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The preparation of porous polyamide-imide nanofiber membrane by using electrospinning for MF application

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ABSTRACT

A membrane material based on polyamide-imide (PAI) has received a great attention lately due to its thermal resistance, outstanding mechanical property, and low thermal expansion coefficient. In this study, we have focused on the preparation of porous PAI nanofiber membranes (PNMs) for water treatments. The preparation of PNMs was completed via the electrospinning method using PAI in a mixed solvent of dimethylacetamide and tetrahydrofuran. The resulting PNMs were then thermally treated to improve mechanical properties. These PAI-based membranes were characterized by scanning electron microscope, tensometer (tensile strength and elongation), pore characteristic, contact angle analyzer (contact angle), and dead-end cell device (water flux). We noticed that the pore diameter (1.0–0.3 μm) of PNMs was systematically controlled by simply increasing the number of PNMs layers. As these nanofiber membranes were found to be highly hydrophobic, we also attempted to prepare hydrophilic PNMs with a PAI solution containing 2–4 wt.% of diethylene glycol prior to the electrospinng. Based on contact angle tests, these modified PNMs exhibited very hydrophilic characteristics that could be utilized in water-filtration systems.

Keywords: Polyamide-imide; Nanofiber; Electrospinning; Diethylenegylcol; MF

1. Introduction

Membrane systems are used on a large scale to produce drinking water from sea water and to clean industrial effluents by reverse osmosis, to recover valuable chemical elements by electrodialysis, to separate alcohol from alcohol–water mixtures by pervaporation, to remove toxins from the blood stream in an artificial kidney by diffusion dialysis, and to use as fuel cells [1–4]. In particular, polymeric membranes can be prepared by phase inversion and electrospinning techniques. The phase inversion technique is a conventional method to prepare commercially available membranes. Electrospinning technique is relatively new preparation method for microfiltration (MF) or ultrafiltration (UF) membranes. It has been introduced to make a nonwoven

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nanofibrous mat or nanofibrous membrane [5–7]. In this technique, electrostatic charge is introduced to the solution jet, causing a thin fiber with high surface areas; hence it can be used in the applications where high surface area-to-volume or length-to-diameter ratios are required. Although nanofiber mat has many potential advantages for the water treatment membrane, it has not been used commercially so far because of the extremely low mechanical property, difficulty of mass production and limited electrospinning conditions [5].

In this study, the polyamide-imide nanofiber membrane (PNM) was prepared by using the electrospinning method and characterized in terms of application as a MF membrane. The electospinning conditions were optimized to obtain the PAI nanofibers having narrow diameter. The pore diameters were also controlled by increasing the number of PNMs layers. In addition, the water flux and contact angle of PNMs were investigated for MF applications.

2. Experiments

2.1. Materials

Materials used to manufacture the polymer nanofibers were polyamide-imide (PAI) powder (Mw = 69,700, offered by KRIEST; Korea Research Institute of Chemical Technology), diethylene glycol (Yakuri Pure Chemicals, >99%), THF (Tetrahydrofuran, >99.5%) and DMAc (*N*,*N*-Dimethlyacetamide, >99%) purchased from DUKSAN PURE CHEMICALS CO., Ltd. In order to remove water, PAI powder was treated at 110˚C in Dry-oven for 24 h, and the other chemicals were used without any purification.

2.2. Preparation of poly amide-imide nanofiber membranes (PNMs)

The PAI nanofiber membranes were prepared by the electrospinning method [5,8], after the preparation of electrospinning solution by mixing PAI powder and diethylene glycol (DEG) with DMAc and THF as solvent. The composition of the solution is listed in Table 1. The prepared solution was then filled into a 5 mL syringe with a 22 gauge needle. The syringe was positioned vertically for 30 min. By pushing the end of the syringe, the air was completely removed. The ejection speed was controlled by KDS100 (KD Scientific Inc.), and the voltage supply equipment used was a CPS 60K02VIT (CHUNGPA EMT co. Ltd.). The humidifier was used to control the humidity. The following electrospinning conditions were used: flow rate 0.7 mL/h, voltage 17 kV, TCD (tip to collector distance) 10 cm, duration 5 h, and relative humidity 40–50%.

To improve the physical property, the PNMs were thermally treated into the dry-oven at 160˚C for 24 h after stacking PNM's layers and placing between glass plates. After peeling off the membrane from the glass plates, the membranes were rinsed with methanol and distilled water to eliminate the residues.

