

Studies of Thermal Annealing on Suppression of Plasticization of the Asymmetric Hollow Fiber Mixed Matrix Membranes

¹T.D. Kusworo, ²A.F. Ismail, ²A. Mustafa and ¹Budiyono

¹Department of Chemical Engineering, University of Diponegoro,
Jl. Prof. Sudharto, Tembalang, Indonesia

²Advanced Membrane Research Technology Center (AMTEC),
Faculty of Chemical and Natural Resources Engineering,
Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor Bahru, Malaysia

Abstract: Combinations of polymer blending and heat treatment have been investigated to improve the performance of hollow fiber mixed matrix membrane for gas separation. Two types of membranes with polymer blending and combination of polymer blending-heat treatment were prepared to study the effect of combination process on its permeation properties. Asymmetric hollow fiber mixed matrix membranes for gas separation were spun using the dry/wet spinning process from spinning solutions containing polyimide/polyethersulfone blends and *N*-methyl-2-pyrrolidone (NMP) as a solvent. CO₂ permeance of the membrane with polymer blending but without heat treatment showed a slight increase with increasing feed pressure, indicating that a small amount of CO₂ plasticized the membrane material. As for the heat treated membrane, the effects of temperature and duration of heat treatment were investigated to study the reduction of undesirable CO₂ plasticization. Experimental results showed that the heat treatment at near and above glass transition temperature was sufficient to suppress the CO₂ plasticization. The better adherence of zeolite particles in the polymer matrix combined with formation of charge transfer complexes (CTCs) and cross-linking might be the main factors to enhance the anti-plasticization on the PI/PES-zeolite mixed matrix membrane. Field emission scanning electron microscopy (FESEM) micrographs showed that the selective layer and the substructure of hollow fibers became denser and more compact after the heat treatment. The FESEM micrographs also showed that the polymer blending and heat treatment was increased the adherence of zeolite particle and polymer. Mixed matrix membranes treated at 280 °C for 2 hours indicated no plasticization effect and the CO₂ permeance remain practically constant over the applied feed pressures.

Key words: Mixed matrix membrane • Heat treatment • Charge transfer complex

INTRODUCTION

Currently, membrane offering wide range applications for many gas separation processes such as natural gas processing, air separation and hydrogen recovery. As for the polymeric membrane material, glassy polymers such as polysulfone, polyethersulfone, polycarbonates and polyimide are considered as superior compared to other polymers due to the desired mechanical property and the flexibility to be used for gas processing processes. It is

well known that the gas streams often contain high levels of plasticizing or condensable vapors, which degrade membrane performance thereof, making the separation process less economic. Glassy polymer gas separation membranes for natural gas treating are offer preferred over rubbery polymer membranes due to their higher CO₂/CH₄ selectivity [1]. As previously discussed [2], glassy polymer membranes exhibit increasing permeability with increasing feed pressure due to CO₂-induced plasticization of the polymer matrix. This plasticizing

action of CO₂ decreases the ability of the membrane to separate molecules on the basis of size, thereby causing the reduction in selectivity. Recently, changes of such magnitude in membrane performance clearly explain the significant industrial and academic interest in this phenomenon. Plasticization phenomena in glassy polymer membranes are depended on many factors such as membrane material, membrane morphology (dense membrane), thickness of the membrane, feed composition, pressure and temperature [1-6]. Due to the enormous potential of membrane technology, continual effort to develop and improve the economics of extant membrane processes for gas separation, as well as to extend the range of applications of this technology is essential. Bos *et al.* [5] demonstrated that blending of a polymer is a simple method to suppress plasticization. Kapantaidakis *et al.* [1] have also studied the effect of polyethersulfone-polyimide blend to suppress the plasticization effect. They reported that CO₂ plasticization of pure polyimide membrane occurred at 4 bars. They observed that the PES/PI 80/20 blend hollow fiber membrane exhibited the highest resistance against plasticization. Chung *et al.* [6] observed that the CO₂ induced plasticization occurred when feed pressure varied 20 to 200 psi for asymmetric 6FDA-2,6DAT hollow fiber membrane. When the heat treatment temperature was increased above 250°C CO₂ induced plasticization was successfully reduced. The propylene plasticization of polyimide Matrimid 5218 may cause the continuous increase of pressure-normalized fluxes was reported by previous study [7]. They were applied annealing process to stabilize the membrane. The stabilized membrane did not show a minimum in the pressure-normalized fluxes as a function of pressure. The plasticization was suppressed by thermal annealing due to a densification of the polymer matrix and results in a reduction of chain mobility. Ismail and Lorna [8] studied the effect of heat treatment to reduce plasticization of polysulfone membrane. They reported that the membranes were stabilized against CO₂ plasticization by subjecting the membrane to heat treatment above 140°C. Heat treatment above T_g can cause the disruption of chain rigidity of polymers.

Meanwhile, beside the CO₂ plasticization, polymeric membrane materials have seemingly reached a limit in the trade-off between productivity and selectivity [9]. Pure polymer membranes oftentimes show several limitations as low selectivity, high temperature instability and swelling and decomposition in organic solvents. While carbon molecular sieves and zeolites possess very attractive permeation properties with permeabilities and

selectivities significantly higher than polymeric materials, processing challenges and high costs obstruct their industrial application [9].

Currently, many researchers have focused to investigate mixed matrix membrane to enhance gas separation performance. Hybrid membrane materials, or mixed matrix membranes, are a new class of membrane materials that offer the potential of significantly advancing the current technology. This concept involves the incorporation of highly selective molecular sieves within a polymeric matrix, resulting in a hybrid membrane material with superior selectivity over that of polymer matrix alone, while maintaining processability under current membrane formation technology [10-11]. Therefore, the main objective of the present study is to investigate the effect of thermal annealing process and polymer blending on the performance of asymmetric zeolite mixed matrix membranes for gas separation system. The present study also studied the CO₂ plasticization behaviour in asymmetric mixed matrix membrane. To our knowledge, there is no documentation on the use of thermal treatment and polymer blending to reduce the plasticization effect on the performance of hollow fiber mixed matrix membrane. The present paper also is to examine the time-dependent aging of two different untreated and thermal treated zeolite mixed matrix membranes with periodic CO₂ exposure.

