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Novel interfacially-polymerized polyamide thin-film composite membranes: Studies on characterization, pervaporation, and positron annihilation spectroscopy

Wei-Chi Chao^a, Shu-Hsien Huang^{b,**}, Quanfu An^d, Der-Jang Liaw^c, Ying-Chi Huang^c, Kueir-Rarn Lee^{a,*}, Juin-Yih Lai^a

^a R&D Center for Membrane Technology, Department of Chemical Engineering, Chung Yuan University, Chung Li 32023, Taiwan

^b Department of Chemical and Materials Engineering, National Ilan University, I-Lan 26047, Taiwan

^c Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

^d Department of Polymer Science and Engineering, Key Laboratory of Macromolecule Synthesis and Functionalization (Ministry of Education),

Zhejiang University, Hangzhou 310027, China

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ABSTRACT

To improve the pervaporation performance of thin-film composite membranes, novel thin-film composite membranes were prepared via interfacial polymerization by reacting 5-nitrobenzene-1,3-dioyl dichloride (NTAC) or 5-tert-butylbenzene-1,3-dioyl dichloride (TBAC) with triethylenetetraamine (TETA) on the surface of a modified polyacrylonitrile (mPAN) membrane (TETA-NTAC/mPAN and TETA-TBAC/mPAN). The effect of the acyl chloride monomers chemical structure on the pervaporation separation of an aqueous ethanol solution was investigated. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and water contact angle measurements were applied to analyze the chemical structure, surface chemical composition, surface roughness and hydrophilicity of the polyamide active layer of the composite membrane. To correlate the variations in the free volume of the polyamide active layers with the pervaporation performance, positron annihilation spectroscopy (PAS) experiments were performed with a variable monoenergetic slow positron beam. From the results of the PAS and XPS experiments, the S parameter, o-Ps annihilation lifetime τ_3 (corresponding to free volume size) and its intensity I_3 (corresponding to free volume concentration), the τ_3 and I_3 of TETA-NTAC polyamide layer (positron incident energy of 1–1.7 keV) were both higher than those of TETA-TBAC polyamide layer. The S parameter for TETA-NTAC polyamide layer was also higher than that of the TETA-TBAC polyamide layer even though the former was more crosslinking than that of the latter. In the aqueous ethanol solution dehydration experiments, the TETA-NTAC/mPAN membrane produced both a higher permeation rate and water concentration in the permeate than the TETA-TBAC/mPAN membrane.

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1. Introduction

Ethanol aqueous solution, a biofuel, is a product of sugar fermentation in biomass resources, such as the stems of corn. It is a new energy source being studied to address the concerns associated with a lack of petroleum resources. Generally, the concentration of the ethanol produced from fermentation is low. To obtain high purity ethanol, ethanol dehydration is performed using a separation processes, such as distillation. Traditional distillation processes are

** Corresponding author. Tel.: +886 3 9357400; fax: +886 3 9357025.

generally used to concentrate ethanol aqueous solutions. However, water/ethanol azeotropes in the ethanol aqueous solution restrict further concentration of the ethanol. To break the azeotrope, azeotropic distillation with an azeotrope-breaking component (entrainer) or a hybrid system of multistage evaporation and distillation is used. These two processes consume large amounts of energy and are not economical. Pervaporation, an important membrane separation process in chemical industries, can effectively separate azeotropic mixtures and decrease the cost and energy consumption. Therefore, the pervaporation separation process is suitable to be applied in the dehydration of ethanol.

A composite membrane combines the advantages of a dense membrane and an asymmetric membrane. It has the potential to obtain a high permeation rate and a high selectivity during



^{*} Corresponding author. Tel.: +886 3 2654190; fax: +886 3 2654198.

E-mail addresses: huangsh@niu.edu.tw (S.-H. Huang), krlee@cycu.edu.tw (K.-R. Lee).

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pervaporation. Interfacial polymerization is a useful technique to apply a thin selective top layer to a composite membrane. Polyamides are an excellent material for the dense selective layer because of its high selectivity, high thermal stability, good mechanical strength and high resistance to organic solvents. Interfacially-polymerized polyamide thin-film composite membranes are usually studied for reverse osmosis [1–5] or nanofiltration applications [6–10], but there have been few reports on pervaporation [11–15]. In this study, polyamide thin-film composite membranes were prepared via interfacial polymerization of the amine monomer TETA and two novel acyl chlorides, NTAC and TBAC, on the surface of modified polyacrylonitrile (mPAN) support membranes. The effect of the monomer chemical structure on the pervaporation separation performance of a 90 wt% aqueous ethanol solution was investigated. The polyamide layer characteristics (i.e., surface roughness, hydrophilicity, degree of crosslinking and free volume) were correlated with the pervaporation performance.