2.3. Characterization

2.3.1. Morphology of PNMs

The morphology of the PNMs was observed by SEM (Jeol-JSM-5410). These membranes were completely dried into a vacuum oven at 25˚C for 24 h, and gold particles were coated on the membranes by using an ion-coater.

2.3.2. Pore size and porosity measurement

To analyze the pore sizes of the PNMs, Capillary Flow Porometer (CFP-1000AEL, Porous Materials Inc.) was used and the galwick possessing a surface tension of 15.9 Dynes/cm was used for wetting of sample as measurement solution.

In order to measure the porositym, the PNMs (5×5 cm) were soaked in *n*-butanol (Junsei Chemical Co. Ltd.) at room temperature for 2 h. The membranes were then taken out from the solvent and wiped with tissue to remove excess *n*-butanol on the surface. The mass of these wet membranes (W_{wet}) was measured. To determine the mass of dry membranes (W_{dry}) and volume (V_{dry}), the wet membranes were dried in the oven at 100˚C for 24 h. The average water uptake values were determined by five measurements.

Table 1
Composition of electrospinning solutions

Sample code	PAI (wt.%)	DEG (wt.%)	DMAc (wt.%)	THF (wt.%)
PNM	19.5	0	48.3	32.2
PNM-EG2	19.5	2	47.1	31.4
PNM-EG4	19.5	4	45.9	30.6

The porosity was determined by the following Eq. (1) [9].

$$\text{Porosity } (\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{\rho_{\text{b}} W_{\text{dry}}} \times 100\% \quad (1)$$

where ρ_{b} is the density of *n*-butanol.

2.3.3. Mechanical properties

The tensile strength and elongation were measured by KYUNG–SUNG Testing Machine with 1 kN capacity load cell. The test was performed using pneumatic grips with 90 psi and 25×25 mm rubber jawface. The test was measured according to ASTM D882, and samples were compared before and after the thermal treatment.

2.3.4. Contact angle measurement

To examine hydrophilicity and hydrophobicity of the surface of prepared membranes, the contact angle was measured via Contact Angle Analyzer (Phoenix 150, SEO).

2.3.5. Water flux measurement

The water flux of the membrane samples was performed by a dead-end-cell device with a filtration area of 38.5 cm^2. The schematic diagram of the filtration system is shown in Fig. 1. The distilled water was prepared in a bomb filter and mixed well using a magnetic stirrer to eliminate bubbles in the membranes. The filtration pressure was maintained by a compressed N_2. The filtrate was collected into a receiver on a balance. The mass of filtrate was recorded during the filtration, which was plotted against time [10]. Water flux was then determined according to the following Eq. (2).

$$\text{Water flux } (\text{kg/m}^2\text{h}) = \frac{m_{\text{x}} C_{\text{t}}}{\tau A_{\text{x}}} \quad (2)$$

m_{x} = the weight of the filtrate (kg); C_{t} = temperature constant; t = filtration time (h); A_{x} = effective area of membrane (m^2).

The temperature constant (C_{t}) was calculated by Eq. (3). The temperature constant is close to 1 where temperature is estimated to be 25°C. The effective area of membrane is fixed at 38.5 cm^2.

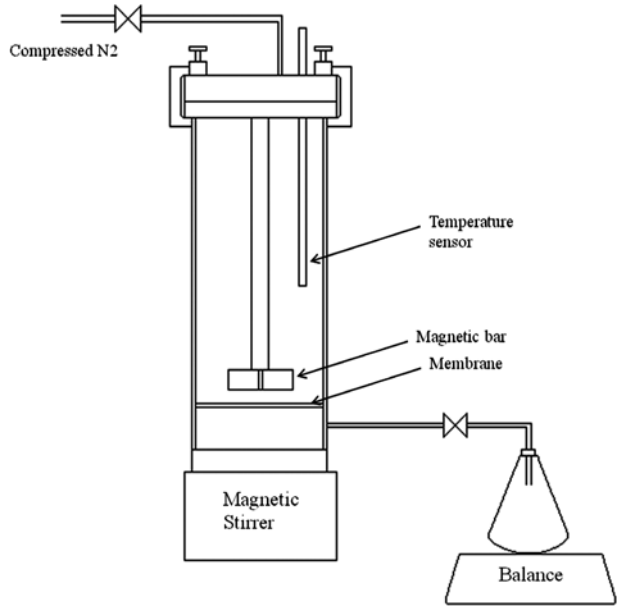

Fig. 1. Schematic diagram of dead-end-cell device.