Experimental

Material Selection: Polyimide (Matrimid 5218) resin was supplied by Alfa Aesar Johnson Matthey Mexico and polyethersulfone by Solvay Advanced Material (USA). The polymers were dried in a vacuum oven at 120°C overnight before dope preparation; N-methylpyrrolidinone (NMP) from Merck was used as the solvent due to its low toxicity. The inorganic filler molecular sieve involved was zeolite 4A purchased from Aldrich and the particle size was about 1 µm. In order to remove the adsorbed water vapour or other organic vapors, all zeolite particles were dehydrated at 300°C for 3 h before use. The chemical structure of the polyimide and polyethersulfone are shown in Figure 1.

Fabrication of Asymmetric Hollow Fiber Mixed Matrix Membrane: In this study, the polymer solution consists of 25 wt % polymer (blend PI/PES, 20/80), 75 wt% NMP and 20 wt% zeolite in the total solid. The homogeneous polyimide and polyethersulfone were prepared according to the following procedure; the inorganic molecular sieve particles were dispersed into the solvent and stirred for

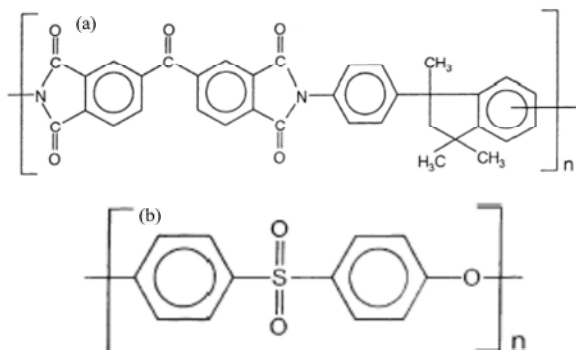


Fig. 1: Chemical structure of (a) Polyimide and (b) Polyethersulfone

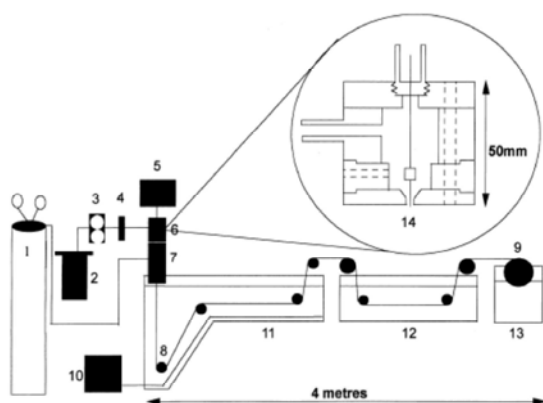


Fig. 2: Schematic of the dry-wet spinning apparatus used in this study (1) nitrogen; (2) dope reservoir; (3) gear pump; (4) 7 mm tube; (5) syringe pump; (6) spinneret; (7) forced convection tube; (8) roller; (9) wind-up drum; (10) refrigeration/heating unit; (11) coagulation bath; (12) washing/treatment bath; (13) wind-up bath; (14) schematic of a spinneret.

24 hours followed by the addition of a desired amount of polyimide. The solution was agitated with a stirrer at least 24 hours to ensure complete dissolution of the polymer. Then, a desired amount of polyethersulfone was added to the homogenous solution. This solution was further agitated by stirring at high speed for at least 2 days. Before spinning, the homogeneous solution so prepared was degassed under vacuum for 3 hours. Asymmetric hollow fibers mixed matrix membranes were prepared according to the dry-jet wet spinning process. The spinneret has an o.d. and i.d. of 0.6 mm and 0.3 mm, respectively. The extrusion rate of the spinning dope was controlled either by nitrogen pressure or the pump flow rate using the adjusting valve. The internal coagulant was controlled by using syringe pump. The external

coagulant bath is filled with tap water at room temperature. The detailed spinning equipment is shown in Fig 2. The nascent fiber appeared from the end of the centrally located needle of the spinneret and passed through a air gap before entering the coagulant bath. After coagulation, the hollow fiber was guided through the roller and then coiled into the storing tank. To ensure all of the solvent in the membrane structure is removed, membranes were immersed in an aqueous bath for 1 day, followed by immersion in methanol for 4 hours and air-dried for 24 hours at room temperature. The mixed matrix membranes were finally dried in a vacuum oven at 150 for 15 hours to remove all the residual solvents.

Post-Treatment Procedure: Hollow fibers mixed matrix membrane after the air drying were dried in an oven at different temperatures (100, 200, 280 °C). Furthermore, heat treatment for different durations (20 and 120 min) at 280 °C was also carried out. After the treatment the membranes were cooled down slowly to room temperature. The treated membrane after being subjected to different heat treatment methods were tested using a pure gas permeation testing system.

Characterization of Blend Hollow Fiber Mixed Matrix Membrane: A Supra 35 VP Field Emission Scanning Electron Microscopy (FESEM) was used to ensure the asymmetric structure and to determine the dimension of the fibers. Membrane samples were fractured in liquid nitrogen. The membranes were mounted on an aluminium disk with a double surface tape and then the sample holder was placed and evacuated in a sputter-coater with gold.

