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Effects of Montmorillonite (MMT) Inorganic Fillers on Polyvinylidene (PVDF) Mixed Matrix Membrane

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Abstract. Asymmetric nanoclay-polyvinylidene (PVDF) mixed matrix membranes (MMMs) were prepared by the reaction of various amount of montmorillonite (MMT) nanoclay mineral with PVDF. The MMMs were fabricated via dry-wet phase inversion method with *N,N*-dimethyl-acetamide (DMAc) as the solvent and ethanol as the coagulant. The fabricated MMMs were characterized by means of fourier-transform infrared (FTIR) and scanning electron microscopy (SEM). The separation performances of the prepared membranes were evaluated by pure gases (CO_2 and CH_4). From the FTIR spectrum, MMMs exhibited new peaks compared to pristine PVDF membrane, indicating assimilation of MMT into the PVDF membrane. The morphology of the membranes depends on the clay mineral loading as confirmed by SEM. PVDF/3wt% MMT MMM showed the highest CO_2 permeance and CO_2/CH_4 selectivity relative to neat PVDF membrane.

Introduction

Mixed matrix membranes (MMMs), consisting of inorganic fillers dispersed in a polymer matrix, represent a viable opportunity for enhancing the separation capabilities of polymeric membranes whilst retaining the desirable characteristics of inorganic fillers. In fact, a wide range of inorganic fillers such as clays, zeolites and carbon molecular sieves have been utilized for a variety of applications [1]. Yet, the selection of suitable polymer-inorganic components remains a challenge in order to prepare defect-free MMMs with good adhesion between the two phases.

In general, polymeric materials like polyvinylidene (PVDF), polyacrolonitrile (PAN) and polyethersulfone (PES) have been widely used in gas separation applications. Interestingly, according to an investigation by Zahidi (2009), PVDF exhibits better separation properties in comparison with PAN and PES [2]. Montmorillonite (MMT), a type of clay from the smectite family, has been employed predominantly in polymer-clay nanocomposite synthesis. It shows promise as inorganic filler to enhance the barrier properties of polymeric materials [3, 4]. There is also evidence that clay increase the free-volume between polymer chains; which in turn increase the gas diffusion properties of membrane [5].

In this study, MMMs were prepared from hybrid materials made of PVDF and MMT using dry/wet phase inversion method. The effects of the presence of the clay inorganic fillers on the structure of the MMMs were investigated. By understanding the morphology and physical features, the performance of the membrane can be predicted.

Experimental

Materials. Polyvinylidene (PVDF) was supplied by courtesy of MTDC lab, Universiti Sains Malaysia. *N,N*-Dimethylacetamide (DMAc) purchased from Merck was used as the solvent, while 99% ethanol was used as the coagulant. The inorganic filler, surface modified montmorillonite (MMT) with 25-30% methyl dihydroxyethyl hydrogenated tallow ammonium was purchased from Sigma Aldrich. PVDF was dried in oven at 80°C to remove trapped moisture. All other materials were used as received.

Membrane Fabrication. In the present study, pristine PVDF membrane and PVDF/MMT MMM were fabricated. Preliminary study was performed to determine the optimum wt% of PVDF for membrane synthesis by incorporating 15, 18, 20 and 25 wt% of polymer in the dope solution, the remaining of which consisted of DMAc. Then, different MMT concentration (0wt%, 1wt%, 3wt% and 5wt%) was added to the casting dope. The dope solution was stirred at 70°C until the polymer and clay dissolved completely. The mixed solution was degassed and sonicated by using ultrasonic degasser to remove trapped air bubbles and to ensure homogenous dispersion of clay. The dope solution was left standing at room temperature for at least 12 hours before casting using an automated casting machine. The membrane film was then immersed into ethanol solution for 24 hours. Finally, the membranes were air-dried for 24 hours at room temperature.

Gas Permeation Test. Gas permeation test was conducted in a permeation cell with an effective membrane area of 19.63cm^2. The fabricated membranes were exposed to CH_4 and CO_2 gases. The permeation tests were carried out at room temperature and feed side pressure of 2, 5 and 8 bar. The gas flux and selectivity was subsequently calculated.

Membrane Characterization. Fourier-transform infrared (FTIR) spectra of the membranes were recorded on Perkin Elmer FTIR 1650 spectrophotometer at resolution between 400 and 4000 cm^{-1}. The morphology of the membranes was examined using Tabletop SEM, model Hitachi TM-3030. The samples were sputter-coated with 15nm of gold before analysis.

Results and Discussion

Characterization of Pristine PVDF Membrane and PVDF/MMT MMMs using FTIR

FTIR spectra of pristine PVDF membrane and PVDF/MMT MMMs are shown in Fig. 1. The frequency and assignment of each vibrational mode observed are listed in Table 1.

