Investigation of Multilayer Pervaporation Membrane by Positron Annihilation Spectroscopy

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ABSTRACT: To investigate the polyamide thin-film composite membranes structure in regard to the variation in the free volume in thin-film composite membrane polyamide active layers, positron annihilation spectroscopy (PAS) experiments using a slow positron beam were performed. The correlation between the pervaporation performance and polyamide active layer free volume explored using the slow positron beam technique was also investigated. The composite membranes were prepared via the interfacial polymerization reaction between ethylenediamine (EDA) and trimesoyl chloride (TMC) on the surface of a modified polyacrylonitrile (mPAN) membrane (EDA−TMC/mPAN). The variations in the *S* parameter at positron incident energies of 0.5−2.5 keV indicate a decrease in the *S* parameter when the concentration of EDA in aqueous solution increased from 0.5 to 10 wt %. The positron annihilation took place at the surface of the polyamide active layer for the variations at low *S* parameters and high *W* parameters (positron incident energy <0.5 keV). The positron annihilation occurred at the free volume in the polyamide active layer for the variations at high *S* parameters and low *W* parameters (positron incident energy: 0.5−2.5 keV). From the o-Ps lifetime results, the density of EDA−TMC polyamide active layer decreases along the thin-film growth direction from the aqueous phase toward the organic phase in the range of 1−2 keV positron incident energy. From the positron annihilation lifetime spectroscopy, the variation in the free volume in the EDA−TMC active layer showed a good correlation with the pervaporation performance.

Introduction

Pervaporation separation processes offer potentially more economical alternatives than other separation processes for separating liquid mixtures that cannot be separated or concentrated by distillation method. Alcohol dehydration is one of the important developing areas in pervaporation separation processes, in which membrane materials are used. Polyamide membranes have been regarded as promising membrane materials because of their excellent mechanical strength and high resistance to organic solvents.

However, one of the disadvantages of pervaporation separation processes that use dense polyamide membranes is the low permeation rate. To increase the permeation rate of polyamide membranes without sacrificing selectivity, the membrane must be converted from a dense thick structure into an asymmetrical or thin-film composite structure.

Interfacial polymerization is an effective technique for producing a composite membrane with a thin interfacially polymerized selective layer. This technique is based on a polymerization reaction that forms a thin film of polymer at the interface between two immiscible phases (an aqueous phase of a monomer and an organic phase of a second monomer). The preparation of the thin-film composite membrane involves the following steps. (1) The asymmetrical porous substrate is immersed in an aqueous solution containing highly reactive amine monomers. (2) The excess amine solution is removed from the asymmetrically porous substrate. (3) The asymmetrically porous support membrane soaked with the amine solution is contacted with an organic solution containing highly reactive acyl chloride monomers. A thin active layer of polyamide is formed on the surface of the asymmetrically porous support membrane via interfacial polymerization.

Studies on thin-film composite membranes are usually on RO or NF.[1−4] Singh et al.[5] prepared thin-film composite RO membranes by allowing polyamide coating to form on two polysulfone membranes, type 1 and 2, with an average pore size distributions of 0.07 and 0.15 μm, respectively. With the use of ATR-IR, the thickness of the polyamide composite membrane was estimated by calculating the depth of amide groups penetrating into the membrane. Type 1 membrane has a thicker skin layer (twice as much) than type 2 membrane. The pores of the type 2 membrane are plugged with polyamides.

Zhou et al.[6] investigated the effect of the chemical structure, characterized by X-ray photoelectronic spectroscopy (XPS), of an interfacially polymerized layer on RO performance. The flux was found to increase, but the NaCl rejection decreases when the linear part with pendant −COOH in the barrier layer of RO membrane increases.

Only a few studies, however, have reported on the use of thin-film composite membrane for pervaporation.[7,8] Morgan proved the direction of growth of ultrathin polymeric membrane formed by interfacial polymerization.[9] However, there is a lack of studies on free volume, density variation, and membrane

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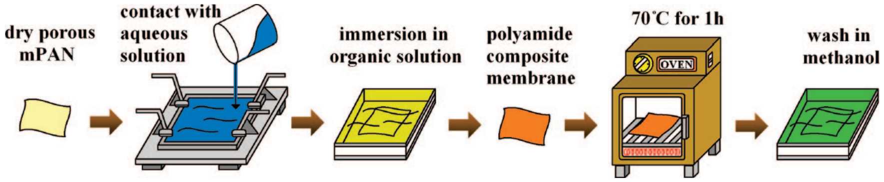


Figure 1. Schematic representation of polyamide active layer formation on the surface of mPAN support membrane.

morphology of the interfacially polymerized membrane, which are very important aspects of research on interfacially polymerized membrane used in pervaporation separation processes.

