

# Effects of the Polymerization and Pervaporation Operating Conditions on the Dehydration Performance of Interfacially Polymerized Thin-Film Composite Membranes

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**ABSTRACT:** The disadvantage of dense polyamide membranes when applied in the pervaporation separation process is their low permeation rates. To improve the pervaporation performance, polyamide thin-film composite membranes were prepared via the interfacial polymerization reaction between ethylenediamine (EDA) and trimesoyl chloride (TMC) on the surface of modified polyacrylonitrile (mPAN) membranes. These composite membranes were applied in the pervaporation separation of alcohol aqueous solutions. On the basis of the best pervaporation performance, the desired polymerization conditions for preparing the polyamide thin-film composite membranes (EDA-TMC/mPAN) were as follows: (1) the respective concentration and contact time of the EDA

aqueous solution were 5 wt % and 30 min and (2) the respective concentration of and immersion time in the TMC organic solution were 1 wt % and 3 min. The polyamide thin-film composite membranes (EDA-TMC/mPAN) exhibited membrane durability when applied in the pervaporation separation of a 90 wt % isopropyl alcohol aqueous solution at 70°C, which indicated that the polyamide thin film composite (TFC) membranes were suitable for the pervaporation separation process at a high operating temperature. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1511–1522, 2009

**Key words:** composites; membranes; polyamides; polycondensation; separation techniques

## INTRODUCTION

Interfacial polymerization is an effective technique for fabricating a composite membrane, which consists of a thin interfacially polymerized selective layer on the surface of a porous support membrane. This technique is based on a polymerization reaction that forms a polymer film at the interface between two immiscible phases (aqueous and organic phases), each of which has a highly reactive mono-

mer dissolved in it. The polymer film formed at the interface usually grows from the aqueous phase toward the organic phase. This concept of polymer film growth at the interface has been proven by Morgan.<sup>1</sup>

The preparation of a thin-film composite membrane requires the following steps: (1) an asymmetric porous substrate is allowed to contact an aqueous phase solution containing a monomer, (2) the excess aqueous solution is removed from the asymmetric porous substrate, and (3) this asymmetric porous support membrane is contacted with an organic phase solution containing its own monomer. A thin active layer is formed on the surface of the asymmetric porous support membrane via the process of an interfacial polymerization reaction between the two different monomers.

Interfacially polymerized thin-film composite membranes are usually investigated in studies on reverse osmosis or nanofiltration,<sup>2–9</sup> but they have also been examined in a few reports on

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pervaporation.<sup>10–13</sup> Alcohol dehydration is one of the important development areas in pervaporation separation processes.

The key to the pervaporation process success is the fabrication of suitable membranes. Polyamides have been regarded as one suitable membrane material because of their high thermal stability, excellent mechanical strength, and high resistance to organic solvents. However, the disadvantage of dense polyamide membranes when applied in the pervaporation separation process is their low permeation rates. To increase the permeation rate of polyamide membranes without sacrificing selectivity, the membrane must be transformed from a dense thick structure into an asymmetric or a composite structure.

The performance of an asymmetric single-material membrane is restricted by its characteristics. A composite membrane would be better, as it is characterized by a selective top layer formed onto a chemically different asymmetric porous membrane substrate. The combination of independent polymeric layers can be advantageous as far as obtaining the desired membrane performance is concerned. A composite membrane with an ultrathin selective layer can be prepared by the interfacial polymerization technique.

In this study, to improve the permeation rate of polyamide membranes, polyamide thin-film composite membranes were prepared via an interfacial polymerization reaction between ethylenediamine (EDA) and trimesoyl chloride (TMC) on the surface of a modified polyacrylonitrile (mPAN) membrane. These composite membranes were applied in the pervaporation process. The permeation rate across the interfacially polymerized polyamide thin-film composite membrane (EDA–TMC/mPAN) was expected to improve without the sacrifice of the selectivity when applied for the dehydration of the alcohol aqueous solution. The effects of the interfacial polymerization and pervaporation operating conditions on dehydration performance were investigated.

## EXPERIMENTAL

### Materials

Polyacrylonitrile (PAN) polymer, used as the support layer for the composite membrane prepared by interfacial polymerization, was supplied by Tong-Hua Synthesis Fiber Co., Ltd. (Hsinchu, Taiwan). Reagent-grade *N*-methyl-2-pyrrolidone (NMP) was the solvent used to prepare the casting solution of PAN. EDA was purchased from Acros Organics Co. (USA) 1,3,5-Benzenetricarbonyltrichloride (i.e., TMC) was purchased from Aldrich Co. (Steinheim, Germany) EDA and TMC were used as the aqueous phase monomer and the organic phase monomer, respec-

tively, for the formation of the polyamide active layer. Distilled water was used to prepare aqueous solutions, and toluene was used as the organic solvent.

### Preparation of the porous mPAN support membrane

A flat porous support membrane was prepared by the casting of the PAN–NMP solution onto nonwoven polyester fabrics. In the preparation process, an NMP solution containing 15 wt % PAN polymer was cast onto a polyester nonwoven substrate with the use of a casting knife (200- $\mu\text{m}$  gap) to fabricate the flat porous PAN support membrane. The cast membrane was precipitated by immersion in a bath of water. The resulting porous PAN membrane was washed in water several times for more than 1 day to remove the remnant of NMP solvent, and it was then dried at atmospheric temperature.

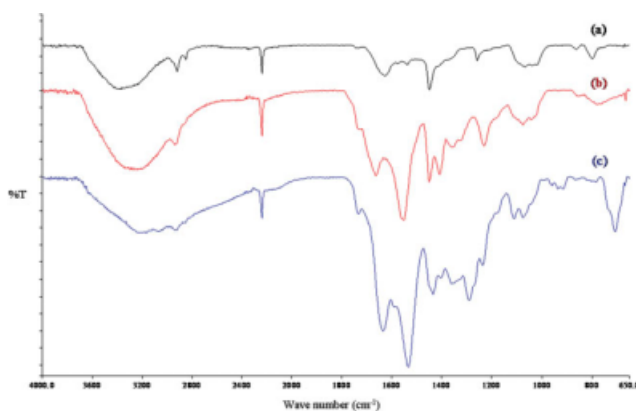
The porous mPAN membrane was prepared by the immersion of the PAN support membrane in a 2M NaOH solution at 50°C. The partial –CN groups of PAN could be converted into –COOH or –CONH<sub>2</sub> groups after hydrolysis with a NaOH solution.<sup>3,14</sup> The porous mPAN support membrane was washed in a water bath for several hours, and it was then dried at atmospheric temperature.

### Preparation of the EDA–TMC/mPAN composite membrane

The mPAN support membrane was fixed in a special framelike device, and its surface was exposed to the atmosphere. An aqueous solution of EDA was poured onto the membrane and was allowed to contact the membrane surface for a period of time. Then, the mPAN membrane soaked with the EDA aqueous solution was removed from the special framelike device. A rubber rod was used to remove the excess amount of EDA aqueous solution from the surface of the mPAN membrane support. This support membrane was immersed in a toluene solution containing TMC for a period of time to carry out the process of interfacial polymerization, which resulted in the formation of a thin polyamide layer on the surface of the mPAN membrane. Finally, to attain the desired stability in the structure, the resulting EDA–TMC/mPAN composite membrane was subjected to heat treatment for 60 min in an oven at 70°C.

