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High Performance Cross-Linked Poly (Vinyl Alcohol)/Piperazine Glycinate Polymer Membrane for CO₂ Gas Separation

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ABSTRACT : Global warming, a subject of increased emphasis in the recent years, is caused by the emission of greenhouse gases like CO₂ in the atmosphere. This work studies the synthesis, characterization and gas separation performance of CO₂ selective cross-linked poly (vinyl alcohol)(PVA)/piperazine glycinate(PG)/ polyethersulfone(PES) facilitated transport composite membranes synthesised via solution casting methodology. The synthesized membrane is characterized via Thermo gravimetric analysis (TGA), Differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and FESEM. The effect of membrane performance on gas transport properties such as CO₂ and N₂ flux (10⁻⁶cm³(STP) /cm².sec), CO₂ and N₂ permeability (Barrer) (10⁻¹⁰ cm³(STP)cm/cm².sec.cmHg), and CO₂/N₂ selectivity with variation in amine content, temperature, and gas relative humidity was thoroughly studied. The feed gas stream consisted of 20% CO₂ and 80% N₂ by volume. At 100⁰C and 4.5 atm feed absolute pressure optimum performance was observed with CO₂ permeance of 38 GPU and CO₂/N₂ selectivity of 200 respectively.

KEYWORDS : Polymeric membrane, Poly (vinyl alcohol), Piperazine glycinate, Permeability, CO₂/N₂ selectivity.

NOMENCLATURE

P_{CO_2}/L	CO ₂ Permeance	J_{CO_2}	CO ₂ Flux
PCO ₂			CO ₂ gas permeability
PN ₂			N ₂ gas permeability
L			Thickness of the membrane
P_{fCO_2}			Partial pressure in the feed side
PPCO ₂			Partial pressure in the permeate side

I. INTRODUCTION

Greenhouse gases (GHGs) trap the heat radiating from the surface of earth when solar energy is being transmitted through the atmosphere thus increasing the global surface temperature. The Intergovernmental Panel on Climate Change (IPCC) has predicted that the sea level will rise by 0.09 to 0.88 meters from 1990 to 2100, which is a matter of serious concern. Post-combustion capture is important application because of its flexibility and easy addition to the operational units. Although conventional separation techniques such as absorption, cryogenic distillation and adsorption have huge applications, advanced technologies such as membrane separation have been extensively used due to advantages of less energy consumption, light weight, space efficiency and compact modular design[1-3]. Polymeric membranes are hugely applied due to its advantages of low cost and easy processability. However, it faces hiccup due to its trade-off limitation between permeability and selectivity as stated by the Robeson upper bound curve. This sometimes poses a great challenge for its long term usability for industrial purposes. Incorporation of suitable amine carriers into the polymer backbone, crosslinking and blending of polymer matrix is useful for the enhancement of CO₂ transport property with increase in the stability throughout the membrane.[4] In this work, poly (vinyl alcohol) (PVA), a synthetic polymer having high hydrophilicity, good film-forming capability, enhanced chemical, thermal and mechanical properties is chosen as the polymer matrix for CO₂/N₂ separation. Piperazine glycinate (PG) salts are synthesized and added to the PVA aqueous solution. These salts act as the mobile carrier thereby leading to a considerable enhancement of the CO₂ transport properties as compared to pure PVA films.[5] In the synthesis process, novel crosslinked poly (vinyl alcohol) (PVA) membranes were doped with piperazine glycinate mobile carrier in

different weight composition by solution casting methodology. The final polymer solution was cast over polyethersulfone (PES) support having a pore size of

0.03 μm . 60mol% of formaldehyde (HCHO) was used as the cross-linking agent.

The CO_2 permeance and CO_2/N_2 selectivity can be defined by the following equations:

$$\text{CO}_2 \text{ permeance} = P_{\text{CO}_2}/L = J_{\text{CO}_2} / (P_{\text{fco}_2} - P_{\text{PCO}_2}) \quad (1)$$

$$\text{CO}_2/\text{N}_2 \text{ selectivity} = P_{\text{CO}_2}/P_{\text{N}_2} \quad (2)$$

Where P_{CO_2}/L is the CO_2 permeance, GPU (1 GPU =

$10^{-6} \text{ cm}^3(\text{STP})/(\text{s} \cdot \text{cm}^2 \cdot \text{cmHg})$, J_{CO_2} is the CO_2 flux, P_{co_2} and P_{N_2} is the CO_2 and N_2 gas permeability, L is the membrane selective layer thickness, P_{fco_2} and P_{pc_2} are the partial pressure of CO_2 in the feed and permeate sides respectively.