Recently, there is an increasing interest in positron annihilation spectroscopy (PAS) and in its use in studies on free volume size and distribution in polymeric membranes. PAS is an important method for detecting vacancy defects, from single atom vacancies to large voids, and it is used for probing the variation in the free volume in the active layers of thin-film composite membranes. With this method, a variable energy positron beam with an adjustable energy and a narrow energy distribution allows depth-resolved measurements useful in thin-film defect studies. The PAS technique is based on a study on annihilation phenomena after injecting positrons in the membrane. When a positron is implanted into a condensed matter, it annihilates with an electron and emits two 511 keV gamma quanta. The energy spectrum is Doppler broadened by the finite momentum of the annihilating pair, which is dominated by the electron momentum. This spectrum is characterized using the line-shape parameters S and W. An increase in positrons trapping to vacancy-related defects results in a narrowing of the spectrum and an increase in the S parameter. This occurs if the size or concentration of the positron trapping defect open volume increases.[10,11] The depth profile of the free volume through the polymeric composites can be probed by the analysis of S parameter as a function of positron incident energy (depth). Thus, the variation in S parameter through the polyamide thin-film composite membrane can be used to detect the variation in free volume.[11] The W parameter is related to the chemical environment where the positron annihilation takes place.[12] Different materials indicate different chemical environments; thus, the values of W parameter are different. This can detect the interface between two different materials. In general, the positron annihilations with the valence electrons increase at the open volume defects, resulting in increasing S parameters but decreasing W parameters.[13] This indicates the $S-W$ plot can exhibit the difference in chemical composition coupling with the variation in free volume in different materials. Therefore, the variation in free volume of multilayer structure can be observed indirectly from the $S-W$ plot.

To estimate the variation in the free volume in the polyamide active layer of a thin-film composite membrane, EDA−TMC/mPAN thin-film composite membranes were examined by conducting PAS experiments using a variable monoenergy slow positron beam. Also, the correlation between the variation in free volume in the EDA−TMC active layer of the EDA−TMC/mPAN composite membrane and the pervaporation performance was investigated.

Experimental Section

Materials. Polyacrylonitrile (PAN) polymer, used as the support layer in the composite membrane prepared by interfacial polymerization, was supplied by Tong-Hua Synthesis Fiber Co. Ltd. (Taiwan). Reagent grade *N*-methyl-2-pyrrolidone (NMP) was the solvent used in preparing PAN solution. Ethylenediamine (EDA) was purchased from Acros Organics Co. 1,3,5-Benzenetricarbonyl trichloride (trimesoyl chloride, TMC) was purchased from Aldrich Co. Distilled water was used in aqueous solutions, and toluene was used as the organic solvent.

Preparation of Modified PAN (mPAN) Porous Membrane Support. Flat porous membrane support was prepared by casting PAN−NMP solution onto nonwoven polyester fabrics. In the preparation process, a polymer solution containing 15 wt % of PAN was cast onto a nonwoven polyester with the use of a casting knife of 200 μm gap. The cast membrane was precipitated by immersion in a bath of water. The resulting PAN porous membrane was washed in water overnight and was then dried at atmospheric temperature. To improve the hydrophilicity of the mPAN membrane and to facilitate the spread of the aqueous solution of amine over its surface, the mPAN membrane was hydrolyzed in 2 M $NaOH_{(aq)}$ solution at 50 °C. The −CN groups of PAN on the surface of the support membrane layer can be converted into −COOH groups after the hydrolysis with $NaOH_{(aq)}$ solution. An ionic bond can be formed by an acid−base reaction between the −NH or $-NH_2$ groups of the amine and the −COOH of the modified PAN membrane.[2] The modified PAN porous membrane support was washed in a water bath for several hours and was then dried at atmospheric temperature.

Preparation of EDA−TMC/mPAN Composite Membrane. The mPAN membrane support was fixed in a special framelike device, and an aqueous solution of EDA was poured onto it and contacted the exposed surface of the membrane for a period of time. The excess amount of EDA solution on the mPAN membrane support was removed. The composite membrane was prepared via interfacial polymerization by immersing the mPAN membrane soaked with the EDA solution into a toluene solution containing TMC. Finally, to attain the desired stability in structure, the resulting membrane underwent heat treatment in an oven at 70 °C for 60 min. The schematic representation of the polyamide active layer formation on the surface of the mPAN support membrane is shown in Figure 1.

