Positron annihilation study on thin-film composite pervaporation membranes: Correlation between polyamide fine structure and different interfacial polymerization conditions

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ABSTRACT

To investigate the variation in the fine structure of polyamide thin-film composite (TFC) membranes prepared via two different interfacial polymerization conditions (IP-I and IP-II), experiments on Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), water contact angle, and positron annihilation spectroscopy (PAS) coupled to a slow positron beam were conducted. Polyamide TFC membranes were prepared via the interfacial polymerization reaction between triethylenetetramine (TETA) and trimesoyl chloride (TMC) on the surface of a modified polyacrylonitrile (mPAN) membrane. Compared with the polyamide TFC membrane prepared via IP-I, the polyamide layer prepared via IP-II showed a shorter S plateau length (thinner thickness), a higher o-Ps intensity I_3 value (higher free-volume concentration), and a smaller o-Ps lifetime τ_3 value (smaller free-volume size), resulting in higher permeation rate and separation factor obtained from the pervaporative separation of a 70 wt% isopropanol aqueous solution at 25 °C.

1. Introduction

Interfacial polymerization is based on a reaction that forms a polymer film at the interface between two immiscible phases. In each of these phases, a highly reactive monomer is dissolved. Polyamide TFC membranes, which are prepared by the interfacial polymerization of amines and acyl chlorides on porous support membranes, are studied usually in reverse osmosis [1–5] or nanofiltration [6–10] processes. However, there have been few reports on pervaporation [11,12].

Polyamide TFC membranes are multilayered. Characterization of multilayered membranes includes mostly chemical and physical structures. Characterization of chemical structures using instruments such as Fourier Transform Infrared Spectroscopy (FTIR) [13,14] and Electron Spectroscopy for Chemical Analysis (ESCA) [15], results in the detection of configuration and conformational variations. Characterization of physical structures using instruments such as Atomic Force Microscopy (AFM) [16,17], Scanning Electron Microscopy (SEM) [16] and Transmission Electron Microscopy (TEM) [18] results in the probe of properties such as morphology and surface roughness. Each analytical technique has its advantages and shortcomings in structural determination and elemental sensitivity. It is essential to characterize multilayered membranes by using several techniques. A novel physical technique, positron annihilation spectroscopy (PAS), can be utilized to measure physical properties of membranes with multiple layers, such as free volumes [19,20] at the atomic and molecular levels as a function of chemical changes and molecular modifications at different depths in a multilayer system. PAS is a potential physical technique. This is because many studies on the physical properties of polymeric materials probed by PAS have been investigated recently [21–26]. However, there are few studies on polymeric TFC pervaporation membranes investigated with PAS [20,27,28].

In this study, the polyamide TFC membranes were prepared via two different interfacial polymerization conditions (IP-I and IP-II) of triethylenetetramine (TETA) and trimesoyl chloride (TMC) on a modified asymmetric polyacrylonitrile (mPAN) membrane and were applied in pervaporation separation process. How to prepare a high performance pervaporation membrane via the simplest interfacial polymerization process parameters, such as the supporting membrane and membrane-making conditions, reaction

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time, monomer concentration, and post-treatment conditions, is the main goal and original idea of our present study. In the case of IP-I, a dry mPAN membrane was used to prepare a polyamide TFC membrane for pervaporation. This TFC pervaporation membrane prepared via IP-I exhibited good separation performance, but it required higher monomer concentration, longer polymerization time, and even more severe annealing condition, in comparison to the membrane fabricated via IP-II. However, in the case of the revised conditions IP-II, as opposed to IP-I, only lower monomer concentration and shorter polymerization time at room temperature were required to prepare a high performance polyamide TFC pervaporation membrane. Based on the TFC membrane having good pervaporation performance, it is interesting to understand the correlation between the polyamide fine structure and the different interfacial polymerization conditions (IP-I and IP-II) by means of a positron annihilation study. Thus, the effect of the interfacial polymerization conditions on the variations in the fine structure and the free volume of the polyamide TFC pervaporation membrane was detected by Doppler broadening energy spectroscopy (DBES) and positron annihilation lifetime spectroscopy (PALS) which were conducted by using a variable monoenergy slow positron beam. The results of PAS were correlated with the pervaporation performance of the polyamide TFC membranes. The effect of the interfacial polymerization conditions on the morphologies of the polyamide TFC membranes was also investigated with SEM and AFM.