Experimental section

Materials : Poly (vinyl alcohol) (99mol% hydrolyzed powder, $M_w = 130,000$), 2-methylimidazole [$\text{C}_4\text{H}_6\text{N}_2$] were procured from Sigma-Aldrich, USA. Formaldehyde solution (37wt % in H_2O), Glycine (Assay > 99%), piperazine (99%), Zinc nitrate hexahydrate [$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$], Methanol was purchased from Merck, India. All chemicals were used without any further purification. Microporous poly(ether sulfone) supports (thickness: 150 μm and pore size: 0.03 μm) were provided by Sterlitech USA. The feed gas (20% CO_2 and 80% N_2) used for the gas permeation analysis was procured from Vadilal Pvt. Ltd., India.

Synthesis of PVA/PG polymeric membrane: The

PVA aqueous solution (12wt% solid weight) was prepared by continuously stirring at a temperature of 90°C which is maintained constant via oil bath. The PVA solution was cross-linked in formaldehyde at a ratio already optimized through our previous studies. Finally, the prepared PG salt solution was added fixed in the weight ratio of 70 and 30 weight ratio of PVA solution to form the final cross-linked PVA/PG polymer solution. The air bubbles formed were removed by centrifugation at 10,000 rpm for 30 min. The final centrifuged solution was cast onto the porous PS support (average pore size: 0.03 μm) kept over a glass plate. The thickness of the polymer film was maintained by the use of micrometer adjustable film applicator (GARDCO, Paul N. Gardner, USA).

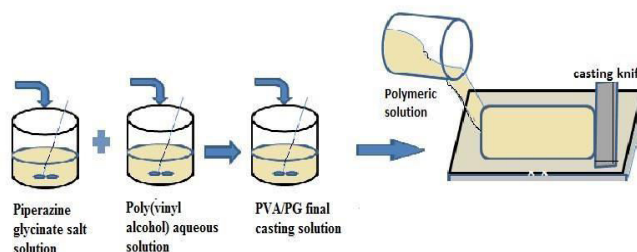


FIGURE 1: Synthesis procedure of PVA/PG polymer solution

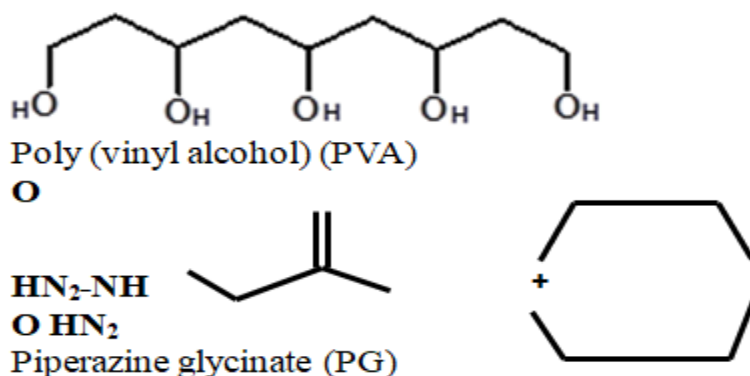


FIGURE 2: Chemical structure of PVA polymer and piperazine glycinate salt

Membrane Characterization: The synthesised membranes were characterized via various techniques. The thermal stability of the synthesized active layer was carried out using TGA/SDTA 851[°] system (MATTLE TOLEDO, Switzerland). Nitrogen atmosphere was used for conduction of the analysis. DSC analysis was carried out using DSC 1/400 STAR[°] system (METTLER TOLEDO, Switzerland) under nitrogen purge gas stream. The samples were subjected to heating/cooling/heating cycle in the range from -30°C to 350°C at a scan rate of 10°C/min. The DSC curves were obtained from the second heating cycle. The functional groups present in the active layer of the prepared membranes were confirmed via Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) (SHIMADZU, IRAffinity 1, Japan). FTIR spectra were obtained in the range of wavenumber from 4000 to 400 cm⁻¹ with 40 scans per sample and 4 cm⁻¹ resolution. The crystal structure of all active layers was examined using Bruke D8, advanced X-ray diffraction measurement for 2 θ angles between 10[°] and 60[°]. Cu K α radiation of wavelength λ = 1.54056 Å was considered. The morphology and distribution of the silica nanoparticles in the synthesized membrane were investigated via top surface and cross sectional views of FESEM imaging. To observe the membrane cross section, the samples were first fractured in liquid nitrogen and then sputter-coated with gold film prior to FESEM observation.

