

H₂ Purification with PVDF/GTA Blended Membranes

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ABSTRACT

In this research blended membranes with poly(vinylidene fluoride) (PVDF) and Glycerol Triacetate (GTA) were fabricated for CO₂/H₂ separation. GTA has been added to polymeric solution in different mass ratios to study its effect on membrane permeability. Membranes cross-sectional morphology was investigated by SEM and remarkable changes in membrane structure were observed. Also, FTIR spectra were used to investigate functional groups of the membranes. Permeation results showed that CO₂ permeation almost doubled, whereas the H₂ permeation remained almost constant and thus CO₂/H₂ selectivity showed acceptable enhancement.

Key Words: H₂ Purification, Blended Membranes, Glycerol Triacetate (GTA), PVDF

INTRODUCTION

Membrane technology for gas separation purposes is widely on the increase due to low cost, interesting efficiency and acceptable processability [1]. CO₂ capture and H₂ purification are the most important fields that can use membranes for separation [2, 3]. In the past few decades many efforts have been done to in this field with various types of membranes, however, polymeric materials are quite well known to be interesting for this application [4]. Several types of modifications have been taken into consideration in order to improve membranes' separation ability and the most common methods are: incorporation of inorganic particles in membrane matrix (nanocomposite and mixed matrix membrane:MMM) [5, 6] and fabrication of blended membranes (which are mixing of polymers with low molecular weight additives) [7-9].

Selection of suitable inorganic particles and additives are of great importance and pre-determined criteria based on the desired application and materials properties should be applied [10]. Glycerol Triacetate (GTA) is a CO₂-phil compound and has an interesting separation factor as a liquid (in particular for CO₂/H₂ separation) [11] and its ability in membrane processes has been considered as well [7, 9, 12]. Furthermore, poly(vinylidene fluoride) (PVDF) which is an inexpensive membrane with good chemical and

mechanical resistance, is an excellent choice for host polymer.

In this study, PVDF and GTA have been selected as the main blending materials in order to fabricate dense blended membranes with high separation ability for CO₂/H₂ separation. GTA as a plasticizer possesses very low vapor pressure and its ability to separate CO₂ from H₂ as a solvent is high (with CO₂/H₂ solubility selectivity of around 100) [7, 11]. It should be mentioned that polymers used commercially in gas separation applications (such as separating air into oxygen-enriched and nitrogen-enriched streams) are usually made of glassy materials [13, 14].

EXPERIMENTAL

PVDF was supplied from Kynar. 1-methyl 2-pyrrolidone (NMP) which was used as the solvent was purchased from Merck. Glycerol triacetate (GTA) was purchased from Sigma-Aldrich.

The membranes were fabricated by simple blending method and after PVDF is completely dissolved in NMP, GTA at different mass ratios to polymer (PVDF:GTA = 3:1, 2:1, 1:1, 1:1.5, 1:2) was added to solution. NMP was a good solvent for both PVDF and GTA. The procedure of membrane preparation is solvent evaporation. The homogenous solution was then casted on petri dish and it was put in oven at 70 °C for 12 hr for solvent evaporation. The fabricated films were subsequently put in vacuum oven for 6 hr in order to eliminate residual solvent. The membranes were put in desiccator before characterization and performance tests.

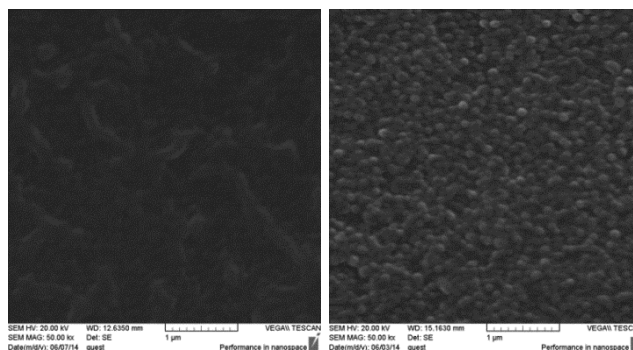


Figure (1): Cross sectional SEM images of the membranes, Left: neat PVDF, Right: 50% GTA, 50% PVDF

RESULTS AND DISCUSSION

The membranes were characterized by SEM to investigate the effect of GTA on the morphology. As it can be seen in Figure (1), remarkable changes are resulted and it seems that GTA addition has led to heterogeneous and shapeless structure which can affect permeation properties considerably [7]. Similar observations have been experienced by other blended membranes. The reason is mainly due to plasticization effect of GTA and as it locates among polymer chains, it leads to more mobility and consequently lower homogeneity. It has been reported in many other works that changes in membrane morphology and structure can significantly affect transport properties, specially diffusion coefficients [9, 15].