Characterization. SEM (Hitachi S-3000N) was used to observe the morphologies of the polyamide composite membranes. FTIR-ATR (Perkin-Elmer Spectrum One) spectroscopy was used to examine the chemical structures of the active layers of the polyamide composite membranes. Two peaks are shown in FTIR-ATR spectra[8] at the wave numbers 1642 and 1542 cm^{-1}, which indicate C═O (amide I) and N−H (amide II), respectively. The spectra confirmed that the thin-film composite membrane active layer was composed of aromatic polyamide.

Positron Annihilation Spectroscopy (PAS). To investigate the variation in the free volume in the active layers of the polyamide composite membranes, PAS experiments using the slow positron beam, which measures a parameter as a function of positron incident energy (0−30 keV), were performed at room temperature under a vacuum of $\sim 10^{-8}$ Torr. Doppler broading energy spectra were described by using the line-shape parameters, S and W. The multilayer structure was obtained by VEPFIT program analysis of the S parameter. All of the positron annihilation lifetime spectra were analyzed by a finite-term lifetime analysis method using the PATFIT program and by a continuous lifetime distribution using the MELT program. These have been reported in our previous paper.[11] We employed the results of o-Ps lifetime to obtain the volume of free volume holes.

Pervaporation Measurement. The apparatus for pervaporation experiment was depicted in a previous paper.[14] The effective surface area of the membrane in direct contact with the feed solution was 11.64 cm^2. The permeation rate was determined as follows: measuring the weight of permeate collected for a period of operation time and then dividing it with the effective membrane area. The

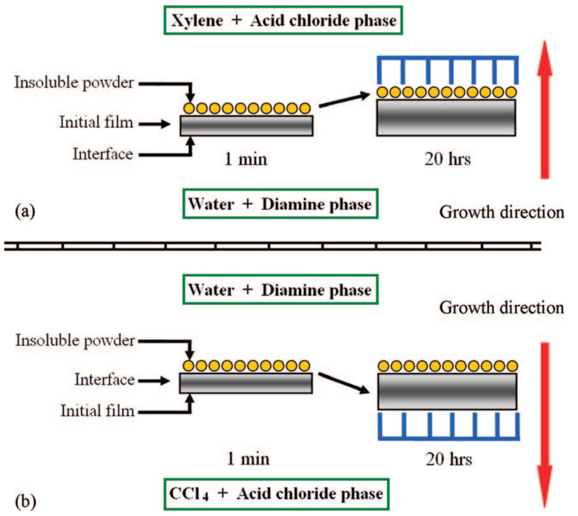


Figure 2. Diagrams of polymer film growth at liquid interface during interfacial polymerization.[9]

compositions of the feed solution and permeate were measured with gas chromatography (GC China Chromatography 8700 T).

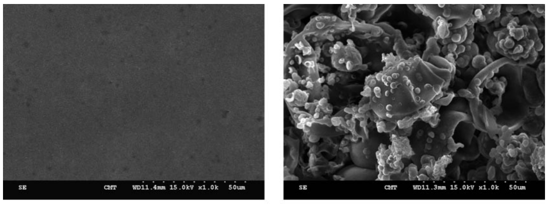
Results and Discussion

Characterization of EDA−TMC/mPAN Composite Membrane Structure. The interfacial polymerization technique is based on a polymerization reaction that forms a polymer film at the interface between two immiscible phases (an aqueous phase of a monomer and an organic phase of a second monomer). The film formed via interfacial polymerization usually grows from the aqueous phase toward the organic phase. This was proven by Morgan,[9] who showed the direction of growth of ultrathin polymeric membrane formed by interfacial polymerization. In his study, the colored insoluble powders were deposited on the surface of the thin film formed initially as a result of interfacial polymerization. After 20 h, the locus of the powder was observed. Figure 2 shows the behavior of polymer film growth during interfacial polymerization. When the organic phase is above the aqueous phase, the powder is embedded inside the polymerized film during interfacial polymerization (Figure 2a). When the aqueous phase is above the organic phase, the powder is still on the surface of the polymerized film and is not embedded inside that (Figure 2b).[9] These experiments confirmed that interfacial polymerization occurs in the organic phase.

According to Morgan's experiment, the ultrathin polymeric membrane density is not constant. The thickness of the polymeric membrane interface increased with interfacial polymerization time, and the reason for this is that the aqueous phase monomer penetrated through the interface and reacted with the organic phase monomer. However, as the interface thickness increased, the amount of aqueous phase monomer that could penetrate decreased.

There is, however, a lack of studies on the variation in density and membrane morphology of interfacially polymerized membrane. These are very important aspects of research on interfacially polymerized membrane used in pervaporation separation process.