The free volume has a significant effect on the separation performance of the membrane in the pervaporation operation. However, the measurement of the free volume is difficult because the free volume is a dynamic pore. Positron annihilation spectroscopy (PAS) with a variable monoenergetic slow positron beam is a powerful technique to measure the free volume of a material. The chemical and structural effects of the polymer on the free volume have been reported [16–19], but there has not been much work on the depth profile for the free volume variation in the thin-film composite membranes [14]. The variations in the free volume of these novel polyamide thin-film composite membranes were measured by positron annihilation spectroscopy (PAS) with a variable monoenergetic slow positron beam.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN) polymer was supplied by the Tong-Hua Synthesis Fiber Co. Ltd. in Taiwan. Reagent grade N-methyl-2-pyrrolidone (NMP) was used in preparing the casting solution of the PAN polymer. Triethylenetetraamine (TETA) was purchased from Merck Co. 5-Nitrobenzene-1,3-dioyl dichloride (NTAC) and 5-tertbutylbenzene-1,3-dioyl dichloride (TBAC) were synthesized in our laboratory. Amine (TETA) and acyl chloride monomers (NTAC and TBAC) were used for the interfacial polymerization to form the polyamide active layer. Distilled water was used in preparing the aqueous amine solution, and reagent grade tetrahydrofuran (THF) was used as the acyl chloride monomer solvent. The chemical structures of the monomers used to prepare the polyamide active layers via interfacial polymerization are shown in Fig. 1.

2.2. Synthesis of monomer NTAC acyl chloride

The diacyl chloride monomers of 5-nitrobenzene-1,3-dioyl dichloride were synthesized from a mixture of 5-nitrobenzene-1,3-dioic acid (3 g, 14.21 mmol), thionyl chloride (30 mL, 0.413 mol) and 1 mL of DMF. The mixture was placed in a round-bottomed flask, equipped with a reflux condenser. After refluxing for 24 h, thionyl chloride was removed by distillation at 120 °C. The crude product was purified by vacuum distillation (5 mm Hg, 120 °C) twice to obtain white particles with 76% yield (2.67 g, 10.79 mmol). The synthesis of NTAC was shown in Scheme 1(a). The spectroscopic data for ¹H NMR (500 MHz, CDCl₃, ppm): δ 9.2161–9.2128 (d, 2H, Ar–H, *J* = 1.9278 Hz); δ 9.1149–9.1083 (t, 1H, Ar–H, *J* = 1.0000 Hz). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 165.60, 148.88, 137.38, 136.01, 130.84.

Amine:



Fig. 1. Chemical structures of the monomers used in preparing the polyamide active layers. (a) TETA, (b) NTAC, (c) TBAC.

2.3. Synthesis of monomer TBAC acyl chloride

The diacyl chloride monomers of 5-tert-butylbenzene-1,3-dioyl dichloride were synthesized by a mixture of 5-tert-butylbenzene-1,3-dioic acid (3 g, 13.50 mmol), thionyl chloride (30 mL, 0.413 mol) and 10 drops of DMF. The mixture was placed in a round-bottomed flask, equipped with a reflux condenser. After refluxing for 24 h, thionyl chloride was removed by distillation (120 °C). The crude product was purified by vacuum distillation (5 mmHg, 120 °C) twice to obtain white particles with 71% yield (2.48 g, 9.58 mmol). The synthesis of TBAC was shown in Scheme 1(b). The spectroscopic data for ¹H NMR (500 MHz, CDCl₃, ppm): δ 8.4947–8.4919 (t, 1H, Ar–H, *J* = 1.0000 Hz); δ 8.2741–8.2711 (d, 2H, Ar–H, *J* = 2.0553 Hz); δ 1.3879 (s, 9H, –CH₃, *J* = 9.7501 Hz). ¹³C NMR (125 MHz, CDCl₃, ppm): δ 166.22, 151.82, 130.59, 130.15, 127.76, 34.70, 30.89.

