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Thin film composite nanofiltration membrane prepared by the interfacial polymerization of 1,2,4,5-benzene tetracarbonyl chloride on the mixed amines cross-linked poly(ether imide) support

Yuyan Hai, Jinli Zhang, Chang Shi, Ayang Zhou, Chengying Bian, Wei Li*

Key Laboratory for Green Chemical Technology MOE, Collaborative Innovation Center of Chemical Science and Chemical Engineering (Tianjin), Tianjin University, Tianjin 300072, China

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ABSTRACT

A novel thin film composite (TFC) nanofiltration (NF) membrane was prepared by the interfacial polymerization of 1,2,4,5-benzene tetracarbonyl chloride (BTC) on the cross-linked poly(ether imide) (PEI) support via the mixed amines of the linear ethylenediamine (EDA) and the hyperbranched poly(ethyleneimine) (HPEI). Characterized by attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, Raman mapping, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), etc.; it is indicated that the TFC NF membrane is synthesized through the interfacial polymerization between BTC and the terminal amine groups on the EDA-HPEI cross-linked PEI support. The optimal TFC NF membrane exhibited the methanol permeance of 14.2 L m^{-2} h^{-1} MPa^{-1} and a RB rejection of 100%. After the solvent activation of dimethylformamide (DMF) and dimethylsulfoxide (DMSO), the TFC NF membrane exhibited the methanol permeance of 30.4 L m^{-2} h^{-1} MPa^{-1} and 51.5 L m^{-2} h^{-1} MPa^{-1} with the RB rejection of 90.4% and 74.4%, respectively. Characterized by ATR-FTIR, SEM and Doppler broadening energy spectroscopy (DBES), the effects of solvent activation via DMF and DMSO respectively were investigated on the PEI-based TFC NF membranes.

1. Introduction

Nanofiltration (NF) membrane separation has been widely used in aqueous systems including the drinking water production and wastewater treatments [1–7], however, it is still a challenge to explore NF membranes suitable to remove pharmaceutical residues with low molecular weight (MW) from organic solvents [8–12]. Organic solvent nanofiltration (OSN) membranes are generally prepared as integrally skinned asymmetric (ISA) membranes through the phase inversion or thin film composite (TFC) membranes via the interfacial polymerization [13–20]. The diamine crosslinking has been adopted to improve the solvent stability of NF membranes [21–26]. For instance, Vanherck et al. [27] prepared the cross-linked asymmetric Matrimid polyimide membranes with p-xylylenediamine and obtained the ISA membrane exhibiting the isopropanol permeance of 5–32 L m^{-2} h^{-1} MPa^{-1} and a rejection of 61–99% for Bengal Rose (RB, MW 1017). Solomon et al. [28] prepared polyamide TFC membranes via the interfacial polymerization of trimesoyl chloride (TMC) and m-phenylenediamine on the hexanediamine cross-linked Lenzing P84 polyimide support membranes and obtained the optimal TFC membranes exhibiting the methanol permeance of 15 L m^{-2} h^{-1} MPa^{-1} and the molecular weight cut-off (MWCO) about 400 Da. Hermans et al. [29] prepared polyamide TFC membranes via interfacial polymerization between TMC and the mixture of hexanediamine (as a cross-linker) and m-phenylenediamine (as a monomer for top-layer formation) on the Matrimid polyimide membranes, and the membrane exhibited the ethanol permeance of 1.7 L m^{-2} h^{-1} MPa^{-1} and the RB rejection of 97.5%. Poly(ether imide) (PEI) is one of the popular polymers to prepare NF membranes, it is reported that ethylenediamine (EDA) cross-linking can improve its solvent resistance property in dimethylformamide (DMF) [30] and dimethylacetamide (DMAc) [31]. However, few reports on the PEI-based NF membranes have been found so far to show the superior separation performance in organic solvents.

EDA can be used not only as the cross-linking agent but also as the reactive monomer simultaneously [32,33]. For instance, Li et al. [34] reported that enough terminal amine groups existed on the surface of the optimized EDA-crosslinked PEI, which can react with the monomer TMC to generate polyamide NF membrane with higher water permeance of 42.5 L m^{-2} h^{-1} MPa^{-1} and the glucose

* Corresponding author.
E-mail address: liwei@tju.edu.cn (W. Li).

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rejection of 93.8%. In the view of membrane structural design, the monomer 1,2,4,5-benzene tetracarbonyl chloride (BTC) has the significant structural advantage for interfacial polymerization, comparing with TMC [10,35–37]. As shown in Fig. S1 of the supplementary information, the molecular simulation results indicate that the monomer BTC has four acyl chloride substituent groups with a stereoscopic structure, while the monomer TMC has a planar structure. The stereoscopic structure of BTC is beneficial to increase the chain flexibility during the interfacial polymerization in order to improve the membrane performance, comparing with the planar structure of TMC. On the other hand, EDA has the short linear molecule structure, it is probably to use a compensating amine with a long and branched chain structure to facilitate the synthesis of the superior TFC membranes. Hyperbranched poly (ethyleneimine) (HPEI) has long and branched polymeric chains enriched with amine groups [38,39], it is intriguing to study whether or not the amine mixture of EDA and HPEI can enhance the anti-solvent property of PEI material as well as the separation performance of PEI-based NF membranes.