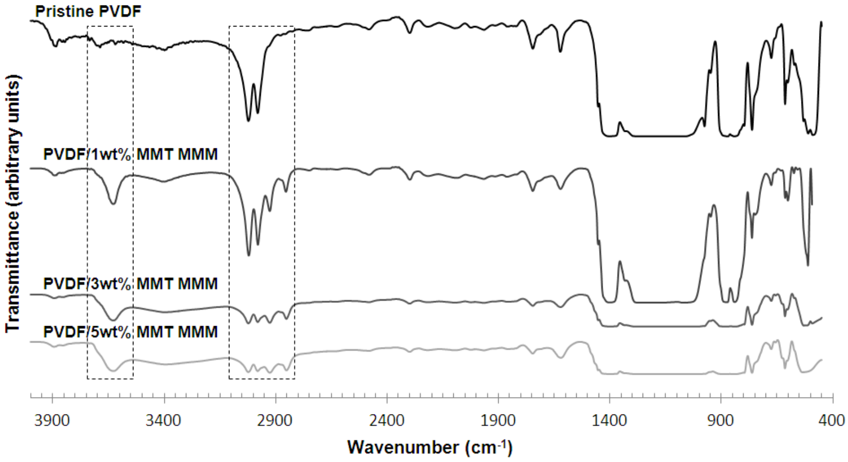


Figure 1: FTIR spectra (400-4000cm^{-1}) for PVDF membrane and MMMs

Table 1: Positions and assignments of the IR vibration bands

Wavenumber (cm^{-1})	Group
3628	O–H stretching of water
2854–2977	Symmetric stretching of C–H
1047	Si–O stretching
976, 762, 614	Crystalline phase α conformation
871, 843, 510	Crystalline phase β conformation
536	Al–O–Si stretching

For pristine PVDF membrane, the absorptions in the spectrum indicate that its crystalline phase is present in α and β conformations. The signals at 976, 762 and 614 cm^{-1} were assigned to α conformation whereas the signals at 871, 843 and 510 cm^{-1} were attributed to β conformation. Other signals which correspond to vibrations of the polymer amorphous phase were also observed. These results are in agreement with the spectrum given in literature [6, 7]. Compared to the pristine PVDF membrane, the MMMs exhibited a new band at each spectrum at 3628 cm^{-1}. This peak was assigned to O–H stretching of water due to the hydrophilic nature of MMT [8]. The bands between 2854 and 2977 cm^{-1} were assigned to the symmetric and asymmetric stretching vibrations of the methylene groups. There were only small differences in the peak positions and intensity caused by the intercalation of MMT into the PVDF matrix. From Fig. 1, it can be deduced that the characteristic peaks of the MMMs were mainly a superposition of the peaks from both PVDF and MMT, indicating assimilation of MMT into the PVDF membrane.

Characterization of MMMs using SEM

SEM is performed to investigate the extent of adhesion between inorganic filler particles and the polymeric matrix. These properties affect the MMMs performance. The morphology of the membrane is largely dependant on nanoclay loading. Fig. 2 shows the surface morphology of PVDF/MMT MMMs. According to Fig. 2a and b, the inorganic particles were scattered uniformly throughout the polymer matrix. However, when nanoclay loading was increased to 5wt%, agglomerates were found to be distributed unevenly over the membrane (Fig. 2c), resulting in formation of larger voids which may significanlty affect the membrane performance.

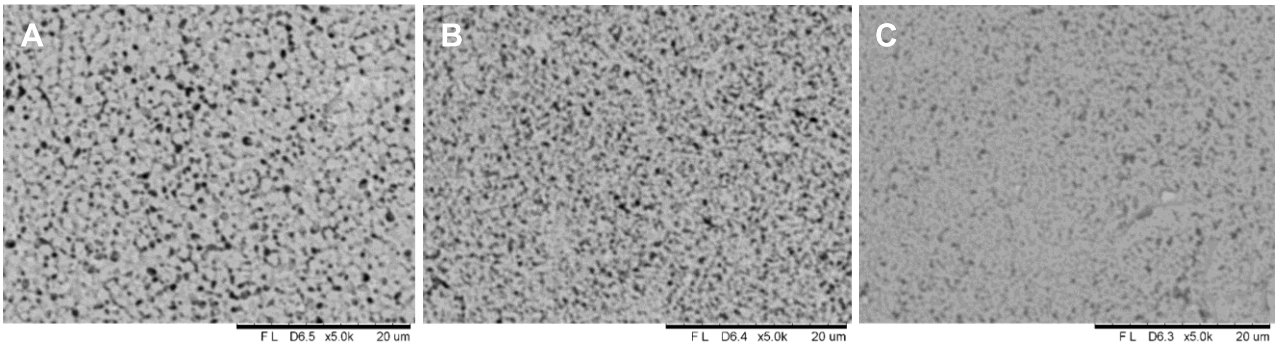


Figure 2: SEM surface view of membranes: (a) PVDF/1wt% MMT (b) PVDF/3wt% MMT (c) PVDF/5wt% MMT