### Characterization

Scanning electron microscopy (SEM; S-3000N, Hitachi, Tokyo, Japan) and atomic force microscopy (AFM; Digital Instruments, DI-NS3a, Santa Barbara, CA) were used to observe the morphologies of the



**Figure 1** FTIR-ATR spectra for (a) a pristine PAN support membrane, (b) an mPAN support membrane (as a result of PAN treatment in a 2M NaOH solution at 50°C), and (c) a polyamide thin-film EDA-TMC/mPAN composite membrane (the concentration of and contact time with the EDA aqueous solution were 5 wt % and 30 min, respectively; the concentration of and time of immersion in the TMC organic solution were 1 wt % and 3 min, respectively). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

polyamide thin-film composite membranes. Fourier transform infrared/attenuated total reflection (FTIR-ATR) spectroscopy (Spectrum One, PerkinElmer, Bucks, England) was used to examine the chemical structures of the membranes. To estimate the conversion from PAN to mPAN in the hydrolysis with the NaOH solution, the elemental composition and concentration ratio data for the PAN and mPAN membranes were obtained with SEM/energy-dispersive X-ray spectroscopy (EDX; S-3000N, Hitachi). The chemical surface characterization of the polyamide thin-film composite membranes was carried out with X-ray photoelectron spectroscopy (XPS; VG ESCA Scientific Theta Probe, East Grinstead, UK). The thermal properties of the membranes were measured by a PerkinElmer (Norwalk, CT) dynamic mechanical analyzer (PerkinElmer DMA7e) with the thermal mechanical analysis (TMA) controlled force mode with a quartz penetration probe at a static force of 100 mN and a heating rate of 5°C/min from 0 to 350°C. To understand the surface hydrophilicity of the polyamide thin-film composite membranes, the water contact angle was estimated with the use of an automatic interfacial tensiometer (FACE Mode 1 PD-VP) (Kyowa Interface Science Co., Ltd., Saitama, Japan).

### Pervaporation measurement

The pervaporation apparatus used in this study was described in our previous study.<sup>15</sup> The effective surface area of the membrane in direct contact with the feed was 11.64 cm<sup>2</sup>, and the operating temperature (feed solution temperature) was 25°C. The concentrations of the feed solution and the permeate were

measured by gas chromatography (8700 T, China Chromatography, Taipei, Taiwan). The permeation rate ( $P$ ) was calculated with the following equation:

$$P = \frac{W}{A \times t} \quad (1)$$

where  $W$  is the weight of the permeate,  $A$  is the effective membrane area, and  $t$  is the sampling time.

## RESULTS AND DISCUSSION

### Characterization

The FTIR-ATR spectra for the PAN and mPAN membranes are shown in Figure 1. Compared with the spectrum for the PAN membrane [Fig. 1(a)], the mPAN membrane had four peaks at wave numbers 3200–3400, 1735, 1664, and 1555 cm<sup>-1</sup>, as shown in Figure 1(b). The first two peaks corresponded to the —OH and C=O, respectively, of the carboxylic acid group. The last two peaks corresponded to the C=O and —NH, respectively, of the acryl amide group. Such spectra revealed that the partial —CN groups of the PAN membrane were converted to —COOH or —CONH<sub>2</sub> groups, as a result of PAN hydrolysis in the NaOH solution.

Table I shows the elemental composition and concentration ratio data for the PAN and mPAN membranes from the SEM/EDX measurement. Compared to the PAN membrane, the O/C and O/N ratios for the mPAN membrane increased, but the N/C ratio decreased slightly. These data indicate that the formation of the —COOH and —CONH<sub>2</sub> groups in the mPAN membrane was a result of the conversion of partial —CN groups in the PAN membrane. The percentage of —CN conversion to —COOH, which was estimated from the O/N ratio for the repeating units in the mPAN structure, was about 26%.

The FTIR-ATR spectra for the mPAN and polyamide thin-film composite membranes are shown in Figure 1. Compared with the spectrum for the mPAN membrane [Fig. 1(b)], two peaks were present in the spectrum for the polyamide thin-film composite membrane [Fig. 1(c)] at wave numbers 1636 and 1535 cm<sup>-1</sup>, corresponding to C=O (amide I) and N—H (amide II), respectively. This result confirms that the thin-film composite membrane active layer was composed of aromatic polyamide.

**TABLE I**  
Elemental Composition and Concentration Ratio Data for PAN and mPAN Membranes from SEM/EDX Measurements

Membrane	C (%)	O (%)	N (%)	O/C	N/C	O/N
PAN	75.50	2.78	21.72	0.04	0.29	0.13
mPAN	70.51	12.15	17.34	0.17	0.25	0.70

mPAN resulted from the hydrolysis of PAN in a 2M NaOH solution at 50°C.

**TABLE II**  
Surface Elemental Composition, Elemental Concentration Ratio, and Crosslinking Portion Data for Polyamide Thin-Film Composite Membranes from XPS Measurements

Membrane	C (%)	O (%)	N (%)	O/C	N/C	O/N	<i>m</i> (%) <sup>b</sup>
EDA-TMC/mPAN prepared with 5 wt % EDA <sup>a</sup>	74.28	15.70	10.03	0.21	0.14	1.57	34
EDA-TMC/mPAN prepared with 10 wt % EDA <sup>a</sup>	68.39	16.54	15.06	0.24	0.22	1.10	86

<sup>a</sup> The contact time with the EDA aqueous solution was 30 min; the concentration of and time of immersion with the TMC organic solution were 1 wt % and 3 min, respectively.

<sup>b</sup> The fractions of the crosslinked portion (*m*) and the linear portion (*n*) were calculated from the relative ratios of the atomic concentrations. In the calculation,  $m + n = 1$  and  $O/N = (3m + 4n)/(3m + 2n)$  according to the chemical formulas of the crosslinked portion and the linear portion:

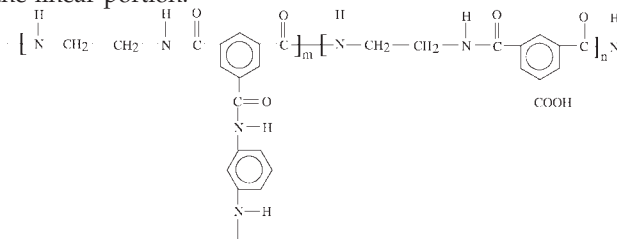
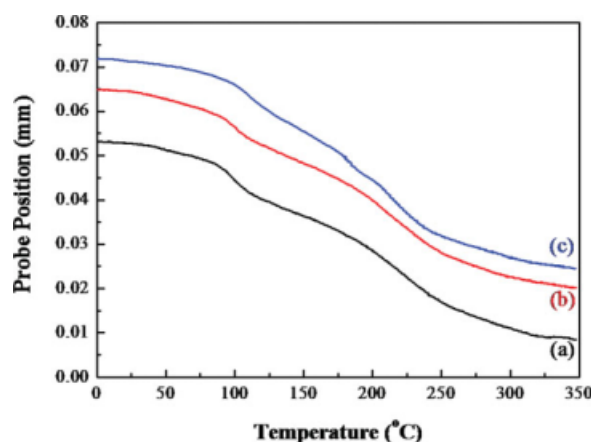


