



Effect of free volume and formation mechanisms of polyamide layers on nanofiltration membrane



Wei-Song Hung^{a,*}, Jui-Han Liang^a, Rumwald Leo G. Lecaros^a, Quan-Fu An^b, Chien-Chieh Hu^a, Kueir-Rarn Lee^a, Juin-Yih Lai^{a,c}

^a R&D Center for Membrane Technology, Department of Chemical Engineering, Chung Yuan University, Chungli 32023, Taiwan

^b Beijing Key Laboratory for Green Catalysis and Separation, College of Environmental and Energy Engineering, Beijing University of Technology, Beijing 100124, China

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

ARTICLE INFO

Article history:

Received 23 February 2017

Received in revised form 19 May 2017

Accepted 6 June 2017

Available online 7 June 2017

Keywords:

Nanofiltration

Free volume

Polyamide

Formation mechanisms

Interfacial polymerization

ABSTRACT

Amine monomers of different chemical structures and multiple reactive functional groups, namely tris(2-aminoethyl)amine (TAEA), triethylenetetramine (TETA), and 1,3-diaminopropane (DAP) was reacted with acyl chloride monomers such as 1,3,5-benzenetricarbonyl chloride (TMC) and suberoyl chloride (SC) to synthesize polyamide thin film composite membranes through interfacial polymerization. The effect of membrane formation mechanisms on nanofiltration was investigated. A variable monoenergy slow positron beam was used to explore the differences in the free volume diameters of polyamide layers composed of different chemical structure. The results revealed that the polymerization degree, free volume diameter, and selective layer thickness of the polyamide layers were strongly correlated with each other. Specifically, a high polymerization degree induced a small free volume diameter and a thin selective layer. The cross-linked TAEA-TMC polyamide layer exhibited a free volume diameter of 3.9 Å and was the thinnest (168 nm) among the synthesized membranes, whereas the linear DAP-SC polyamide layer was the thickest (873 nm) with a free volume diameter of 4.7 Å. Finally, a stability test on the TAEA-TMC/PAN showed a slight fluctuation during the 36 h filtration, salt rejection maintained stability at around 97% and water flux of 22.3 L m⁻² h⁻¹.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Polyamide thin film composite (TFC) membranes are the primary type of membrane used in reverse osmosis, nanofiltration (NF), and forward osmosis [1–6]. Interfacial polymerization is applied to synthesize a dense and thin polyamide layers on a porous support. Specifically, this technique involves dissolving an amine monomer and an acyl chloride monomer, both of which contain multiple functional groups, in an aqueous solution and an organic solution, respectively [7]. The polymerization of polyamide occurs at the immiscible interface between the aqueous and organic solutions. The surface density of a polyamide TFC membrane determines the selectivity of a separation process. The porous support helps on increasing the mechanical strength and permeability of the membrane. Generally, interfacial polymerization occurs at the organic phase because amine monomers dissolve easily in an organic solution, whereas the low solubility of acyl chloride in the aqueous phase can be overlooked [8–10]. Addition-

ally, polyamide synthesized through this method contains unreacted amine and hydrolyzed carboxylic groups that can increase membrane hydrophilicity and electric charge, affecting the water adsorption and electrolyte rejection ability of the membrane [11,12].

Ultra-thin polyamide layers directly determine the usability and functions of a TFC membrane. Consequently, researchers have invested greatly in exploring thin film surface patterns [13], internal structures [14], and chemical compositions [15] to examine the structures and functions of selective layers. This facilitates establishing membrane formation mechanisms and kinetic models [16–19]. However, previous study results have contradicted with the generally accepted theoretical models, including uneven density and charge distributions of polyamide layers and partial occurrence of interfacial polymerization in the aqueous phase [20]. These contradictions are attributed to how nonlinear reaction rates [21], increased polymer molecular weights, or cross-links can induce self-limiting and unstable interface properties [22]. Thus creating difficulty on formulating membrane formation mechanisms and kinetic models for estimating polyamide synthesis.

* Corresponding author.

E-mail address: wshung@cycu.edu.tw (W.-S. Hung).

Various techniques featuring specific functions and various advantages have been developed to examine ultra-thin polyamide layers [13,23–27]. The free volume diameter is an essential factor that affects the separation capability of a TFC membrane. However, few techniques can be used to determine the free volume diameter. Positron annihilation spectroscopy is a nondestructive examination method to characterize free volume size, distribution, and layer structure of a material on a nanoscale [28–32]. After a positron and an electron form a positronium, it is captured in a low activity free volume or space and undergoes an annihilation process. Information regarding free volume diameter can be obtained by observing the positronium lifetime. Specifically, a long positronium lifetime indicates a large free volume diameter. Therefore, this method can be used to examine the microstructural changes in ultra-thin polyamide layers and facilitates establishing comprehensive membrane formation mechanisms and kinetic models [33,34]. The present study used amine monomers and acyl chloride monomers with different molecular structures to conduct interfacial polymerization and synthesize polyamide TFC membranes as well as to investigate the differences in the membrane formation mechanisms, free volume size, and physicochemical properties of the synthesized polyamides. Additionally, factors affecting the separation efficiencies of the synthesized products were explored.

