Characterizing free volumes and layer structures in polymeric membranes using slow positron annihilation spectroscopy

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Abstract. Positron annihilation spectroscopy coupled with a newly built slow positron beam at National University of Singapore has been used to study the free volume, pore, and depth profile (0 - 10 µm) in cellulose acetate polymeric membrane at the bottom and top sides of membranes for ionic separation in water purification applications. The S and R parameters from Doppler broadening energy of annihilation radiation representing free volumes (0.1-1 nm size) and pores (>1 nm- m) as a function of depth have been analyzed into multilayers, i.e. skin dense, transition, and porous layers, respectively. The top side of membrane has large free volumes and pores and the bottom side has a skin dense layer, which plays a key role in membrane performance. Positron annihilation lifetime results provide additional information about free-volume size and distribution at the atomic and molecular scale in polymeric membrane systems. Doppler broadening energy and lifetime spectroscopies coupled with a variable mono-energy slow positron beam are sensitive and novel techniques for characterization of polymeric membrane in separation applications.

1. Introduction
An asymmetric polymeric membrane system has a multilayered structure usually consisting of a thin surface or dense skin layer, an intermediate layer, and a highly porous substrate [1]. While polymeric materials and layer systems have been used a long time for separation, purification, and storage, the basic understanding of physical structures and membrane interactions is still primitive. There is limited understanding of the causes for performance in polymeric membrane systems, i.e. permeability and selectivity, at the molecular level. Positron annihilation spectroscopy (PAS) was developed as a useful tool to probe the nanoscopic properties of polymeric materials [2]. Most investigations in polymeric membranes and film systems have been reported mainly in the bulk and few in thin films.
using positron annihilation lifetime and Doppler broadening energy techniques [3-12]. Using a variable mono-energy positron beam (from kT to several ten keV) [13] coupled with positron annihilation lifetime and momentum density measurements is capable of probing depth profiles from the surface, interfaces and to the bulk. In this paper, we present the results of both Doppler broadening energy spectroscopy (DBES) and positron annihilation lifetime (PAL) spectroscopy using a newly built variable mono-energy positron beam at National University of Singapore in one of important membrane systems, i.e. cellulose acetate (CA) on both sides of the membranes for water filtration applications [14-16]. In addition to the use of PAS technique, characterization of this CA membrane from FESEM, ATR-FTIR, AFM measurements has been made and reported elsewhere [17].

2. Experiments

2.1 Polymeric Membrane Preparation

We first prepared polymer solutions by dissolving cellulose acetate, 22.5 wt% CA-398-10 (supplied by Eastman Chemical Company) to a mixed solution of acetone (5 wt%) and NMP (72.5 wt%). Solutions were then cast on a glass plate with a 50 μm casting knife, followed by immediate immersion in a tap water bath at 25°C. After removal of residual solvents, membranes were ready for use or underwent heat treatment prior to use. The prepared CA membranes were removed from the glass plate, dried and two sides of membranes were measured in positron experiments, the top side without contact with the glass and the bottom side directly interacted with the glass plate. While both two sides have skin layers, the top layer has been known to be thicker (~0.9 μm) but with nm pores and the bottom layer contains a dense thin skin layer (~0.1 μm), which controls the separation performance. Figure 1 shows the FESEM cross sectional structure of the double-layer CA membrane assemble and our focus is on the bottom side of the membrane, which plays a key role for membrane performance. Detailed experimental procedures could be found elsewhere [17].

2.2. Positron Annihilation Spectroscopy and Slow Beam

A newly built slow positron beam at the Department of Chemical and Biomolecular Engineering, National University of Singapore (NUS) is shown in Figure 2. This beam was designed and built similar to that at the University of Missouri-Kansas City (UMKC) [18,19] and at Chung Yuan Christian University (CYCU) [20] in Taiwan. This new beam has been calibrated and its performance is as good as or better than that of existing radioisotope beams: slow positron converting efficiency = 6 x 10⁻⁴, beam diameter < 5 mm using PC-control focus for positron energies 0-30 keV.