$$C_{\text{t}} = -0.575 \ln T(^{\circ}\text{C}) + 2.85 \quad (3)$$

3. Results and discussion

3.1. Preparation of polyamide-imide nanofiber membranes (PNMs)

The electrospinning solution generally consists of a polymer, a good solvent, and a poor solvent. The nanofiber membranes could be continuously produced with optimized concentrations of the polymer solution. The thickness could be controlled by varied electrospinning time. This method is suitable for mass production. Completely formed sheets using numbers of PAI nanofiber layers were prepared for the optimization of pore size and porosity. The optimized pore size and porosity of PNMs could be obtained by controlling the layer of PAI nanofiber after treatment of final PAI nanofiber layers.

3.2. Morphology of PNMs

The morphology was observed by SEM. The nanofibers are well formed when the applied voltage is higher than the surface tension of polymeric solution. The micrographs of the top surface of PAI nanofiber are shown in Figs. 2 and 3. From the SEM images, the PAI nanofibers were nicely formed under 17 kV applied voltage. Although many bead-type objects were formed under this voltage, simply

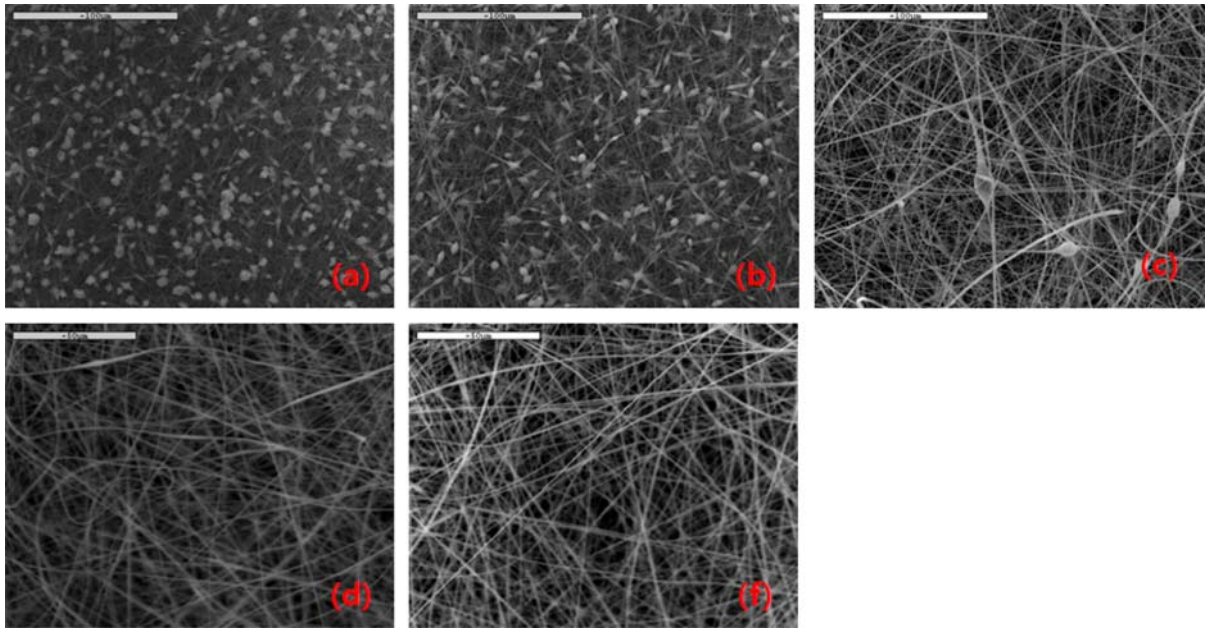

Fig. 2. SEM images of PNM samples under varied conditions; (a) 10 kV, (b) 13 kV, (c) 17 kV, (d) 17 kV, R.H. 40%, (f) 17 kV, R.H. 50%.

