



Correlating the microstructure of novel polyamide thin-film composite membranes with ethanol dehydration performances

Wei-Chi Chao^a, Yun-Hsuan Huang^a, Der-Jang Liaw^c, Yun-Ying Hsieh^a, Wei-Song Hung^a, Shu-Hsien Huang^{b,**}, Kueir-Rarn Lee^{a,*}, Juin-Yih Lai^a

^aR&D Center for Membrane Technology, Department of Chemical Engineering, Chung Yuan University, Chung Li 32023, Taiwan

^bDepartment of Chemical and Materials Engineering, National Ilan University, I-Lan 26047, Taiwan

^cDepartment of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 10607, Taiwan

ARTICLE INFO

Article history:

Received 1 August 2012

Received in revised form

19 December 2012

Accepted 8 January 2013

Available online 12 January 2013

Keywords:

Polyamide

Pervaporation

Positron annihilation

lifetime spectroscopy (PALS)

ABSTRACT

Polyamide thin-film composite (TFC) membranes were prepared by interfacial polymerization. The purpose is to improve the pervaporation performance of polyamide membranes in separating an aqueous ethanol solution. A novel amine monomer 2,2'-dimethylbenzidine hydrochloride (m-tolidine-H) was reacted with an acyl chloride monomer trimesoyl chloride (TMC) on the surface of a modified polyacrylonitrile (mPAN) membrane. The effects of the following interfacial polymerization conditions on the TFC membrane pervaporation performance were investigated: monomer concentration, immersion time of mPAN in aqueous m-tolidine-H solution, and interfacial polymerization (IP) time for reacting m-tolidine-H with TMC. Attenuated total reflectance Fourier transform infrared spectroscopy and scanning electron microscopy were used to characterize the chemical structure and the morphology of the membranes, respectively. To probe the variation in the fine-structure of the polyamide active layer and the free volume depth profile in the TFC membranes, positron annihilation lifetime spectroscopy (PALS) experiments coupled to a variable monoenergy slow positron beam were conducted. The densest portion of the polyamide layer was at the interface of the two immiscible monomer solutions, as detected based on the smallest o-Ps annihilation lifetime at positron incident energies of 1 and 2 keV with 0.05 and 0.5 wt% TMC, respectively. A high pervaporation performance of 2191 g/m²h permeation flux and 99 wt% water content of permeate was delivered by the polyamide TFC membrane that was prepared by immersing the mPAN membrane in a 1.5 wt% aqueous m-tolidine-H solution for 10 s, followed by contacting it with a 0.05 wt% organic TMC solution for 10 s.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Membrane separation techniques are applicable to liquid mixtures that are difficult to separate or purify by solvent extraction or distillation. A technique that separates the desired component in a feed solution through a suitable membrane by a solution-diffusion mechanism is known as pervaporation. It has been widely regarded as an alternative separation process to traditional ones for azeotropic mixtures, close-boiling-point mixtures, and isomers [1–10]. It is a cost-effective way of dehydrating aqueous ethanol solutions to prepare a technical grade of ethanol used for producing a biofuel, which is one of the novel energy sources that

are considered as possible solutions to the problem of depleting petroleum resources [11].

A suitable pervaporation membrane has a high thermal stability, an excellent mechanical strength, and a high resistance to organic solvents. A material with these properties is a polyamide membrane. It has shown high selectivity in dehydrating alcohols at a wide range of water concentrations [12–14]. Its high selectivity can be attributed to two factors: (1) the high diffusion selectivity because of the low free volume and the low mobility; however, the permeation flux is low due to the low free volume and the low solubility of water in the membrane, and (2) the smaller size of water relative to alcohol molecules.

To improve the permeation flux through a polyamide membrane without sacrificing the selectivity, the membrane morphology must be converted from a dense into an asymmetric or a composite film. In this connection, a feasible alternative is the so-called asymmetric thin-film composite (TFC) membrane, which

* Corresponding author. Tel.: +886 3 2654190; fax: +886 3 2654198.

** Corresponding author. Tel.: +886 3 9317505; fax: +886 3 9357025.

E-mail addresses: huangsh@niu.edu.tw (S.-H. Huang), krlee@cycu.edu.tw (K.-R. Lee).

consists of a thin dense top layer and a porous supporting layer. With this type of membrane, the permeation flux can be enhanced during pervaporation due to its thin selective skin layer with a low mass transfer resistance. An effective technique for fabricating a TFC membrane is interfacial polymerization, which involves a fast reaction rate between two monomers at atmospheric conditions.

