

양전자 소멸시간 분광분석을 통한 방향족 폴리아미드 역삼투 분리막의 수투과 향상 메커니즘 제시

김성호, 박승엽
서울대학교 재료공학부

Positron Annihilation Lifetime Spectroscopic Analysis to Demonstrate Flux-Enhancement Mechanism of Aromatic Polyamide Reverse Osmosis Membranes

Sung Ho Kim and Seung-Yeop Kwak
School of Materials Science and Engineering,
Seoul National University

1. Introduction

Flux-enhancement mechanism of thin-film-composite (TFC) membranes for the reverse osmosis (RO) process was newly explained by positron annihilation lifetime spectroscopy (PALS) that has been found to be applied for detecting molecular vacancies or pores having sizes that are equivalent to salt or hydrate ions in RO membrane.

2. Theory

PALS is a unique and valuable technique that characterizes the free-volume hole properties in the solid polymeric systems on the basis of the detection of γ -radiation [1-2]. The o -Ps lifetime was related to the radius of free-volume holes in polymer chains:

$$\tau_{o\text{-Ps}} = \frac{1}{2} \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right]^{-1}$$

where $\tau_{o\text{-Ps}}$ is o -Ps lifetime (ns), R is radius (\AA) of free hole space, and R_0 is $R + \Delta R$ where the fitted empirical electron layer thickness ΔR is 1.66\AA .

3. Experimental

Aromatic polyamide TFC membranes were made from the interfacial polymerization of *m*-phenylenediamine (MPD) in aqueous phase and trimesoyl chloride (TMC) in organic phase (n-hexane). The MPD solution was coated over the microporous polysulfone support, the excess amine solution was removed, and TMC solution was coated thereon. Then, the resulting membrane was dried at 95 C for 210 s. The resulting aromatic polyamide TFC membranes shall hereinafter be referred to as A1, A2, and A3, respectively.

Positron annihilation lifetime spectra were measured for the same aromatic polyamide polymers as thin-film layers of TFC membranes using the conventional fast-fast coincidence system at room temperature. The γ -rays with energies of 1.27 MeV (emitted from a β -decay of ^{22}Na source) and those of 0.511 MeV (emitted from a positron annihilation in a sample) were measured by the start and the stop counters, respectively. The lifetime spectrum was analyzed by using PATFIT program [3] and maximum entropy lifetime (MELT) program [4,5].

4. Results and Discussion

Table 1 showed the RO transport performance data of water flux and salt rejection for the aromatic polyamide TFC membranes. The addition of DMSO led to great enhancement of the water flux of TFC membrane without any considerable rejection loss.

Table 1. Formation and Transport Characteristics of Aromatic Polyamide TFC Membranes

sample	aqueous phase			organic phase	RO performance	
	MPD (wt%)	DMSO (wt%)	TEA/CSA (wt%)	TMC (wt%)	flux (L/m ² h)	rejection (%)
FT-30	2.0	—	1.1/2.3	0.1	25.8	96.4
A1	2.0	1.0	1.1/2.3	0.1	83.6	95.1
A2	2.0	2.0	1.1/2.3	0.1	87.4	93.1
A3	2.0	3.0	1.1/2.3	0.1	116.8	89.6

The spectra of positron annihilation in the aromatic polyamide thin-film polymers were represented in Fig. 1. The decay curves were first analyzed by the maximum entropy method using MELT program. The hole radius distributions obtained using the MELT program were shown in Fig. 2.

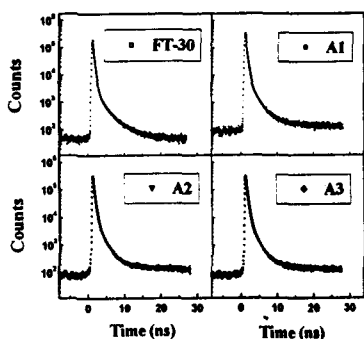


Figure 1. Positron annihilation decay curve

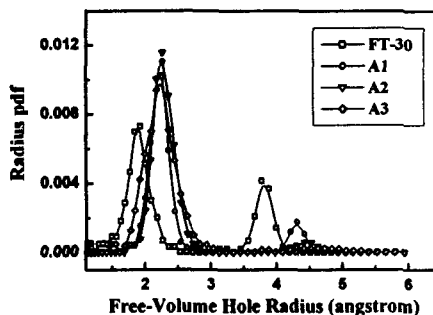


Figure 2. Free-Volume hole radius distribution

The MELT results indicate that the thin-film polymers of TFC membranes are composed of two characteristic domains having radii of about 1.5-2.5Å and 3.5-5.0Å. These PALS results support the interstitial-void model proposed by Sourirajan et al [6-8]. According to the model, solute permeation takes place only in the larger aggregate pores, and solvent permeation in both the smaller network pores as well as the aggregate pores. Adding the DMSO into the membrane formation process increased the number of the smaller network pores, while decreasing that of the larger aggregate pores. The increased network pores make it possible to enhance water flux without a significant salt rejection loss in the high-flux TFC membranes.

5. References

1. D. M. Schrader, Y. C. Jean, "Positron and Positronium Chemistry: Studies in Physics and Theoretical Chemistry", Elsevier, Amsterdam (1988).

2. V. P. Shantarovich, T. Suzuki, C. He, V. A. Davankov, A. V. Pastukhov, M. P. Tsyurupa, K. Kondo, Y. Ito, *Macromolecules*, **35**, 9723, 2002.
3. P. Kirkegaard, M. Eldrup, O. E. Mogensen, N. Pedersen, *Comput. Phys. Commun.*, **23**, 307, 1981.
4. A. Shukla, M. Peter, L. Hoffmann, *Nucl. Instrum. Meth. A.* **335**, 310, 1993.
5. C. Wastlund, F. H. Maurer, *J. Nucl. Instrum. Meth. B.* **117**, 467, 1996.
6. T. D. Nguyen, K. Chan, T. Matsuura, S. Sourirajan, *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 655, 1985.
7. T. D. Nguyen, K. Chan, T. Matsuura, S. Sourirajan, *Chem. Eng. Commun.*, **54**, 17, 1987.
8. A. Kulkarni, D. Mukherjee, W. N. Gill, *J. Appl. Polym. Sci.*, **60**, 483, 1996.