Structural characterization of neat PVDF and PVDF /GTA blended membrane was investigated by FTIR-ATR analysis as shown in Figure (2). The main functional groups of GTA and PVDF have been shown in their spectra. As it can be seen, with GTA addition the peak related to O=C=O loses its sharpness, as this functional group does not exist in PVDF structure. Also peaks related to symmetric and asymmetric -C-O will appear in the blended membranes which are due to GTA addition [7]. From the FTIR spectra, it is evident that the main functional groups of GTA possess highly oxygenated and carbonyl groups (C=O). It is generally well-known that materials with these properties are excellent for CO₂ capture [16].

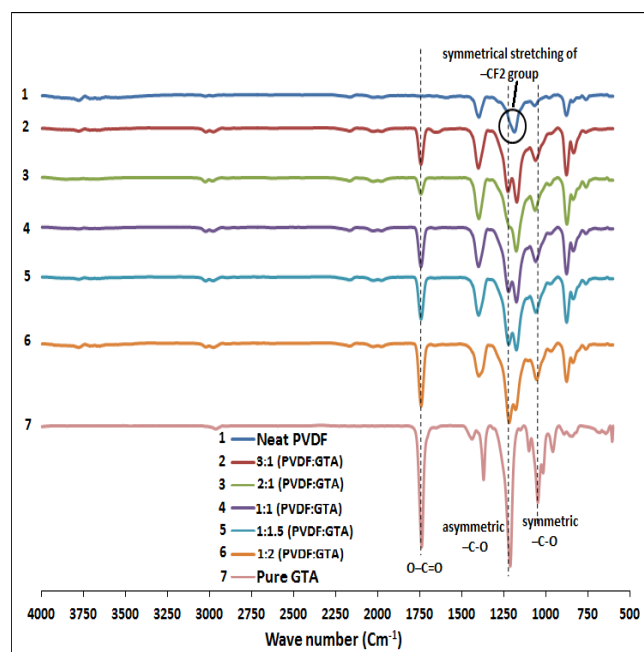


Figure (2): FTIR-ATR spectra of GTA, PVDF and blended membranes

The permeation performance of the prepared membranes was evaluated by constant volume method at 30°C and 4 bar. The membrane set-up and cell are completely described in our previous works [5, 7]. In order to measure permeability via constant volume method, the following equation has been used:

$$P = \frac{V}{A} \cdot \frac{273.15}{T} \cdot \frac{l}{p_s \Delta p} \cdot \frac{dp}{dt} \quad (1)$$

where, V is volume of permeate (cm³), A is membrane area (cm²), l is membrane thickness (cm), T is operating temperature (K) and p_s standard pressure (1 bar). Δp is pressure difference across the membrane (mmHg) and $\frac{dp}{dt}$ is pressure increment in permeate vessel with time (bar/sec). Eq.(1) gives permeability in Barrer unit where 1 Barrer = 10⁻¹⁰ cm³(STP) cm cm⁻² s⁻¹ cmHg⁻¹.

The results are shown in Figure (3) from which it can be seen that the permeation of CO₂ and H₂ increases when GTA mass content rises. The reason for this observation is that GTA as a plasticizer possesses higher permeability in comparison with the neat PVDF membranes [12]. However, this increment is much higher for CO₂ than for H₂ and that is why CO₂/H₂ selectivity rises as GTA content increases. The main reason for this phenomenon is that GTA is highly CO₂-selective due to its functional groups and has oxygenated structure with carbonyl functional groups that are quite well known for CO₂ capture [16].

With increment in the amount of GTA in membrane structure, as the membrane morphology become more amorphous (it can be seen in SEM), molecules of gases diffuse easier, thereby for all the tested gases permeability increases.