Table II shows the surface elemental composition and elemental concentration ratio data for the polyamide thin-film composite membranes from the XPS measurement. As shown in Table II, there was an increase in the N/C ratio and a decrease in the O/N ratio when the concentration of the EDA aqueous solution used to prepare the polyamide layer was increased from 5 to 10 wt %. This result shows that more polyamide linkage groups formed in the polymerized layer with increasing concentration of the EDA aqueous solution used for the interfacial polymerization. The fraction of the crosslinking portion of

the polyamide layer was estimated from the O/N ratio for the repeating units in the polyamide structure, as shown in Table II. The fraction of the crosslinking portion of the polyamide layer increased with increasing concentration of the EDA aqueous solution.

To investigate the thermal properties of the mPAN and polyamide thin-film composite membranes, TMA was conducted. Figure 2 shows the TMA curves for the mPAN and polyamide thin-film composite membranes. There were two obvious drops for all of the curves in the ranges 80–120 and 160–240°C, corresponding to the glass-transition temperature ( $T_g$ ) and initial decomposition temperature ( $T_{d,i}$ ) values, respectively, of the mPAN. The  $T_g$  and  $T_{d,i}$  values for the mPAN and polyamide thin-film composite membranes are shown in Table III. The result shows that both the  $T_g$  and  $T_{d,i}$  values shifted to higher temperatures when the concentration of the EDA aqueous solution used to prepare the polyamide layer was increased from 5 to 10 wt %. This might have been

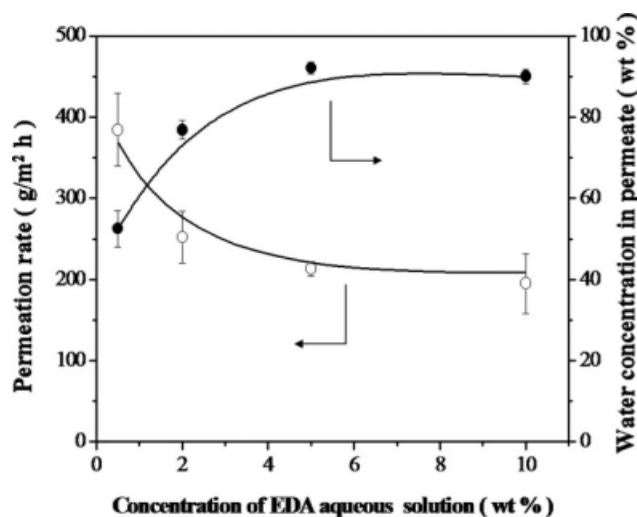


**Figure 2** TMA curves for (a) an mPAN support membrane and (b,c) polyamide thin-film composite membranes prepared by contact with a 5 or 10 wt % EDA aqueous solution, respectively, for 30 min and then immersion in a 1 wt % TMC organic solution for 3 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE III**  
 $T_g$  and  $T_{d,i}$  Values of mPAN and Polyamide Thin-Film Composite Membranes

Membrane	$T_g$ (°C)	$T_{d,i}$ (°C)
mPAN	92	193
EDA-TMC/mPAN prepared with 5 wt % EDA <sup>a</sup>	94	196
EDA-TMC/mPAN prepared with 10 wt % EDA <sup>a</sup>	104	206

<sup>a</sup> The contact time with the EDA aqueous solution was 30 min; the concentration of and time of immersion in the TMC organic solution were 1 wt % and 3 min, respectively.



**Figure 3** Effect of the concentration of an EDA aqueous solution on the pervaporation performance of polyamide thin-film composite membranes for dehydrating a 90 wt % isopropyl alcohol aqueous solution at 25°C (the contact time with the EDA aqueous solution was 30 min; the concentration of and time of immersion in the TMC organic solution were 1 wt % and 3 min, respectively).

because the dense polyamide layer formed on the mPAN membrane became thicker (as shown later in Fig. 4) with an increase in the concentration of the EDA aqueous solution, which resulted in a delay in the  $T_g$  and  $T_{d,i}$  of the mPAN.

#### Concentration and contact time effects of EDA aqueous solutions on the pervaporation performance

To obtain the desired interfacially polymerized thin-film composite membrane that could be applied in isopropyl alcohol dehydration by pervaporation, the effect of the interfacial polymerization conditions on the pervaporation performance was investigated. The concentration effect of the EDA aqueous solution on the pervaporation performance of the polyamide thin-film composite membranes for dehydrating a 90 wt % isopropyl alcohol/water solution at 25°C was studied, and the result is exhibited in Figure 3. The figure shows a decrease in the permeation rate and an increase in the water concentration in the permeate with an increase in the concentration of the EDA aqueous solution from 0.5 to 5 wt %. This was due to the increase in the thickness of the polyamide active layer with the increase in the concentration of the EDA aqueous solution (Fig. 4).