II. RESULTS AND DISCUSSIONS

TGA characterization: Thermo gravimetric analysis of the prepared PVA/PG polymer membrane is shown in Fig. 3. TGA plot indicates weight change of sample when heated at the rate of 10°C min⁻¹ rate. For, pure PVA/PEG blend membrane, the initial weight loss at a temperature below 120°C is due to the loss of absorbed and bound moisture from atmosphere and other volatile matters. The weight loss in the second stage from 230°C-320°C is due to the eradication of hydroxyl groups and free amine groups. The final weight loss at 405°C is attributed to the breakdown of the C-C polymer backbone. [1-2] The analysis showed a stable polymer with loss of weight in three distinct stages.

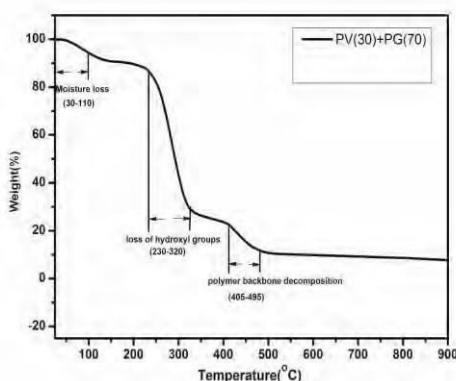


FIGURE 3: TGA characterization of the synthesised PVA/PG polymer membrane.

Effect of Temperature: The effect of temperature (°C) on CO₂ and N₂ flux, CO₂ and N₂ permeability, and CO₂/N₂ selectivity for pure PVA/PG/PES polymer membrane was investigated for temperature range from 25 to 80°C. The pressure at feed and sweep side was maintained at 1.5atm and 1atm, respectively. The water flow rates at the feed and sweep sides were kept constant at 0.03 and 0.05ml/min, respectively. The gas flow rates of the feed gas (20% CO₂ balance N₂) and sweep gas (Ar) were kept constant at 30 and 40 ml/min, respectively. The effect of temperature on CO₂ and N₂ flux, CO₂ and N₂ permeability and CO₂/N₂ selectivity for the synthesized membrane is represented in Fig.4. It was observed that with the increase in temperature, the CO₂ flux, CO₂ permeance, and CO₂/N₂ selectivity increased gradually with the increase from room temperature to temperature as high as 90°C. At higher temperatures, the increased gradually becomes constant. [3] The N₂ gas undergoes separation only by solution diffusion mechanism. Hence, the N₂ flux, and N₂ permeance almost remained constant. The increase in CO₂/N₂ selectivity, CO₂ permeance and CO₂ flux is due to the enhanced rate of reaction between the CO₂ gas and amine carriers in presence of moisture and increase in temperature. For an active layer thickness of 18μm and temperature of 80°C, CO₂ permeance of 38 GPU along with CO₂/N₂ selectivity of 200 and a high CO₂ flux of 3000 was observed.

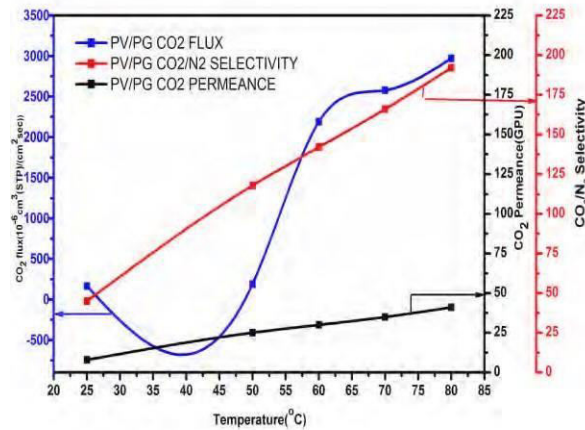


FIGURE 4: Effect of temperature on CO₂ permeance(GPU),and CO₂/N₂ selectivity for pure PVA/PG PM at feed absolute pressure=1.5 atm, sweep absolute pressure=1 atm, and water flow rates = 0.03/0.04 ml/min (feed/sweep).

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