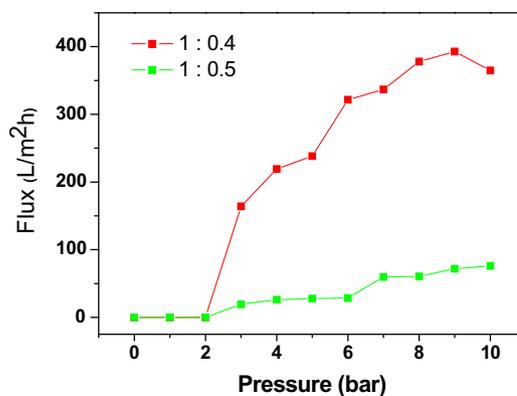


Fig. 1. Flux through 1/0.4 and 1/0.5 CA/IL composite matrices at various water pressures.

observed water flux was attributable to the penetration of water through the weakened polymer chains resulting from the plasticization effect of the ionic liquid, BMIM-BF₄. However, even though the BMIM-BF₄ content could be increased beyond the aforesaid ratios, further increase in flux was not observed. This may be attributed to the increased interaction between CA and BMIM-BF₄ at higher concentrations of the ionic liquid. The best performance was observed at the ratio of 1:0.4.

Scanning electron microscopy (SEM) was used to investigate the pores generated in the polymer. Fig. 2 showed the porosity generated in 1:0.4 CA/BMIM BF₄ matrices at water pressures of 4–5 bar. Vertically interconnected pores were observed, and the pore sizes increased with pressure, indicating that water pressure could generate interconnected pores in weakened polymer chains resulting from the plasticization effect of the incorporated ionic liquid. On the other hand, the polymer chains without ionic liquid remained constant as a support due to the relatively high the mechanical property. These phenomena was also observed in porous polymer prepared by Draft method to generate the pores in amorphous region. Since the mechanical property in amorphous region was relatively weaker than that in crystalline region, the attractive force in a certain direction could generate the pores in weakened amorphous region. Similarly, the weakened region by ionic liquid in CA polymer could be easily torn by external physical force, i.e. water-pressure, resulting in the nano-porous structure.

Fourier transform infrared (FT-IR) spectra were obtained for the CA/IL matrix using a VERTEX 70 FT-IR spectrometer (Bruker Optics Inc.). Fig. 3 showed the FT-IR spectra of 1/0.4 CA/ILs at various water pressures. The peak observed in the 2800–3100 cm⁻¹ range for BMIM-BF₄ disappeared after the polymer matrix was subjected to various water pressures. The peaks observed at 1100–1350 cm⁻¹ and 500–900 cm⁻¹ also disappeared after the polymer was treated at various water pressures. These changes in the spectra indicated that when the polymer was exposed to high water pressures, most of the BMIM-BF₄ was removed from the polymer matrix. These results were attributable to the water-path into polymer to contain ionic liquid. Since the water only could flow through the physically weakened polymer chains to contain ionic liquid, the BMIM-BF₄ could be easily removed by water-pressure with the favorable chemical interaction between ionic liquid and water molecules. Thus, the remove for amount of ionic liquids to generate the pores indicated that there was a strong possibility to be applied as nano-porous membrane, separator in battery and porous fiber.

Thermogravimetric analysis (TGA) was carried out to confirm the thermal stability of porous polymer matrix using a Universal V4.5A (TA Instruments). Fig. 4 shows that neat CA decomposed at

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