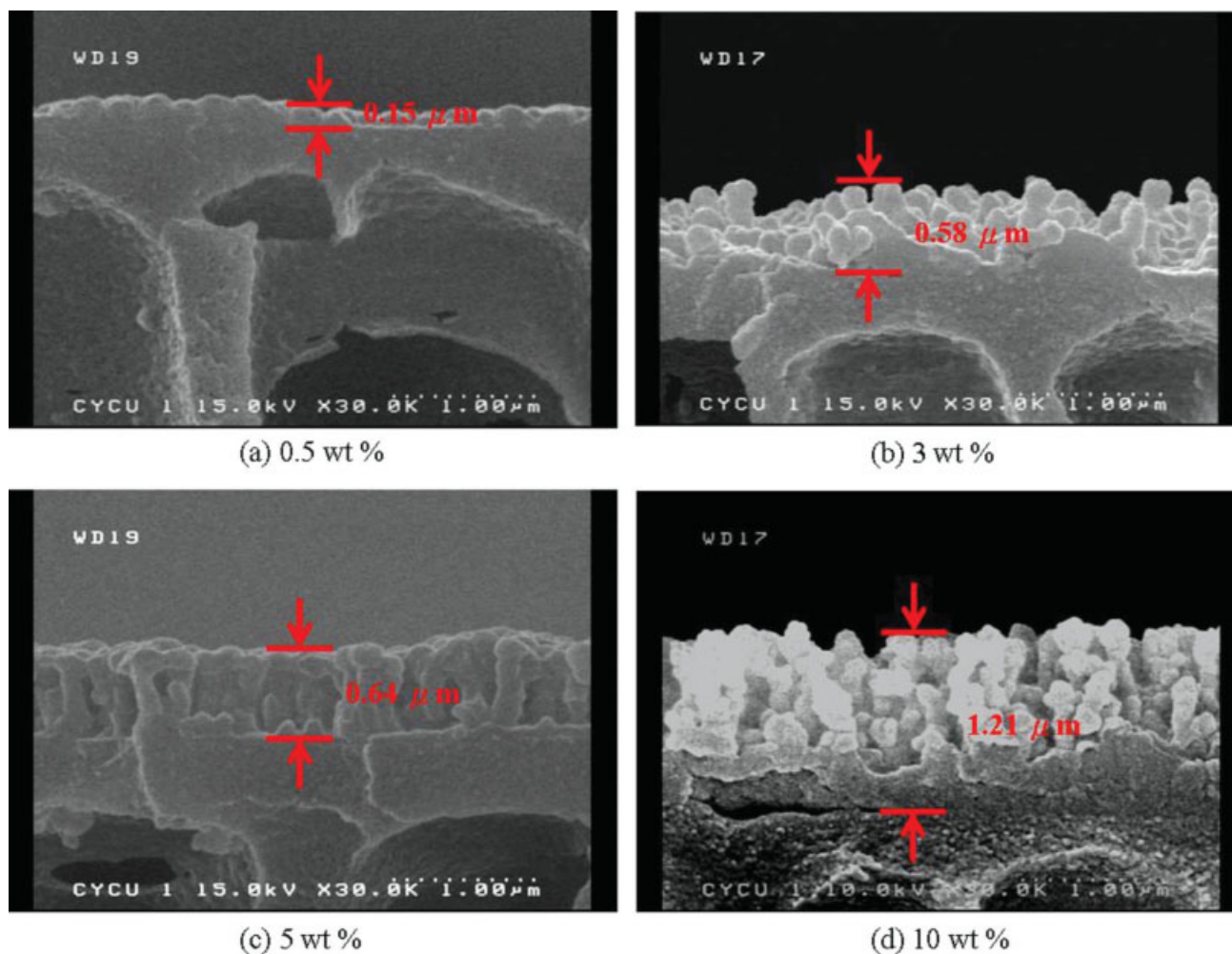
Figure 4 displays the cross-sectional SEM images of the polyamide thin film composite membrane active layers prepared from the contact of the mPAN surface with different concentrations of EDA aqueous solutions for 30 min and then its immersion in a 1 wt % TMC organic solution for 3 min. Figure 4 indicates an increase in the thickness of the poly-

amide active layer from 0.15 to 0.64  $\mu\text{m}$  with an increase in the concentration of the EDA aqueous solution from 0.5 to 5 wt %. This may be because the higher monomer concentration increased the opportunity for the monomers to collide and react with each other, which caused a high polymerization rate. As a result, the thickness of the polymerized layer increased. Hence, the permeation rate decreased, and the water concentration in the permeate increased, as shown in Figure 3.

On the basis of the SEM images in Figure 4, the polyamide active layer near the surface of the mPAN support membrane appeared denser, whereas that far from the surface of the mPAN support membrane appeared to have a looser structure.<sup>16</sup> This phenomenon may be explained as follows: the dense polymerized layer was formed instantly from the reaction of EDA with TMC when the aqueous and organic phase solutions contacted each other at the surface of the mPAN support membrane. The polymerized polyamide layer near the surface of the mPAN support membrane gradually became dense with the passage of time or as the reaction proceeded. As the layer formed, the amount of EDA in the aqueous solution that could penetrate the polymerized polyamide layer before it reacted with the TMC in the organic solution gradually decreased. This resulted in a looser structure in the polymerized layer far from the surface of the mPAN support membrane.

The permeation rate and the water concentration in the permeate leveled off when the concentration of the EDA aqueous solution exceeded 5 wt % (Fig. 3). This phenomenon was attributed to the following: the polyamide active layer near the surface of the mPAN support appeared dense enough to attain good performance in separating a 90 wt % isopropyl alcohol/water solution. The increasingly looser structure in the polyamide active layer far from the surface of the mPAN support did not affect the pervaporation performance.

The most asymmetric support membrane prepared with the wet-phase inversion method possesses a dense skin layer. Therefore, it is necessary to allow enough time for the skin layer of the asymmetric support membrane to swell. This swollen state permits the aqueous diamine monomer to penetrate into the membrane and causes the reactive sites to increase to facilitate the formation of a denser polymerized layer. The contact time effect of the EDA aqueous solution on the pervaporation performance for dehydrating a 90 wt % isopropyl alcohol/water solution was investigated, and the result is exhibited in Figure 5. The data indicated a decrease in the permeation rate and an increase in the water concentration in the permeate when the contact time of the EDA aqueous solution increased from 5 to 30 min. The permeation rate and the water concentration in



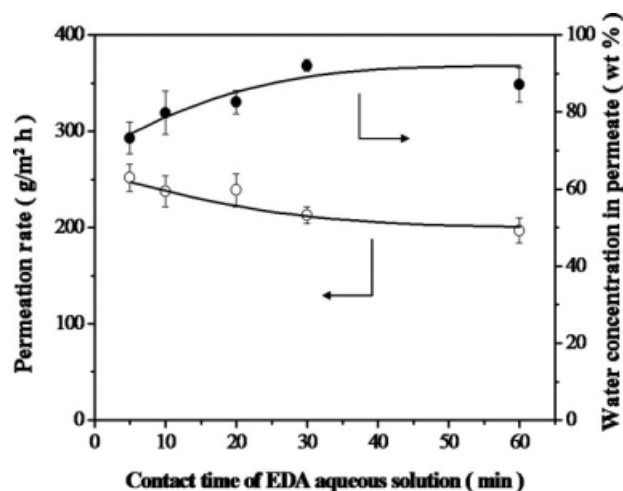
**Figure 4** Effect of the concentration of an EDA aqueous solution on the thickness of the polyamide active layer. Polyamide thin-film composite membranes were prepared by contact with (a) 0.5, (b) 2, (c) 5, and (d) 10 wt % EDA aqueous solutions for 30 min and then immersion in a 1 wt % TMC organic solution for 3 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the permeate changed slightly when the contact time of the EDA aqueous solution was longer than 30 min. It was demonstrated that an increase in the contact time of the EDA aqueous solution could make the skin layer of the asymmetric support membrane swell, which increased the reactive sites and facilitated the formation of a denser polymerized layer. This resulted in an improvement in the pervaporation performance. On the basis of the results given in Figures 3 and 5, the desirable conditions for the EDA aqueous solution to obtain better pervaporation performance were a concentration of 5 wt % and a contact time of 30 min. These desirable conditions were used in the following experiments.