2. Experimental

2.1. Materials

Polyacrylonitrile (PAN) polymer was supplied by Tong-Hua Synthesis Fiber Co. Ltd. (Taiwan). N-methyl-2-pyrrolidone (NMP) of reagent grade was used as the solvent for PAN. Triethylenetetramine (TETA) was purchased from Merck Co. Trimesoyl chloride (TMC) was purchased from TCI Co. TETA and TMC were used as monomers for the polyamide active layer. Distilled water was used in preparing amine aqueous solution, and reagent grade toluene was used as the solvent for acyl chloride. Isopropanol used to mix feed solutions for pervaporation experiments was purchased from Echo Chemical Co., Ltd. in Taiwan.

2.2. Preparation of asymmetric modified PAN (mPAN) porous membrane support

In preparing the flat asymmetric PAN porous membrane by a continuous procedure, an NMP solution containing 15 wt% PAN polymers was cast onto a polyester nonwoven substrate with a casting knife of 200-μm gap. The cast membrane was precipitated by immersion in a bath of water. The resulting asymmetric PAN porous membrane was washed in water overnight and was then stored in a bath of water prior to its use.

The asymmetric modified PAN (mPAN) porous membrane was prepared by immersing the asymmetric PAN membrane support in a 2-M NaOH solution at 50 °C for 2 h. Partial –CN groups of the asymmetric PAN membrane can be converted into –COOH and –CONH₂ groups after the hydrolysis with NaOH solution. The resulting mPAN porous membrane was washed in a water bath for several hours, and was then stored in another water bath before its use for interfacial polymerization.

2.3. Preparation of polyamide TFC membrane

Interfacial polymerization conditions I (IP-I) is illustrated in Fig. 1(a). In IP-I, the time of contact between the surface of the dry mPAN membrane and the 2 wt% TETA aqueous solution at 50 °C is 300 s. The excess amount of the TETA aqueous solution that remains on the surface of the mPAN membrane is removed. To carry out interfacial polymerization, the mPAN membrane soaked with TETA aqueous solution is immersed in a toluene solution containing 1 wt% TMC at atmospheric temperature for 180 s. After removal from the toluene solution, the resulting polyamide TFC membrane undergoes heat treatment in an oven at 70 °C for 60 min to attain the desired membrane structure. Finally, the resulting membrane is washed in methanol.

Interfacial polymerization conditions II (IP-II) is illustrated in Fig. 1(b). In IP-II, the wet mPAN membrane was immersed in a 0.1 wt% TETA aqueous solution at atmospheric temperature for 5 s. The excess amount of the TETA aqueous solution that remained on the surface of the mPAN membrane was removed. Then to carry out interfacial polymerization, the surface of the mPAN membrane soaked with TETA aqueous solution was contacted with a toluene solution containing 0.05 wt% TMC at atmospheric temperature for 10 s. The resulting polyamide TFC membrane was dried at atmospheric temperature and then washed in methanol.

2.4. Characterization

The chemical structures of the active layers of the TFC membranes were studied by using FTIR-ATR (Perkin Elmer Spectrum One) spectroscopy. The surface and cross-sectional morphologies of the polyamide TFC membranes were observed with SEM (HITACHI S-3000N and S-4800). The surface roughness and area of the polyamide TFC membranes were probed by using an AFM (Digital Instruments, DI-NS3a USA) with scanning area of
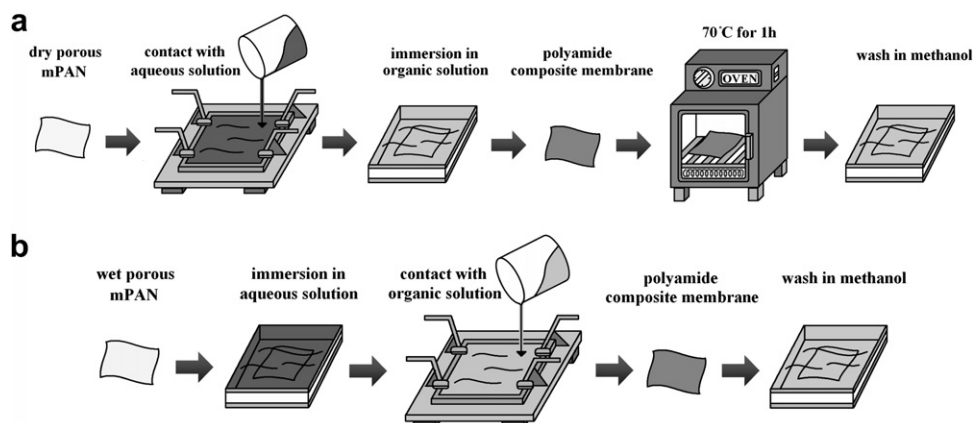

Fig. 1. Illustration of (a) IP-I and (b) IP-II.