2.4. Preparation of modified PAN (mPAN) porous membrane supports

Flat PAN porous membrane supports were prepared by casting PAN onto non-woven polyester fabrics. In a continuous preparation, a polymer solution, containing 15 wt% of PAN, was cast onto the non-woven polyester fabric by the use of a casting knife with 200 μ m gap. The cast membrane was precipitated by immersion in a water bath. The resulting PAN porous membrane supports were washed in water several times for more than 1 day to remove the remnants of the NMP solvent. In order to enhance the hydrophilicity of membrane support to benefit the sorption of the amine



Scheme 1. Synthesis of diacyl chloride monomer (a) NTAC or (b) TBAC.

monomer in it, the PAN porous membrane support was hydrolyzed by NaOH solution [20]. The modified PAN porous membrane was prepared by immersing the PAN porous membrane support in a 2 M NaOH solution at 50 °C. The partial –CN groups of PAN can be converted into –COOH and –CONH₂ groups after undergoing hydrolysis in a NaOH solution. The mPAN porous membrane was washed in a water bath for several hours to remove the remnants of the NaOH solution.

2.5. Preparation of the polyamide thin-film composite membrane

The polyamide thin-film composite membrane was prepared by the interfacial polymerization of the amine monomer TETA and the acyl chloride monomer (NTAC or TBAC). The mPAN membrane was first immersed in a 1 wt% aqueous amine solution for 30 s. Then, the excess aqueous amine solution on the surface of the mPAN membrane was removed. The mPAN membrane, soaked with the aqueous amine solution, was brought into contact with a 1 wt% organic acyl chloride solution for 30 s to carry out the interfacial polymerization. Finally, the resulting polyamide thin-film composite membrane was washed in methanol and then dried at atmospheric temperature. The schematic diagram for the chemical reaction showing the structure of the synthesized polyamide as a result of the interfacial polymerization between TETA and diacyl chloride (NTAC or TBAC) on the surface of the mPAN membrane was shown in Scheme 2.

2.6. Surface characterization

The surface roughness of the polyamide thin-film composite membranes was observed with an atomic force microscope (AFM; Digital Instruments, DI-NS3a, USA). Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR; PerkinElmer Spectrum One) and X-ray photoelectron spectroscopy (XPS; ThermoFisher Scientific K-Alpha) were used to characterize the chemical structure and the surface composition of the polyamide active layer of the thin-film composite membrane, respectively. To understand the surface hydrophilicity of the polyamide thin-film composite membrane, the water contact angle was estimated with an automatic interfacial tensiometer (FACE Mode 1 PD-VP).

2.7. Light transmission experiment

The reactivity between the aqueous amine solution and the organic acyl chloride solutions was observed with the light transmission experiments. In the light transmission experiment, the beaker containing the aqueous TETA solution was placed on a detector, and a light source was installed above the beaker vertically. The light source was turned, letting the light transmit through the aqueous TETA solution until the light transmission value reached steady state. The organic diacryl chloride (NTAC or TBAC) solution was poured into the beaker carefully and slowly along its inside wall. When the organic diacryl chloride solution contacted the light, the light transmission value was started to be recorded by the detector. The light transmittance was calculated by the following equation:

$$Light transmittance = \frac{E_i}{E_0}$$
(1)

where E_0 is the initial light transmission value (light transmission value before pouring organic diacryl chloride solution into the beaker), and E_i is the light transmission value after pouring organic diacryl chloride solution into the beaker at each time interval.

When the organic diacryl chloride solution contacted the aqueous TETA solution, a free-standing polyamide membrane was formed at the interface between the solutions by means of interfacial polymerization. With the passage of time, the growth of the free-standing polyamide membrane affected the variation in the light transmittance, which was used to observe the reactivity between the aqueous amine solution and the organic acyl chloride solution.

2.8. Positron annihilation spectroscopy

PAS was used to estimate the free volume variations in the depth profile of the polyamide thin-film composite membrane. A variable monoenergetic slow positron beam as a function of the positron incident energy (0–30 keV) at atmospheric temperature under a vacuum of ~ 10^{-8} torr. The radioisotope beam used 50 mCi of ²²Na as the positron source. Two positron annihilation spectrometers were installed in this beam—Doppler broadening energy spectroscopy (DBES) and positron annihilation lifetime spectroscopy



Scheme 2. Schematic diagram for the chemical reaction showing the structure of the synthesized polyamide as a result of the interfacial polymerization between TETA and diacyl chloride (NTAC or TBAC) on the surface of the mPAN membrane.

