



Highly stable “pore-filling” tubular composite membrane by self-crosslinkable hyperbranched polymers for toluene/*n*-heptane separation

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ABSTRACT

The stability of membrane is a key issue for pervaporation separation of aromatic/aliphatic hydrocarbon mixtures. In this study, in order to enhance the stability, composite membrane with “pore-filling” structure was formed on porous ceramic tubular substrate. A simple self-crosslinking strategy based on the unique hyperbranched macromolecule, Boltorn W3000, was utilized in the preparation procedure. The hydroxyl and carboxyl groups on Boltorn W3000 molecules reacted at intramolecular and intermolecular during thermal cross-linking process, and then hyperbranched polymers were assembled onto the top layer and sublayer of the ceramic substrate. The morphologies and structures of “pore-filling” composite membrane were characterized by FTIR, SEM, and Nano Indenter. Moreover, “non-pore-filling” membrane was also prepared by the same method with an additional “plugging-holes” step. Both of these two composite membranes were used for separating toluene/*n*-heptane mixtures. The results indicated that the “pore-filling” membrane showed more stable separation performance, due to its excellent anti-swelling properties. This work thus not only illustrated a new approach for the preparation of “pore-filling” membrane, but also produced a potentially useful organic/inorganic composite membrane for aromatic/aliphatic hydrocarbon mixtures separation.

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1. Introduction

Separation of aromatic/aliphatic hydrocarbon mixtures is an important and difficult process in petrochemical industry. Azeotropic distillation and extractive distillation are two traditional techniques for carrying out this separation. However, due to their high energy consumption and large equipment investment [1], the development of efficient and economic technology has been of great concerns. In recent years, pervaporation has been recognized as one of the most promising approaches, due to its economy, simplicity, and minimal environmental impact [2–4]. Based on the solution-diffusion mechanism for pervaporation, the separation performance of a membrane is mainly affected by membrane materials and structures. To achieve superior selectivity in aromatic/aliphatic separation process, the membrane materials should have high affinity to aromatic component. Aromatic compounds containing π electron cloud usually have stronger affinity to polar polymeric materials. Besides, polymer which has the hexagonal carbon rings and unsaturated groups could also contribute to a higher selectivity, due to their

similar structure with aromatic compounds. The σ - and π -bond interactions between membrane material and aromatic compounds could improve the separation performance. However, high affinity may lead to an excessive swelling of the membrane, which would damage the integrity of the membrane and reduce the selectivity. Therefore, it is a challenge for reducing the excessive swelling during the pervaporation process to obtain a stable separation performance [5]. For this purpose, membrane materials and structures should be considered as the significant factors.

Various polymeric materials have been investigated to prepare membranes for separating aromatic/aliphatic mixtures [6,7]. Among these materials, block copolymer is considered as a promising material for fabricating membrane with anti-swelling behavior using for aromatic/aliphatic separation [8]. For example, polyacrylonitrile-block-poly(methyl acrylate) (P(AN-*b*-MA)) block copolymer was used as the membrane material for reducing the excessive swelling. Polyacrylonitrile is resistant to swelling in aromatic/aliphatic solution and polymethylacrylate is selective to aromatic component [9]. It was found that the increasing of acrylonitrile content in P(AN-*b*-MA) copolymer led to a lower degree of swelling of membrane. In addition, other commercial soft-hard block copolymer, such as polyurethane and poly(ether block amide) were also investigated for aromatic/aliphatic separation [10–12]. The separation performance of the

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membrane could be adjusted by changing the ratio of soft and hard segments in the block copolymer.

Besides materials, membrane structures could also be tuned to suppress the excessive swelling. “Pore-filling” structure membrane, which was first purposed by Yamaguchi et al. [13], provided an approach to improve the stability of polymeric membrane. For “pore-filling” membrane, the high-selectively separation layer was formed onto the surface of porous anti-swelling substrates and into the sublayer pores. To obtain the “pore-filling” structure, small monomers were introduced into the pores, subsequently initiated to polymerize inside the support by plasma graft-filling or UV photo grafting technology [14–16]. Due to the covalent anchoring of the grafting polymer on the substrate, these obtained membranes demonstrated good performance and stability in separation of aromatic/aliphatic mixtures. Moreover, in our previous studies, [17] poly(vinyl alcohol)-graphene oxide nanohybrid “pore-filling” membrane was fabricated by a dynamic pressure-driven method. The separation performance could be controlled by negative pressure. These research works indicated that the “pore-filling” structure is beneficial for aromatic/aliphatic separation. However, most of these studies formed “pore-filling” structure on polymeric porous substrate. Compared with the polymeric porous substrate, ceramic substrate could provide better anti-swelling property. Tanaka et al. prepared cross-linked PDMS/PMHS membrane on a porous alumina tubular support. The alumina substrate could inhibit the excessive swelling of PDMS/PMHS [18]. Therefore, the stability of the organic/inorganic composite membrane could be further improved.