In this study, a free-standing EDA−TMC interfacially polymerized membrane was prepared. The SEM micrographs are shown in Figure 3, which shows that the surface density of the aqueous phase is much higher than that of the organic phase. Moreover, the surface roughness of the aqueous phase is much lower than that of the organic phase. These phenomena correspond well to Morgan's theory. Nevertheless, ultrathin interfacial polymerized membrane is difficult to use in pervaporation separation processes because of its poor mechanical properties.



Aqueous phase surface Organic phase surface

Figure 3. Surface view of free-standing EDA−TMC interfacially polymerized membrane.

In this study, the EDA−TMC/mPAN composite membrane was prepared via the interfacial polymerization reaction between EDA and TMC, resulting in the formation of active layer of polyamide on the surface of the asymmetric mPAN membrane. To investigate on the polyamide thin-film composite membrane structure in regard to the free volume variation in the thin-film composite membrane consisting of polyamide active layers and to correlate the variation with pervaporation performance, positron annihilation spectroscopy experiments using a slow positron beam were carried out. The polyamide active layer free volume can be measured with a standard γ-ray spectrometer equipped with a Ge detector; for this purpose, a Doppler-broadened energy spectrum (DBES) (one of the positron annihilation techniques) was used. This technique is based on measuring the width of the annihilation gamma photon line, center at 511 keV.

The Doppler-broadened line width is described using simple line-shape parameters S (shape) and W (wing). The S parameter is defined by the ratio of the central part of the annihilation spectrum to the total spectrum reflecting positron annihilation using low-momentum valence electrons. The W parameter is defined by the ratio of the edge of the annihilation spectrum to the total spectrum reflecting positron annihilation using high-momentum electrons (core electrons). The W parameter is related to the chemical environment where the annihilation takes place. The S parameter value increases if the relative contribution from low-momentum electrons to the positron annihilation increases in the open volume defects. DBES can, therefore, be used to probe the variations in the free volume.

Figure 4 shows that the S parameter as a function of the positron incident energy for the polyamide thin-film composite membrane prepared initially by contacting the mPAN membrane support with various concentrations of EDA−water solution for 30 min, and the membrane was then immersed into a 1 wt % organic TMC solution for 3 min. From the variation in the S parameter, the positron annihilation in the polyamide active layer was at low positron incident energies (about 0.5−2.5 keV) and that in the mPAN support membrane was at positron incident energies higher than 2.5 keV. The variations in the S parameter at positron incident energies of 0.5−2.5 keV show that the S parameter decreased when the concentration of EDA in the aqueous solution increased from 0.5 to 10 wt %. This was because higher monomer concentration caused higher polymerization rate, resulting in lower free volume (higher density) in the polyamide active layer. There was a horizontal, plateau-like curve of S parameter at positron incident energies of 0.5−2.5 keV. The length of the horizontal, plateau-like curve increased with an increase in the concentration of EDA in the aqueous solution. This phenomenon might be due to the fact that the polyamide active layer (EDA−TMC) thickness increased with the concentration of EDA solution in water. Figure 5 shows the SEM images of the EDA−TMC/mPAN composite membranes. The thickness of the polyamide active layer was

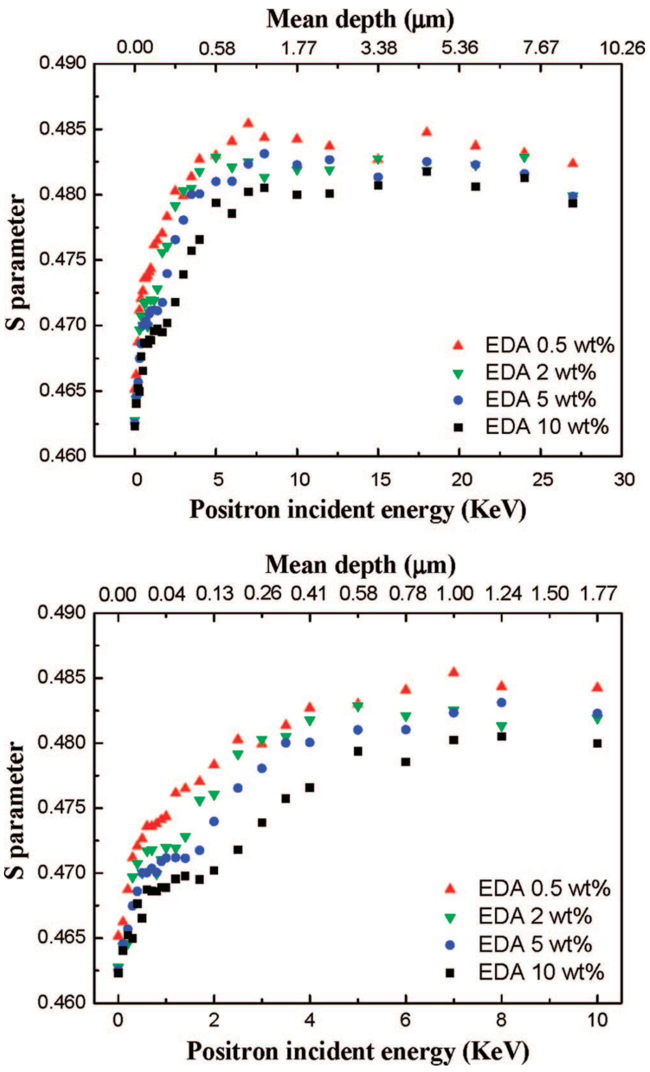
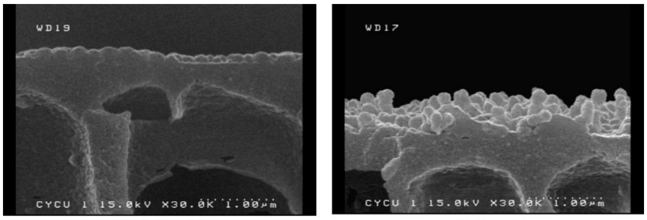


