

Study of the Porosity in Cellulose Acetate Membranes by 3γ annihilation of positrons

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A series of cellulose acetate membranes with different porosities were prepared. The porosity of the membrane was adjusted by adding different molecular weights and contents of polyethylene glycol (PEG), which acts as pore-forming agent in the preparation process. Positron annihilation lifetime measurement and γ -ray energy spectroscopy were employed to evaluate the porosities of the membranes. The lifetime results indicate the size of the free-volume holes in all the membranes are nearly the same. The 3γ annihilation results suggest that, with the increase of porogen content: if the molecular weight of the porogen is low (PEG200, PEG400), pore combination is dominant in the preparation process; while if the molecular weight of the porogen is higher (PEG1000, PEG2000), new pores are formed and/or pores are enlarged.

1. Introduction

Separation membranes have been widely applied in many fields, such as the water treatment, chemical engineering, medicine production and so on [1]. Many achievements such as Tsuru's model [2], Bowen's model [3], etc. have been developed to interpret the correlation between the membrane nanostructure and the performance. In previous work, we found that the membrane performance, e.g. rejection and flux, is influenced by the holes in the membrane [4, 5]. For such membranes, the kind and content of the pore-forming agent is important for membrane preparation.

In this paper, a series of cellulose acetate membranes with different porosities were prepared through adding polyethylene glycol (PEG) with different contents and molecular weights. The obtained membranes were characterized by positron annihilation techniques to find the effect of the PEG on the porosity of the membrane.

2. Experimental

2.1 Membrane preparation

Cellulose acetate (CA) casting solution was prepared by dissolving 20 wt% CA in acetone with polyethylene glycol (PEG) as a pore forming agent for 4 hours at room temperature. The molecular weights of PEG were chosen as 200, 400, 1000, and 2000, respectively. For each kind of PEG, the content in the solution was 8 wt%, 10 wt%, and 15 wt%, respectively. The samples were labeled as PEG200, PEG400, PEG1000, and PEG2000 (the number after PEG denotes the molecular weight of PEG), respectively. The solution was cast onto a glass plate using an 800- μ m casting knife. The membranes were then obtained by rinsing with distilled water for 12 hours.

Table I Water flux and positron annihilation lifetime results for each of the membranes studied.

Sample	Water flux [L m ⁻² h ⁻¹]	τ_3 [ns]	I_3 [%]
PEG200 8 wt%	12	2.13±0.01	14.01±1.75
PEG200 10 wt%	90	2.12±0.01	14.68±0.42
PEG200 15 wt%	200	2.10±0.01	14.63±0.40
PEG400 8 wt%	26	2.09±0.01	14.80±1.69
PEG400 10 wt%	110	2.11±0.01	15.37±0.57
PEG400 15 wt%	260	2.15±0.01	15.79±0.57
PEG1000 8 wt%	35	2.08±0.01	13.06±0.42
PEG1000 10 wt%	170	2.09±0.01	16.29±0.42
PEG1000 15 wt%	500	2.11±0.01	15.07±0.47
PEG2000 8 wt%	70	2.08±0.01	15.29±0.40
PEG2000 10 wt%	100	2.12±0.01	13.89±1.82
PEG2000 15 wt%	410	2.09±0.01	14.91±0.42

2.2 Water flux measurements

Pure water flux (J) was evaluated in a laboratory-scale dead end cell with deionized water at 0.1 MPa. The effective membrane area in the cell was 12.5 cm².

2.3 Positron annihilation characterization

The membranes were characterized by conventional positron annihilation lifetime measurement [4–6] and positron annihilation γ -ray spectroscopy [4,5]. A 0.5-MBq ²²Na positron source was sandwiched between the sample sheets. The total counts for the lifetime measurement and γ -ray spectroscopy are 1 million and 5 million, respectively. The positron 3 γ -annihilation probability was characterized as the ratio of the counts in a low-energy window (365 keV–495 keV) to those in the 511 keV annihilation photo peak of the spectrum.

3. Results and Discussion

The water flux and the positron annihilation lifetime results for the cellulose acetate membranes with different porosities are presented in Table I. In this study, PEG was used as the porogen. Generally, increasing the content of porogen would lead to higher porosity in the membrane, resulting in a higher water flux during the filtration process which is confirmed by the water flux data.

According to the spur model, positrons implanted into polymers may combine with one of the spur electrons to form Ps. In free space, spin-parallel triplet *ortho*-Ps (*o*-Ps) annihilates into 3 γ rays with an intrinsic lifetime of 142 ns, while spin-antiparallel singlet *para*-Ps (*p*-Ps) annihilates into 2 γ -rays with a shorter lifetime of 125 ps. If *o*-Ps is localized in a sub-nanometer hole, it annihilates with a lifetime of around several nanoseconds through a 2 γ pick-off process upon collision with electrons on the hole walls. The *o*-Ps lifetime by 2 γ pick-off annihilation is well correlated with the hole dimension, so the subnanometer-sized free volume can be examined by the positron annihilation lifetime technique [7]. This quantum confinement of *o*-Ps reduces the probability of 3 γ annihilation. In the presence of the pores far larger than 1 nm, some *o*-Ps may be trapped therein before annihilation. Because of the reduced overlap of the Ps wave function with the electrons on the pore walls, such *o*-Ps dominantly undergoes 3 γ annihilation.

