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Polymeric composite membrane fabricated by 2-aminoterephthalic acid chemically cross-linked polyvinylamine for CO_2 separation under high temperature

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ABSTRACT

Improvement of the performance of CO_2 separation membrane under high temperature is of great importance in industrial applications. In this work, 2-aminoterephthalic acid (AA) was used to chemically cross-link polyvinylamine (PVAm) to fabricate PVAm-AA aqueous solution. PVAm-AA/polysulfone(PSf) composite membrane was then prepared by coating PVAm-AA aqueous solution on PSf support membrane. Through the chemical cross-linking by AA, the polymer chain mobility was restrained, resulting in the enhancement of thermal stability. The introduction of AA also increased the effective carrier content for CO_2 separation. Therefore, CO_2 permeance and CO_2/gas selectivity of PVAm-AA/PSf membrane under relatively high temperature were greatly improved. For CO_2/N_2 mixed gas (15/85 by volume), PVAm-AA/PSf membrane showed a CO_2 permeance of 661 Gas Permeation Unit (GPU) and CO_2/N_2 selectivity of 95 at 0.3 MPa and 120 °C. Excellent performance stability was shown during the operation for 250 h at 120 °C. Moreover, PVAm-AA/PSf membrane displayed excellent separation performance and thermal stability for the separation of CO_2/CH_4 and CO_2/H_2 mixed gases.

1. Introduction

CO_2 separation technology based on membranes has shown great potentials in the application of CO_2 capture from flue gas, CO_2 removal from natural gas and syngas due to the inherent advantages of low capital cost, operational simplicity and low pollution [1–3]. It can make a great contribution to the environmental protection and the efficient use of energy [4]. Polymeric membranes are considered as one potential option for CO_2 separation from large volume gas streams due to its simple commercial preparation [5]. Several polymeric materials, such as cellulose acetate [6], silicon rubber [7], polyimide [8], and polyvinylamine (PVAm) [4,5] have been used to fabricate CO_2 separation membranes. Among the polymeric membranes, the fixed carrier membrane, combining solution-diffusion and reaction-diffusion through the reversible reactions between reactive carriers (such as amine groups) and the targeted gas-CO_2, was expected to achieve a high CO_2 permeance and selectivity simultaneously [9]. In our previous studies, the fixed carrier membranes using PVAm (as shown in Scheme 1(a)) as the active layer showed good separation performance under the room temperature [2,4,10,11]. However, the temperatures of industrial gases are sometimes over 100 °C for certain applications [12–18]. The cost and energy consumption for cooling the gases will be reduced if the separation membrane can be used under high temperature. Generally, the physical structure of fixed carrier membrane material would be changed under high temperature, such as the densification of the polymeric matrix [19], which would lead to the reduction of the separation performance [20–22]. The loss of separation performance under high temperature would weaken the techno-economical competitiveness of the membrane [2,23]. As known to us, studies on the improvement of separation performance of PVAm under high temperature have seldom been reported. It is necessary to investigate the modification of PVAm to improve the separation performance under high temperature.

Generally, the chemical cross-linking can restrain the polymer chain mobility [21,22,24,25], and is an effective method to enhance thermal stability of the membrane [19,26–28]. However, the

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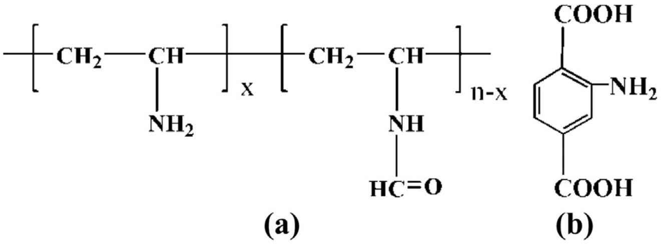

Scheme 1. Chemical structure of (a) PVAm and (b) AA.

chemical cross-linking would influence the gas separation performance of the membrane. In most cases, chemical cross-linking would increase CO_2/gas selectivity but decrease CO_2 permeance of the membrane. The studies of Dong et al. [29] and Yi et al. [30] indicated that CO_2/CH_4 selectivity of PVAm/PSf membrane increased but CO_2 permeance declined sharply after the chemical cross-linking of PVAm by glutaraldehyde. The results were ascribed to the densification of the polymer matrix and the carrier depletion induced by the cross-linking, which would reduce the solution-diffusion and the reaction-diffusion, respectively [2,29,30].

In some cases, chemical cross-linking could improve the CO_2 permeance of the membranes. Koros and his co-workers [19,26,31] investigated the chemical cross-linking of the polyimide membranes by phenyl radical or ethylene glycol and found the cross-linking could increase the CO_2 permeance of the membranes. It was because the cross-linkers functioned as the “spacers” between the polymer chains to disrupt chain packing and increase the polymer free volume [31]. Besides, Cao et al. [32] chose the agents containing ether oxygen and amine groups to cross-link the polyimide membranes. The results indicated that the cross-linked membranes showed higher CO_2 permeance and CO_2/gas selectivity due to the improvement of the solubility selectivity and the chain mobility of the polymer by ether oxygen and amine groups. Nevertheless, in the above-mentioned researches, the CO_2/gas selectivity was not increased by a satisfying extent due to the significant increase in other gas (N_2, CH_4 or H_2) permeances.

