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CO₂ separation using thermally stable crosslinked poly(vinyl alcohol) membrane blended with polyvinylpyrrolidone/polyethyleneimine/tetraethylenepentamine

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ABSTRACT

This article reports structural characterizations and permeation of novel CO₂-selective crosslinked thin film composite poly (vinyl alcohol) (PVA)/polyvinylpyrrolidone (PVP) blend membranes doped with suitable amine carriers. The characteristic properties of the active layer were examined by Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). The effects of active layer thickness, feed pressure, temperature, and sweep side water flow rate on transport properties (CO₂ and N₂ flux, CO₂ permeance, and CO₂/N₂ selectivity) were investigated with a mixed gas stream containing 20% CO₂ and 80% N₂ by volume. The temperature, feed pressure and sweep side water flow rate were varied from 90 to 125 °C, 1.7 to 6.2 atm and 0.02 to 0.075 cm³/min, respectively. The selective dense layer containing amine carrier displays both high selectivity and permeance. The maximum CO₂/N₂ selectivity of 270 and a CO₂ permeance of 29 GPU were obtained for the composite membrane with 45 μm active layer thickness at 2.8 atm feed side absolute pressure and 100 °C temperature. Crosslinked-PVA-PVP with blended amines membrane also exhibited a good stability during a 300 h test.

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1. Introduction

Carbon dioxide emission due to industrial era has been increasing at an alarming rate in the recent times posing a great threat to the environmental ecology. This has led to an intensity of research in the field to mitigate its adverse effects on the environment. CO₂ capture has a wide number of applications from mitigating greenhouse gas effect to production of fuel with enhanced energy content, natural gas sweetening and gas purification with the prevention of corrosion problems [1]. Purification of CO₂ remains a challenging task due to economical and environmental reasons. Conventionally, CO₂ is removed from flue gas by absorption into amine solvents but this process is highly energy intensive due to the regeneration process of CO₂ loaded amine solvents [2]. Polymer membrane based separation may become a potential method to capture CO₂ with less energy consumption due to light weight and space efficiency as well as compact modular design. Also, a separating agent is not required hence no regeneration is required [3,4]. Polymer membranes such as cellulose acetate, cellulose triacetate or polyimide are used industrially for CO₂ removal.

These membranes are normally suffered by low CO₂ permeability as well as low CO₂/N₂ selectivity. Wind et al. [5] reported a CO₂ permeability of 4 Barrers and a CO₂/N₂ selectivity of 26 for cellulose acetate membranes. However, most of the industrially available polymeric membranes are made of common polymeric materials and separation is governed by solution-diffusion mechanism. Relative solubility and diffusivity of the components in the gas mixture limits the selectivity of conventional polymeric membrane. Blending of suitable carriers into the polymer matrix can enhance the CO₂ transport property by reacting reversibly with the target compound and hence can enhance CO₂-selective properties. Miscibility between polymers and amines is a key factor, since it affects the mechanical properties, such as morphology, permeability, degradation and thermal stability. Improvement of thermal stability of polymeric membrane is one of the most important characteristics in any industrial application because most of the polymeric membranes are affected by high temperature application. Crosslinking and blending with a thermally stable polymer matrix is one of the alternative ways to improve thermal stability of polymer hydrogels. There are several investigations that have been reported in the literature for improvement of thermal stability of polymers [6–10] and amine blends due to their useful applications in the field of CO₂ removal and gas separation [11–24]. Poly (vinyl alcohol) (PVA), a 1,3-diglycol polymer, is an excellent hydrophilic material and useful for many practical

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applications due to ease of its preparation as well as its excellent film-forming ability, good compatibility with amine, and good thermal stability [25]. However, its hydrophilicity and thermal stability can be improved using crosslinking agents such as aldehydes, carboxylic acids, anhydrides and also by blending with thermally stable polymer matrix like polyvinylpyrrolidone (PVP) [6–10]. There is an increasing interest for the crosslinked PVA hydrogels doped with amine carrier in the gas separation application because of their high permeability as well as high thermal stability [14–22]. The important literature on CO₂ separation using different polymeric membranes are given in Table 1. Cai et al. [11] studied the separation of CO₂ from CH₄ and N₂ mixture using PVA containing poly(allylamine) composite membrane. The CO₂ permeance and CO₂/N₂ selectivity observed was around 24 GPU and 80 against 0.98 atm feed pressure at room temperature (25 °C) [11]. Deng et al. [12] have used a defect-free ultra-thin (0.3 μm) PVAm/PVA blend membrane for CO₂ separation from 10% CO₂ and 90% N₂ gas mixture. The CO₂ permeance of 214 GPU and CO₂/N₂ selectivity of 174 was observed against 1.97 atm feed pressure and at room temperature (25 °C) [12]. Francisco et al. [14] have studied the effect of different alkanolamines (MEA/AMP/DEA/MDEA) in PVA membranes. Pure CO₂ permeance and CO₂/N₂ selectivity was found to be about 8 GPU and 88, respectively, against the feed pressure difference of 0.5 atm at 24 °C. They have reported that DEA (20 wt%) gives the satisfactory result among all other alkanolamines [14]. Matsuyama et al. [16] have reported the CO₂ permeance and CO₂/N₂ selectivity using PVA/PEI blend membrane as 4 GPU and 160, respectively at CO₂ partial pressure of 0.065 atm with 220 μm membrane thickness [16]. The effect of zeolite 5A has been carried out using PVA with PEG polymer matrix. CO₂ permeability and CO₂/CH₄ selectivity was reported around 250 Barrer and 20 respectively, at 10.2 atm feed pressure and 39 °C temperature [21]. However, the literature on CO₂/N₂ separation using crosslinked PVA membrane containing blended amine carriers at high temperatures are limited.