Two positron annihilation spectroscopies were used in this study: Doppler energy spectroscopy (DBES) and positron annihilation lifetime (PAL) spectroscopy. The S and W parameters from DBES represent the relative value of the free volume (Å to 1 nm) depth profile from o-Ps 2γ radiation (pick-off annihilation) in polymeric systems. The other parameter R, which is the 3γ to 2γ annihilation ratio and it gives information about the existence of large pores (nm to μm), where o-Ps undergoes 3γ annihilation. The S parameter in Si waffle was measured this new beam and the result is compared with those obtained at UMKC [18,19] and CYCU [20] beams. Figure 3 shows good agreements on data obtained among those three slow positron beams. The beam-PAL spectrometer uses the secondary electrons as the starting signal and the lifetime resolutions were found to be about 450 ps at the positron energy > 2 keV. The PAL data contain quantitative information on the free-volume and pore properties in polymeric systems. Analyzed o-Ps pick-off lifetimes (τ₃) from PATFIT fitting are on the order of 1-5 ns in polymeric materials, and were used to calculate the mean free-volume radius (Å to nm) from an established semi-empirical correlation equation [21] based on Tao’s spherical-hole infinite potential quantum model [22]. The long o-Ps lifetime, τ₄ contains pore (>nm-μm) information. Detailed descriptions of slow positron beam and data analysis could be found elsewhere [2,18,19,21].

3. Results and Discussion
Figure 4 shows the results of S and R parameters vs. positron incident energy (which is also expressed as the mean depth according to an established equation [13]) for both the top and bottom sides of CA membrane. From the S data, we have the following observations: (1) S near the surface increases sharply as the positron energy increases; (2) S reaches a maximum and then decreases. The detailed variations contain multilayer structural and chemical composition information. We have employed a computer program VEPFIT [23] to fit the S vs. depth data. We found that the results from 3-layer model fits have good chi-squares (< 1.5) and give stable results and reasonable error bars as lines plotted in Figure 4. These three layers are assigned as: the dense skin layer, the transition layer between the dense skin and the porous layer, and the porous layer of CA membrane. The resolved 3-layer structure is also consistent with the findings of most asymmetric membranes [24,25]. The results of VEPFIT fitted layer thickness are shown in Table 1 for both top and bottom modes of CA membrane. It is found that the top side of the membrane has a much thicker skin layer (852 nm) than that of the bottom side (98 nm). This result is consistent with the FESEM result as shown in Figure 1.

The R parameter represents 3γ annihilation radiation which is either from o-Ps localized in large pores (> nm- µm) of CA membrane or in the beam chamber. The R result vs depth has the following features: (1) Near the surface, R is large due to the backscattering and back diffusion of o-Ps to the vacuum; (2) it decreases as the positron enters the surface of CA and reaches a low value due to the pick-off 2γ annihilation in the dense skin layer; and (3) R increases as the positron enters the transition and then at a large value in the porous region of CA. We employed the VEPFIT program to fit R vs depth in 3-layer model and the result of the skin, transition, and porous layers is shown in Table 1. In general, we found the layer thickness and structure are consistent with that from S fit, i.e. bottom side of CA has thinner skin and transition layers than top side. However, the thickness (260 nm) of the dense skin layer of bottom side from R fit is larger than that of S fitted result (98 nm) while the transition layer from R fit (865 nm) is smaller than S fitted result (2210 nm). This difference is understandable from the intrinsic difference between R and S, which are from 3γ- and 2γ- o-Ps annihilation, respectively. And the layer structures from R and S are schematically shown in Figure 5, which reflect the pores (> nm) and free volumes (< nm) information, respectively.

We analyzed the obtained PAL spectra into four lifetime components: (τ1= 0.125 ns, constrained), (τ1 ~0.45 ns), (τ3 ~ 2-3 ns), and (τ4 ~ 12-40 ns). The o-Ps pick-off lifetime (τ3) of CA polymer is in agreement with the values of common polymers as o-Ps annihilation lifetime and the corresponding free-volume radius ranges from 0.25 to 0.40 nm. The long o-Ps lifetime (τ4) of CA membrane is also consistent with porous membranes on the order of > nm. The variations of τ3 and τ4 vs. depth are shown in Figure 6 and the corresponding intensities, I3 and I4 are shown in Figure 7. Those results are consistent with that expected from the multi-layer structures as resolved by S and R parameters above. The result of τ3, τ4, I3 and I4 at 1.0 and 1.5 keV of positron energy (30 nm, 58 nm mean depth) of the skin layer is shown in Table 2. This result indicates that heating (annealing) reduces the pores and possibly free volume content of CA membrane. We also analyzed the positron lifetime distributions using the MELT program and the τ3 results (with corresponding free-volume radius distributions) are shown in Figure 8. The kinetic radius of water (1.3 Å) [26] is much less than free volumes of CA , however, the hydrated ions, such as Na+, and Cl− are between 1.5 Å and 3.5 Å [27], which are in the range of free-volume radius distribution of CA. The free-volume size distribution is valuable information for the understanding of ionic selectivity in membranes.