(PALS). The DBES was measured using an HP Ge detector at a counting rate of approximately 2000 cps. The total number of counts for each DBES was 1.0 million. The DBES is based on the measured width of the annihilation gamma photon line, centered at 511 keV. The Doppler-broadened linewidth can be described with simple lineshape parameters, such as the shape (S) parameter. The S parameter, defined as the ratio of the central part of the annihilation spectrum to the total spectrum, reflects the positron annihilation with low momentum valence electrons. The S parameter data from DBES was fitted by VEPFIT program. The PALS experiment provides more quantitative information on the free volume properties in polymeric systems. The PALS data were obtained by taking the coincident events between the start signal detected by a multichannel plate (MCP) from the secondary electrons and the stop signal discerned by a BaF₂ detector from the annihilation photons at a counting rate of approximately 200-300 cps. A PALS spectrum contains 2.0 million counts. From the analysis of positron annihilation lifetime spectrum, positron lifetimes (τ_1 , τ_2 and τ_3) and relative intensities (I₁, I₂ and I₃), which result from the positron and positronium annihilation in polymeric membranes, can be determined. The lifetime τ_3 from pick-off annihilation of ortho-positronium (o-Ps) and electron, which is on the order of 1–5 ns in polymeric membranes, is related to the size of the free volume [21]. τ_3 is usually used to calculate the mean free-volume radius. I3 may directly indicate the concentration of the free volume because of the amount of the formed Ps annihilating with the electrons in microcavities may correspond to the free volume. That is, an increase in I_3 is approximately equivalent to an increase in the concentration of the free volume. Therefore, τ_3 and I₃ from PALS can be used to explore the depth profiles of the size and concentration distributions of the free volume in polymeric thin-film composite membranes. All of the positron annihilation lifetime spectra were analyzed by a finite term lifetime analysis method using the PATFIT program [22].

2.9. Pervaporation and sorption measurements

The pervaporation separation of an aqueous ethanol solution through the polyamide thin-film composite membrane was performed. The pervaporation apparatus has been described in an earlier study [23]. The feed solution directly contacted the polyamide side of the composite membrane. The effective area of the membrane for pervaporation was 10.24 cm². The operating temperature (feed solution temperature) was 25 °C. The concentrations of the feed solution and the permeate were measured by gas chromatography (GC; China Chromatography 8700 T). The permeation rate (*P*) and the pervaporation separation factor of water/ethanol (α_P) were calculated from the following equations:

$$P = \frac{W}{At} \tag{2}$$

$$\alpha_P = \frac{Y_W/Y_E}{X_W/X_E} \tag{3}$$

where *W* is the weight of the permeate, *A* is the effective membrane area and *t* is the sampling time. X_W and X_E are the respective weight fractions of water and ethanol in the feed. Y_W and Y_E are the respective weight fractions of water and ethanol in the permeate. The sorption of 90 wt% aqueous ethanol solution or water vapor by the polyamide thin-film composite membrane was measured at 25 °C. The sorption measurements and apparatus were described in our previous study [24]. The solution separation factor of water/ ethanol (α_S) was obtained from the following equation:

$$\alpha_S = \frac{Z_W/Z_E}{X_W/X_E} \tag{4}$$

where X_W and X_E are the weight fractions of water and ethanol in the feed. Z_W and Z_E are the weight fractions of water and ethanol in the membrane, respectively.

The water vapor ratio, which was absorbed in the membrane, was calculated from the following equation:

Water vapor sorption ratio
$$\binom{\%}{W_D} = \frac{W_S}{W_D}$$
 (5)

where W_D and W_S are the weights of the dry membrane and the water vapor absorbed in the membrane, respectively.

3. Results and discussion

3.1. Characterization of the polyamide thin-film composite membranes

The chemical structures of the polyamide thin-film composite membranes were characterized by ATR-FTIR. Fig. 2 shows the ATR-FTIR spectra of the mPAN and polyamide thin-film composite membranes. Compared with the spectrum of mPAN (Fig. 2(a)), an increase in the intensity of the peaks at wave number 1580 cm⁻¹, corresponding to the N–H (amide II) of the amide group, is shown in the spectra for the polyamide thin-film composite membranes (TETA-NTAC/mPAN and TETA-TBAC/mPAN) (Fig. 2(b) and (c)). A shift of the amide I peak from 1631 cm⁻¹ (C=O of the acrylamide group in mPAN) to 1664 cm⁻¹ (C=O of the amide group in the polyamide) is shown in the spectra (Fig. 2). In addition, the peak at 1613 cm⁻¹, corresponding to the vibrational modes and the C=C stretching of the aromatic ring, is shown in Fig. 2(b) and (c). The results reveal that the active layers of the thin-film composite membranes were composed of aromatic polyamides.