The changes in the chemical structure caused by thermal annealing and polymer blending were identified using Fourier transform infrared spectroscopy (FTIR). The IR absorption spectra were obtained at room temperature in a range from 4000 to 500 cm^{-1} with a spectral resolution of 8 cm^{-1} and averaged over 16 scans. The glass transition temperature of each cast film was determined using differential scanning calorimetry (Mettler Toledo DSC 822e). A small piece of membrane or pure polymer sample was first stored under vacuum at 100 °C for 24 hours to remove adsorbed water; then weighed and placed into aluminium DSC pans. The scanning range was 50- 320 °C with scanning rate of 10 °C min^{-1} in the first DSC cycle to remove thermal history and then cooled from 320 to 25 °C at the rate of 10 °C min^{-1} ; finally the second cycle was carried out with the same procedure.

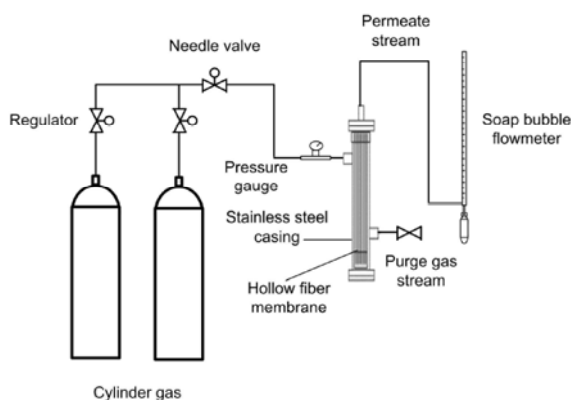


Fig. 3: Schematic diagram of hollow fiber testing equipment (1) CO₂ or CH₄ (2) hollow fiber module; (3) bubble soap meter.

Module Fabrication and Gas Permeation Experiment: In this study, the hollow fiber membranes were tested in a pure, O₂, N₂, CO₂ and CH₄ gas system using a variable volume method using an upstream pressure up to 10 bars while the downstream pressure was effectively atmospheric. Figure 3 illustrated the schematic diagram of a testing apparatus to measure the gas permeation performance of hollow fibers. Permeation experiments were carried out at room temperature. The permeance was measured after the steady state was reached, which took about 10 min. the permeate flow rate was measured by means of a soap bubble flow meter reading to 0.05 cm³. The down stream side was always purged with the test gas prior to the permeation measurement. For time dependent permeation experiment, the CO₂ permeation was measured at 10 bar as a function of time for both untreated and thermal annealing treated mixed matrix membranes. The experimentation time is generally 4 days. Five fibers with a length of 15 cm were assembled into a bundle. One end of the bundle was sealed with epoxy resin while the shell side of the other end was glued onto an aluminium holder using hysol epoxy adhesive. The prepared bundle was fitted into a stainless steel tube, the i.d. of which was 2.2 cm, respectively. The permeance or pressure-normalized flux, (P/L) , is calculated by:

$$(P/L) = \frac{Q_i}{(\Delta p)(n\pi D l)} \quad (1)$$

where Q_i is the volumetric flow rate of gas 'i' at standard temperature and pressure, Δp is the transmembrane pressure drop (cmHg), n = number of tested fibers;

D = outer diameter of the fibers (cm); l = effective length of the fibers (cm). Permeances are expressed in gas permeation units, GPU, (1GPU = $1 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$)

The ideal separation factor (gas A over gas B) of the hollow fiber membrane was determined by

$$\alpha = \frac{(P/L)_A}{(P/L)_B} \quad (2)$$

RESULTS AND DISCUSSION

Gas Permeation Behaviour of Mixed Matrix Membranes:

Figure 4 depicts the effect of feed pressure on the permeance of O₂, N₂, CH₄ and CO₂ gases on the PI/PES-zeolite mixed matrix membrane. The permeances of slow gas such as CH₄ and N₂ were relatively unchanged with increasing feed pressure. Contrary to slowly gases, the CO₂ permeation increased slightly when the feed pressure was increased from 1 to 10 bars. This was due to small plasticization that occurred on the PI/PES 20/80-zeolite 4A hollow fiber mixed matrix membrane. As illustrated in Figure 4, the type of plasticization on the PI/PES-zeolite 4A hollow fiber mixed matrix follows the second type [2]. The permeance of CO₂ firstly decreases at low pressure until 7 bars, in accordance with the dual mode sorption theory. Above 7 bars CO₂ permeance starts to increase. The decrease in permeability, in the low pressure region, is dominated by a decrease in solubility with increasing pressure. According to Kapantaidakis and Koops [3], the plasticization pressure of pure polyimide membrane was 4 bars. Another researcher, Wang *et al.* [12] found that the plasticization pressure of the 6 FDA polyimide membranes occurred at feed pressure about 2.75 bars. However, the CH₄ permeance was almost constant as feed pressure increased from 8 to 11 bars. Therefore, from the results we can conclude that the polymer blending can reduce the plasticization effect on the PI/PES hollow fiber membranes. Figure 5 compares the CO₂ permeance of PI/PES neat and PI/PES-zeolite. As can be seen from Figure 5, the trends of CO₂ permeance of both membranes are quite similar. However the CO₂ permeance of neat PI/PES membrane above 7 bars was increases about 59.1 %, meanwhile, the CO₂ permeance of PI/PES-zeolite was increased about 49 %. This result indicated the important role of zeolite pore size in gas transport properties of mixed matrix membrane. The small increasing of CO₂ permeance of PI/PES-zeolite indicated that the plasticization behaviour on PI/PES-zeolite was smaller than on PI/PES neat. This phenomenon probably

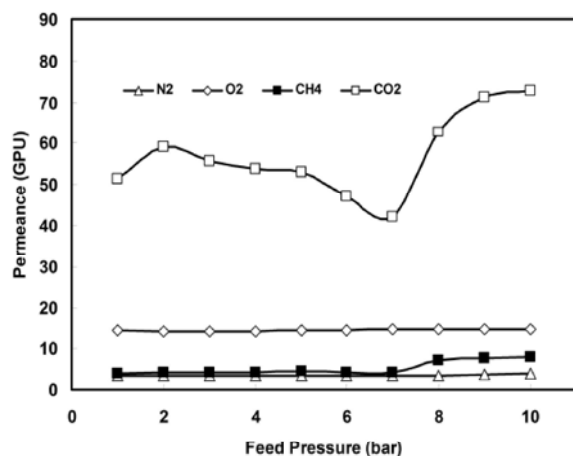


Fig. 4: Permeation rate of all gases for asymmetric PI/PES blend mixed matrix membrane as a function of feed pressure at 35°C.

