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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.

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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 $-CONH_2$ 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

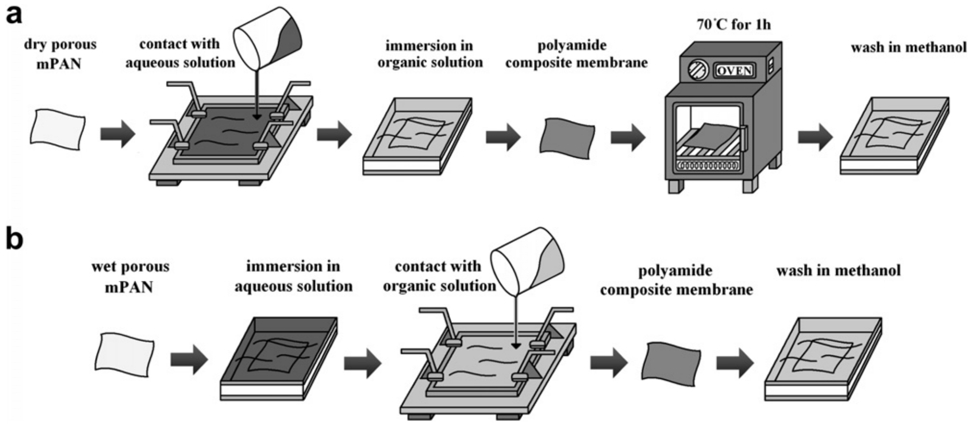

Fig. 1. Illustration of (a) IP-I and (b) IP-II.

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