#### Concentration and immersion time effects of TMC organic solutions on the pervaporation performance

In addition to the EDA aqueous solution, the TMC organic solution played an important role in the

polymerized layer's morphology and the pervaporation performance of the polyamide thin-film composite membranes. Hence, the concentration and the immersion time effects of the TMC organic solution were investigated. Table IV tabulates the data regarding the concentration effect of the TMC organic solution on the pervaporation separation of a 90 wt % isopropyl alcohol/water solution at 25°C. The tabulation indicates that the permeation rate decreased and then increased and that the water concentration in the permeate increased when the concentration of the TMC organic solution increased from 0.1 to 1.0 wt %. The rationale behind these phenomena may be given as follows: the active layers prepared by interfacial polymerization had different chemical structures, which changed the hydrophilic-hydrophobic properties of the composite membranes. In general, two side reactions occur when a diamine reacts with TMC during interfacial polymerization. One side reaction is the crosslinking



**Figure 5** Effect of the contact time of an EDA aqueous solution on the pervaporation performance of polyamide thin-film composite membranes for dehydrating a 90 wt % isopropyl alcohol aqueous solution at 25°C (the concentration of the EDA aqueous solution was 5 wt %; the concentration of and time of immersion in the TMC organic solution were 1 wt % and 3 min, respectively).

reaction between a diamine molecule with the terminal acyl chloride group of TMC to form an amide linkage (—CONH—) in the backbones of the polymer chains. This results in the formation of a network chain-branching structure in polyamide. The other side reaction is the hydrolysis reaction of the third or terminal acyl chloride group of TMC, which forms a carboxylic acid. This results in the formation of a linear hydrophilic structure in the polyamide.<sup>17</sup> The proportion of the crosslinking network and the linear hydrophilic structures in the polyamide affect the hydrophilic–hydrophobic properties of the composite membrane.

When the concentration of the TMC organic solution increased from 0.1 to 0.5 wt %, a higher poly-

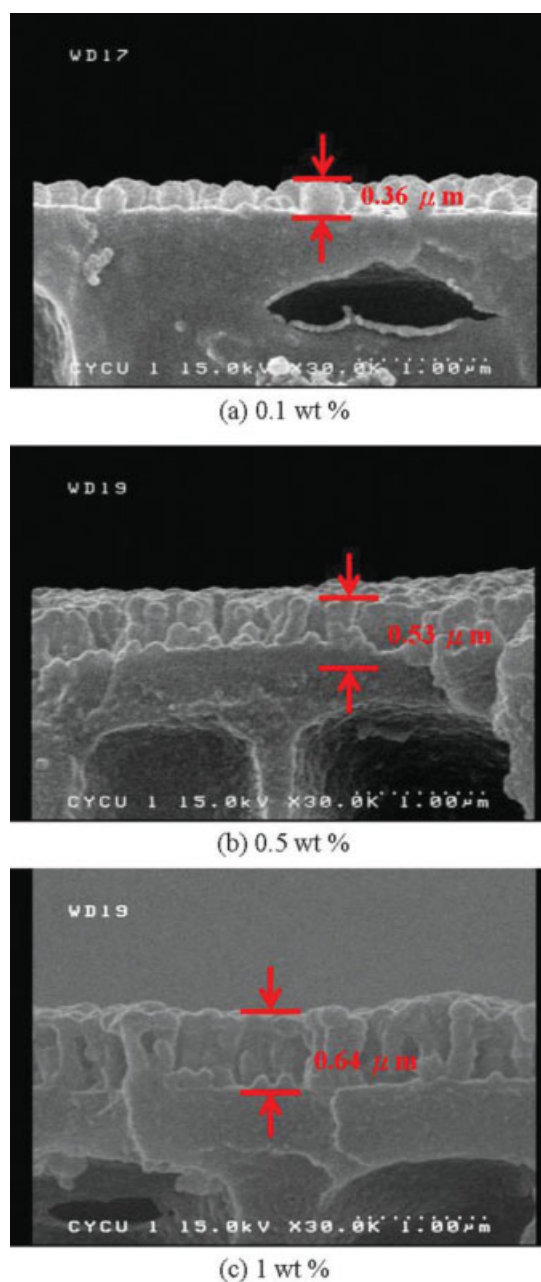
**TABLE IV**  
Effect of the Concentration of the TMC Organic Solution on the Pervaporation Performance of Polyamide Thin-Film Composite Membranes for Dehydrating a 90 wt % Isopropyl Alcohol/Water Solution at 25°C

Concentration of the TMC organic solution (wt %) <sup>a</sup>	Pervaporation performance	
	Permeation rate (g/m <sup>2</sup> h)	Water concentration in the permeate (wt %)
0.1	213 ± 5	71.9 ± 2.3
0.5	181 ± 10	82.4 ± 4.0
1.0	213 ± 9	92.1 ± 1.5

The concentration of and contact time with the EDA aqueous solution were 5 wt % and 30 min, respectively; the time of immersion in the TMC organic solution was 3 min.

<sup>a</sup> When the concentration of the TMC organic solution was greater than 1 wt %, TMC showed poor solubility.

merization rate was achieved. This caused the thickness of the EDA–TMC polymerized layer to increase from 0.36 to 0.53 μm. The cross-sectional SEM images of these polyamide layers are shown in Figure 6. The surface hydrophilic–hydrophobic properties of the composite membrane were examined directly by measurement of the water contact angle. A decrease in the water contact angle indicated an



**Figure 6** Effect of the concentration of a TMC organic solution on the thickness of the polyamide active layer. Polyamide thin-film composite membranes were prepared by contact with a 5 wt % EDA aqueous solution for 30 min and then immersion in an organic solution of (a) 0.1, (b) 0.5, or (c) 1 wt % TMC for 3 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