5 μm × 5 μm. In order to understand the surface hydrophilicity of the polyamide TFC membranes, the water contact angle was estimated with the Automatic Interfacial Tensiometer (FACE Mode 1 PD-VP).

2.5. Positron annihilation spectroscopy (PAS)

A newly built slow positron beam with variable mono energy at the R&D Center for Membrane Technology, Chung Yuan University, Taiwan was used for this study to investigate the free-volume variation and the boundaries in a multilayer structure of polyamide TFC membranes. This slow positron beam measures a parameter as a function of positron incident energy (0–30 keV), and the investigation with the use of such beam was conducted at room temperature under a vacuum of $\sim 10^{-8}$ torr. This new radioisotope beam uses 50 mCi of ^{22}Na as the positron source. Two positron annihilation spectrometers were installed in this beam—Doppler broadening energy spectroscopy (DBES) and positron annihilation lifetime spectroscopy (PALS). These spectrometers use the secondary electrons emitted from the sample surface as the starting signal. The DBES spectra were measured using an HP Ge detector at a counting rate of approximately 2000 cps. The total number of counts for each DBES spectrum was 1.0 million counts. The PALS data were measured using a BaF$_2$ lifetime detector at a counting rate of approximately 200–300 cps. Each PALS spectrum contains 2.0 million counts. PALS can quantitatively detect the variation in the free volume. From the analysis of positron annihilation lifetime spectrum, positron lifetimes (τ_1, τ_2 and τ_3) and relative intensities (I_1, I_2 and I_3), 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 [20]. τ_3 is usually used to calculate the mean free-volume radius. I_3 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 I_3 from PALS can be used to explore the depth profiles of the size and concentration distributions of the free volume in polymeric TFC membranes. All of the positron annihilation lifetime spectra were analyzed by a finite-term lifetime analysis method using the PATFIT program. Doppler broadening energy spectra were described by using the line-shape S parameter, which indicates the variation in free volume qualitatively. The multilayer structures were obtained by the VEPFIT program analysis of the S parameter. The S parameters (which are defined as the ratio of low momentum part of the peak region to the total 2γ annihilation near 511 keV energy) of Doppler broadening energy spectra (DBES) were measured as a function of depth using the slow positron beam (0–30 keV). Since the S parameter represents the relative value of the low momentum part of positron-electron annihilation radiation, it is sensitive to the change of the positron and positronium (Ps) states due to microstructural changes. When the positron and Ps are localized in a free volume with a finite size, the observed S parameter is a measure of the momentum broadening according to the uncertainty principle: a larger free volume results in a larger S parameter value. The S parameter has been successfully used in detecting the free-volume depth profile in polymeric systems [20,21,24].

2.6. Pervaporation measurement

The pervaporation separation of alcohol aqueous solutions through polyamide TFC membranes was conducted. The pervaporation apparatus was described in our previous study [29]. The feed solution was contacted directly with the membrane. The effective area of the membrane for pervaporation was 11.64 cm^2. The operating temperature (feed solution temperature) was 25 °C. The concentrations of the feed solution and permeate were measured by gas chromatography (GC; China Chromatography 8700 T). The permeation rate (P) and the pervaporation separation factor of water/alcohol ($\alpha_{W/A}$) were calculated from the following equations:

$$P = \frac{W}{At} \tag{1}$$

$$\alpha_{W/A} = \frac{Y_W/Y_A}{X_W/X_A} \tag{2}$$

where W is the weight of the permeate, A is the effective membrane area, t is the sampling time, X_W and X_A are the respective weight fractions of water and alcohol in the feed, Y_W and Y_A are the respective weight fractions of water and alcohol in the permeate.

3. Results and discussion

3.1. Chemical structure

FTIR-ATR spectra for pristine PAN membrane support, modified PAN (mPAN) membrane support (result of PAN treatment in 2 M NaOH solution at 50 °C) and polyamide TFC membranes prepared via IP-II and IP-I are shown in Fig. 2. Compared with the spectrum for the PAN membrane (Fig. 2(a)), the mPAN membrane has four peaks at wave numbers 3300–3400, 1738, 1664 and 1564 cm^{-1}, as shown in Fig. 2(b). The first two peaks correspond to –OH and C=O of carboxyl acid group, respectively. The last two peaks correspond to C=O (amide I) and –NH (amide II) of acryl amide group, respectively. Such spectra revealed that partial –CN groups of PAN membrane were converted to –COOH or –CONH$_2$ groups, as a result of PAN hydrolysis in NaOH solution.