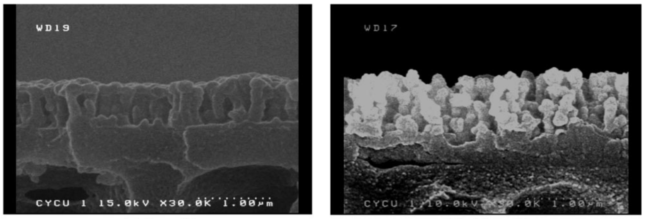
Figure 4. *S* parameter as a function of positron incident energy for polyamide thin-film composite membrane prepared by contacting mPAN membrane with (▲) 0.5, (▼) 2, (●) 5, and (■) 10 wt % aqueous EDA solution for 30 min and then immersing into a 1 wt % organic TMC solution for 3 min.

found to increase with the EDA solution concentration. This result was in agreement with that of the variation in *S* parameter at positron incident energies of 0.5−2.5 keV.

In general, the positron is trapped in the open volume defects and then annihilated with increasing valence electrons, resulting in an increase in *S* parameters but a decrease in *W* parameters. Another useful approach is to present experimental data in terms of the *S*−*W* plot, which allows obtaining certain conclusions about the evolution of the defects participating in positron trapping.[10,11] Figure 6 shows the *W* parameter as a function of the *S* parameter for the 5 wt % EDA−TMC/mPAN composite membrane. A two-step variation was found. The positron annihilation took place at the surface of the polyamide active layer for the variations at low *S* parameters and high *W* parameters (positron incident energy <0.5 keV). The positron annihilation occurred at the free volume in the polyamide active layer for the variations at high *S* parameters and low *W* parameters (positron incident energy: 0.5−2.5 keV). Moreover, the *S*−*W* plot is distinguished into two regions at 0.469 *S* value at positron incident energies of 0.5−2.5 keV. The region of higher *W* and lower *S* indicates the EDA−TMC polyamide active layer. The region of lower *W* and higher *S* indicates the (EDA−TMC) + skin layer of mPAN. The different slopes indicate a chemical composition transition (*W* variation) coupling with a variation in free volume (*S* variation) in the depth profile near the surface of polyamide thin-film composite membrane, which is a transition from the EDA−TMC polyamide layer to the (EDA−TMC) + skin layer of mPAN. These observations agree with the result shown in Figure 4 very well. From the observation of *S* parameter variation, the free volume variation is qualitatively estimated.



(a) 0.5 wt % (b) 2 wt %



(c) 5 wt % (d) 10 wt %

Figure 5. Effect of concentration of aqueous EDA solution on the thickness of the polyamide active layer. The polyamide thin-film composite membranes were prepared by contacting mPAN membrane with (a) 0.5, (b) 2, (c) 5, and (d) 10 wt % aqueous EDA solution for 30 min and then immersing into a 1 wt % organic TMC solution for 3 min.

