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Improving Gas Separation Performance of Poly(Vinylidene Fluoride) Based Membranes Containing Ionic Liquid

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***Abstract*—**Polymer based membranes are one of the low-cost technologies available for the gas separation. Three major elements required for a commercial gas separating membrane are high permeability, high selectivity, and good mechanical strength. Poly(vinylidene fluoride) (PVDF) is a commercially available fluoropolymer and a widely used membrane material in gas separation devices since it possesses remarkable thermal, chemical stability, and excellent mechanical strength. The PVDF membrane was chemically modified by soaking in different ionic liquids and dried. The thermal behavior of modified membranes was investigated by differential scanning calorimetry (DSC), and thermogravimetry (TGA), and the results clearly show the best affinity between the ionic liquid and the polymer support. The porous structure of the PVDF membranes was clearly seen in the scanning electron microscopy (SEM) images. The CO_2 permeability of blended membranes was explored in comparison with the unmodified matrix. The ionic liquid immobilized in the hydrophobic PVDF support exhibited good performance for separations of CO_2/N_2. The improved permeability of modified membrane (PVDF-IL) is attributed to the high concentration of nitrogen rich imidazolium moieties.

***Keywords*—**PVDF, gas permeability, polymer membrane, ionic liquid.

I. INTRODUCTION

MEMBRANE-BASED separation is one of the low cost technologies available and it has been widely used for many tasks involving gas/liquid separations. Polymer based membranes considered as efficient membranes due to easy processability, flexibility, and structural stability of the polymer. Their chemistry can be tailored to attain great selectivity. Porosity is an important factor, which can influence the selectivity and permeability of the gas to a great extent and the pore diameter of the polymer must be smaller than the mean free path of gas molecules. Membrane based carbon dioxide separation is one of the main solutions to defend factors in the rise of global warming, because it significantly prevents emission of CO_2 from reducing the atmosphere of greenhouse gases from fossil fuels. Therefore, the development of an efficient and economically valuable gas capturing system is highly in demand [1]. The conventional process of CO_2 capture and storage requires large amount of energy compared to the membrane based separation technique [2]. The advancement of efficient gas separation membrane materials, which can separate CO_2 from other gases such as H_2, N_2, CH_4, is a major task to researchers [3], [4]. Polymer based membranes are one of the most popular materials studied for CO_2/light gas separation owing to their structural stability easy processability and also easy to tailor any functional moieties [5]. Recently polymers of intrinsic microporosity (PIMs), poly(ethylene oxide) (PEO), and PVDF are attractive candidates for different applications ranging from separating gases and liquids, and all of them have high selectivity, permeability, and strong affinity to CO_2/N_2 gas pair. [6]-[8]. Ionic liquid modified membranes are the best performing among other polymers due to a higher diffusion coefficient of CO_2 in ionic liquid. The CO_2 permeability increased simultaneously with CO_2/N_2 selectivity as the content of ionic liquid in these polymer gels increased [9]; however, further improvement of PVDF is needed in order to achieve optimum separation. The PVDF membranes were usually prepared by well-known phase inversion technique with appropriate additives [10]. Addition of excess amount of ionic liquid in the membrane casting solution, would adversely affect the mechanical strength of the resulting membrane by the plasticizing effect [11]. So, it is worth adding nanofillers to improve porosity and mechanical strength. The introduction of carbon nanotubes (CNTs) into PVDF mainly improves the mechanical and thermal properties along with microstructural changes [12]. The aim of this study is to conduct a systematic investigation on the molecular architecture and modification of the PVDF as well as to produce useful membranes which have high CO_2 permeability, with excellent chemical and mechanical stability. The modification of the PVDF membrane will be achieved by incorporating with CO_2-philic ionic liquids (IL), which will produce high performance porous membrane with excellent gas separation performance for the clean energy applications.

