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Enhanced pervaporation performance of SA-PFSA/ceramic hybrid membranes for ethanol dehydration

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ABSTRACT

In this study, sodium alginate (SA)-perfluorinated sulfonic acid (PFSA)/ceramic hybrid membranes were successfully prepared by dip-coating method. The contorted rigid structure of PFSA immobilized the loose structure of SA as well as improved the interconnectivity so as to demonstrated high separation factors. Meanwhile, the ion clusters formed by $-SO_3H$ groups of PFSA possessed high affinity for water, resulting in high water flux. The viscosity of blend solution, structures and properties of the hybrid membranes were investigated by viscometry, Fourier transform infrared (FTIR), scanning electron microscopy (SEM), water contact angle meter and pervaporation dehydration. The effects of SA-PFSA ratio, PFSA content, feed composition and temperature on the separation performances of the hybrid membranes were investigated. The hybrid membrane fabricated by 2.0 wt % SA and 2.0 wt% PFSA demonstrated a high flux of 1155 g m^{-2} h^{-1} coupled with separation factor of 1149 by dehydration of 15 wt% water content ethanol-water mixture at 75 °C, reflecting superior pervaporation processing capacity.

1. Introduction

Compared with conventional separation processes, pervaporation (PV) is considered as an efficient and environmental friendly membrane separation process that provides several advantages, such as low energy consumption, high selectivity, and uncomplicated process design [1]. In addition, PV demonstrates tremendous potential for separating azeotrope and close-boiling mixtures [2]. Usually, ethanol-water separation is used as a kind of standard to test the effectiveness of a PV membrane due to it is difficult to remove one of these solutions from each other. As for the dehydration of alcohol-water solution, highly hydrophilic membranes which yield high permeability, good selectivity and sufficient mechanical strength are preferred [3–5]. Therefore, various hydrophilic materials [2,3] have been reported as PV membrane materials, including poly (vinyl alcohol) [6], polyimides [7], polyamides [8,9], polysaccharides [10], and polyelectrolytes [11–13].

Sodium alginate (SA) is a natural polysaccharide that possesses excellent performances (e.g., hydrophilicity) as a PV membrane material for the dehydration of alcohol-water mixture [14]. Its carbohydrate chains consist of sugar moieties which contain a large number of carboxyl groups and hydroxyl groups, endowing SA membrane with outstanding hydrophilicity and excellent permselectivity nanochannels for water [15]. However, high hydrophilicity of SA leads to instability in aqueous solution during PV. Apart from its water solubility, mechanical weakness of SA membrane has also been a weak point in its possible use in PV [16]. Therefore, great efforts have been devoted to improving the performance of SA PV membranes. A popular modification method is crosslinking [17,18]. It is widely reported that cross-linking with different organic cross-linkers successfully enhances the chemical structure and solves the polymeric chains relaxation of SA membrane [19]. However, a serious drawback for cross-linking is that this chemical reaction is difficult to control (e.g., extent of reaction), which greatly influences the degree of cross-linking [20,21] and thus impacts the performance of the SA membrane. Another frequently used modification method is incorporating nanomaterials with well-defined pore structures, such as metal-organic frameworks (MOFs) [10,22–24] , carbon nanotubes [25], graphenes [26] and nanoparticles [27–29]. However, dispersion of nanomaterials in the polymeric matrix is a great challenge because the nanomaterials trend to agglomerate to create defects in the membranes, resulting in a decrease in selectivity [30].

Polymer blends are attractive alternative materials for modification of SA membranes due to ease of processing and synergetic properties of polymer blends. Moreover, blend method can avoid the drawbacks of cross-linking (e.g., control of cross-linking degree) and incorporating nanomaterials (e.g., dispersion). Perfluorinated sulfonic acid (PFSA) is considered as a good blend polymer due to its excellent chemical,

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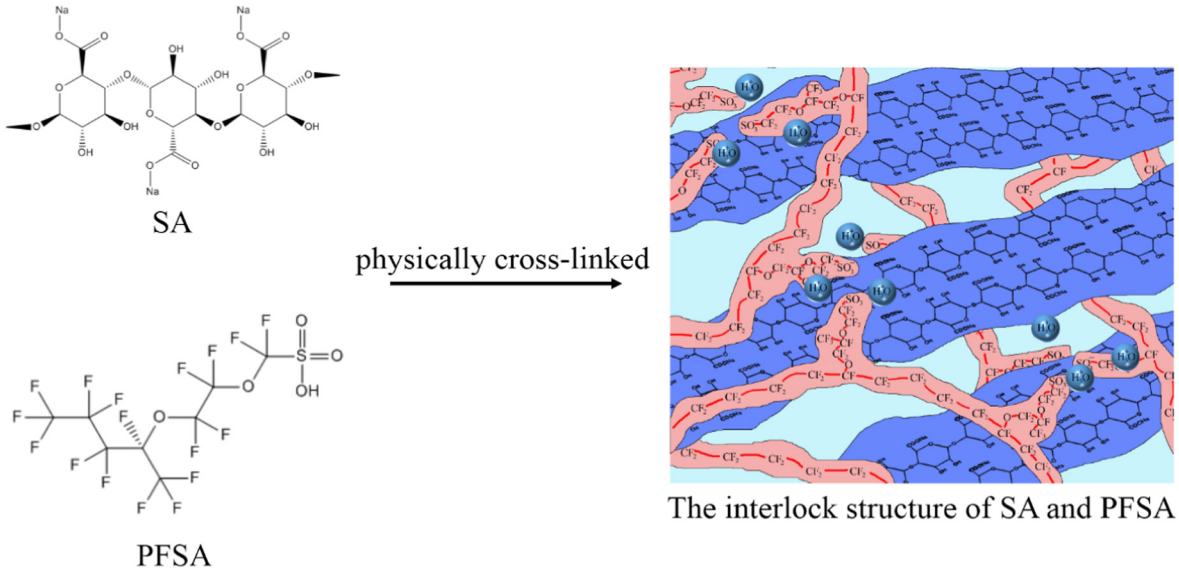