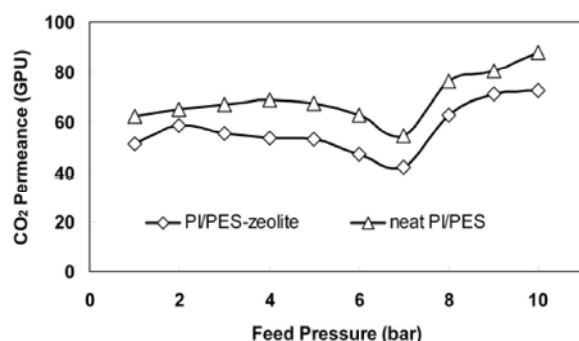


Fig. 5: CO₂ Permeance for asymmetric neat PI/PES membrane and PI/PES-zeolite mixed matrix membrane as a function of feed pressure at 35°C.

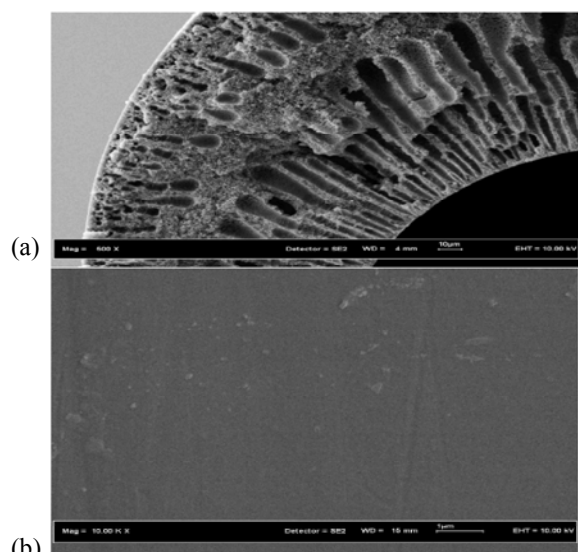


Fig. 6: Cross-sectional and surface images of neat PI/PES membrane

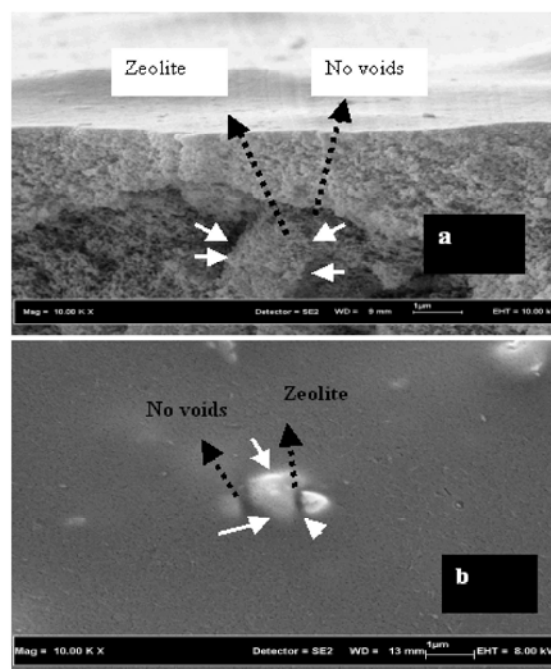


Fig. 7: Cross-sectional and surface images of PI/PES-zeolite mixed matrix membrane

attributed to better interaction between zeolite particles with polymer matrix. Figures 6-7 represent the cross-sectional as well as the top surface and surface FESEM image of neat PI/PES membrane and PI/PES-zeolite 4A mixed matrix membrane. As can be seen in Figures 7(a)-(b), the picture demonstrates that zeolite 4A molecular sieves are well embedded in the dense layer. As shown in Figure 7(b), the ruptures of surface active layers of PI/PES-zeolite fiber were significantly suppressed due to better adherence of zeolite particles with polymer matrix. Moreover, the smooth surface of PI/PES-zeolite mixed matrix membrane as shown in Figure 7(b) also indicates that the zeolite particle adheres well to the polymer matrix and does not show any unselective void between the sieve particles. Hence, the resulting fibers from PI/PES-zeolite mixed matrix membrane might be less the chain mobility which can reduce the plasticization behaviour. The properties of zeolite 4A having open crystal structure and relatively small pore size could induced a resistant to the diffusion of the gas penetrant through the zeolite pore. Moreover, due to its small pore size, zeolite can discriminate gas penetrant on the basis of the differences in molecular size and shape.

The effect of plasticization can be observed as the reduction in selectivity, as shown in Fig. 8. The figure shows that the ideal selectivity of CO₂/CH₄ gas pair

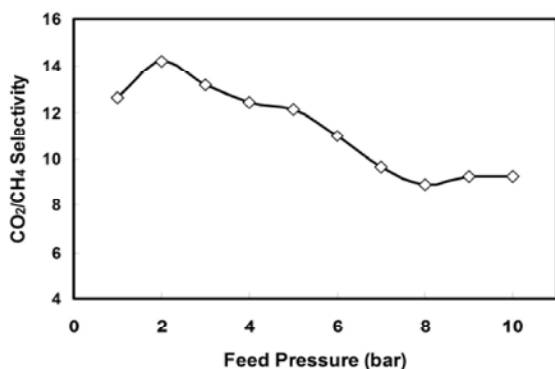


Fig. 8: CO₂/CH₄ selectivity of asymmetric PI/PES blend mixed matrix membrane as a function of feed pressure at 35°C.