Compared with the spectrum for the mPAN membrane, the peaks of C=O (amide I) and –NH (amide II) of amide group shift from 1664–1668 cm^{-1} and from 1564–1558 cm^{-1}, respectively, as shown in the spectra for the polyamide TFC membrane prepared via IP-II (Fig. 2(c)). The spectrum for the polyamide TFC membrane prepared via IP-I (Fig. 2(d)) also exhibits two peaks at wave numbers 1638 and 1547 cm^{-1}, corresponding to C=O (amide I) and N–H (amide II) of amide group, respectively. The spectra in Fig. 2 confirmed that the TFC membrane's active layer is composed of polyamide.
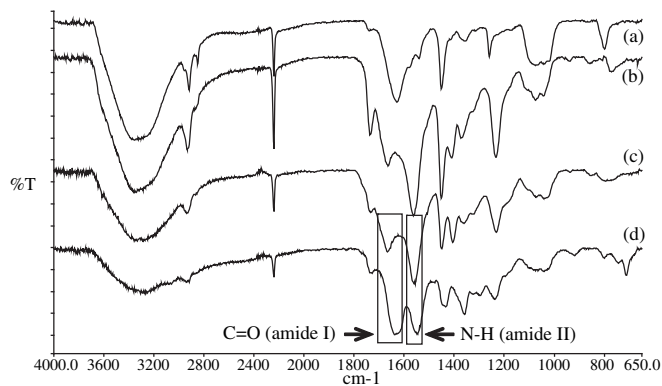

Fig. 2. FTIR-ATR spectra for (a) pristine PAN membrane support, (b) modified PAN (mPAN) membrane support (result of PAN treatment in 2 M NaOH solution at 50 °C) and polyamide TFC membranes prepared via (c) IP-II and (d) IP-I.

Table 1
Comparison between two different interfacial polymerization (IP) conditions in terms of operating and processing conditions and of resulting pervaporation performances of polyamide TFC membranes.

IP conditions	Support membrane state	Amine aqueous solution			Acyl chloride organic solution			Temp./time of heat treatment (°C/h)	Permeation rate[b] (g/m² h)	Separation factor[b] ($\alpha_{water/IPA}$)
		Process	Temp. (°C)	Conc./time (wt%/sec)	Process	Temp. (°C)	Conc./time (wt%/sec)			
I	Dry	Contact	50	2/300	Immersion	r.t.[a]	1/180	70/1	1102 ± 24	167.6 ± 12.1
II	Wet	Immersion	r.t.[a]	0.1/5	Contact	r.t.[a]	0.05/10	r.t.[a]/1	1296 ± 82	736.5 ± 176.4

[a] r.t.: room temperature.
[b] pervaporative separation of 70 wt% isopropanol (IPA) aqueous solution at 25 °C.

3.2. Influence of interfacial polymerization conditions on polyamide TFC membranes' morphology and pervaporation performance

Table 1 shows a comparison between two different IP conditions in terms of operating and processing conditions and of the resulting pervaporation performances of polyamide TFC membranes. It was found that the polyamide TFC membrane prepared via IP-II showed superior pervaporation performance than that prepared via IP-I. In IP-I, the dry asymmetric mPAN membrane was used as support for preparing the polyamide TFC membrane. As such, it was difficult for the monomer (TETA) dissolved in the aqueous solution to penetrate into the denser skin layer of dry asymmetric mPAN membrane, even though the mPAN membrane was soaked with the monomer of higher concentration in the TETA aqueous solution and then immersed in the organic solution of higher TMC concentration at a longer polymerization time. The resulting membrane was dried at a post-annealing temperature of 70 °C for 1 h. The process of forming the polyamide active layer via IP-I has still some difficulty to produce a membrane of a form conducive for obtaining good pervaporation performance.

In IP-II, the wet asymmetric mPAN membrane was used as support. When the wet asymmetric mPAN membrane was immersed in the TETA aqueous solution, the TETA monomers could easily penetrate into the membrane by capillary phenomena and could easily fill the cavities throughout the membrane, even though the concentration of the TETA aqueous solution was lower. The

whole surface of mPAN membrane being uniformly filled with TETA monomers was beneficial to prepare a defect-free polyamide active layer by just contacting the surface with the lower TMC concentration in the organic solution at a shorter polymerization time in the case of IP-II. The resulting membrane was allowed to dry naturally without undergoing an annealing process.