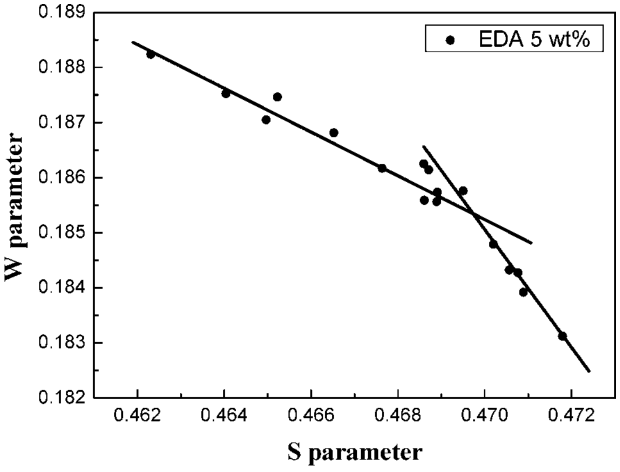


Figure 6. *W* parameter as a function of *S* parameter for polyamide thin-film composite membrane prepared by contacting mPAN membrane with 5 wt % aqueous EDA solution for 30 min and then immersing into a 1 wt % organic TMC solution for 3 min.

To further explore the free volume and structure variations in each layer of the multilayer system quantitatively, positron annihilation lifetime spectroscopy (PALS) experiments were carried out, in which o-Ps lifetime data as a function of positron incident energy for the EDA−TMC/mPAN composite membrane with 5 wt % EDA in water solution were obtained. (From Figure 4, the 5 wt % EDA *S* data show an evident plateau of the top layer.) The resulting o-Ps annihilation lifetime (τ_3) and intensity (I_3) vs positron incident energy plots are shown in Figure 7. In general, τ_3 mirrors the size of the free volume. An increase in τ_3 means an increase in free volume size. I_3 may not directly indicate the amount of the free volume because the Ps formation also depends on the decay rates and chemical environments, and the experiments due to these effects are not

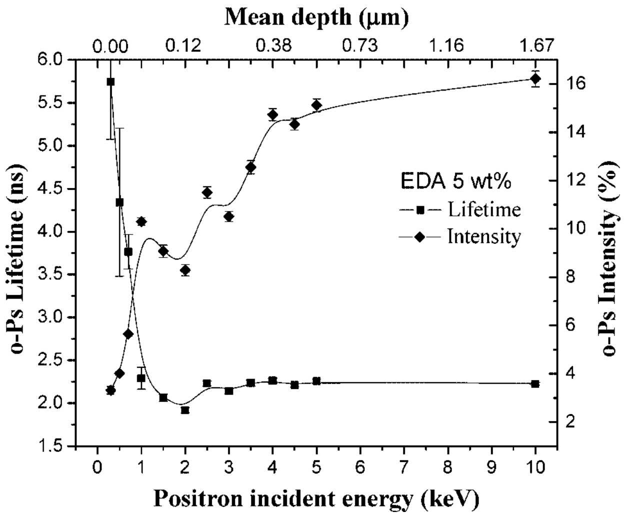


Figure 7. o-Ps annihilation lifetime (τ_3) and intensity (I_3) vs positron incident energy for EDA−TMC/mPAN composite membrane prepared by contacting mPAN membrane with 5 wt % aqueous EDA solution for 30 min and then immersing into a 1 wt % organic TMC solution for 3 min.

carried out in this study. 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 amount of free volume.

The following observations are based on Figure 7: (1) A sharp decrease in τ_3 and a sharp increase in I_3; these general phenomena for o-Ps annihilation near the polymer surface due to the back-diffusion and -scattering of o-Ps from the surface to the vacuum, which results a long o-Ps lifetime (positron incident energy <0.5 keV). (2) A decrease in both the o-Ps lifetime and I_3 intensity with increase in the positron incident energy from 1 to 2 keV; that is, the free volume size and o-Ps formation decrease gradually. (3) An increase in τ_3 until it comes to a plateau; in other words, the free volume size increases.

There is a transition layer from the EDA−TMC polyamide layer to (EDA−TMC) + dense skin layer of mPAN because the skin of mPAN has a larger free volume than the EDA−TMC polyamide (2−2.5 keV). In the same keV range, I_3 jumps to another high value; that is, the amount of the free volume increases. On the basis of both DBES and PALS data, the multilayer structure of the EDA−TMC/mPAN composite membrane is systematically shown in Figure 8. The resulting multilayer structure is as follows: the top layer is the EDA−TMC polyamide, the second layer is a transition layer of (EDA−TMC) + dense skin layer of mPAN, and the third layer is the porous mPAN. From the o-Ps lifetime results (Figure 7), the density of EDA−TMC polyamide active layer decreases along the thin-film growth direction from the aqueous phase to the organic phase in the range of 1−2 keV positron incident energy. These phenomena correspond well to Morgan's theory.