In this study, a commercially available hyperbranched polymer (HBP), Boltorn W3000, was used as the membrane material for forming separation layer on ceramic tubular substrate. W3000 is a dendritic polymer, which was grafted with unsaturated fatty acid chains and polyethylene glycol chains (reported by the manufacturer). The polar groups and unsaturated bonds in W3000 contributed to a high affinity to aromatic compounds [19]. Moreover, an industrial ceramic tube was used as the porous substrate to improve the mechanical properties and stability [20]. A simple self-crosslinking strategy was utilized to fabricate “pore-filling” membrane for the pervaporation of aromatic/aliphatic hydrocarbon mixtures (Scheme 1). In order to improve the adhesion force between HBP layer and substrate, the Al_2O_3 substrate was pre-treated by silane coupling agent. Due to the low viscosity and small molecular volume, Boltorn W3000 was introduced into pores in substrate by a simple immersion process. Subsequently, thermal cross-linking was applied as the two different groups ($-\text{OH}$ and $-\text{COOH}$) in Boltorn W3000 molecules could react with each other. Comparing with “pore-filling” membrane, “non-pore-

filling” membrane was prepared with additional “plugging-hole” treatment. The morphology and structure of the composite membrane were characterized by FTIR, SEM and Nano Indenter. The as-prepared organic/inorganic composite membrane was used for separating toluene/*n*-heptane mixtures. The performance and stability of the composite membrane were investigated.

2. Experimental

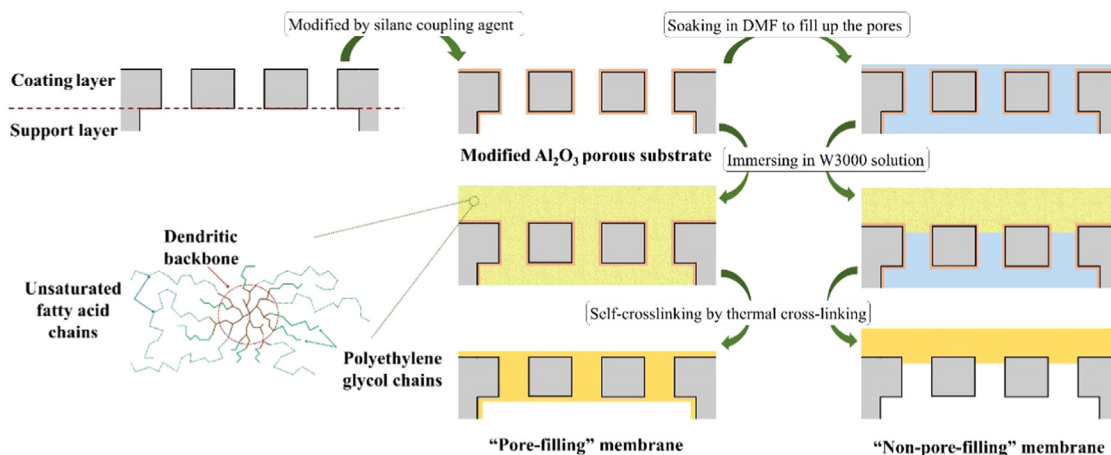
2.1. Chemicals and materials

Hyperbranched polymer (Boltorn W3000, Mw 9000) was purchased from the Perstorp Specialty Chemicals AB (Sweden) [21]. Alumina (Al_2O_3) substrates, with 100 mm-long tubular membranes with inner and outer diameters of 8.5 and 13.5 mm respectively, were obtained from JieXi LiShun Technology Co., Ltd, China. N, N-Dimethylformamide (DMF), toluene, and *n*-heptane were provided by Beijing Chemical Factory. The silane coupling agent, 3-aminopropyltrimethoxysilane (Mw 179.29), was purchased from Aldrich. All chemicals were used as received without further purification.

2.2. Membrane formation

A certain amount of Boltorn W3000 was dissolved into DMF to form a slightly yellow transparent solutions. The ceramic tubular substrate was pre-treated with the method in our pervious study [22]. Firstly, the tube was immersed in a mixture of 95 wt% ethanol aqueous solution and 8 g/L silane coupling agent for 2 h, followed by rinsing with deionized water. Then the substrate was dried in an oven at 110 °C for 2 h. After that, the ceramic tube was immersed into the Boltorn W3000 solution for 10 min. Then the tube was taken out and put in an oven for 1 h at 150 °C for the followed thermal cross-linking treatment. Immersing and thermal cross-linking steps were repeating once to ensure the formation of defect-free film. “Pore-filling” membrane was thus obtained following the above process.

To compare with “pore-filling” membrane, composite membrane with “non-pore-filling” structure was also prepared. In order to fill up the pores in the substrate, the pre-treated tube was soaked in DMF for enough time. After that, the membrane was removed and quickly wiped with filter paper to remove the solvent on the surface of the substrate. Then, the same immersion and thermal cross-linking procedures were taken for this membrane. The non-pore-filling membrane was prepared after the above process. All membranes were preserved in air for further use.



Scheme 1. Schematic illustration of the preparation process of Boltorn W3000 composite membrane with simple self-crosslinking strategy. (For interpretation of the references to color in this scheme, the reader is referred to the web version of this article.)

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