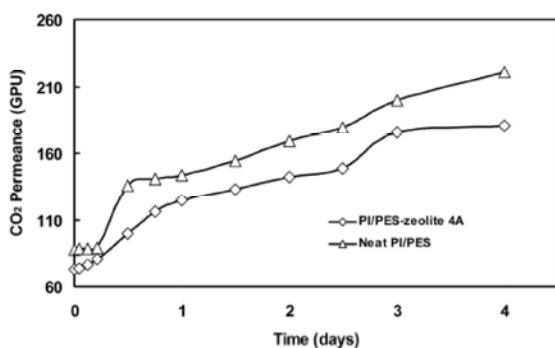


Fig. 9: Time dependent of CO₂ permeation rate of PI/PES blend and PI/PES mixed matrix membrane at 10 bars

decreased by 7 % from the highest to the lowest value. The reduction in ideal CO₂/CH₄ selectivity is might be due to the fact that membranes tend to swell when tested at high feed pressure. The other phenomenon contributed from the CO₂ plasticization is the time dependent permeance at feed pressures above the plasticization pressure. Figure 9 shows the CO₂ permeance as a function of time for the neat PI/PES membrane and the PI/PES-zeolite mixed matrix membrane when both were tested at a feed pressure of 10 bars. The CO₂ permeance of the neat PI/PES hollow fiber membrane did not reach a steady state value within the given period. The total increase in permeance was more than 55 % after 12 hours. On the other hand, the PI/PES-zeolite hollow fiber mixed matrix membrane reached a steady state value. The latter membrane reached a steady value of permeance after 12 hours, which is 36 % higher than the initial value. Therefore, these results also suggest that polymer blending is one of effective methods in the mixed matrix membrane fabrication for enhance the adhesion between

sieve and polymer matrix and also can suppress the CO₂-induced plasticization. This phenomenon can be explained by the mechanism of gas transport through PI/PES-zeolite mixed matrix membrane might be occur through three dominant pathway, which are through dense active layer of PI/PES matrix, highly selective of zeolite and through non selective gaps or voids between the matrix and sieve particles. The gas transport through zeolite particles is offer most selective pathway because zeolite is capable of discriminating between size and shape differences of the gas penetrants. The gas transport the voids are assumed to be Knudsen diffusion. As depicted in Figure 7a-b, the PI/PES mixed matrix membranes show no evidence of unselective voids or the gaps size between the zeolite particles and polymer matrix. Therefore, the permeation of gas via Knudsen diffusion mechanism was suppressed. Moreover, more penetrant gases were directed to flow through zeolite particle. Therefore, the CO₂ plasticization in the PI/PES-zeolite mixed matrix membrane was successfully suppressed because the zeolite particle can't be swelling with CO₂ gas.

Effect of Heat Treatment Temperature on Morphology and Gas Separation Performance of Mixed Matrix Membrane:

Plasticization of glassy polymers occurs due to the reduction of the interaction between adjacent segments of the neighbouring polymer chains [13]. As a result, the polymer materials will change in the chain segmental motion and increase in the mobility and consequently in the gas permeability. The polymer membrane material after plasticization will be generally swelled upon sorption of CO₂ and accelerating the permeation of CH₄, hence is reducing the selectivity of CO₂/CH₄. Therefore, plasticization process is highly undesirable in the membrane production. Suppression of plasticization means suppression of polymer chain flexibility through polymer blending, cross-linking of the polymer matrix or by thermal curing of polymer. As discussed in section 3.1, polymer blending could suppress the plasticization of hollow fiber mixed matrix membrane. However, it seems that the polymer blending did not completely suppress the plasticization. This result is consistent with the previous studies by Bos [14] and Kapantaidakis *et al.* [5]. Bos observed that polymer blending of Matrimids and Thermids did not adequately suppress the plasticization of the glassy polymer membrane. While Kapantaidakis *et al.* [5] found that the ideal selectivity of CO₂/N₂ for PES/PI 80/20 significantly reduced, thus indicating that plasticization occurred in the membrane.

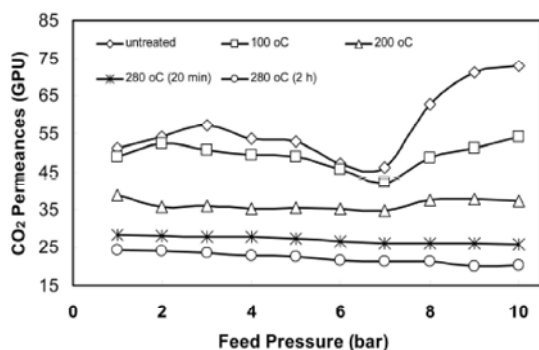


Fig. 10: CO₂ permeance as a function of feed pressure for asymmetric PI/PES blend mixed matrix membrane at different thermal annealing temperature.

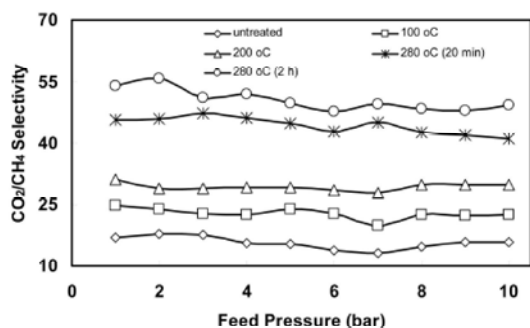


Fig. 11: CO₂/CH₄ selectivity as a function of feed pressure for asymmetric PI/PES blend mixed matrix membrane at different thermal annealing temperature.