The surface chemical compositions of the polyamide thin-film composite membranes were investigated by XPS analysis. Fig. 3 shows the C_{1s} X-ray photoelectron spectra of the polyamide thin-film composite membranes, and their relative bond assignments from these spectra are shown in Table 1. There are two peaks that correspond to the -N-C=0 and -COOH groups at 287.6 eV and 288.9 eV, respectively, in the C_{1s} spectra of the TETA-NTAC/mPAN and TETA-TBAC/mPAN membranes. The -N-C=0 group was formed by the reaction of an amine group with an acyl chloride group during the interfacial polymerization process, and the -COOH group was generated by the hydrolysis of the unreacted



Fig. 2. ATR-FTIR spectra for (a) the pristine PAN membrane support and the polyamide thin-film composite membranes: (b) TETA-NTAC/mPAN and (c) TETA-TBAC/mPAN.



Fig. 3. C1s X-ray photoelectron spectra of the polyamide thin-film composite membranes: (a) TETA-NTAC/mPAN and (b) TETA-TBAC/mPAN.

acvl chloride group. A greater number of -COOH groups on the polymer chain of the interfacially-polymerized polyamide indicates that many acyl chloride groups did not react with amine groups, resulting in a shorter polymer chain and a lower polymer chain entanglement. As shown in Table 1, the concentration of the -N-C=O and -COOH groups were 8.39% and 1.92% for the TETA-NTAC/mPAN membrane and were 2.98% and 3.85% for the TETA-TBAC/mPAN membrane, respectively. The relative ratio of the -COOH to -N-C=0 groups was higher for the TETA-TBAC/ mPAN membrane than the TETA-NTAC/mPAN membrane. This implies that the TETA-NTAC/mPAN membrane had a greater degree of polymer chain entanglement and/or crosslinking than the TETA-TBAC/mPAN membrane. Thus, a higher selectivity in the pervaporation separation process was obtained, resulting from the membrane with a higher polymer chain entanglement and a higher polymer chain packing density.

3.2. DBES of the polyamide thin-film composite membranes

To investigate the effects of the acyl chloride chemical structure on the fine structure of the polyamide active layer, PAS experiments, coupled with a variable monoenergetic slow positron beam, were performed to obtain the DBES. The S parameter increases concomitantly with increase in the relative contribution of low momentum electrons to the positron annihilation in the polymeric membranes [14.21.25–27]. Thereby, the DBES can be applied to measure the variation in the fine structure of a composite membrane, and the multilayer structure of a composite membrane can be analyzed by the variation in the S parameter. Fig. 4 shows the S parameter versus the positron incident energy (or mean depth) for the polyamide thin-film composite membranes. The S value close to the surface increases rapidly with an increase in the positron incident energy lower than 0.5 keV. This is due to the backdiffusion of the positron annihilation. The S value shows a peak-like region for the positron incident energies from 0.7 keV to 2.0 keV, which penetrate deeper into the membrane. This region corresponds to the polyamide active layer. And then the S value comes to

 Table 1

 Relative bond assignments from the C1s X-ray photoelectron spectra of the polyamide thin-film composite membranes.

Membranes	C—C and C—H	C=C and C-H	C—N and C—O	N-C=0	-соон
TETA-NTAC/mPAN	15.57%	11.62%	30.25%	8.39%	1.92%
TETA-TBAC/mPAN	22.20%	9.32%	32.80%	2.98%	3.85%



Fig. 4. S parameter versus the positron incident energy (mean depth) for the polyamide thin-film composite membranes: (\bullet) TETA-NTAC/mPAN and (∇) TETA-TBAC/ mPAN.

a plateau-like region for the positron incident energies from 2.0 keV to 5.0 keV. This region corresponds to the transition layer from polyamide layer to dense skin layer of mPAN support. For the positron incident energies from 5.0 keV to 15 keV, the S value increases to a maximum. This region is a transition layer from dense skin to porous support layer in the mPAN. The S value decreases when the positron incident is energy higher than 15 keV. This region remains in the porous support of the mPAN. In general, the effective separation layer of a composite membrane is the dense top layer. Thus, we focused on the variation in the S parameter for this region of the polyamide active layer. As shown in Fig. 4, the S parameter was higher for the TETA-NTAC polyamide layer than the TETA-TBAC polyamide layer. This indicates that the free volume size of the TETA-NTAC polyamide layer.