TFC membranes prepared by interfacial polymerization are generally used in nanofiltration or reverse osmosis [15–24], only few studies on pervaporation have been reported [1,25,26]. Parthasarathy et al. [25] prepared TFC hollow fiber membranes by interfacial redox polymerization or interfacial photopolymerization to apply them in a simple pervaporation-type experiment. The transport rate of the liquid through the hollow fiber was determined by following the change in mass of the liquid-filled fiber as a function of time. Mass-time data were obtained for two different neat liquids: methanol and methyl tert-butyl ether (MTBE). Transport selectivity coefficients were obtained from the ratio of the slopes for the mass–time transients of methanol and MTBE. They concluded that the interfacially polymerized TFC membrane had potential for pervaporation separation processes. Kim et al. [1] prepared polyimide composite membranes by the interfacial polymerization/thermal imidization method. These composite membranes were applied to separate a mixture of ethanol/water by pervaporation. The polyimide composite membrane prepared at the proper condition exhibited a high separation factor of over 240 and a high permeation flux of 1.7 kg/m²–h for a 90/10 (w/w) ethanol/water mixture. The result demonstrated that interfacial polymerization/thermal imidization could be a very effective method for the preparation of a composite membrane with an ultrathin skin layer of polyimide suitable for the dehydration of ethanol/water mixtures. Zuo et al. [26] fabricated high-performance hollow fiber membranes consisting of a TFC polyamide layer and a porous Torlon® polyamide-imide substrate by means of interfacial polymerization for the pervaporation dehydration of isopropanol. With optimal interfacial polymerization conditions, the TFC hollow fiber membrane showed the best separation factor of 624 with a flux of 1282 g/m²–h and a permeate water concentration of 99.1 wt% using a feed composition of 85/15 wt% isopropanol/water at 50 °C. After post methanol treatment, the flux could be enhanced to 1920 g/m²–h with a slight decrease in the permeate water concentration of 98.4 wt%. In our previous studies [3,7,27–30], a series of PA TFC membranes was prepared by means of the interfacial polymerization of various amine monomers and TMC on the surface of a modified asymmetric polyacrylonitrile (mPAN) membrane. These composite membranes were applied to the dehydration of aqueous alcohol solutions by pervaporation.

The separation performance of a polymeric membrane during the pervaporation process is greatly influenced by the membrane free volume. However, the measurement of free volume is not straightforward because of its dynamic characteristics. A powerful technique that directly measures the free volume in a polymeric material is called positron annihilation lifetime spectroscopy (PALS). The effect of the membrane chemical structure on free volume has been extensively investigated [31–35]. Furthermore, some work on the depth profile of the free volume variation in TFC membranes has also been reported [6,7,36,37].

A novel diamine monomer, 2,2'-dimethylbenzidine hydrochloride (m-tolidine-H), was synthesized in this study. It differs from commercial diamine monomers, such as m-phenylenediamine (MPD) that consists of amine groups on the meta-position of benzene, as it has amine groups on the para-like position of dimethylbenzidine and has a longer molecular chain, which can form a molecular structure with an ordered arrangement in the polyamide layer. Also, m-tolidine-H has two pendent methyl groups, one of which is attached to one of the two benzene rings in its structure and the other methyl group to the second benzene. These methyl groups can bring about steric hindrance effect, causing restriction on the rotation and packing of the molecular chain. These conditions result in making the molecular chain more stable and in increasing the free volume. The aforementioned reasons are favorable for the improvement in the permeation flux and maintaining high water concentration in permeate during the pervaporative dehydration of ethanol.

In this study, polyamide TFC membranes were prepared by the interfacial polymerization reaction between a novel amine monomer m-tolidine-H and an acyl chloride monomer trimesoyl chloride (TMC) on the surface of a modified polyacrylonitrile (mPAN) membrane. The effects of interfacial polymerization conditions on the membrane pervaporation performance were investigated. These conditions were the concentration of the monomers used, the immersion time of mPAN in the aqueous phase solution, and the polymerization time. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was used to characterize the membrane chemical structure. Field emission scanning electron microscopy (FE-SEM) was applied to determine the morphology of the membranes. The variations in the fine-structure of the novel polyamide TFC membranes were measured through PALS experiments.

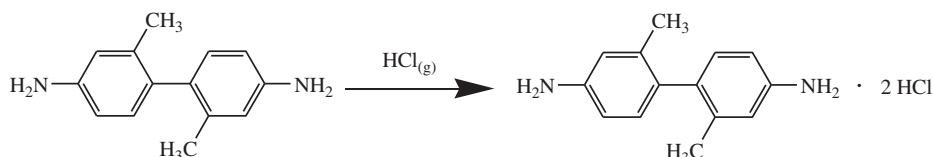
2. Experimental

2.1. Materials

Polyacrylonitrile (PAN) polymer was supplied by Tong-Hua Synthesis Fiber Co. Ltd. in Taiwan. Reagent grade N-methyl-2-pyrrolidone (NMP) was used in preparing the PAN polymer casting solution. The synthesis route of the novel amine monomer m-tolidine-H is shown in Scheme 1. The monomer m-tolidine-H was synthesized through the reaction between 2,2'-dimethylbenzidine and gaseous HCl (generated from sodium chloride and sulfuric acid) [38,39]. Acyl chloride monomer TMC was purchased from TCI Co. Distilled water was used in preparing the aqueous amine solution, and reagent grade toluene was used as the solvent of the acyl chloride monomer. These two monomer solutions were reacted with each other during the interfacial polymerization process to form the polyamide active layer.

2.2. Preparation of porous modified PAN membrane supports

Flat porous PAN membrane supports were prepared by casting PAN onto non-woven polyester fabrics. In a continuous preparation, a polymer solution containing 15 wt% PAN was cast onto polyester



Scheme 1. Reaction in synthesizing m-tolidine-H monomer.

Download English Version:

<https://daneshyari.com/en/article/5182868>

Download Persian Version:

<https://daneshyari.com/article/5182868>

[Daneshyari.com](https://daneshyari.com)