The original colour of the PI/PES-zeolite hollow fiber mixed matrix membrane is light yellow. The yellow colour is characteristic of most polyimides, which is attributed to charge-transfer complexes (CTCs). The properties of aromatic polyimide generally depend on the existence of charge transfer complexes as described by transfer of one electron charge from the electron-rich donor molecule to the electron deficient acceptor molecule. The electron donors are attributed to the six-membered rings of dianhydride while the electron acceptors correspond to the five-membered rings of imide. The polymer chain motion would be hampered since the formation of charge transfer complex occurs between closely located rings by the shift of π -electron. Hasegawa *et al.* [15-16] found that the formation of the complex in the polyimide strongly depended on the curing temperature during preparation of the membrane.

In the present study, the PI/PES-zeolite mixed matrix membranes were subjected to different kinds of heat-treatment both below and above T_g to study the

possibility of reducing the CO₂ plasticization. Figure 10 and Tables 1 and 2 show the effect of heat treatment temperature on the CO₂ permeance of PI/PES-zeolite mixed matrix membranes and some physical properties of these membranes, respectively. Figure 11 displays the ideal CO₂/CH₄ selectivity of PI/PES blend mixed matrix membranes. As we can see from Fig. 10, the CO₂ permeance decreased by the heat treatment. With the mild heat treatment (thermal curing at 100 °C), the CO₂ permeance slightly decreased with increasing feed pressure when the pressure was below 7 bar. However, the CO₂ permeation started to when the pressure was above 7 bars. The behaviour indicates that the CO₂ plasticization still occurs even after the heat treatment. However, significant reduction in permeance occurred when the heat treatment was performed at near and above the glass transition temperature of PI/PES-zeolite mixed matrix membrane. A 20 minutes heat treatment at 280 °C resulted in a 44 % reduction of CO₂ permeance as compared to the untreated PI/PES blend mixed matrix membrane. While the CO₂ permeance decreased by 56 % for heat treated for 2 hours at 280 °C (Fig. 10). The reduction of CO₂ permeances indicates that the segmental mobility of polymer is reduced by the heat treatment as evidenced by an parallel increase in T_g (Table 2).

The suppression of CO₂ plasticization can also be seen in the permeance change with feed pressure. Contrary to the strong pressure dependence of the untreated membrane, the CO₂ permeance of the PI/PES mixed matrix membrane became little pressure dependent after the heat treatment at 280 °C (above T_g), suggesting that the CO₂ induced plasticization could be removed almost completely.

The effect of heat treatment on the ideal selectivity of CO₂/CH₄ is depicted in Fig. 11. Increasing the heat treatment temperature significantly increased the ideal CO₂/CH₄ selectivity of the PI/PES blend mixed matrix membrane. This phenomenon is attributed to the combined effects of heat treatment on densification of the selective layer and cross-linking and formation of the charge transfer complexes (CTCs). After heat treatment was performed, the thickness of dense layer was slightly increased (Fig. 12) and more densified (Table 2) compare to the untreated membrane. Hence, the diffusion rate big gas molecule such as CH₄ the is increased compared to the small gas likes CO₂. The result was in agreement with the work by Chung *et al* [17].

As discussed earlier, polyimide has been characterized by the formation of charge transfer complexes. Kawakami *et al.* [18] observed that the

Table 1:

Asymmetric mixed matrix membrane	Color	λ (UV) nm	$\Delta\lambda$ (UV shift) nm
Untreated	Light yellow	258.7	0
Heat treatment 100 °C (20 min)	Light yellow	260.3	1.6
Heat treatment 200 °C (20 min)	Yellow	299.0	40.3
Heat treatment 280 °C (20 min)	Dark yellow	305.3	46.6
Heat treatment 280 °C (2 hours)	Dark yellow	311.5	52.8
Heat treatment 280 °C (4 hours)	Darker yellow	375.8	117.1

Table 2:

Asymmetric mixed matrix membrane	T_g (°C)	Density g/cm
Untreated	230.00	1.0024
Heat treatment 100 °C (20 min)	230.35	1.0218
Heat treatment 200 °C (20 min)	231.50	1.0220
Heat treatment 280 °C (20 min)	234.50	1.0223
Heat treatment 280 °C (2 hours)	235.00	1.0225
Heat treatment 280 °C (4 hours)	235.10	1.0228

formation of charge transfer complexes was accompanied by the change of colour, increase in density and glass transition temperature. Indeed, the membrane colour changed significantly from light yellow to dark yellow by heat treatment in our experiments (Table 1). The colour remained unchanged at 100 °C. This indicates that charge transfer complexes were not formed at this temperature. Above 100°C, however, the colour change was noticed and the higher the temperature, the darker was the yellow colour. The colour change during the heat treatment can be attributed to the formation of charge transfer complexes as mentioned before [16, 18-19]. The alternating electron acceptor and donor endow the polyimides with the ability to form CTCs. Generally, the CTCs in solid state polyimides are most likely in a non-equilibrium state [16]. Therefore, heat treatment at higher temperature will be facilitating the formation of CTCs. The formation of CTCs is also shown by the red shift of a UV absorption band (Table 1). Furthermore, when a polymeric membrane is heat-treated, the relatively flexible chains are thermodynamically easier to be reoriented and as a result the treated membrane has better or more perfect chain-packing. As shown in Table 2, the heat treatment did not only increase the density but also the glass transition temperature of the fiber. The increase in density and T_g suggests that the formation of CTCs occurred during the heat treatment process. Kawakami *et al.* [18] also found that the formation of CTCs in the polyimide membrane increased the glass transition temperature. Therefore, from the data shown in Table 1-2 it is firmly concluded that the charge transfer complexes were formed.