II. EXPERIMENTAL

A. Materials & Methods

PVDF (M_w = 275 kg mol^{-1}) and ionic liquid; 1-ethyl-3-methylimidazolium dicyanamide were purchased from Sigma-Aldrich and used as received. Polar solvent DMF procured locally. The FT-IR spectra were recorded on a Shimadzu FT/IR-6300. Microscopic technique implemented is SEM (SEM: JEOL Model 6300). The thermal profile (DSC) of the PVDF and its blends were evaluated using DSC 60 A plus Shimadzu with a heating rate of 10 K/min starting from 30 to

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220 °C. Thermal degradations were performed in a thermogravimetric analyzer (TA) (Discovery TGA). Degradations were performed from 40 °C up to 600 °C, in a nitrogen atmosphere and at a heating rate of 10 °C/min. The TGA and differential thermogravimetric (DTG) curves were plotted.

B. Preparation of Membrane

The polymer solution was prepared by heating a mixture of PVDF and DMF (15 wt.%) at 80 °C for 2h. The solution was kept at same temperature for 1h in order to eliminate the air bubbles. This solution was cast on glass plate using a doctor blade and dried in air. PVDF membrane is cast from DMF, a high boiling point solvent that evaporates slowly. Non-solvent water from humid atmosphere is fully miscible with DMF and penetrates the wet membrane by diffusion. A highly porous PVDF membrane with pore diameters ranging from microns to sub-microns was prepared. Similarly, PVDF-IL blends were also prepared.

C. Permeability Measurement

The instrument *Convergence Inspector* is designed for testing polymeric and other inorganic membranes for gas-gas permeation, having pressurized gas containers connected to six inlets (higher inlet pressure than working pressure). See Fig. 1 for the flow sheet.