Fig. 3 shows the SEM images of the polyamide TFC membranes prepared via different IP conditions. The surface and cross-sectional SEM images of the polyamide TFC membranes prepared via IP-I are shown in Fig. 3(a) and (c). It was found that the polyamide layer prepared via IP-I show a rough profile of peak-and-valley structures with some defects present. This might be the result of the uneven distribution of the TETA monomers on the surface of the mPAN membrane during interfacial polymerization. However, a defect-free and a thinner polyamide layer was obtained in IP-II, as shown in Fig. 3(b) and (d). They show a smooth profile composed of well-dispersed tiny nodules beneficial to obtain good pervaporation performance. This might be the result of the uniform distribution of the TETA monomers on the surface of the wet mPAN membrane during interfacial polymerization.

The AFM images of the polyamide TFC membranes prepared by different IP conditions are shown in Fig. 4. Compared with the polyamide TFC membrane prepared via IP-II (Fig. 4(b)), that prepared via IP-I displays a higher surface roughness as is shown in Fig. 4(a). The surface roughness of the polyamide TFC membranes based on Fig. 4 is given in Table 2. It reveals that the polyamide TFC
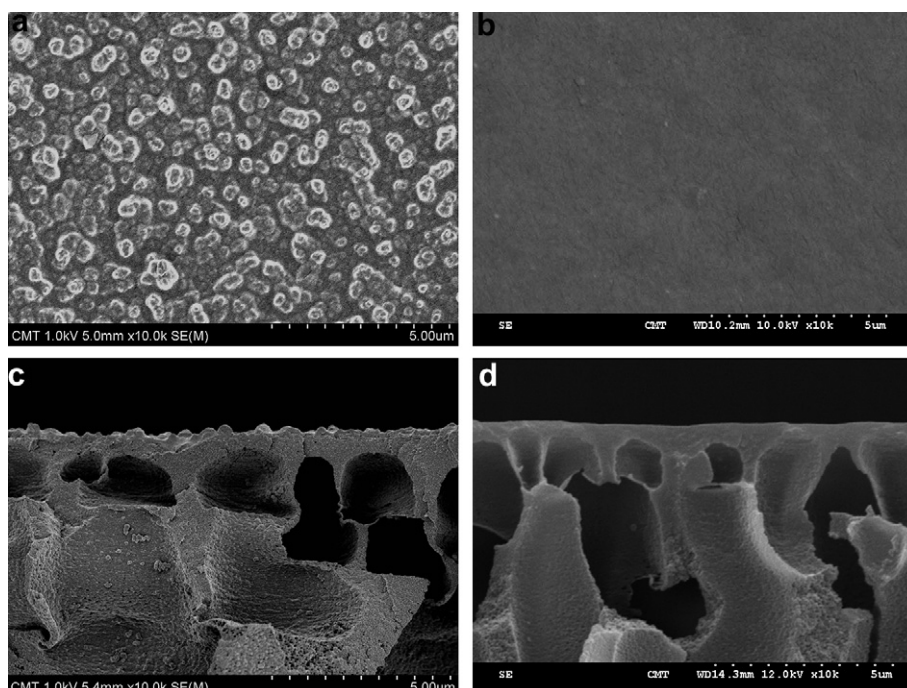

Fig. 3. SEM images of polyamide TFC membranes prepared via IP-I ((a), (c)) and IP-II ((b), (d)).
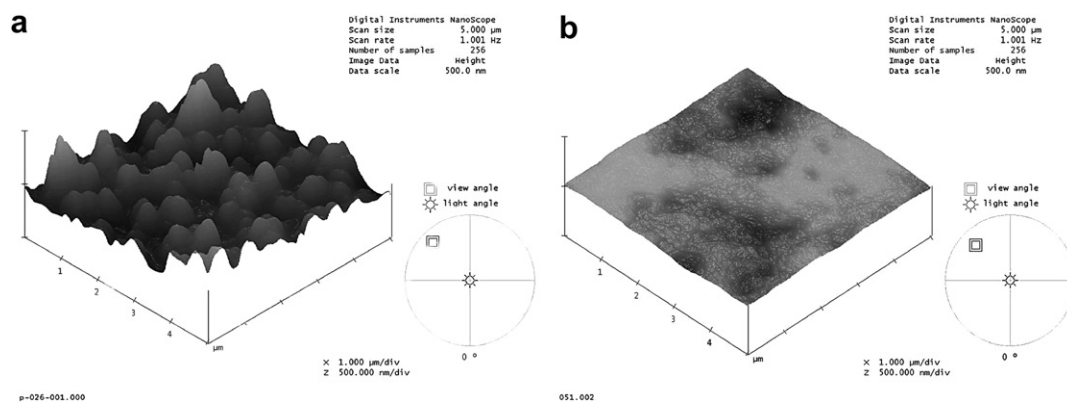
Fig. 4. AFM images of polyamide TFC membranes prepared via IP-I (a) and IP-II (b).

membrane prepared via IP-I shows higher data on root mean square roughness (R_{ms}), average roughness (R_a), maximum roughness (R_{max}) and surface area than that prepared via IP-II. These results might be due to the variation in the uniformity of the TETA monomers distribution on the surface of the mPAN membrane, brought about by the two different interfacial polymerization conditions.