Moreover, according to Wallace [20] the cross-linking phenomenon could be characterized by the dissolution and infra red methods. Therefore, the effect of thermal

Table 3:

Asymmetric mixed matrix membrane	Dissolution time
Untreated	20 min
Heat treatment 100 °C (20 min)	25 min
Heat treatment 200 °C (20 min)	6 hours
Heat treatment 280 °C (20 min)	3 days
Heat treatment 280 °C (2 hours)	Insoluble no visible swelling
Heat treatment 280 °C (4 hours)	Insoluble no visible swelling

annealing on the dissolution of fibers in NMP solvent was studied. Table 3 shows the time required to dissolve PI/PES blend mixed matrix membranes in NMP after the fibers were treated under different temperatures. The untreated fiber and the fiber treated at 100 °C needed 20 and 25 min, respectively, to dissolve in NMP. These results suggest that the treatment temperature up to 100 °C is not enough to cause any cross-linking. Further increase in heat treatment temperature to 200°C prolonged the dissolution time to 6 hours, indicating that the low intensity of cross-linking was formed at this temperature. Subsequent increase of heat treatment temperature to 280 °C or above glass transition temperature further increased the insoluble property of the fiber; i.e. even submerged for 15 days the membrane did not dissolve in NMP, indicating complete formation of cross-linking at this temperature. Moreover, a membrane becomes insoluble in a solvent after heat treatment due to the formation of complete cross-linking. According to Figure 10, the mild heat treatment (100 °C) was not sufficient to suppress the CO₂ plasticization. On the other hand, increasing the heat treatment temperature to 200 °C and 280 °C significantly suppressed the CO₂ plasticization. Hence, it can be concluded that if the degree of cross-linking is really low, the charge transfer complexes (CTCs) may be the main factor for the densification of the fiber. These results are in agreement with the statement made by Bos *et al.* [16] and Kawakami *et al.* [18] that the combination of cross-linking and formation of charge transfer complexes were responsible for suppressing the CO₂ plasticization in the fiber. Moreover, combination of polymer blending and heat treatment on the PI/PES-zeolite mixed matrix membrane has been increased the adhesion of zeolite particle with polymer matrix as shown in Figure 12e.

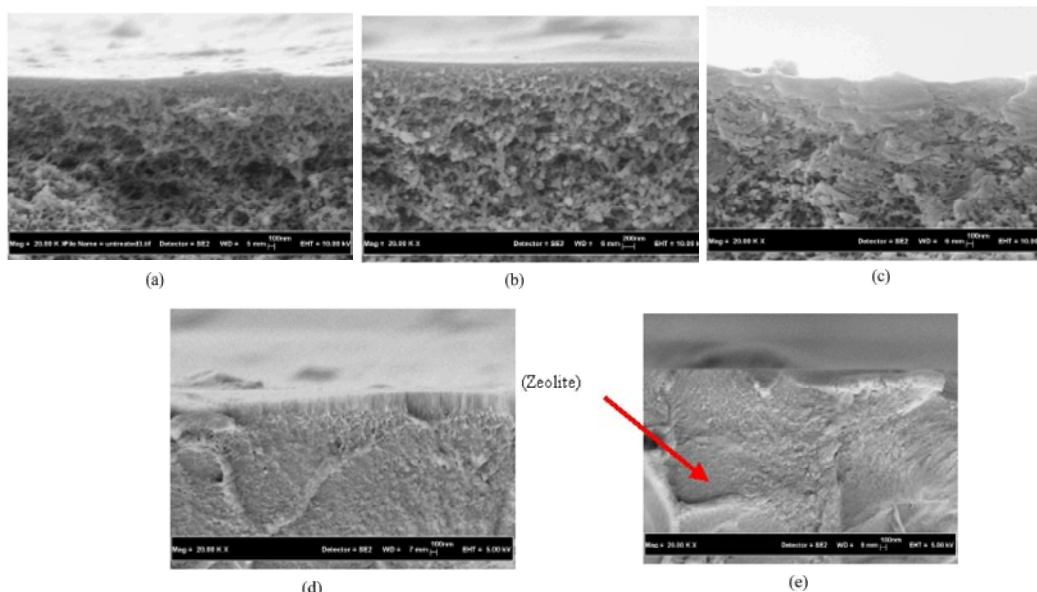


Fig. 12: Cross-section of asymmetric PI/PES blend mixed matrix membrane at different temperature (a)100 oC, (b) 200 oC, (c) 280°C 20 min, (d) 280 2 h e; zeolite at skin layer.

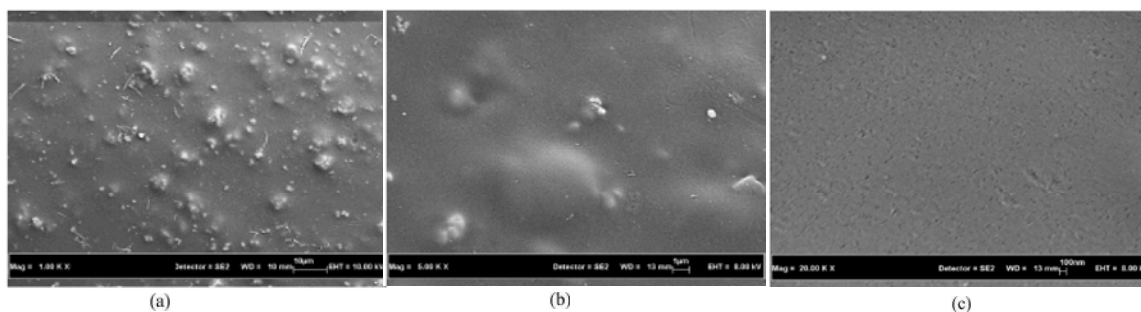


Fig. 13: Surface section of asymmetric PI/PES blend mixed matrix membrane at different temperature (a)100 oC, (b) 200°C, (c)280°C.

In addition, no separate layer was observed between the zeolite particles and PI/PES matrix. As discussed earlier, the better adherence of zeolite particles with the polymer matrix was caused by penetrant gases which directed to flow through zeolite pathway. Therefore, the plasticization was reduced because the zeolite particle was not swell with CO₂ gas.