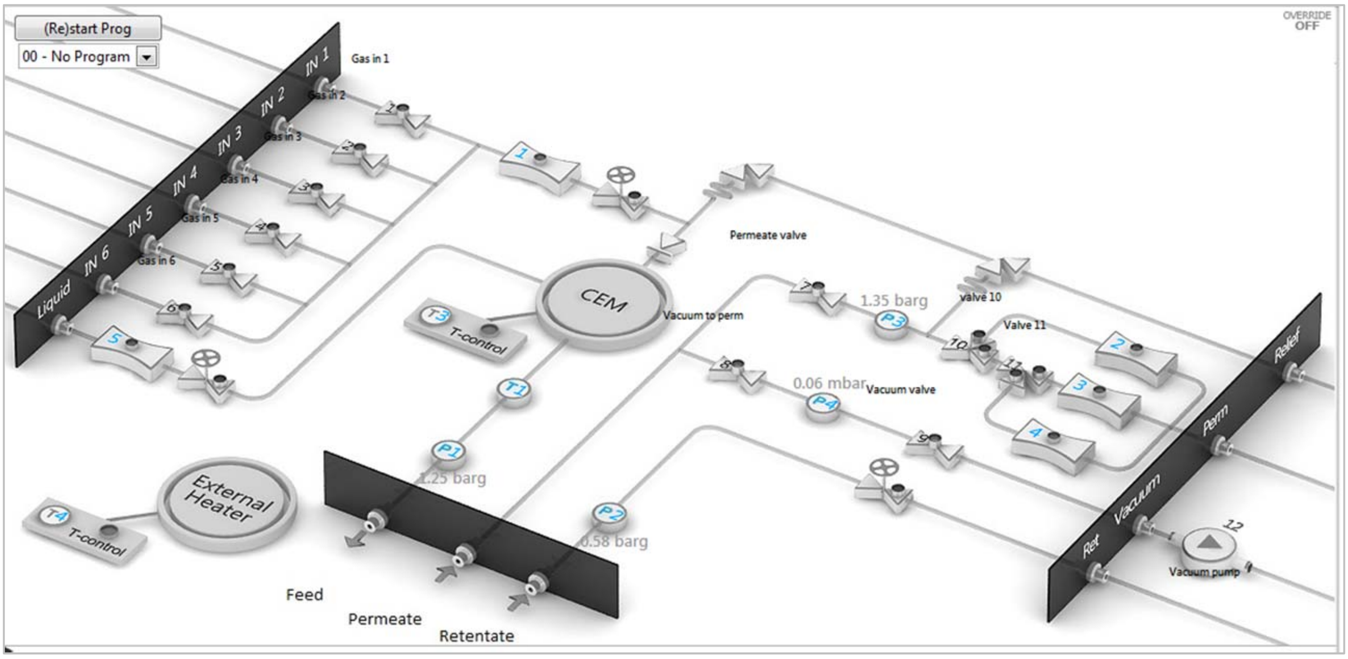

Fig. 1 Gas permeability process flow diagram

At the feed side a gas flow can be generated with constant pressure difference. The feed mixture can be heated with a heating system around the cell up to 35 °C. The gas that does not pass through the membrane is via the flow controller led to the exit of the installation. The permeate flow is measured with multiple flowmeters (covering a high permeability range of 0.02 – 200 mL/min. The permeate side of the membrane can be vacuumed, and the pressure increase can be measured over time. The system is protected with two pressure relief valves, one of +/- 20 bar on the feed side and one of +/- 4 bar on the permeate side. When the gas permeates from the feed side through the membrane to the permeate side, the pressure increases and the pressure rise is used to calculate the permeability. The permeability can be calculated using (1):

$$Permeability\ (P) = \frac{flow\ rate\ x\ thickness}{area\ x\ pressure\ diffrence} \qquad (1)$$

III. RESULTS AND DISCUSSION

A. FTIR Spectroscopy

The FTIR spectra of the Pure PVDF and its blends with ionic liquid membrane were represented in Fig. 2. The transmittance bands at 2924 and 2854 cm^{-1} corresponding to the CH_2 vibration of PVDF. The band appeared at 1400 cm^{-1} was ascribed to CH_2 wagging vibration. The C-C band of pure PVDF was observed at 1166 cm^{-1}. The peaks at 875 and 833 cm^{-1} were attributed to C-C-C asymmetrical stretching vibration and C-F stretching vibration of PVDF. It was detected that the most of the characteristic transmittance bands of the pure PVDF membranes were retained by the PVDF-IL blend membranes. For example, the bands at 2924 2854 cm^{-1} and 1402 cm^{-1} were displayed. The other major bands ranging from 1232 to at 835 cm^{-1} were also observed. However, compared to PVDF, there were additional dual bands observed in both PVDF-IL-5 and PVDF-IL-10 at 2241-2135 cm^{-1}. The occurrence of the new transmittance band was attributed to cyanamide group present in the ionic liquid; 1-

ethyl-3-methylimidazolium dicyanamide. It indicated that the molecule of 1-ethyl-3-methylimidazolium dicyanamide was well distributed in the blend.

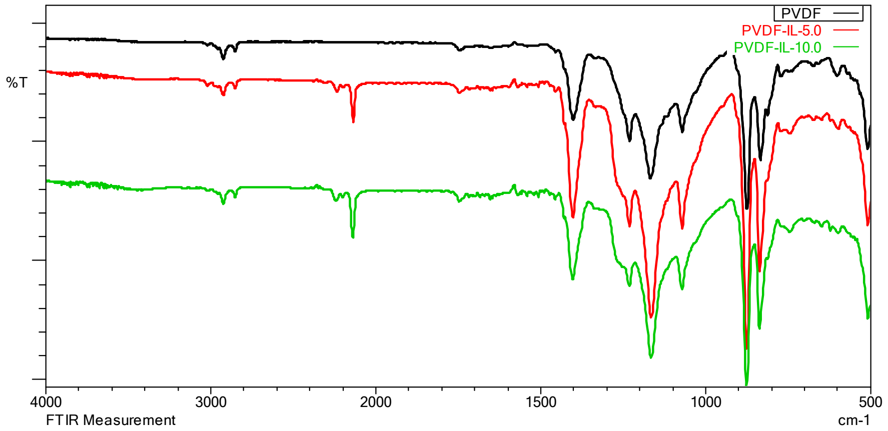

Fig. 2 FTIR spectra of PVDF and its blends with ionic liquid

B. DSC

The melting and crystallization behaviors of PVDF and PVDF-IL blends prepared with different ionic liquid concentrations were analyzed by DSC and the results were tabulated in Table I. For the membranes fabricated with pure PVDF, it showed a melting peak around 172.72 °C. PVDF with different ionic liquid concentration showed a decreasing tendency of the melting behavior as shown in Fig. 3 (a), the curves presented a melting peak at around 166.35 °C, without any shoulder at higher concentration of ionic liquid. The variation in the melting point indicated that the crystal structure of PVDF was altered. This could be attributed to the plasticizing effect of ionic liquid and well compatible with the polymer matrix. The crystallization temperature (T_c) for both PVDF-IL-5 and PVDF-IL-10 was lower (Fig. 3 (b)). Presence of ionic liquid in the PVDF matrix induces the delayed crystallization occurring during cooling process.