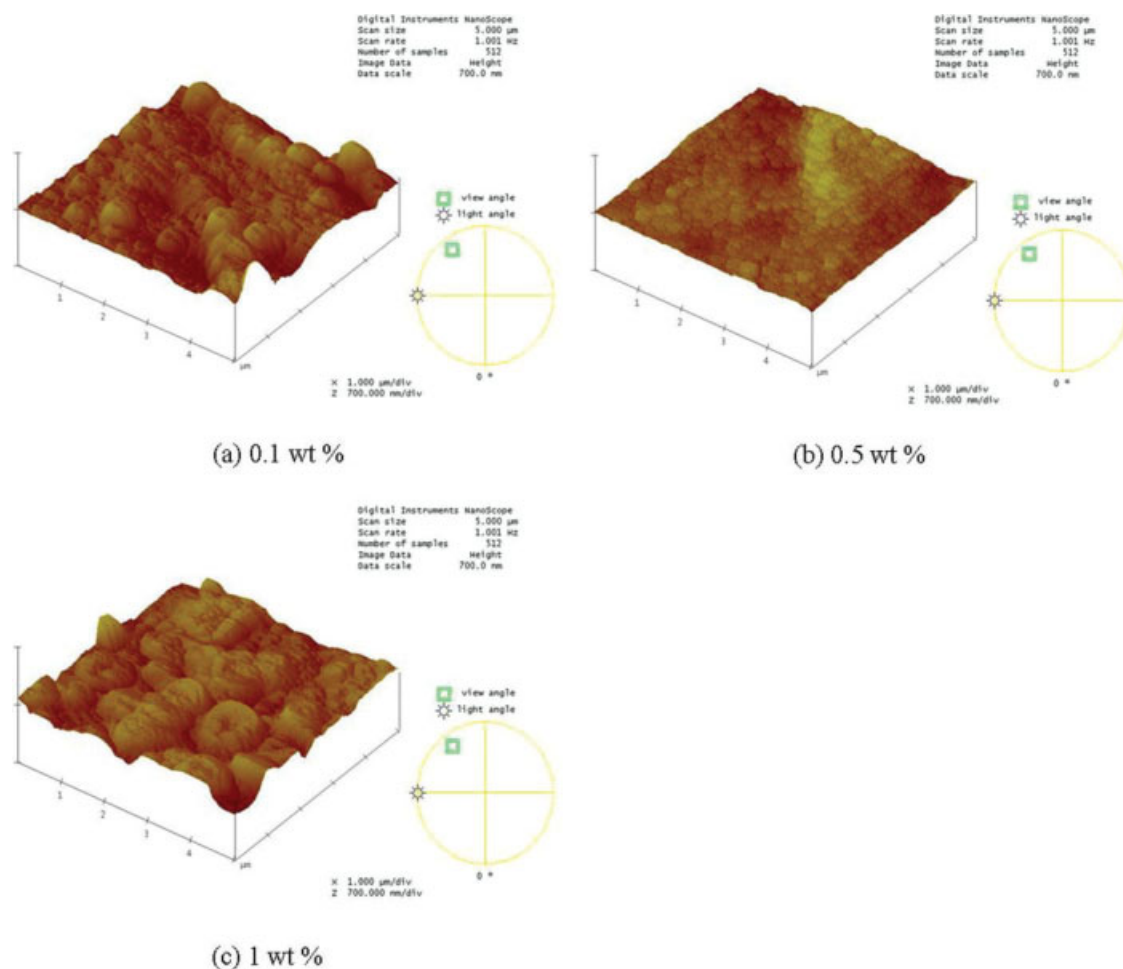
**TABLE V**  
**Effect of the Concentration of the TMC Organic Solution on the Surface Water Contact Angles for Polyamide Thin-Film Composite Membranes**

Concentration of the TMC organic solution (wt %)	Water contact angle (°)
0.1	89 ± 3
0.5	96 ± 2
1.0	77 ± 1

The concentration of and contact time with the EDA aqueous solution were 5 wt % and 30 min, respectively; the time of immersion in the TMC organic solution was 3 min.

increase in the hydrophilicity (this was based on the water contact angle being less than 90°). Table V lists the data on the effect of the concentration of the TMC organic solution on the surface water contact angles for the polyamide thin-film composite membranes. The list indicates an increase in the water contact angle from 89 to 96°, which corresponded to

an increase in the concentration of the TMC organic solution from 0.1 to 0.5 wt %. This was related to the decrease in the hydrophilicity of the polyamide layer. In general, an increase in the membrane surface roughness caused a corresponding increase in the surface area and the membrane hydrophilicity, which improved the efficiency of the pervaporation separation process. The effect of the concentration of the TMC organic solution on the surface roughness of the polyamide thin-film composite membranes was investigated by AFM, and the result is exhibited in Figure 7. The AFM images indicate a decrease in the surface roughness of the polyamide thin-film composite membrane when the concentration of the TMC organic solution increased from 0.1 to 0.5 wt %. This resulted in a decrease in the effective surface area, which caused a decrease in the permeation rate and a decrease in the hydrophilicity (based on the result of the water contact angle measurement). This decrease in the hydrophilicity (an increase in the water contact angle) indicated that



**Figure 7** AFM images of polyamide thin-film composite membrane surfaces. Polyamide thin-film composite membranes were prepared by contact with a 5 wt % EDA aqueous solution for 30 min and then immersion in an organic solution of (a) 0.1, (b) 0.5, or (c) 1 wt % TMC for 3 min. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

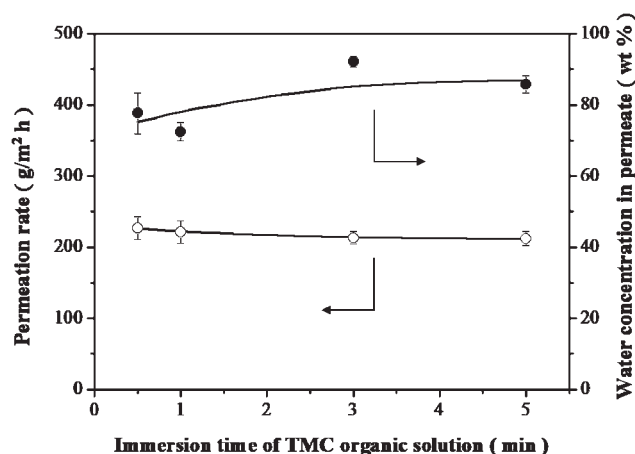


most of the terminal acyl chloride groups of TMC reacted with diamine molecules to form the cross-linking structure. This resulted in an increase in the water concentration in the permeate and a decrease in the permeation rate.

On the basis of the aforementioned results, the reasons for the decrease in the permeation rate and the increase in the water concentration in the permeate when the concentration of the TMC organic solution increased from 0.1 to 0.5 wt % (Table IV) were as follows:

1. An increase in the thickness of the polyamide layer, which corresponded to a decrease in the permeation rate and an increase in the water concentration in the permeate, resulted from a higher polymerization rate.
2. A decrease in the hydrophilicity of the polyamide layer is supposed to be related to the following occurrence: most acyl chloride groups of TMC are joined in the crosslinking reaction, and few acyl chloride groups of TMC are converted into carboxylic acid groups via the hydrolysis reaction. The crosslinking network structure dominates the linear hydrophilic structure in polyamide. This could cause a decrease in the permeation rate and an increase in the water concentration in the permeate.
3. A decrease in the surface roughness of the polyamide thin-film composite membrane indicated a decrease in the effective surface area for permeation during the pervaporation separation, and as a result, the permeation rate decreased.

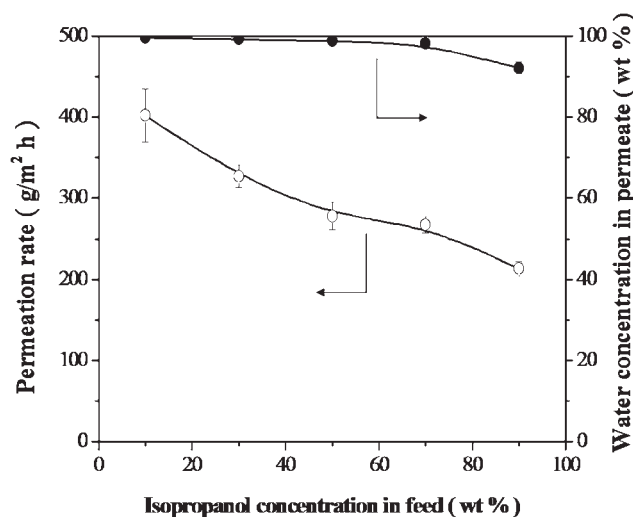
As indicated in Table IV, both the permeation rate and the water concentration in the permeate increased when the concentration of the TMC organic solution increased from 0.5 to 1.0 wt %. This may have been due to the increase in both the hydrophilicity (Table V) and the surface roughness (Fig. 7) of the polyamide thin-film composite membrane, although an increase in the thickness of the polyamide layer from 0.53 to 0.64  $\mu\text{m}$  (Fig. 6) possibly resulted in a decrease in the permeation rate. The decrease in the water contact angle of the polyamide thin-film composite membrane from 96 to 77° as the concentration of the TMC organic solution increased from 0.5 to 1.0 wt % is indicated in Table V. This decrease in the water contact angle corresponded to an increase in the hydrophilicity of the polyamide layer. This was supposed to be related to an increase in the amount of the carboxylic acid groups resulting from the hydrolysis of the unreacted acyl chloride groups of TMC. In other words, the proportion of the linear hydrophilic structure in polyamide increased in comparison to the crosslinking network structure. As a result, both