From the results of SEM and AFM analyses, the two different interfacial polymerization conditions utilizing the same monomers cause the variation in the roughness of the polyamide active layers. To complement the SEM and AFM data, the water contact angle for the polyamide TFC membrane was measured and the values are included in Table 2. The water contact angle data reveal that the polyamide TFC membrane prepared via IP-I show a lower water contact angle than that prepared via IP-II. This result corresponds very well to the results from SEM and AFM analyses. These aforementioned results are in line with a defect-free and a thinner layer of the polyamide TFC membrane prepared via IP-II, and such characteristics are beneficial to obtain a higher permeation rate and separation factor. In this regard, it is interesting to understand to a greater extent the effect of the variation in the fine structure in the depth profile of the polyamide TFC membrane on the pervaporation performance in the following experiments.

3.3. Positron annihilation spectroscopy (PAS) of polyamide TFC membranes prepared via different polymerization conditions

To investigate the free-volume variation and the depth profile of the polyamide TFC membranes, PAS experiments were carried out by means of a slow positron beam. The S parameter as a function of the positron incident energy from DBES for the polyamide TFC membranes prepared via IP-I and IP-II is shown in Fig. 5. Compared with the S parameter for the membrane prepared via IP-II, the observation drawn from the S parameter for the polyamide TFC membrane prepared via IP-I reveals a very small plateau existing near the membrane surface, as shown in Fig. 5(b).

From the results of the S curves in Fig. 5, the rapid increase in the S value near the membrane surface at the positron incident energy

value of lower than about 0.5 keV is a typical phenomenon of positronium annihilation. After its rapid increase, the S value comes to a plateau, increases, and then decreases with increasing positron incident energy. The variation in the S parameter, resulting from the variation in the fine structure such as free volume, indicates a multilayer structure of the polyamide TFC membrane, based on the positron annihilation characteristic differences between the layers. 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. We tried to fit 3-layer and 4-layer models from the VEPFIT analysis to analyze the layer boundary for each S curves for IP-II and IP-I prepared TFC membranes. We found that the S curves for IP-I and IP-II fit using a 3-layer model and a 4-layer model, respectively, showed good average χ^2 values (<2.5) and gave stable results and reasonable error bars as a result of the fitting process (S curve for IP-II prepared TFC membrane fit using a 3-layer model showed poor resolution). The resulting fitted lines are also plotted in Fig. 5, from which we can clearly see good fitting results of the three-layer and four-layer models for the polyamide TFC membranes prepared via IP-I and IP-II, respectively. As a result of the VEPFIT analysis, the polyamide TFC membrane prepared via IP-II was divided into four layers whose boundaries are demarcated with three vertical broken lines, as shown in Fig. 5(a). The multilayer structure is described in the following order: (I) The top layer is the polyamide thin layer. (II)
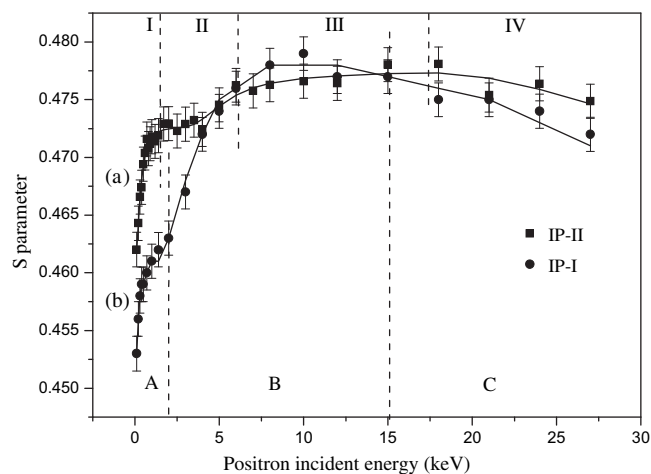
Table 2
Surface roughness, surface area, and water contact angle for polyamide TFC membranes prepared via IP-I and IP-II.

IP procedure	R_{ms} (nm)	R_a (nm)	R_{max} (nm)	Surface area (μm^2)	Water contact angle (°)
I	87.2	67.8	603.1	29.23	72.1 ± 2.8
II	21.3	17.5	114.6	25.11	79.7 ± 1.5

R_{ms}: root mean square roughness.
R_a: average roughness R_{max}: maximum roughness.