TABLE I
DSC CHARACTERISTICS OF PVDF AND ITS BLENDS

Samples	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)
PVDF	172.72	38.24	135.61	35.24
PVDF-IL-5	171.19	34.37	129.03	31.02
PVDF-IL-10	166.35	33.11	125.19	30.85

C. Morphology

The SEM technique was used to explore the surface morphologies of PVDF and PVDF/IL blend samples. The surface morphology of cross section of PVDF (Fig. 4) exhibits approximately the same surface morphologies seen with the exception of more interconnected pores in PVDF-IL-10 (Fig. 5). The phase separation is generally induced by exposing the polymer solution with a non-solvent in the liquid or vapor phase [13]. The exchange of solvent and non-solvent induces a thermodynamic flux in the polymer solution causing phase separation, consequently formation of cellular polymer with micropores. The morphology of the membrane materials mainly depends on the conditions under which the phase separation is carried out. Addition of ionic liquid into polymeric materials mainly imparts plasticization effect. Adding proper amount of ionic liquid in to the polymer solution could improve the formation and growth of micropores, and thereby could increase porosity and permeability.

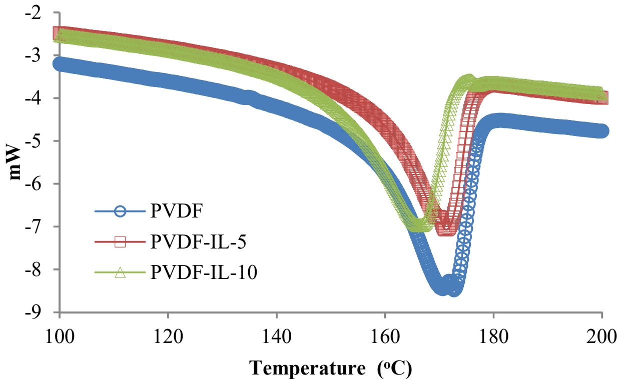

Fig. 3 (a) Melting curves of PVDF and its blends; PVDF-IL-5 & PVDF-IL-10)

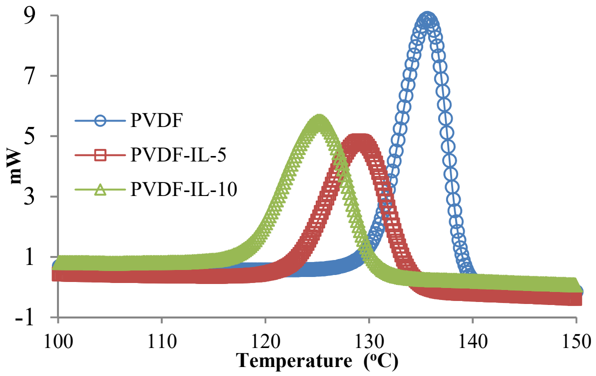

Fig. 3 (b) Crystallization curves of PVDF and its blends; PVDF-IL-5 & PVDF-IL-10)

D. TGA

The effect of blending ionic liquid on the thermal behavior of PVDF membrane materials was analyzed by TGA. The TGA traces are shown in Fig. 6. Considering PVDF, the thermal stability of the PP/ionic liquids was decreased with increasing the ionic liquid. Comparing PVDF the onset degradation temperature (T_{onset}) values of the PP-IL-5 and PVDF-IL 10 showed a substantial decrease. The maximum degradation temperature (T_{dmax}) exhibited a decrease from 464 (PVDF) to 302 (PP-IL-10). This is attributed to the effective plasticization by the inclusion of ionic liquid. Comparing the results obtained over the thermal degradation showed the clear effect of ionic liquid and how distinct they were during thermal degradation. While comparing the derivative curves, it was observed that both PVDF-IL-5 and PVDF-IL 10 were decomposed via a single step degradation process similar to a pure PVDF membrane. However, when ionic liquid was added to the PVDF, the initiation and maximum decomposition temperatures are shifted towards lower temperature, this effect is explained by the fine dispersion of the ionic liquid, which increases the polymer permeability to both oxygen and the volatile decomposition products.