2. Experimental section

2.1. Materials

Polyacrylonitrile (PAN) polymer was supplied by the Tong-Hua Synthesis Fiber Co. Ltd. (Taiwan). N-Methyl-2-pyrrolidone (NMP) used as solvent was of reagent grade. 1,3,5-Benzenetricarbonyl (TMC), Suberoyl chloride (SC), Tris(2-aminoethyl)amine (TAEA) and 1,3-Diaminopropane (DAP) were purchased from Acros Organics Co. Triethylenetetramine (TETA) was purchased from TCI Co. Diamines including TAEA, TETA and DAP the DI water were used as the solvent; and acyl chlorides including SC and TMC the DMF were used as the solvent the polyamide active layer formed by interfacial polymerization method. Synthesis of polyamide TFC

membrane is performed with interfacial polymerization of aqueous solution with organic solution were shown in Fig. 1.

2.2. Preparation of polyamide thin-film composite (TFC) membranes

A flat asymmetric PAN membrane, with a thickness of 45 μm , was fabricated through a wet-phase inversion method. A solution of PAN (15 wt% in NMP) was cast using a casting knife (200 μm gap) onto a non-woven polyester fabric. By immersing the cast film in a water bath, a porous PAN membrane was formed. Pores on the PAN membrane surface are 20–30 nm in size with the water permeability 174 ± 12 LHM/bar.

The polyamide active layer was synthesized through interfacial polymerization technique. The PAN support was first immersed in 2wt% aqueous amine solution for 2 min. The excess amount of aqueous amine solution remained on the PAN support was removed. The PAN membrane soaked in the aqueous amine solution was contacted with 1wt% organic acyl chloride solution for 2 min to carry out the interfacial polymerization. Finally, the resulting polyamide thin-film composite (TFC) membrane was washed in methanol and then dried at atmospheric temperature.

2.3. Characterization

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR; Perkin Elmer Spectrum One) and X-ray photoelectron spectroscopy (XPS; ThermoFisher Scientific K-Alpha) were used to characterize the chemical structure of the polyamide TFC membranes. The cross-sectional morphologies of the polyamide TFC membranes were observed with SEM (HITACHI S-4800). The surface roughness of the polyamide TFC membranes were probed by using an AFM (Digital Instruments, DI-NS3a USA) with scanning area of 5 μm x 5 μm . In order to understand the surface hydrophilicity of the polyamide TFC membranes, the water contact angle was estimated using the Automatic Interfacial Tensiometer (FACE Mode 1 PD-VP). A light transmission instrument (Tecpel 536 light meter) was used to observe the changes in the light transmissions during the growth of the polyamides.

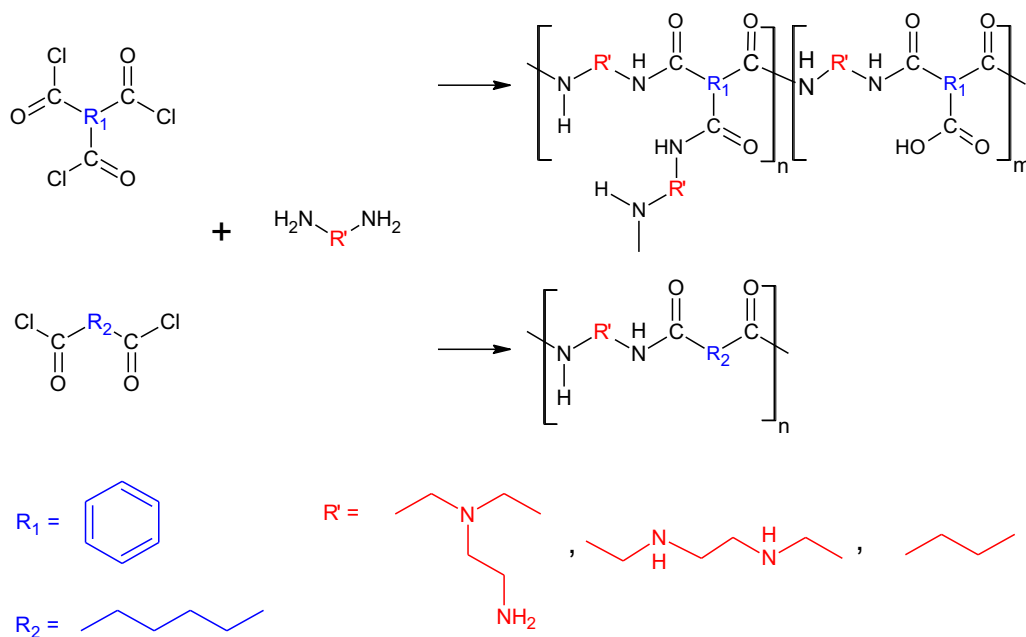


Fig. 1. Chemical structures of aqueous and organic monomer used in preparing polyamide TFC membranes.

Download English Version:

<https://daneshyari.com/en/article/4989592>

Download Persian Version:

<https://daneshyari.com/article/4989592>

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