In Table I, τ_3 is around 2.1 ns for each membrane, which indicates that the free-volume holes in all the membranes are nearly the same size, while the intensity of the τ_3 component shows only slight differences.

The variation of the $3\gamma/2\gamma$ ratio of each membrane as a function of PEG content is shown in Fig. 1. It can be found that, for PEG200 and PEG400, the $3\gamma/2\gamma$ ratio decreases with increasing PEG content whereas for PEG1000 and PEG2000, the $3\gamma/2\gamma$ ratio increases with increasing PEG content. Moreover, the slope of the variation obviously increases with increasing PEG molecular weight. In other words, the $3\gamma/2\gamma$ ratio exhibits a clear decrease with PEG content for PEG200 and a slight decrease for PEG400, while the $3\gamma/2\gamma$ ratio exhibits a slight increase for PEG1000 and a clear increase for PEG2000. The results in table 1 show that for low molecular weight PEG, the intensity increases with increasing the PEG content, but for high molecular weight PEG, it decreases with the PEG content. Since the membranes are cellulose acetate material with different pore structures. The difference in I_3 might be due to *o*-Ps annihilation via the 3γ process. If the number of pores (larger than 1 nm) increases, the possibility of 3γ annihilation should increase, resulting in a decrease of 2γ annihilation. Thus the decrease of I_3 is related to an increase of $3\gamma/2\gamma$ ratio.

If the pores (larger than 1 nm) are enlarged, the probability of *o*-Ps decay via 3γ annihilation would increase. In addition, if the number of the pores (larger than 1 nm) increased, the probability of 3γ annihilation would also increase. In both cases, either enlarging the pore size or increasing the number of pores can induce a higher 3γ annihilation probability.

The water flux results suggest that for each kind of porogen, the membranes exhibit higher porosity when increasing PEG content. In this case, the decrease of $3\gamma/2\gamma$ ratio for PEG200 and PEG400 can be only attributed to a decrease in pore number, which means the combining of the pores. In other words, with increasing PEG content, the small pores might prefer to combine together. This leads to pore enlargement while the pore number decreases. As a result, PEG200 and PEG400 exhibit lower $3\gamma/2\gamma$ ratio with increasing PEG content. For PEG1000 and PEG2000, the increase of $3\gamma/2\gamma$ ratio with increasing PEG content implies the membrane contains more pores and/or larger pores at higher PEG content.

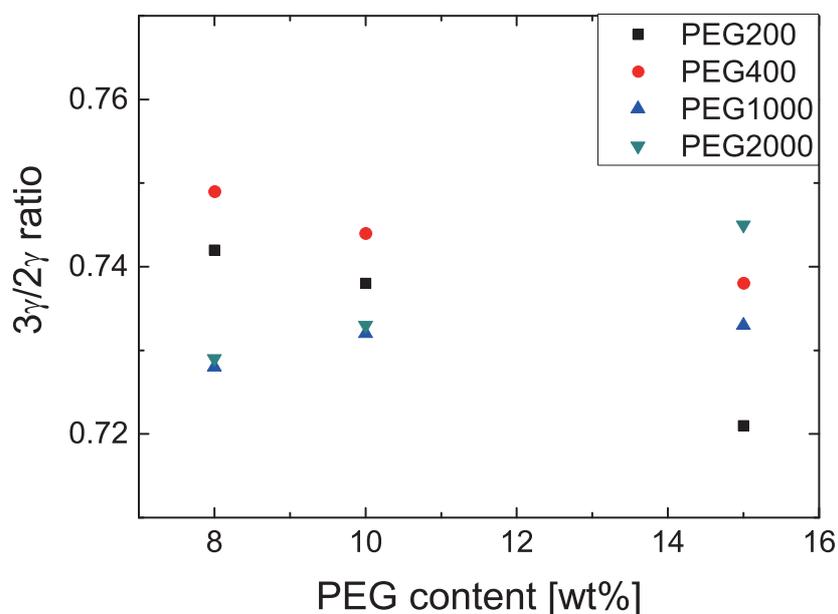


Fig. 1 Variations of the $3\gamma/2\gamma$ ratio for the membranes as a function of PEG content.

4. Conclusion

Positron lifetime measurement and positron annihilation γ -ray energy spectroscopy were employed to characterize the microstructure of cellulose acetate membranes. All membranes exhibited a similar value of the *o*-Ps lifetime component τ_3 , implying that the free-volume hole in the membrane maintains a constant size with increasing PEG content. The $3\gamma/2\gamma$ ratio, obtained from γ -ray energy spectroscopy, decreases with increasing PEG content for PEG200 and PEG400, while the $3\gamma/2\gamma$ ratio increases with increasing PEG content for PEG1000 and PEG2000. Considering the water flux results, it is found that, with increasing porogen content: if the molecular weight of the porogen is low (PEG200 and PEG400), pore combination is dominant in the preparation process; while if the molecular weight of the porogen is higher (PEG1000 and PEG2000), new pores and/or larger pores are formed in the process.

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