**Figure 8** Effect of the immersion time in a TMC organic solution on the pervaporation performance of polyamide thin-film composite membranes for dehydrating a 90 wt % isopropyl alcohol aqueous solution at 25°C (the concentration of and contact time with the EDA aqueous solution were 5 wt % and 30 min, respectively; the concentration of the TMC organic solution was 1 wt %).

the water concentration in the permeate and the permeation rate increased. Moreover, the surface roughness of the polyamide thin-film composite membranes increased when the concentration of the TMC organic solution increased from 0.5 to 1.0 wt %, as depicted in Figure 7. The AFM images indicated an increase in the effective surface area for permeation during the pervaporation separation. This resulted in an increase in the permeation rate. An increase in the surface roughness also indicated an increase in the hydrophilicity, which was in agreement with the result of the water contact angle measurement (Table V). This resulted in the enhancement of the water concentration in the permeate and the permeation rate.

The immersion time effect of the TMC organic solution on the pervaporation separation of a 90 wt % isopropyl alcohol/water solution is described in Figure 8. It shows that the immersion time effect of the TMC organic solution on the permeation rate was not obvious. However, the water concentration in the permeate increased when the immersion time of the TMC organic solution increased from 0.5 to 5 min. This was due to the increase in the thickness of the polyamide active layer from 0.20 to 0.72  $\mu\text{m}$ , which corresponded to the increase in the immersion time of the TMC organic solution. The polyamide thin-film composite membrane (EDA-TMC/mPAN) with the desirable polymerization conditions (contact with a 5 wt % EDA aqueous solution for 30 min and immersion in a 1 wt % TMC organic solution for 3 min) exhibited the best pervaporation performance in the dehydration of a 90 wt % isopropyl alcohol/water solution at 25°C.



**Figure 9** Effect of the isopropyl alcohol concentration in the feed on the pervaporation performance of a polyamide thin-film composite membrane (EDA-TMC/mPAN) under desirable polymerization conditions at 25°C.

Normally, pervaporation performance strongly depends on the operating conditions. Different industries require different operating conditions for their pervaporation separation processes. In this regard, it was interesting to investigate the effect of the operating conditions, such as the feed composition, operating temperature, and type of feed alcohol aqueous solutions, on the pervaporation performance of the polyamide thin-film composite membranes (EDA-TMC/mPAN) with the desirable polymerization conditions, as discussed in the following sections.

#### Effect of the feed composition on the pervaporation performance

Figure 9 illustrates the effect of the isopropyl alcohol feed solution concentration on the pervaporation performance of the EDA-TMC/mPAN composite membrane with the desirable polymerization conditions at 25°C. The water concentration in the permeate remained unchanged except when it decreased slightly in the case of the 90 wt % aqueous isopropyl alcohol solution. The permeation rate decreased with

increasing isopropyl alcohol concentration in the feed. This was because the thin polyamide active layer was easily swollen by the isopropyl alcohol when the isopropyl alcohol concentration in the feed increased. To further confirm the previous phenomenon, contact angle measurements were made. A lower contact angle indicated a greater tendency for the aqueous alcohol solution to wet the membrane surface and, therefore, a higher affinity between them. Table VI gives the data on the effect of the aqueous isopropyl alcohol feed solution concentration on the surface contact angle of the EDA-TMC/mPAN composite membrane with the desirable polymerization conditions. The contact angle decreased with an increase in the isopropyl alcohol concentration in the feed solution. That is, a higher affinity was obtained between the polyamide thin layer and the aqueous isopropyl alcohol solution with a higher concentration. This observation is reflected in the results plotted in Figure 9. Thus, the swollen polymer chain became softer and supplied more free volume (at a higher isopropyl alcohol concentration). The isopropyl alcohol molecules occupied the free volume supplied by the swollen polymer chain, but they could not be desorbed easily from the EDA-TMC active layer because of the higher affinity between the EDA-TMC active layer and the isopropyl alcohol molecules. Thus, the rate of diffusion across the membrane for the water molecules became lower than that for the isopropyl alcohol molecules. This was because water molecules (18 mL/mol) are smaller than isopropyl alcohol molecules (76.4 mL/mol). Therefore, the permeation rate decreased and the water concentration in the permeate changed slightly when the isopropyl alcohol feed concentration increased. In addition, the driving force decreased when the water concentration in the feed solution decreased, which also caused the permeation rate to decrease.

#### Effect of the operating temperature on the pervaporation performance

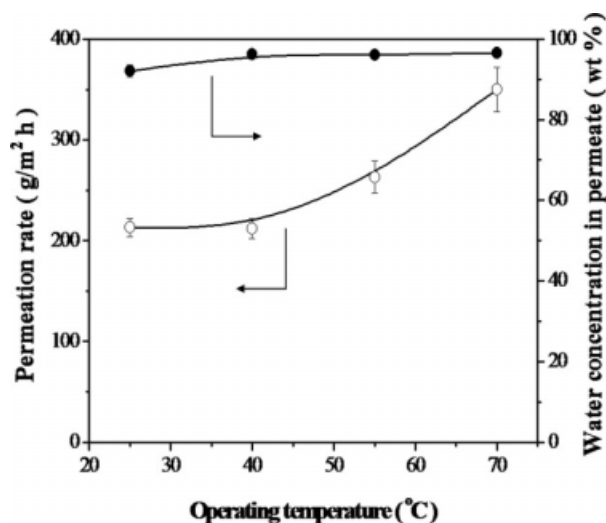
Figure 10 demonstrates the effect of the operating temperature on the pervaporation separation of the

**TABLE VI**  
Effect of the Aqueous Isopropyl Alcohol Solution Concentration on the Contact Angle for EDA-TMC/mPAN Composite Membranes at 25°C

	Isopropyl alcohol concentration (wt %)						
	0	10	30	50	70	90	>99
Contact angle (°)	77.2	42.2	20.6	17.3	14.1	— <sup>a</sup>	— <sup>a</sup>
Standard deviation	1.0	1.9	1.5	0.8	1.5	—	—

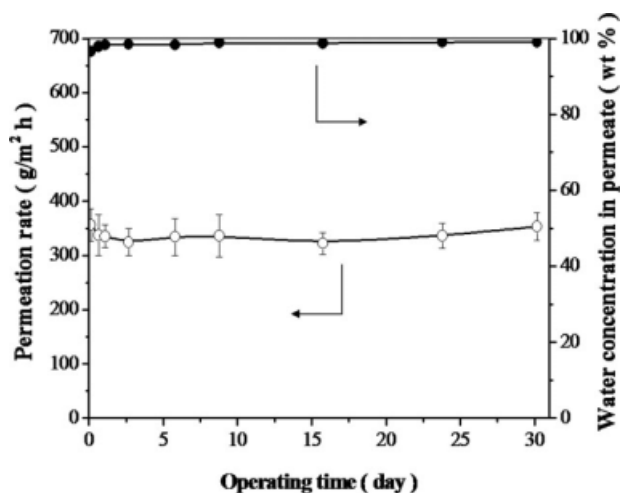
The reaction conditions were contact with 5 wt % EDA/water for 30 min and then immersion in 1 wt % TMC/toluene for 3 min.