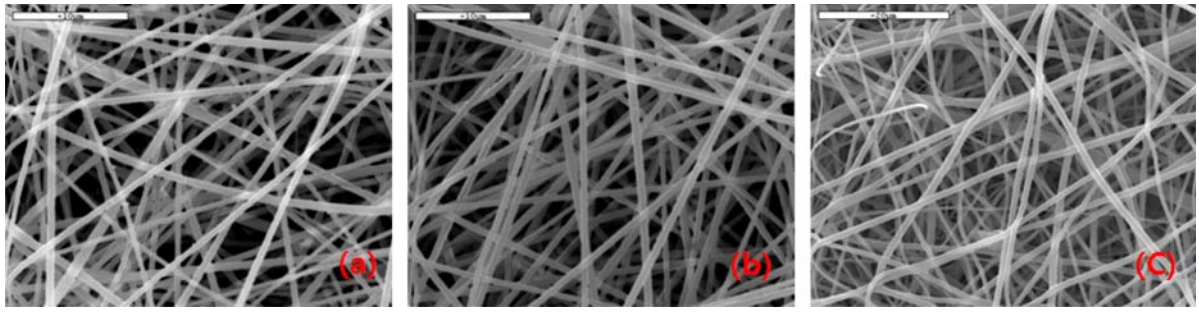

Fig. 3. SEM images of modified PNM samples; (a) PNM-EG2, (b) PNM-EG4, (c) PNM.

controlling the relative humidity of between 40 and 50% allowed for the disappearance of this phenomenon during electrospinning process. Similar results were observed from PNM-EG2 and PNM-EG4 samples.

3.3. Pore size and porosity measurement

The common transport mechanism of membranes depends on sieving and solution-diffusion. In particular, the transport mechanism of the MF-based membranes having a range of 10^{-5}–10^{-7} m pore diameter highly depends on sieving mechanism, and the components that permeate through the membrane are transported by convective flow through micropores under a gradient pressure as a driving. Thus, the pore

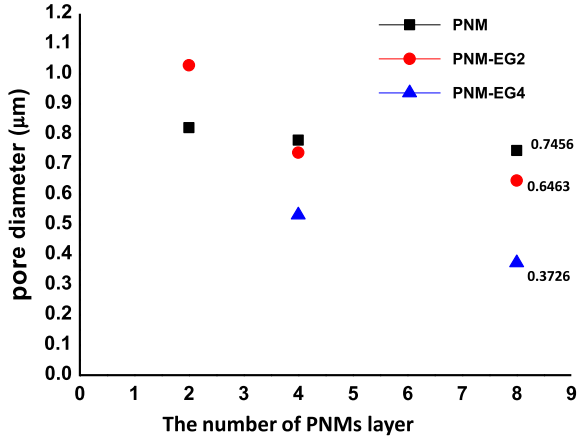

Fig. 4. The pore diameter graph with increasing the number of PNMs layer.

Table 2
The pore properties of 8-layer of PNMs

Sample code	Thickness (μm)	Porosity (%)
PNM	70–80	65 ± 5
PNM-EG2	65–70	52 ± 4
PNM-EG4	65–70	50 ± 6

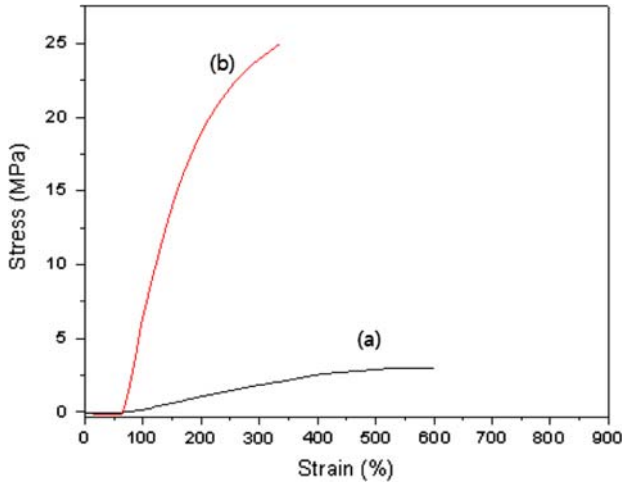

Fig. 5. The tensile strength of PNMs; (a) after and (b) before thermal treatment.

diameter of MF membranes is one of key factors. The pore diameter of prepared PNMs was estimated (Fig. 4). The pore diameters of PNMs were decreased as the increase in both membrane layers and content of DEG. The sample with the smallest pore diameter was PNM-EG4 (0.37 μm) with DEG 4%. However, the smaller pore size of PNMs should be prepared for the commercial application as a MF membrane.