Conclusion

Positron annihilation spectroscopy coupled with a variable energy slow positron beam has been used to determine the layer structures and free-volume properties in an asymmetric CA membrane for forward osmosis (FO) membrane separations. We found a 3-layer structure existed in the bottom side of CA membrane prepared on the glass: a dense skin (96 nm), and a transitional layer from dense skin to porous (0.1-2 µm) and a porous CA layer. Free-volume sizes and distributions of asymmetric membranes are useful information to study the membrane performance, particularly for selectivity.
Positron annihilation spectroscopy coupled with a slow positron beam is a useful method for quantitative analysis of free volume and pore size and distributions for FO water purification and may provide guidance for the design of multi-layer membranes for separation applications.

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Table 1. Results of S and R values and thicknesses (L) from multilayer analysis of CA membranes using VEPFIT.

| Mode* | S1       | S2       | S3       | L1(nm)   | L2**(nm) |
|-------|----------|----------|----------|----------|----------|
| Top   | 0.4841±0.0003 | 0.4783±0.0016 | 0.4830±0.0012 | 852±530  | 2778±1792 |
| Bottom| 0.4824±0.0006 | 0.4793±0.0004 | 0.4813±0.0009 | 98±67    | 2210±1583 |

| Mode* | R1       | R2       | R3       | L1(nm)   | L2**(nm) |
|-------|----------|----------|----------|----------|----------|
| Top   | 0.4010±0.0003 | 0.4600±0.0004 | 0.4200±0.0004 | 693±52   | 4884±269 |
| Bottom| 0.3994±0.0003 | 0.4210±0.0003 | 0.4310±0.0003 | 260±38   | 865±112  |

* Top mode refers to the characterization of the top side of the membrane facing to the air, and bottom mode refers to the characterization of the bottom side of the membrane facing the glass plate.
** L₁ and L₂ are the boundary lengths of the dense and transition sub-layers, respectively.

Table 2. PAL results from PATFIT analysis for the bottom side of CA membrane cast on a glass plate measured at 1.0 and 1.5 keV positron energies (mean depth 30 and 58 nm), respectively.

| Energy (keV) | Membrane       | ₃ (ns)     | ₃ (%)      | ₄ (ns)     | ₄ (%)      |
|--------------|----------------|------------|------------|------------|------------|
| 1.0          | CA-90°C-bottom | 2.02±0.02  | 25.42±0.53 | 12.97±0.54 | 2.31±0.08  |
| 1.0          | CA-RT-bottom   | 2.05±0.03  | 28.26±0.56 | 13.55±0.55 | 2.15±0.07  |
| 1.5          | CA-90°C-bottom | 2.14±0.02  | 25.97±0.34 | 13.31±0.83 | 1.28±0.07  |
| 1.5          | CA-RT-bottom   | 2.17±0.02  | 27.64±0.35 | 13.88±0.84 | 1.14±0.06  |
Figure 1. Schematic diagram and FESEM images of the CA membrane cast on glass plate.

Figure 2. A schematic diagram of variable mono-energy (0-30 keV) slow positron beam at National University of Singapore. This beam includes Doppler broadening energy (DBES) and positron annihilation lifetime (PAL) spectrometers for the free-volume and pore depth profile determination.
Figure 3. Comparison of S parameters obtained in the newly built slow positron beam from Si at National University-Singapore (NUS) with existing two beams at University of Missouri-Kansas City (UMKC) [18,19] and at Chung-Yuan Christian University (CYCU) in Taiwan [20].

Figure 4 The S (left) and R parameter ($3\gamma/2\gamma$ ration) for the bottom side of CA membrane.
Figure 5. Three layers are resolved from S (left) and R (right) parameters data of Figure 4: skin, transition from skin to porous, and porous CA membrane as indicated vertical lines as boundaries from the VEPFIT analysis.

Figure 6. Pick-off $\gamma$-Ps annihilation lifetime ($\tau_3$) and intensity ($I_3$) vs. positron energy (depth) in the bottom mode of CA membrane cast on a glass plate with and without 15 min anneal at 90ºC.
Figure 7. Long o-Ps $3\gamma$ annihilation lifetime ($\tau_4$) and intensity ($I_4$) vs. positron energy (depth) in the bottom mode of CA membrane cast on a glass plate with and without 15 min anneal at 90ºC.

Figure 8. The o-Ps lifetime distributions ($\tau_3$) or free volume radius of the bottom mode of CA membranes cast on a glass plate with and without anneal at 90ºC for 15 min.