Fig. 1. Schematic diagram of blending SA with PFSA.

Table 1
Compositions of SA-PFSA blend solutions.

Blend	SA (wt.%)	PFSA (wt.%)	Ethanol (wt.%)	Water (wt.%)
SA-1.5/PFSA-2.5	1.5	2.5	30.8	65.2
SA-2.0/PFSA-2.0	2.0	2.0	24.0	72.0
SA-2.5/PFSA-1.5	2.5	1.5	16.3	79.7
SA-3.0/PFSA-1.0	3.0	1.0	9.5	86.5

Table 2
Variation of PFSA content in SA-PFSA blend solutions and nomenclature.

Blend	SA (wt.%)	PFSA (wt.%)	Ethanol (wt.%)	Water (wt.%)
SA-2.0/PFSA-1.0	2.0	1.0	24.5	72.5
SA-2.0/PFSA-1.5	2.0	1.5	24.3	72.2
SA-2.0/PFSA-2.0	2.0	2.0	24.0	72.0
SA-2.0/PFSA-2.5	2.0	2.5	23.8	71.7

thermal and mechanical properties [31]. Its fluorocarbon main chain forms a rigid main body (polytetrafluoroethylene backbone) which can effectively improve the mechanical properties of the blend membrane [32]. The terminated hydrophilic sulphonate ionic groups are considered as a cluster-type structure [33] containing aqueous phase ions which can facilitate the transport of water [34].

In the current work, PFSA was blended with SA to prepare PV membranes. A schematic diagram of blending SA with PFSA was shown in Fig. 1. The contorted rigid structure of PFSA can effectively immobilize the loose structure of SA. On the other hand, the blending process enabled PFSA ion clusters to physically cross-link with SA carbohydrate chains (Fig. 1), thus enhancing interconnectivity of intermolecular voids [35]. The physic-co-chemical properties of the obtained PV hybrid membranes were investigated by viscometry, Fourier transform infrared (FTIR), scanning electron microscopy (SEM), and water contact angle meter. The effects of SA-PFSA ratio, PFSA content, feed composition and temperature on the separation performances of the hybrid membranes were investigated by ethanol dehydration.

2. Experimental

2.1. Materials

Sodium alginate (SA, viscosity above 0.02 Pa·s in 1 wt% aqueous solutions at 20 °C) and ethanol were purchased from Sinopharm (China). Perfluorinated sulfonic acid (PFSA, MW = 1130) resin was purchased from Shanghai Baichun Chemical Materials Co., Ltd. (China). The α-Al_2O_3 ceramic tube M20 with a mean pore size of 20 nm was supplied by Hyflux SIP PTE Ltd. Deionized water was used throughout the work.

2.2. Membrane preparation

PFSA was dissolved in ethanol-water (1:1, wt/wt) solution to prepare a 5.0 wt% solution at ambient temperature. A certain amount of SA was dissolved in water under continuously stirring to prepare an aqueous solution. After filtration to remove insoluble materials, a desired amount of PFSA solution was added in SA aqueous solution under continuously stirring to prepare SA-PFSA blend solutions. The compositions of SA-PFSA blend solutions as well as nomenclature were shown in Table 1.

SA-PFSA/ceramic hybrid membrane was prepared by coating the blend solution on the ceramic hollow fiber membrane. Specifically, a 50 mm in length ceramic hollow fiber membrane was connected to a specially made stainless steel tube. The joint between the ceramic membrane and stainless steel tube as well as the other end of the ceramic membrane were sealed by epoxy sealant. After the epoxy sealant dried up, the ceramic membrane was dip-coated with the prepared SA-PFSA blend solution. Every membrane was coated twice and placed upside down during the second drying process to ensure uniform distribution of the active layer along the hollow fiber membrane axis [36]. For convenience, these hybrid membranes share the same names with blend solutions (Table 1).

The PV performance of the obtained membranes made above was investigated and it was found that the one with 2 wt% SA showed the best performance. In order to investigate the effect of PFSA content, another four hybrid membranes were prepared as shown in Table 2, in which SA concentration and ethanol content were remained the same. The hybrid membrane preparation process was the same as above.

2.3. Pervaporation test

In order to systematically investigate the separation performance, the obtained SA-PFSA hybrid hollow fiber membranes were used to dehydrate ethanol-water solution. The effective area of the membrane was 5.0 cm^2. The operating temperature varied from 60 to 75 °C and the