The pore properties of prepared membranes are shown in Table 2. The thickness of PNMs increasing with the number of those layer, but porosity was not much more changed. It could be expected that the

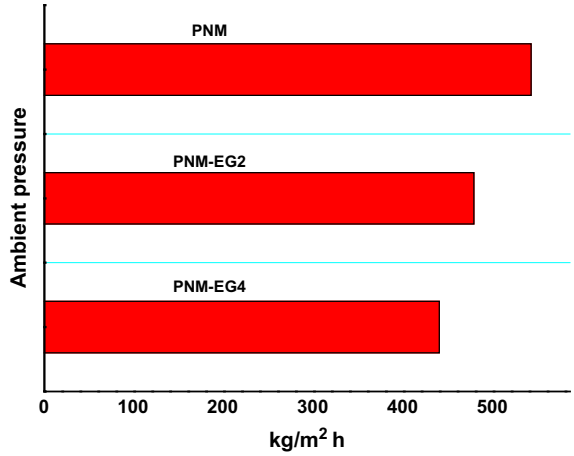

Fig. 7. The water flux of PNMs.

PNMs prepared in this study would be possible to show high permeability due to its high porosity.

3.4. Mechanical properties

As glass transition temperatures (T_g) of PAI and DEG are around 268°C and 245°C, thermal treatment of PNMs was performed at 160°C to minimize defects like pinholes. The tensile strength of PNMs was highly increased after thermal treatment (Fig. 5). However, even though the thermal treatment in PNMs enhances the mechanical strength, it should be cautious because the high temperature treatment might change the properties of PAI itself. It seems that the thermal treatment is one of the methods to enhance the physical property of nanofiber.

3.5. Contact angle measurement

The contact angle is an important parameter in surface sciences. It is a regular measure of the surface hydrophobicity [11,12] and Fig. 6 shows values of contact angle of PNMs. The contact angle was

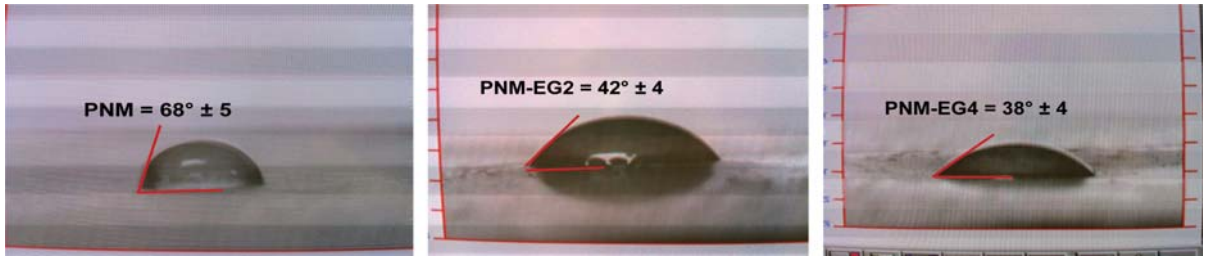

Fig. 6. The contact angle images of PNMs.

decrease with the increase of hydrophilic DEG contents. Based on contact angle tests, these modified PNMs exhibited very hydrophilic characteristics.

3.6. Water flux measurement

The water flux was measured at a dead-end cell device for MF application, the results are shown in Fig. 7. The tests were performed at ambient pressure because PNMs have a relatively large pore diameter. The results of water flux, agree well with the results of pore size and porosity of PNMs. High pore size and porosity make a high water flux although hydrophilic materials are included in the nanofiber membrane. However, the water flux of PNM-EG4 which has much lower pore size and lower porosity then PNM decreased not much compared with PNM water flux. We think that this result attribute to the DEG's hydrophilic property. However, after several water flux tests, it was found that the membranes still preserved the extremely high hydrophilic characteristics due to the diethylene glycol inside of nanofiber membranes.

4. Summary and conclusion

In this study, we have focused on the preparation of porous PAI nanofiber membranes (PNMs) for possible water treatment. The preparation of PNMs was completed via the electrospinning method using a PAI solution containing a mixture of dimethylacetamide and tetrahydrofuran. The resulting PNMs were then thermally treated to improve tensile strength (25 Mpa). The pore diameter (1.0–0.3 μm) of PNMs was systematically controlled simply by increasing the number of PNMs layers. The porous structure of these PAI-based membranes was examined by scanning electron microscope and porosity measurement. As these nanofiber membranes are found to be highly hydrophobic, we also attempted to prepare hydrophilic PNMs with a PAI solution containing 2–4 wt.% of diethylene glycol prior to the electrospinng. Based on contact angle tests, these modified PNMs exhibited very hydrophilic characteristics that could be utilized in water-filtration systems.

Acknowledgments

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