Fig. 5. S parameter as function of positron incident energy for polyamide TFC membranes prepared via IP-II (a) and IP-I (b). Lines drawn through data for S parameter are fitted results from VEPFIT program analysis. Vertical broken lines demarcate boundaries from layer to layer.

The second layer is the dense skin layer of mPAN. (III) The third layer is a transition layer from the dense skin layer to the porous support layer of mPAN. (IV) The fourth (bottom) layer is the porous support layer of mPAN. However, the polyamide TFC membrane prepared via IP-I was divided, also as a result of the VEPFIT analysis, into just three layers separated by two vertical broken lines to mark the boundaries, as shown in Fig. 5(b). The multilayer structure is described in the following order: (A) The top layer is polyamide layer. (B) The second layer is a transition layer from the dense skin to the porous mPAN support. (C) The third (bottom) layer is the porous mPAN support. Therefore, the fine structure of the polyamide TFC membranes could not be identified based from the VEPFIT analysis.

In general, the length of the S plateau in DBES indicates the thickness of the layer. The higher the S value, the greater is the free volume. The effective selective layer of the TFC membrane is the polyamide layer. Fig. 5(a) indicates that the polyamide layer prepared via IP-II shows a higher S value and a shorter S plateau length. However, the opposite trend was observed in the case of the polyamide layer prepared via IP-I (Fig. 5(b)). It indicates that the former TFC membrane has a greater free volume and a thinner thickness than that of the latter TFC membrane. This causes the polyamide TFC membrane prepared via IP-II to have a higher permeation rate than that prepared via IP-I. Nevertheless, the polyamide TFC membrane prepared via IP-II shows a higher separation factor than that prepared via IP-I, as is shown in Table 1. This result can not be explained reasonably by using just the S parameters from DBES. To understand more extensively the variations in the fine-structures of the polyamide layers prepared by the two different interfacial polymerization conditions, the o-Ps lifetimes (τ_3) and their corresponding intensities (I_3) in the polyamide layers were investigated by PALS coupled to a slow positron beam. The o-Ps lifetime (τ_3) and its corresponding intensity (I_3) correspond to the size and the concentration of the free volume, respectively.

Fig. 6 plots the o-Ps lifetime (τ_3) as a function of the positron incident energy for the polyamide TFC membrane prepared via IP-I and IP-II. Fig. 6(a) shows a rapid drop of τ_3 near the membrane surface at the positron incident energy lower than 0.5 keV. This is a typical phenomenon of positronium annihilation due to the back-diffusion and -scattering of the o-Ps from the surface to the vacuum. A zone with lower τ_3 values at positron incident energies from 0.5 to 1.5 keV corresponds to the polyamide layer. At positron incident energies higher than 1.5 keV, τ_3 curve jumps to higher values
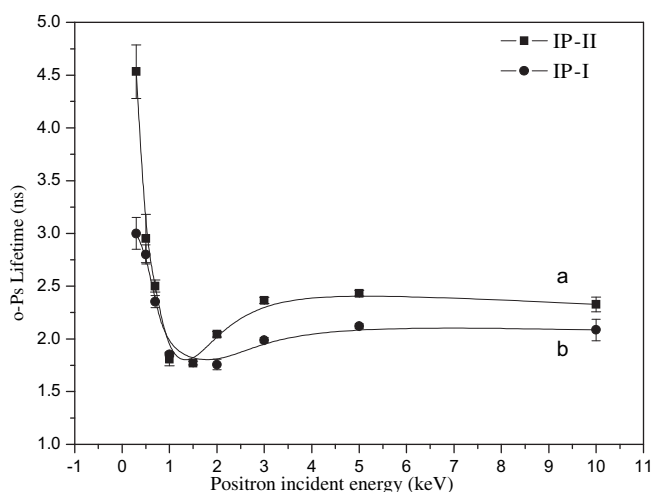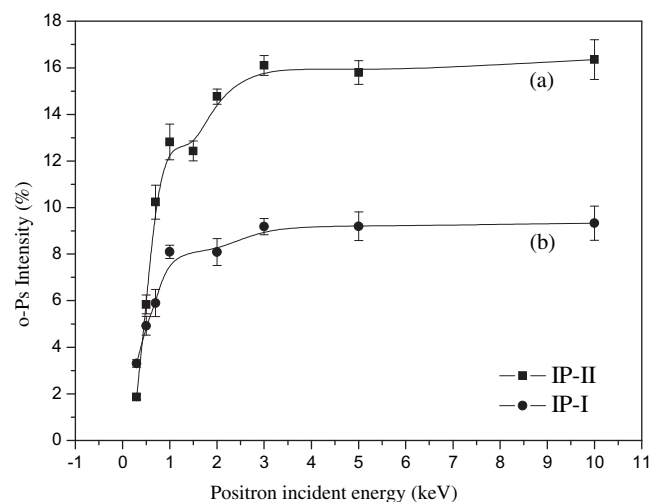