In this study, novel crosslinked PVA membranes blended with polyvinylpyrrolidone (PVP) and doped with amines have been synthesized by the solution casting technique. Here, we have used HCHO as the crosslinking agent and PVP blending to enhance the thermal stability of PVA membrane. PVP enhances the thermal stability of polymer hydrogel because it has high glass transition temperature (T_g) due to the presence of the rigid pyrrolidone group and also has excellent miscibility characteristics with cross-linked PVA hydrogels due to formation of hydrogen bonds between carbonyl group of PVP and the hydroxyl group of PVA. To enhance the CO₂ transport property through the membrane, it is very essential to introduce suitable carrier into the polymer backbone which should have higher CO₂-carrier reaction rate along with high CO₂ loading capacity. Here primary sterically hindered amine, PEI and primary sterically unhindered amine, TEPA and their blends have been used as carriers. The main interest is in the study of glass transition temperature (T_g), melting

temperature (T_m), degree of crystallinity, weight loss of polymer fraction and CO₂ gas transport properties (CO₂ flux, CO₂ permeance, CO₂/N₂ selectivity) against different physical condition like pressure, temperature and moisture content of the crosslinked PVA-PVP-amine thin film composite membranes.

2. Experimental section

2.1. Materials

Poly(vinyl alcohol) (98–99 mol% hydrolyzed powder, M_w = 130,000), polyvinylpyrrolidone (average M_w = 360,000), polyethylenimine (average M_w = 25,000) and tetraethylenepentamine (M_w = 189.3) were procured from Sigma-Aldrich, USA. Formaldehyde (37 wt % aqueous solution) and potassium hydroxide were purchased from Merck, India and used without further purification. Microporous polysulfone supports (thickness: about 150 μm and average pore size: 0.03 μm) were obtained from Sterlitech USA. Feed gas (20% CO₂ and 80% N₂) with certified compositions was purchased from Vadilal Pvt. Ltd., India for the gas permeation tests.

2.2. Membrane synthesis

Active layer of thin-film-composite membranes was synthesized by the solution casting methodology on the porous polysulfone support membrane. The membrane synthesis process is mainly divided into two parts. Firstly, polymer hydrogel was synthesized using crosslinking agent (HCHO) as well as blending with polyvinylpyrrolidone (PVP). Secondly, a suitable amine carrier was introduced into the polymer hydrogel.

Three different compositions of polymer hydrogel active layers were synthesized. These are pure PVA, PVA crosslinked with HCHO and crosslinked-PVA blended with PVP with a PVA:PVP ratio of 1:0.2. The detailed compositions of active layer were 100 wt% PVA, 90 wt% PVA + 10 wt% KOH with 60 mol% degree of crosslinking by HCHO and 75 wt% PVA + 15 wt% PVP + 10 wt% KOH with 60 mol% degree of crosslinking by HCHO. For simplicity these compositions were coded like 100-PVA, 90-PVA and 75-PVA, respectively. These compositions were based on the wt% of each component present in solid polymer film on dry basis. The active layer solution was prepared following our earlier procedure [24,26]. In short, PVA was dissolved in water at 90 °C under vigorous stirring. A stoichiometric amount of formaldehyde and a calculated amount of KOH was added into the PVA aqueous solution to achieve a 60 mol% degree of crosslinking. The PVA/formaldehyde/KOH solution was heated at about 90 °C for the time period of 9 h under stirring. The calculated amount of PVP was then added into the PVA/formaldehyde/KOH solution for the time period of 5 h under continuous stirring. The viscosity of the solution increased significantly. This increase might be due to the crosslinking of PVA and addition of PVP.

Table 1

The important literature on CO₂ separation through different polymeric membrane via facilitated transport mechanism.

References	Membrane type	Pressure difference (atm)	Temperature (°C)	Thickness (μm)	CO ₂ permeance (GPU)	Selectivity
Matsuyama et al. [16]	PVA/PEI blend membrane	0.065 (CO ₂ partial pressure)	25	220	4	CO ₂ /N ₂ : 160
Francisco et al. [14]	Different alkanolamines (MEA/AMP/DEA/MDEA) in PVA membranes	0.5	24	145	8	CO ₂ /N ₂ : 88
Cai et al. [11]	PVA containing poly(allylamine) composite membrane	0.98	25	3	24	CO ₂ /N ₂ : 80
Deng et al. [12]	PVAm/PVA blend membrane	1.97	25	0.3	214	CO ₂ /N ₂ : 174
Xing and Ho [21]	PVA/PEG with zeolite 5A polymer matrix	10.2	39	20–45	12	CO ₂ /CH ₄ : 20

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