Changes in permeation after addition of a low molecular weight additive can be discussed further by looking at the changes in solution and diffusion coefficients. Solubility of CO₂ in GTA is higher than that of H₂ and the CO₂/H₂ solubility selectivity is around 20 [11]. In addition, based on the results reported in the literature [8, 11], GTA shows more solubility coefficients for CO₂ compared to neat PVDF. Thereby, increment in CO₂ solubility with GTA is quite expected. Another coefficient which is also affected by GTA addition is the diffusion coefficient. The rate of gas molecules diffusion in membranes is directly related to their kinetic diameter and molecular size. Therefore, any changes in membranes morphology will change the ability of gases to diffuse in membrane matrix. Addition of GTA, as a plasticizer leads to mobility of polymer chains, as this additive can locate between them and gas molecules should find their way through these chains to diffuse [17]. Hence, GTA addition leads to higher values of diffusion of gases, but this growth in diffusion for CO₂ is relatively higher than that for H₂. Because the kinetic diameter of CO₂ is 3.8 Å

(this number for H₂ is 2.89°A), it is more dependent to changes in the space among polymer chains.

To sum up, increase in diffusion and solubility coefficients of CO₂ is more than those of H₂ and this explains more permeation increment for CO₂ with GTA addition, based on the following equation:

$$P = S \cdot D \quad (2)$$

where, D and S are diffusion and solubility coefficient, respectively.

Thus, it can be said that both solubility and diffusion selectivities of CO₂ over H₂, increase that lead to higher permeation selectivity. These discussions are based on the reported data about the pure components and obvious changes that can be characterized in the chemical and physical properties of the membrane. However, for understanding the exact contribution of diffusion and solubility and compare their effects, separate experiments ought to be carried out to measure their coefficients directly [7, 10, 18].

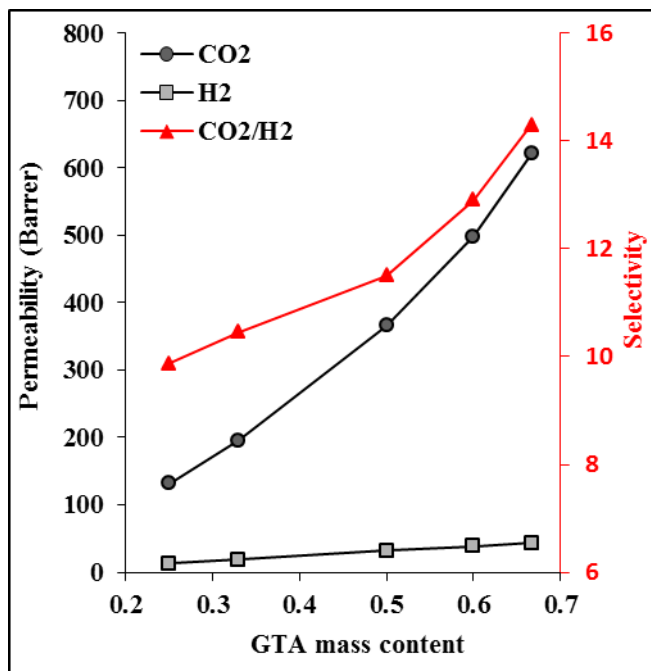


Figure (3): Permeation and selectivity through the membranes at different GTA concentrations

CONCLUSION

Membrane preparation with PVDF and GTA was studied in order to improve properties of PVDF membranes for CO₂/H₂ separation. The membranes were fabricated via commonly used solvent evaporation by using industrially favorable solvent, NMP. The results showed enhancement

in CO₂/H₂ separation by around 45% when GTA/PVDF ratio increases 0.33 to 2. The possible changes in transport properties of the membrane after GTA addition was discussed based on the published articles where much higher increment in CO₂ permeability was mentioned. This observation is quite expected due to separation ability of GTA. The membranes were also characterized by FTIR and SEM to investigate changes in their molecular structure and morphology. The observed changes in membrane structure, as seen in SEM, can be considered as a way to inspect diffusion changes. The obtained enhancement in CO₂/H₂, seems significant.

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