In this work, the chemical cross-linking was expected to improve the thermal stability and gas permselectivity. To achieve this target, from our viewpoint, the chemical cross-linking for fixed carrier membrane should meet the following conditions. (1) The chemical cross-linking could control the degree of densification, improving the CO_2/gas selectivity while not resulting in significant reductions in CO_2 permeance. (2) The chemical cross-linking agent should contain the carrier of CO_2 (such as amine group and carboxyl group [33]), which may enhance the reactivity-selectivity of the membrane.

Based on the idea described above, we deduced that the chemical cross-linking by an agent containing CO_2 facilitated carrier and ring structure could enhance the thermal stability and CO_2 separation performance simultaneously. 2-Aminoterephthalic acid (AA) (as shown in Scheme 1(b)) was used to chemically cross-link PVAm in this work. The CO_2 separation performance of PVAm-AA/PSf membrane under high temperature was expected to be enhanced due to the following points. Firstly, the potential formation of chemical bonds between the carboxylic groups in AA and the amine groups in PVAm could restrain the polymer chain mobility, which was favorable to the improvement of membrane thermal stability. Secondly, the existed amine in AA would increase the carrier content in the membrane, which could promote CO_2 transport in the membrane by taking reversible reactions with CO_2 molecules. Thirdly, AA containing benzene ring possesses large steric hindrance, which could avoid the excessive densification and increase the free volume within the polymeric matrix, thereby enabling fast permeation of CO_2 molecules.

In this work, the coating solutions containing PVAm or PVAm-AA were coated on silicone rubber substrate and PSf support membranes to prepare PVAm or PVAm-AA films and PVAm/PSf or PVAm-AA/PSf composite membranes, respectively. To investigate the changes in physicochemical properties after the cross-linking, PVAm and PVAm-AA films were characterized by attenuated total reflectance infrared (ATR-FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray diffractometer (XRD) and differential scanning calorimetry (DSC). Moreover, the gas separation performance and thermal stability of PVAm-AA/PSf and PVAm/PSf membrane were investigated using CO_2/N_2 under different temperatures and feed pressures. Finally, CO_2/CH_4 and CO_2/H_2 permselectivity of PVAm-AA/PSf membrane was tested to further evaluate its gas separation performance.

2. Experimental

2.1. Material

N-vinylformamide (NVF) was purchased from Aldrich Inc. and was distilled under vacuum before using. 2,2′-azobis (2-methylpropion-amidine) dihydrochloride (AIBA) was purchased from Aldrich Inc. and was recrystallized from ethanol before use. Model 201 × 7 strongly basic anion exchange resin from Chemical Plant of Nankai University (China) was regenerated before using. 2-Aminoterephthalic acid (99.0% purity) was obtained from J&K Scientific Ltd. (China) and used without further purification. N-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDC · HCl, purity 98.5%) and N-hydroxysuccinimide (NHS, purity 98%) were purchased from Aladdin Reagent Co., Ltd. (China), and used as received. The PSf ultrafiltration membrane was purchased from Vontron Technology Co., Ltd. (China) and the average cut-off molecular weight of PSf membrane was 6000.

2.2. Synthesis of PVAm polymer

PVAm was synthesized according to a method reported in the reference [2,34], and a schematic diagram of the reaction process was shown in Scheme 2.

The reaction was conducted as follows. (1) 0.053 g AIBA and 9.83 mL NVF were dissolved in 40 mL deionized water in a flask. (2) The polymerization of poly(N-vinylformamide) (PNVF) was performed in the flask equipped with a stirrer at 52 ± 2 °C for 4 h under nitrogen atmosphere. (3) After polymerization, 30 g 37 wt% hydrogen chloride (HCl) aqueous solution was added into the flask and acidic hydrolysis was performed at 70 ± 2 °C for 2 h or at 85 °C ± 2 °C for 10 h. (4) To remove HCl, the polymer solution was mixed with excessive strongly basic anion exchange resin and was further stirred for 2 h. (5) The solution was placed in ethanol to precipitate a white deposit. The deposit was dried in a vacuum oven at 40 °C for 48 h. Finally, the dried product named PVAm was obtained.

As illustrated in Scheme 2, PVAm with a higher hydrolysis degree contained more amine groups, which should benefit the reaction-diffusion of CO_2. However, when the hydrolysis degree of PVAm was too high, the crystallinity of PVAm would be increased because of the high regularity of the polymer structure. The crystalline region was assumed to be impermeable to gas, thus the increase of crystallinity would lead to the decrease of effective carrier content. Therefore, in the previous work [2,4,10], the hydrolysis degree of PVAm was controlled in a medium level (around 40%). However, the chemical cross-linking could disturb the regularity of the polymer structure, which would avoid the increase of the crystallinity with hydrolysis degree increasing. Therefore, to