In this work, we synthesized a novel PEI-based TFC NF membrane through the interfacial polymerization between BTC and the terminal amine groups on the mixed amines cross-linked PEI support, as shown in Scheme 1, in order to explore an efficient pathway to enhance the separation performance via modulating the top layers of the TFC NF membranes. In combination with characterizations of attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, Raman mapping, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), contact angle, etc., it is indicated that the interfacial polymerization occurs between BTC and the terminal amine groups on the EDA-HPEI cross-linked PEI support, and the optimal TFC NF membrane shows higher permeance and rejection towards RB methanol solution. Characterized by ATR-FTIR, SEM and Doppler broadening energy spectroscopy (DBES), the effects of solvent activation via DMF and dimethylsulfoxide (DMSO) respectively were investigated on the optimal PEI-based TFC NF membranes.

2. Experimental

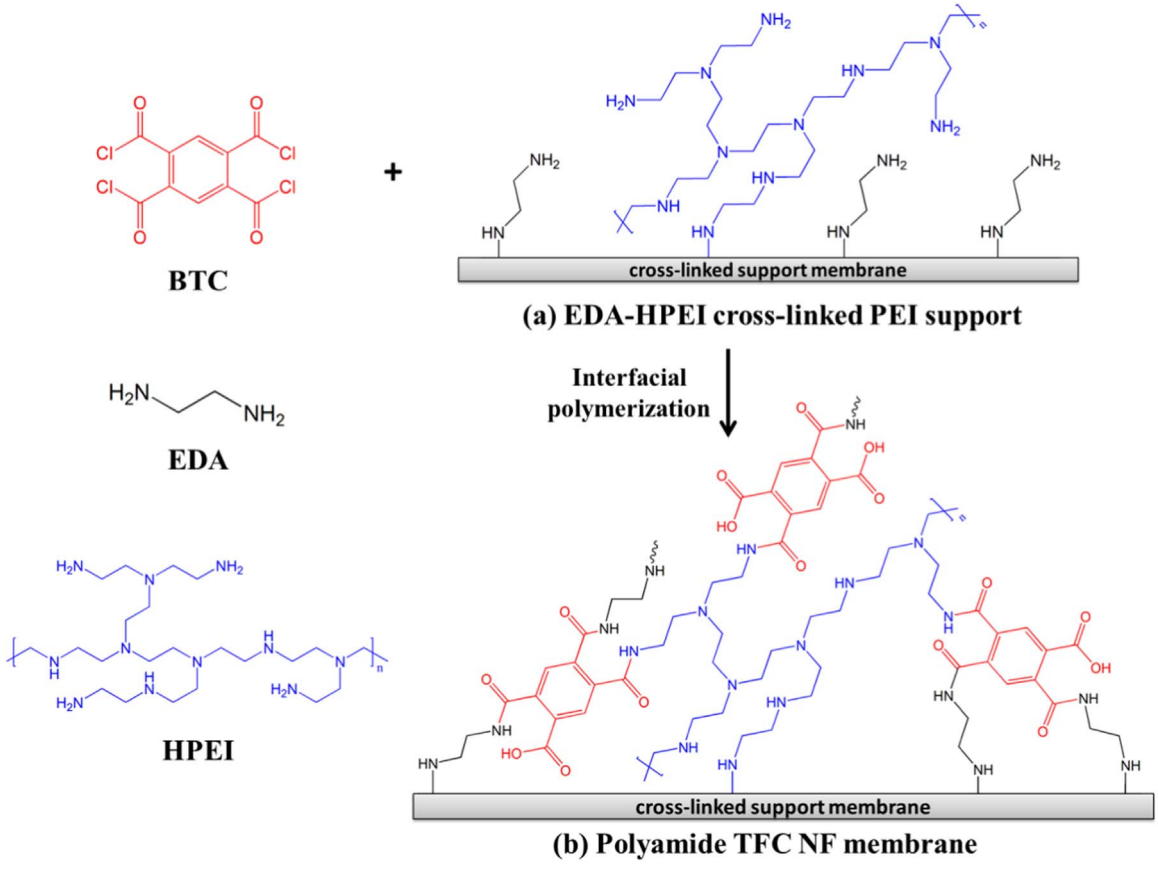
2.1. Chemicals

PEI (Ultem 1000) was purchased from Saudi Basic Industries Corporation (Riyadh, Saudi Arabia) and dried at 150 °C for 5 h before use. BTC was synthesized using pyromellitic dianhydride and phosphoric chloride according to the previous procedure [40,41]. DMF, DMAc, DMSO, EDA, n-hexane and methanol were purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. (Tianjin, China). HPEI (MW 70,000) and RB were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Glucose and tetracycline were purchased from Heowns Biochemical Technology Co., Ltd. (Tianjin, China). All chemicals were of analytical grade and used without further purification. Deionized (DI) water was used throughout the study.

2.2. Preparation of composite membranes

2.2.1. Preparation of PEI support

The PEI support membrane was prepared by casting a 22 wt% PEI solution in DMAc onto a polyester non-woven fabric (purchased from British Belting & Asbestos Company, USA) with a knife gap of 200 μm at room temperature and immersing into a water



Scheme 1. (a) PEI support cross-linked by the mixed amines of EDA and HPEI; (b) polyamide TFC NF membrane prepared via interfacial polymerization between BTC and the terminal amine groups on the cross-linked PEI support.