Fig. 7. o-Ps intensity (I_3) as function of positron incident energy for polyamide TFC membranes prepared via IP-II (a) and IP-I (b).

because the positron penetrates into the dense layer of the mPAN support membrane. The o-Ps annihilation trend of IP-I (Fig. 6(b)) is similar to that for the TFC membrane prepared via IP-II.

Fig. 7 presents the o-Ps intensity (I_3) as a function of the positron incident energy for polyamide TFC membranes. It shows that the I_3 curve corresponding to the concentration of the free volume in the polyamide layer prepared via IP-II is higher than that for the polyamide layer prepared via IP-I. To understand the relationship between the free volume size distribution and the pervaporation performance of polyamide TFC membranes, the positron lifetime distributions and the τ_3 results at 1 keV positron incident energy (with the highest density) were analyzed with the use of positron annihilation spectroscopy (Fig. 7); the analysis is shown in Fig. 8. It shows that the lifetime distribution curves shift to lower lifetime direction, while the wet mPAN membrane was used as the support (IP-II). The free volume radius of the TFC membrane prepared by IP-I and IP-II was 2.73 Å and 2.66 Å, respectively. In line with this finding, the effect of TFC membranes prepared via the different IP conditions on the size and the concentration of the free volume is
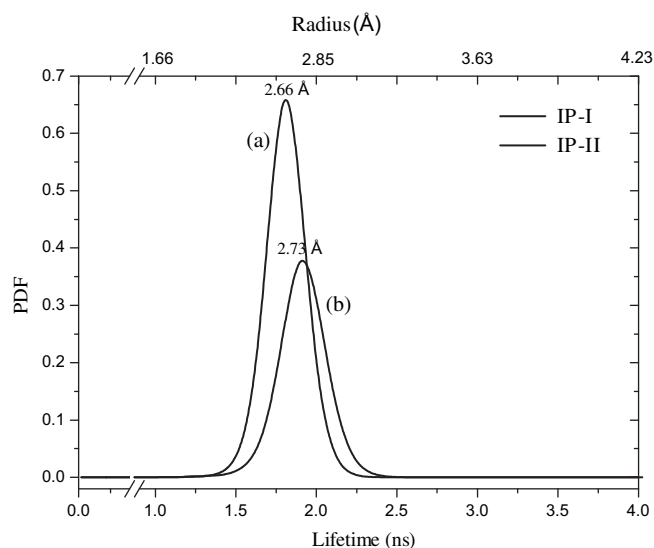

Fig. 6. o-Ps lifetime (τ_3) as function of positron incident energy for polyamide TFC membranes prepared via IP-II (a) and IP-I (b).

Fig. 8. o-Ps lifetime distribution data for polyamide TFC membranes prepared via IP-II (a) and IP-I (b) (PDF: Probability Density Function).

Table 3
o-Ps lifetimes (τ_3) and their intensities (I_3) in polyamide layers prepared via IP-I and IP-II at 1keV positron incident energy.

IP conditions	τ_3 (ns)	I_3 (%)
I	1.85	8.1
II	1.80	12.5

given in Table 3. It indicates that the polyamide layer prepared via IP-II shows a smaller size (τ_3) and a higher concentration (I_3) of the free volume than that for the TFC membrane prepared via IP-I. These resulting characteristics cause the separation factor and the permeation rate for the polyamide TFC membrane prepared via IP-II to be higher than those for the TFC membrane prepared via IP-I (Table 1).

4. Conclusion

In this study, polyamide TFC membranes were successfully prepared via two different interfacial polymerization procedures for reacting TETA and TMC on the surface of mPAN membranes. Based on the results of the SEM, AFM, and water contact angle experiments, the polyamide TFC membrane prepared via IP-II showed lower surface roughness, lower surface area, and lower hydrophilicity than that prepared via IP-I. The results of the positron annihilation studies indicated that thinner thickness, smaller free-volume size, and higher free-volume concentration were obtained for the polyamide layer prepared via IP-II. And from the results of the pervaporative separation of a 70 wt% isopropanol aqueous solution at 25 °C, the respective separation factor and the permeation rate for the polyamide TFC membrane prepared via IP-II were higher than those for TFC membrane prepared via IP-I.

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