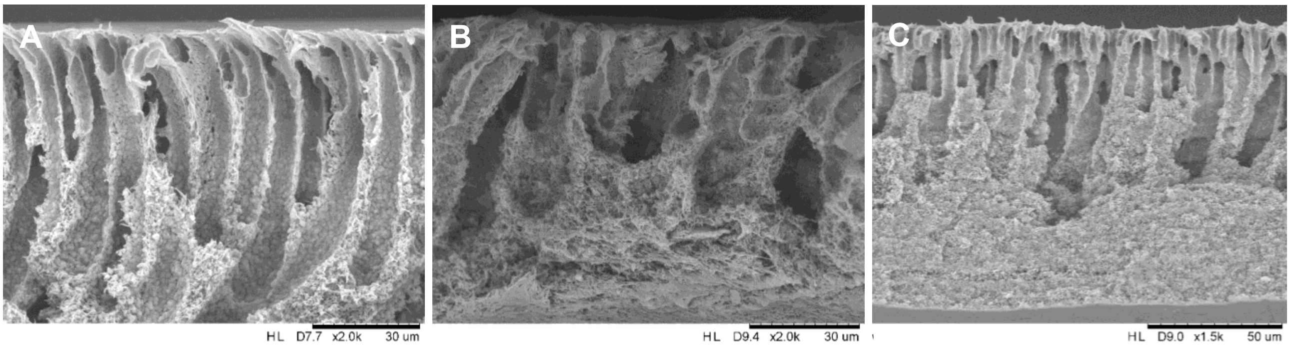


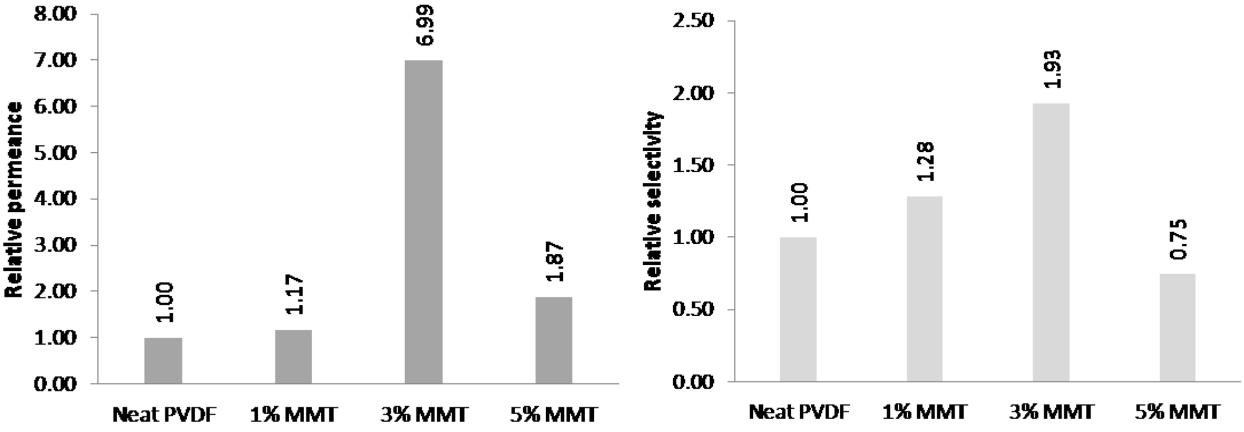
Figure 3: SEM cross sectional view of membranes: (a) PVDF/1wt% MMT (b) PVDF/3wt% MMT (c) PVDF/5wt% MMT

Fig. 3 illustrates the cross-sectional morphology of PVDF/MMT MMM. As the nanoclay content increased, the particle cluster became more significant and bigger agglomerates were formed. Interestingly, MMMs with 5wt% nanoclay content shows good adhesion between the PVDF and MMT. Nevertheless, rigidified polymer layer is believed to have formed around the nanoclay, resulting in reduction in free volume [9].

Gas Permeation

Fig. 4 depicts the influence of MMT loading on the separation properties of MMMs. Permeance exhibits an ascending trend with increasing MMT loading up to 3wt% and then shows a descending trend (Fig. 4a). The decrease in permeance at 5wt% MMT loading can be interpreted due to high aspect ratio of MMT plates which act as barriers across the gas diffusion path [8]. In spite of that, the permeance of these MMMs is still higher than that of neat PVDF membrane. Fig. 4b shows the changes in selectivity as a function of MMT loading. A similar trend is observed, in which 3wt% MMT loading showed the highest selectivity. Obviously this case exhibits an ideal morphology. At

5wt% MMT loading, the MMM experience a dramatic decline in selectivity, which is due to decrease in uniform dispersion of MMTs.



(a) (b)

Figure 4: Effect of MMT loadings on PVDF/MMT MMM (a) CO_2 permeance and (b) CO_2/CH_4 selectivity

Conclusion

Flat sheet PVDF and PVDF/MMT membranes with various nanoclay loadings have been fabricated through dry/wet phase inversion method. It was determined through preliminary study that 25wt% of polymer is optimum for fabrication of pristine PVDF membrane. MMMs have subsequently been fabricated with the incorporation of MMT (1, 3 and 5wt%). FTIR spectrum indicates the assimilation of MMT into the PVDF membrane. At low clay loading of up to 3wt%, nanofillers particles are distributed uniformly throughout the polymer matrix, giving higher CO_2 permeance and selectivity. However, at 5wt% nanoclay loading, the membrane shows dramatic decline in selectivity due to agglomeration of clay particles.

Acknowledgements

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