The polymer chain packing density and light transmittance was affected by the polymer formation rate during the interfacial polymerization. To observe the light transmittance variation of the free-standing polyamide membrane formation during the interfacial polymerization process, light transmission experiments were conducted (Fig. 5). For the TETA-NTAC and TETA-TBAC polyamide layers, the light transmittance decreased during the initial 8 s of the polymerization. This indicates that the polyamide membrane was growing. After the polymerization time exceeded 8 s, there was no significant change in the light transmittance, implying that the polyamide layer had stopped growing. Compared with the TETA-NTAC polyamide layer, the TETA-TBAC polyamide layer had the lower light transmittance. This may have been due to the difference in the polyamide formation rate between the diamine and diacryl chloride monomers. Fig. 5 shows that the polyamide formation rate of TETA-TBAC layer is higher than that of the TETA-NTAC layer. Thus, a high density skin layer forms instantaneously when the aqueous TETA solution and organic TBAC solution come in contact. This results in a better arrangement of the polymer chain at the TETA-TBAC polyamide layer. These results agree with Fig. 4. The lower S parameter of the TETA-TBAC polyamide layer indicates that the polymer chain packing density was higher in the TETA-TBAC polyamide layer than the TETA-NTAC polyamide layer.

In addition, the solubility parameter difference between TETA and TBAC was lower than that between TETA and NTAC (as shown in Table 2), indicating that TETA and TBAC have higher affinity. The



Fig. 5. Light transmittance of the free-standing polyamide membrane formed between the aqueous TETA and the organic acyl chloride solutions in the interfacial polymerization process (\blacksquare) TETA-NTAC and (\bullet) TETA-TBAC.

Table 2

Solubility parameters and their differences for the amine and the acyl chloride monomers.

Monomers	$\delta_{ m t}~({ m MPa}^{1/2})$	$\Delta \delta_t (\mathrm{MPa}^{1/2})^{\mathrm{a}}$
TETA	19.10	_
NTAC	23.78	4.68
TBAC	20.74	1.64

^a The solubility parameter difference of TETA and acyl chloride.

higher affinity between the amine and the acyl chloride monomers increased the likelihood of collision and their subsequent reaction.

In addition, to illustrate the variation in the S parameter along the depth of the composite membrane, the S parameter data as a function of the positron incident energy were fitted by the VEPFIT program analysis in a four-layer model and the results showed in Fig. 6. As shown in Fig. 6, the polyamide thin-film composite membrane was divided into four layers. These four layers indicated are as follows: (I) interfacially-polymerized polyamide (PA) layer, (II) transition layer from polyamide layer to dense skin layer of mPAN support, (III) dense skin + porous support layer of mPAN, and (IV) porous support layer of mPAN. The effective selective layer of the thin-film composite membrane is the polyamide active layer. The thickness of the polyamide active layer also estimated from the VEPFIT program analysis. The thickness of the TETA-NTAC and TETA-TBAC polyamide layers were about 196 and 153 nm, respectively. From the result of DBES analysis, the TETA-NTAC/mPAN membrane had a higher S parameter and a thicker thickness for the polyamide active layer than the TETA-TBAC/mPAN membrane. In the pervaporation separation process, an increase in the free volume and an increase in the thickness for a polymeric membrane are favorable to an increase in the permeation rate and an increase in the selectivity, respectively.

3.3. PALS of the polyamide thin-film composite membranes

In general, the S parameter from DBES experiment qualitatively represents the fine structure of the polymeric membranes. In fact, the fine structure of the polymer can be dominated by the size and the concentration of the free volume quantitatively. To examine the



Fig. 6. Schematic diagram of four-layer depth structure obtained by using VEPFIT program analysis of S parameter data from DBES for (a) TETA-NTAC/mPAN and (b) TETA-TBAC/mPAN membranes. Description of four layers: (1) interfacially-polymerized polyamide (PA) layer, (II) transition layer from polyamide layer to dense skin layer of mPAN support, (III) dense skin + porous support layer of mPAN, and (IV) porous support layer of mPAN.