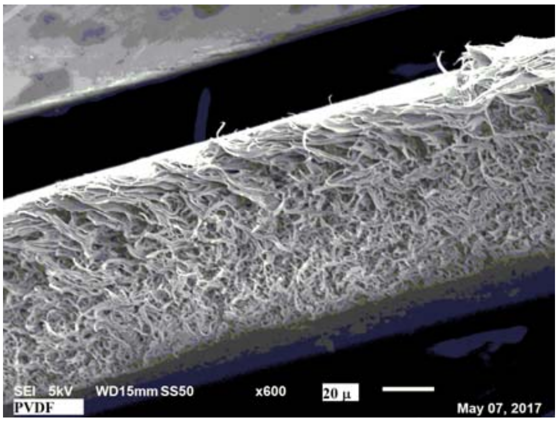

Fig. 4 SEM image of cross section of PVDF

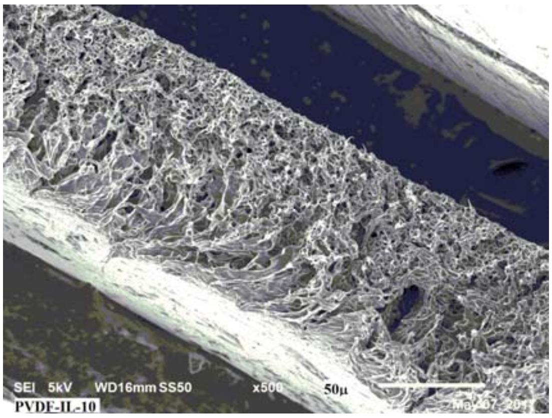

Fig. 5 SEM image of cross section of PVDF-IL-10

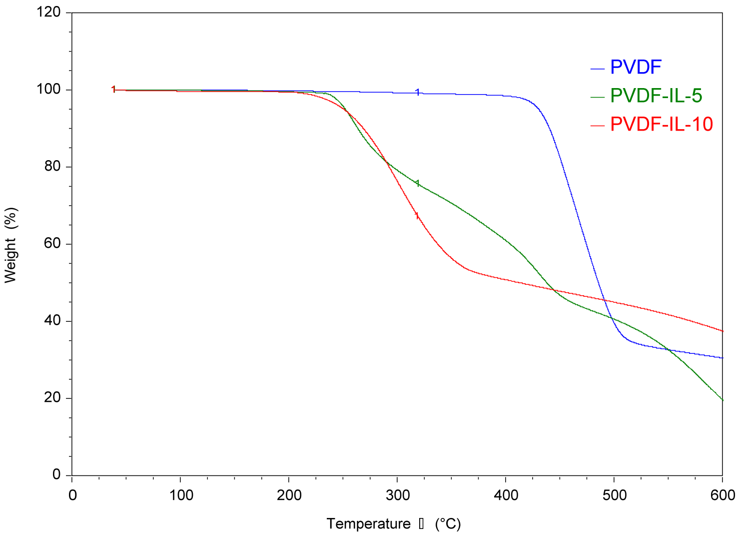

Fig. 6 TGA traces of PVDF and its ionic liquid blends

E. Permeability

The permeabilities of CO_2 and N_2 gases through the PVDF and its blend membranes were measured, and the ideal selectivity was calculated. The permeability values of CO_2 higher value compared to nitrogen which may be attributed to the higher CO_2-philic nature of ionic liquid compared to the nonpolar nitrogen. The CO_2/N_2 selectivity value of blend membrane is 10 times higher than the pure PVDF membrane for separating CO_2 over N_2. Considering the fact that CO_2 is a quadruple gas molecule, introducing imidazole groups into the polymer structure can improve their gas separation performances. The nitrogen-rich structural units are among the most promising material for high selective CO_2 capture and separation which can have a solid impact on the clean energy applications. For example, decorating the pores with imide groups in the framework of porous architectures is expected to enhance their affinity and selectivity towards CO_2.

IV. CONCLUSION

The promising porous structures of PVDF-IL blends may provide an outline for the design of more novel membrane materials with improved gas separation capacity especially applicable for CO_2 separation.

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