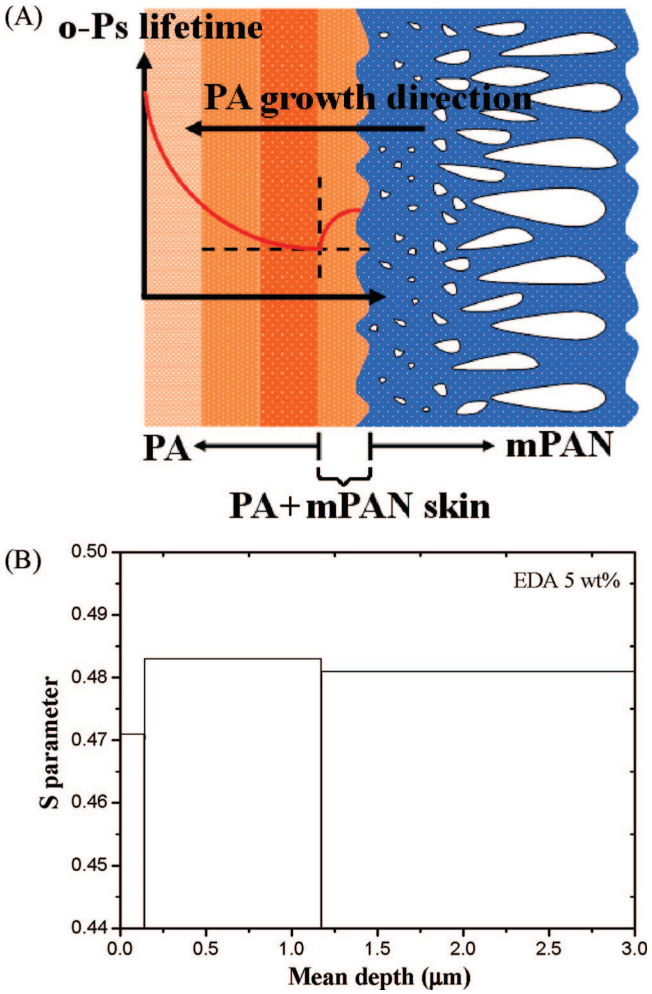


Figure 8. Layer structure of EDA−TMC/mPAN composite membrane: (A) schematic drawing of the formation of composite membrane; (B) schematic diagram of three-layer depth structure obtained by VEPFIT program analysis of *S* parameter from DBES in the EDA−TMC/mPAN composite membrane. (I) EDA−TMC layer, (II) (EDA−TMC) + mPAN skin, (III) porous mPAN (polyamide thin-film composite membrane prepared by contacting mPAN membrane with 5 wt % aqueous EDA solution for 30 min and then immersing into a 1 wt % organic TMC solution for 3 min).

Table 1. Effect of Concentration of Aqueous EDA Solution on Pervaporation Performance of 90 wt % Aqueous Isopropanol Mixture at 25 °C[a]

EDA concn (wt %)	permeation rate (g/(m^2 h))	water concn in permeate (wt %)
0.5	384 ± 45	52.5 ± 4.5
2	252 ± 32	76.8 ± 2.3
5	213 ± 9	92.1 ± 1.5
10	195 ± 37	91.3 ± 1.8

[a] Polyamide thin-film composite membranes (contact time of aqueous EDA solution: 30 min; concentration/immersion time of organic TMC solution: 1 wt %/3 min).

Correlation between EDA−TMC Active Layer Free Volume and Pervaporation Performance. The effect of concentration of EDA in aqueous solution on pervaporation performance of 90 wt % isopropanol−water mixture, which is separated with EDA−TMC/mPAN composite membranes, is exhibited in Table 1. The permeation rate was found to decrease and the water concentration in permeate increased with EDA concentration from 0.5 to 10 wt %. These phenomena might be due to the fact that the polyamide active layer (EDA−TMC) thickness increased with the concentration of EDA solution. This might be because a high polymerization rate was obtained at the higher monomer concentration during interfacial polymerization, resulting in increased active layer thickness.