Fig. 7. o-Ps annihilation lifetime (τ_3) and intensity (I_3) as a function of positron incident energy for TETA-NTAC/mPAN and TETA-TBAC/mPAN membranes.

free volume quantitatively, the PALS experiment was carried out to obtain the o-Ps annihilation lifetime (τ_3) and intensity (I_3) which corresponded to the size and the concentration of the free volume, respectively. The result of the PALS experiment is shown in Fig. 7. In general, τ_3 represents the size of the free volume. An increase in τ_3 means an increase in free volume size. I₃ may not directly indicate the concentration of the free volume because the Ps formation also depends on the decay rates and chemical environments, however, the effects of chemical quenching and chemical inhibition were not observed evident in this study even the -NO₂ functional group still survived in the TETA-NTAC polyamide layer on the mPAN (From Fig. 2(b), the peak at 1052 cm^{-1} is corresponding to the C–N stretching of -NO₂ functional groups). The amount of the formed Ps annihilating with the electrons in microcavities may be in response to the free volume only by assuming in the absence of these effects for the current system. Therefore, an increase in I_3 can be only used very approximately for an increase in the concentration of free volume. The following observations are based on Fig. 7: (1) Gradually decrease in both the τ_3 and I_3 intensity with increase in the positron incident energy from 0.7 to 2 keV for TETA-NTAC/ mPAN membrane and 0.7 to 1.7 keV for TETA-TBAC/mPAN membrane. This means that the free volume size decrease gradually in the region of the polyamide layer. (2) An increase in τ_3 and I_3 after 2 keV for TETA-NTAC/mPAN membrane and 1.7 keV for TETA-TBAC/mPAN. There is a transition layer from polyamide layer to dense skin layer of mPAN support. As shown in Fig. 7, the τ_3 and I_3 of the TETA-NTAC polyamide layer are both higher than those of the TETA-TBAC polyamide layer, that is, the size and concentration of the free volume for the TETA-NTAC polyamide layer are both higher than those for the TETA-TBAC polyamide layer. This result corresponded with the DBES analysis using VEPFIT program in Fig. 6 very well. The higher S parameter for the TETA-NTAC polyamide layer is contributed to the larger free volume size and higher free volume concentration.

Table 3

The surface water contact angle and water vapor sorption values of the polyamide thin-film composite membranes at 25 $^\circ C.$

Membranes	Water contact angle (°)	Water vapor sorption ratio (%)
TETA-NTAC/mPAN	45.5 ± 1.2	8.60 ± 3.58
TETA-TBAC/mPAN	38.5 ± 1.0	11.48 ± 4.08

Table 4

The surface roughness values of the polyamide thin-film composite membranes.

Membranes	$R_{\rm ms}^{a}({\rm nm})$	$R_{a}^{b}(nm)$	$R_{\max}^{c}(nm)$
TETA-NTAC/mPAN	21.5 ± 3.3	16.9 ± 2.8	170.7 ± 38.8
TETA-TBAC/mPAN	34.1 ± 5.7	27.1 ± 4.3	219.3 ± 16.0

^a *R*_{ms}: root mean square roughness.

^b R_a : average roughness.

^c R_{max}: maximum roughness.

3.4. Surface hydrophilicity and roughness

The surface hydrophilicity of the polyamide thin-film composite membrane was estimated by the surface water contact angle and water vapor sorption measurements. The results are shown in Table 3. Compared with the TETA-NTAC/mPAN membrane, the TETA-TBAC/mPAN membrane had a lower water contact angle and a higher water vapor sorption ratio. This indicates that the TETA-TBAC/mPAN membrane had a higher hydrophilicity, resulting in a higher water vapor sorption ratio. In addition to the innate characteristic of the polymeric membrane, the surface roughness affects the water contact angle. For a hydrophilic polymer membrane, a rougher membrane surface produces a lower water contact angle, indicating higher affinity between water molecular and polymer membrane [28,29]. The surface roughness of the polyamide thinfilm composite membranes was measured by AFM, and the results are shown in Table 4. The root mean square roughness (R_{ms}) , the average roughness (R_a) and the maximum roughness (R_{max}) were all higher for the TETA-TBAC/mPAN membrane than for the TETA-NTAC/mPAN membrane. This suggests an increase in the hydrophilicity of the TETA-TBAC/mPAN membrane.