<sup>a</sup> The affinity between the aqueous isopropyl alcohol solution and the EDA-TMC/mPAN composite membrane was too strong for the contact angle to be measured.



**Figure 10** Effect of the operating temperature on the pervaporation separation of a 90 wt % isopropyl alcohol aqueous solution with a polyamide thin-film composite membrane (EDA-TMC/mPAN) under desirable polymerization conditions.

90 wt % isopropyl alcohol aqueous solution through the polyamide thin-film composite membrane (EDA-TMC/mPAN) with the desirable polymerization conditions. The plot indicates an increase in the permeation rate and a slight increase in the water concentration in the permeate with an increase in the operating temperature. This occurred because the polymer chains became more active, that is, they mobilized more easily, at higher temperatures. An increase in the free volume resulted from the motion of the polymer chains at higher operating temperatures. The diffusion rate across the membrane for water molecules became lower than that for isopropyl alcohol molecules. However, the crosslinking structures in the polyamide layer made it difficult for isopropyl alcohol molecules to pass through the membrane compared with water molecules. Therefore, both the permeation rate and the water concentration in the perme-



**Figure 11** Effect of the operating time on the pervaporation performance of a polyamide thin-film composite membrane (EDA-TMC/mPAN) under desirable polymerization conditions at 70°C for dehydrating a 90 wt % isopropyl alcohol aqueous solution.

ate increased with an increase in the operating temperature.

On the basis of the results of the operating temperature effect, the polyamide thin-film composite membrane (EDA-TMC/mPAN) with the crosslinking network structure would be suited for the pervaporation separation operation at high feed temperatures. However, the membrane durability is a critical factor in commercial applications. The long-term membrane operating stability was, therefore, investigated in this study. Figure 11 presents the data for the operating time effect on the pervaporation separation of a 90 wt % isopropyl alcohol/water solution at 70°C. The data indicated that both the permeation rate and the water concentration in the permeate remained unchanged during the operation for 30 days at 70°C. This finding illustrates that the polyamide thin-film composite membrane (EDA-TMC/mPAN) with the crosslinking network structure exhibited membrane durability during the pervaporation separation at a high operating temperature.

**TABLE VII**  
Effect of 90 wt % Alcohol Aqueous Solutions on the Pervaporation Performance of a Polyamide Thin-Film Composite Membrane (EDA-TMC/mPAN) Under Desirable Polymerization Conditions at 25°C

90 wt % alcohol aqueous solution	Pervaporation performance		Molecular length (Å) <sup>a</sup>	Molar volume of the alcohol solvent (mL/mol)
	Permeation rate (g/m <sup>2</sup> h)	Water concentration in the permeate (wt %)		
Methanol	555 ± 31	29.0 ± 0.9	2.9	40.7
Ethanol	360 ± 21	48.8 ± 2.6	4.2	58.6
<i>n</i> -Propanol	240 ± 6	82.0 ± 4.4	5.4	75.1
Isopropyl alcohol	213 ± 9	92.1 ± 1.5	—	76.4

The concentration of and contact time with the EDA aqueous solution were 5 wt % and 30 min, respectively; the concentration of and time of immersion in the TMC organic solution were 1 wt % and 3 min, respectively.

<sup>a</sup> The data were taken from ref. 18.

### Effect of the feed alcohol aqueous solutions on the pervaporation performance

Table VII is a tabulation of data for the effects of different 90 wt % alcohol aqueous solutions on the pervaporation performance of the polyamide thin-film composite membrane (EDA-TMC/mPAN) with the desirable polymerization conditions at 25°C. The pervaporation separation mechanism is based on the solution-diffusion model. The molecular size of the penetrator is important in both the solution and the diffusion process. Table VII indicates a decrease in the permeation rate and an increase in the water concentration in the permeate with an increase in the number of carbon atoms in the alcohol. The molecular size and the shape of the alcohol can explain this result. The molecular lengths of methanol, ethanol, and *n*-propanol are listed in Table VII.<sup>18</sup> As the molecular length increased for this linear alcohol series, the water concentration in the permeate increased and the permeate rate decreased. In addition, the steric hindrance for isopropyl alcohol was higher than that for *n*-propanol. This resulted in a decrease in the permeate rate and an increase in the water concentration in the permeate.

From another viewpoint, the molar volume of the penetrator affected its diffusion behavior across the membrane. A penetrator with a higher molar volume did not easily penetrate the membrane. This resulted in a decrease in the permeation rate and an increase in the selectivity. As indicated in Table VII, the permeation rate decreased and the water concentration in the permeate increased as the molar volume of alcohols increased in the following order: Methanol (40.7 mL/mol) < Ethanol (58.6 mL/mol) < *n*-Propanol (75.1 mL/mol) < Isopropyl alcohol (76.4 mL/mol). The molar volume of water was the smallest compared with all of the alcohols in the feed. This confirmed that the diffusion rate across the membrane for the penetrator increased with an increase in the molar volume of the penetrator. This resulted in a decrease in the permeation rate and an increase in the water concentration in the permeate.

### CONCLUSIONS

Polyamide thin-film composite membranes were prepared successfully via the interfacial polymerization reaction between EDA and TMC on the surface of mPAN membranes. These membranes were

applied in the pervaporation separation of alcohol aqueous solutions. The desirable polymerization conditions for the preparation of the polyamide thin-film composite membrane (EDA-TMC/mPAN) that gave the best pervaporation performance were a 30-min contact with a 5 wt % EDA aqueous solution and a 3-min immersion in a 1 wt % TMC organic solution. The polyamide thin-film composite membrane (EDA-TMC/mPAN) with the crosslinking structure was suitable for the pervaporation separation at a high operating temperature. The permeation rate and the water concentration in the permeate remained unchanged during a 30-day pervaporation separation of a 90 wt % isopropyl alcohol aqueous solution at 70°C. This indicated that the polyamide thin-film composite membrane (EDA-TMC/mPAN) with the desirable polymerization conditions exhibited membrane durability during the pervaporation separation at a high operating temperature.

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