The polyamide active layer near the surface of the mPAN support was found to appear denser in comparison to that farther from the mPAN support surface (this finding is the similar to a previous study[15]). This phenomenon might be attributed to the following: the dense polymerized layer was formed instantly when EDA reacted with TMC after the aqueous and organic phase solutions contacted with each other on the mPAN support surface. The polymerized layer near the mPAN support surface gradually became dense with increasing EDA concentration,

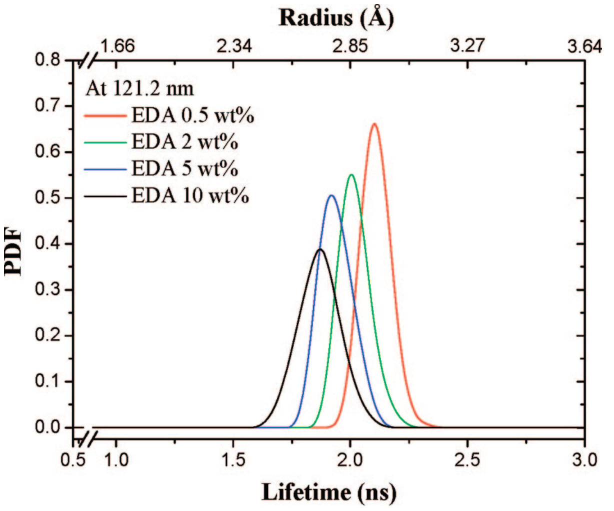


Figure 9. o-Ps lifetime distribution data for EDA−TMC/mPAN composite membrane.

Table 2. Effect of Concentration of Aqueous EDA Solution on o-Ps Annihilation Lifetime[a]

EDA concn (wt %)	τ_3 (ns)	I_3 (%)	radius (Å)	free volume (Å^3)
0.5	2.034 ± 0.033	10.41 ± 0.63	2.880 ± 0.02	100.7 ± 2.6
2	1.981 ± 0.028	9.98 ± 0.75	2.841 ± 0.02	95.8 ± 2.2
5	1.920 ± 0.031	8.29 ± 0.24	2.781 ± 0.03	90.0 ± 2.5
10	1.841 ± 0.164	7.46 ± 0.38	2.705 ± 0.14	82.9 ± 12.7

[a] τ_3 (ns): o-Ps annihilation lifetime; I_3: o-Ps intensity.

causing difficulty for the EDA monomer to penetrate through the polymerized layer to react with the acyl chloride in the organic solution. This resulted in a looser structure in the polymerized layer farther from the mPAN support surface compared to the layer near the mPAN surface. These observations are in good agreement with the SEM images of the EDA−TMC/mPAN composite membranes, as indicated in Figure 5.

To understand the relationship between the free volume size distribution and the pervaporation performance of EDA−TMC/mPAN composite membranes, the positron lifetime distributions and the τ_3 results at 2 keV positron incident energy (mean depth $= 0.12\ \mu$m with the highest density) were analyzed with the use of positron annihilation spectroscopy; the analysis is shown in Figure 9. We employed the results of o-Ps annihilation lifetime (τ_3) to analyze the volume of free volume hole. Table 2 shows the effect of concentration effect of EDA in aqueous solution on the o-Ps annihilation lifetime. It shows that the o-Ps annihilation lifetime and the relative intensity (I_3) decrease with increasing concentration of EDA solution. This result indicates that the size of free volume hole is strongly affected by the concentration of EDA solution. The free volume radius of the EDA−TMC/mPAN composite membrane decreases from 2.89 Å to 2.70 Å with increasing concentration of EDA solution. This revealed that a high-density EDA−TMC active layer was obtained at high concentration of EDA solution, resulting in a decrease in the permeation rate and an increase in the concentration of water in permeate with an increase in EDA concentration from 0.5 to 10 wt %.

Conclusion

In this study, the polyamide thin-film composite membrane was successfully prepared via the interfacial polymerization reaction between EDA and TMC on the surface of mPAN membrane. The polymerized layer near the mPAN support surface gradually became dense with increasing EDA concentration, causing difficulty for the EDA monomer to penetrate through the polymerized layer to react with the acyl chloride in the organic solution. This resulted in a looser structure in the polymerized layer farther from the mPAN support surface compared to the layer near the mPAN surface. The resulting multilayer structure is composed of the following: the top layer, which is the EDA−TMC polyamide, the second layer, which is a transition layer of (EDA−TMC) + mPAN, and the third layer, which is the porous mPAN. From the o-Ps lifetime results (Figure 7), the density of EDA−TMC polyamide active layer decreases along the thin-film growth direction from the aqueous phase toward the organic phase in the range of 1−2 keV positron incident energy. The o-Ps annihilation lifetime and the relative intensity (I_3) decrease with increasing concentration of EDA in aqueous solution. This result indicates that the size of free volume hole is strongly affected by the concentration of EDA solution. A high-density (low o-Ps lifetime) EDA−TMC active layer was obtained at high concentration of EDA solution, resulting in a decrease in the permeation rate and an increase in the concentration of water in permeate with an increase in EDA concentration from 0.5 to 10 wt %.

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