3.5. Pervaporation performance

The pervaporation performance of the polyamide thin-film composite membranes with a 90 wt% ethanol aqueous solution at 25 °C is shown in Table 5. The mPAN support membrane had a poor pervaporation performance with a permeation rate of 2149 g/m²-hr and a water concentration in permeate of 19.6 wt%. To improve the pervaporation performance of the mPAN support membrane, the TETA-NTAC/mPAN and the TETA-TBAC/mPAN composite membranes were prepared via interfacial polymerization. The composite membranes had better pervaporation performances than the pristine mPAN support membrane. Compared with the TETA-TBAC/mPAN membrane, the TETA-NTAC/mPAN membrane had both a higher permeation rate and water concentration in the permeate. This may be a result of the higher relative ratio of -COOH to -N-C=O groups for the TETA-TBAC/mPAN membrane (Table 1). This suggests that the TETA-NTAC/mPAN membrane had greater polymer chain entanglement and/or crosslinking than that of the TETA-TBAC/mPAN membrane. Thus, a higher selectivity in the pervaporation separation process was obtained, resulting from the membrane with a higher polymer chain entanglement and higher polymer chain packing density. In addition, from the result of the PAS experiment (Figs. 6 and 7), the τ_3 and I_3 of the TETA-NTAC polyamide layer are both

Table	5			
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Effect of the acyl chloride monomer chemical structure on the pervaporation performance of the polyamide thin-film composite membranes for 90 wt% aqueous ethanol solutions at 25 $^\circ\text{C}.$

Membranes	Permeation rate (g/m ² -hr)	Water conc. in permeate (%)
mPAN	2149 ± 290	19.6 ± 1.7
TETA-NTAC/mPAN	537 ± 71	98.2 ± 0.8
TETA-TBAC/mPAN	452 ± 52	97.1 ± 1.2

Table 6

Effect of the acyl chloride structure on the sorption and diffusion properties of the polyamide thin-film composite membranes for a 90 wt% aqueous ethanol solution at 25 $^\circ$ C.

Membranes	$\alpha_{\rm P}$	α _s	α _D
TETA-NTAC/mPAN	$\overline{558\pm261}$	59 ± 28	6.7 ± 2.1
TETA-TBAC/mPAN	326 ± 159	129 ± 39	2.7 ± 0.9

 $\alpha_{\rm P}$ = pervaporation separation factor.

 α_{S} = solution separation factor.

 $\alpha_D = diffusion$ separation factor.

higher than those of the TETA-TBAC polyamide layer, that is, the size and concentration of the free volume for the TETA-NTAC polyamide layer are both higher than those for the TETA-TBAC polyamide layer, resulting in a higher pervaporation performance of the TETA-NTAC/ mPAN membrane was obtained.

The effect of the acyl chloride structure on the sorption and diffusion of a 90 wt % aqueous ethanol solution through the polyamide thin-film composite membranes was investigated at 25 °C, and the results are shown in Table 6. The results indicate that α_S was higher than α_D for all polyamide thin-film composite membranes, which implies that the solution dominates the separation behavior of the polyamide thin-film composite membranes. Compared with the TETA-NTAC/mPAN composite membrane, the TETA-TBAC/mPAN composite membrane, the TETA-TBAC/mPAN composite membrane had a higher α_S and a lower α_D . The higher α_S for the TETA-TBAC polyamide layer resulted from a lower surface water contact angle and a higher surface roughness (Tables 3 and 4), signifying a higher hydrophilicity and effective contact area. Thus, the permeation rate of TETA-NTAC/mPAN membranes and the water concentration of the resultant permeate were higher than those of the TETA-TBAC/mPAN composite membranes.

4. Conclusion

The polyamide thin-film composite membranes were successfully prepared via interfacial polymerization of TETA with NTAC or TBAC and were applied to the dehydration of an aqueous ethanol solution. The following conclusions were obtained:

As a result of the PAS experiments, the TETA-NTAC polyamide layer of the composite membrane had a higher S parameter, a higher τ_3 (free volume size), a higher I_3 (free volume concentration), as well as a thicker polyamide layer thickness, compared with the TETA-TBAC polyamide layer.

From the analyses of the XPS, AFM and water contact angle measurements, the TETA-NTAC/mPAN membrane had higher degree of crosslinking, lower surface roughness of the active layer and lower hydrophilicity than the TETA-TBAC/mPAN membrane.

The TETA-NTAC/mPAN membrane showed both a higher permeation rate and water concentration in permeate than the TETA-TBAC/mPAN membrane. The solution effect primarily controlled the pervaporation separation behavior of the polyamide thin-film composite membrane in the dehydration of a 90 wt% aqueous ethanol solution at 25 °C.

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