Characterization of Hollow Fiber Membrane: Figure 12 compares the cross-sections of the PI/PES blend mixed matrix membranes subjected to heat treatment at 100-280 °C for up to 2 hours. As can be seen from the SEM micrographs, of all membranes exhibited the porous structure. The porous structure became increasingly denser as the heat-treatment temperature increased. Moreover, the FESEM micrographs reveal that the dense skin layer formed when the heat-treatment temperature

was higher than 200°C. Furthermore because of the thermal effect the packed chains in the polymer matrix denser and the packed structure in the skin layer provide a high degree of size and shape discrimination between the gas molecules. Therefore, after heat treatment mixed matrix hollow fiber became more compact in the outer skin and substructure as compared to the untreated fiber. As result the permeance for treated membrane was lower than untreated membrane. This is consistent with the reduction of permeance and increasing the selectivity as shown in Figures 10 and 11. The other effect with increasing heat treatment at 280 °C was made the better adherence of zeolite particle with polymer matrix which can enhance the gas selectivity. Furthermore, the defect on the surface of the fiber because of poor adhesion between the polymer and the filler could be reduced as shown in Fig. 13.

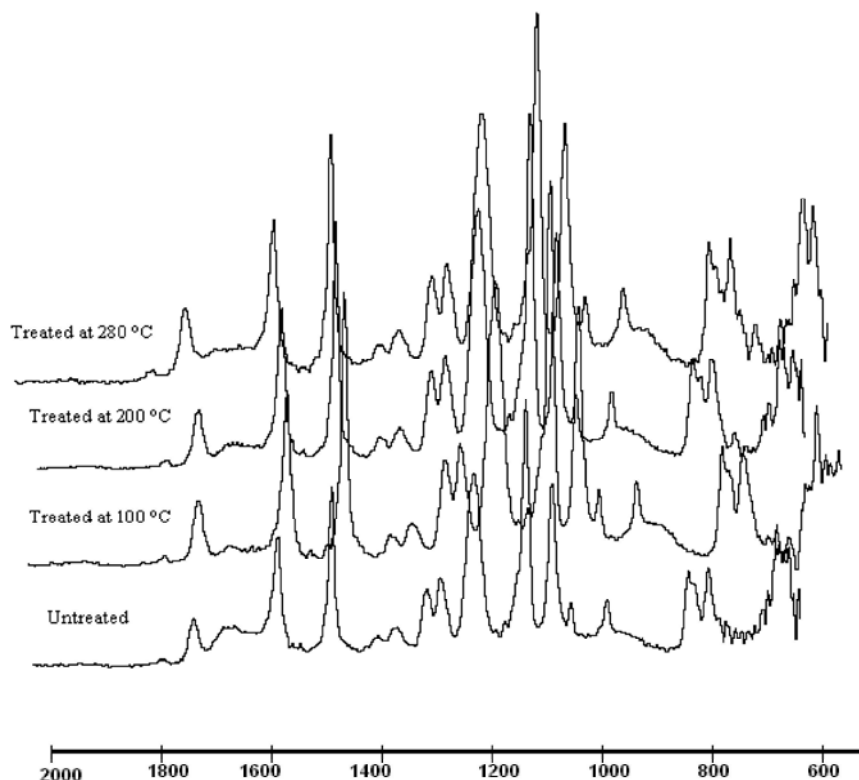


Fig. 14: FTIR of asymmetric PI/PES blend mixed matrix membrane at different temperature.

Figure 14 depicted the FTIR spectra of PI/PES blend mixed matrix membranes with and without heat treatment. The untreated hollow fiber was characterized by bands at around 1775 cm^{-1} (attributed to asymmetric stretch $\text{C}=\text{O}$ in the imide group), 1720 cm^{-1} (attributed to symmetric stretch $\text{C}=\text{O}$ of the imide group), 1319 cm^{-1} (stretch of $\text{C}-\text{N}$ in the imide group), 1010 cm^{-1} (transverse stretch of $\text{C}-\text{N}-\text{C}$ in the imide group) and 710 cm^{-1} (out of plane bending of $\text{C}-\text{N}-\text{C}$ in the imide group). The amide group characteristic was characterized by bands at around 1661 cm^{-1} (stretch of $\text{C}=\text{O}$ in the amide group) and at 1539 cm^{-1} (stretch of $\text{C}-\text{N}$ and/or bend of $\text{N}-\text{H}$ in the amide group). After thermal treatment, we found that the intensities of the characteristic amide group decreased. However the heat treatment at $100\text{ }^{\circ}\text{C}$ did not cause the change in the band intensities compared to the untreated fiber. The results indicate that heat treatment at a mild temperature ($100\text{ }^{\circ}\text{C}$) was not sufficient to change the structure of the fiber. This is consistent with the results presented in Table 3, indicating the fiber readily dissolved in NMP after 25 min. On the other hand, after the heat treatment at $280\text{ }^{\circ}\text{C}$ the intensities bands corresponding to the imide group have almost increased after thermal treatment.

CONCLUSION

In this work, the simultaneous, polymer blending and heat treatment effect on the adhesion of zeolite particle with polymer matrix was investigated. The CO_2 plasticization behavior on the PI/PES-zeolite mixed matrix membrane also determined. Therefore the following conclusion can be drawn from this study:

- Combination of polymer blending and thermal treatment can be used as an effective method to enhance adhesion of zeolite particle with polymer matrix which can control the plasticization effect in asymmetric hollow fiber mixed matrix membranes.
- The better adherence of zeolite particle combined with the cross-linking and charge transfer complexes (CTCs) were main dominant factors to suppress CO_2 plasticization in the PI/PES blends-zeolite mixed matrix membranes.
- It is found that the combinations of polymer blending and heat treatment can effectively improve the performance of mixed matrix membrane with increasing the selectivity of CO_2/CH_4 more than 68 %.

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