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# Hydrogen separation and purification in membranes of miscible polymer blends with interpenetration networks

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## Abstract

This study demonstrates the successful implications of blending technique cum chemical modification for the fabrication of high performance polymeric membranes for gas separation applications. The effect of variation in composition on miscibility and microstructure, gas permeability and selectivity of blend membranes is investigated. It is found that augmentation in PBI composition results in enhancement in gas separation performance of membranes which is attributed mainly to the effect of diffusivity selectivity. Analysis of the microstructure of membranes confirms the variations in chain packing density, *d*-spacing and segmental mobility of polymer chains as a result of blending. Separation performance of membranes is further ameliorated through chemical modification of blend constituents. Modification of PBI phase with *p*-xylene dichloride brings about slight improvements in selectivity performance, especially for $H_2/CO_2$ and $H_2/N_2$. In contrast, the selectivity of membranes is improved significantly after cross-linking of Matrimid phase with *p*-xylene diamine. The results indicate that higher tendency of Matrimid toward cross-linking reaction contributes more in controlling the transport properties of membranes through diffusion coefficient by increase in chain packing density and diminishing the excess free volumes. Results obtained in this study reveal the promising features of developed membranes for gas separation applications with great potential for hydrogen separation and purification on industrial scale.

*Keywords:* Hydrogen separation; Polymer blending; Polybenzimidazole

## 1. Introduction

Hydrogen is anticipated to play an inevitable role as one of the promising sources of energy in the future. According to the latest statistics, the US annual production of hydrogen is appraised to about 9 million tons [1]. The major proportions of produced hydrogen is used to supply the refinery and fertilizer industries. The constant increasing demand for highly purified hydrogen has resulted in attracting more attentions for extensive research studies on advancement of the technologies for generation of hydrogen with higher efficiency and lower production cost.

At present, steam reforming of hydrocarbons is predominantly the established technology for generation of hydrogen and it supplies about half of the world's demand for this viable gas. In this process, a stream of natural gas mainly composed of methane undergoes a water gas shift reaction. The yielded product has to be further processed in a separation process in order to remove unwanted carbon dioxide and other byproducts from the mixtures with hydrogen. Currently, commercially available separation processes for this purpose are pressure swing adsorption, amine absorption and absorption using aqueous solution of potassium carbonate which are highly energy intensive [2–4].

Membranes have received global attention as a promising technology for gas separation and purification. This mainly stems from the small footprint, reliability, considerable high energy efficiency and low capital cost offered in membranes compared to other conventional separation processes [5,6]. It is also worthy noting that hydrogen recovery has been among the first commercial applications of membranes in the field of gas

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separation [7]. The major applications of membranes for hydrogen separation include hydrogen purifications, fuel cell technology and membrane reactor processes [8]. Recovery of hydrogen from hydrocarbon streams, recovery of hydrogen from ammonia streams, and hydrogen composition adjustment in synthetic gases are the widely practiced industrial and petrochemical applications of hydrogen purification [9]. Interestingly, membrane separation systems have good potentials for integration with hydrogen generation equipments that permits the processes to be entirely carried out in a single processing unit.

In recent years, research directions have been focused on both inorganic and organic materials to develop membranes with desirable hydrogen separation properties. There are different approaches for the use of inorganic membranes in hydrogen separation. One is based on a dense metal layer deposited on a ceramic support. In this category, palladium-based membranes are more attractive and generally exhibit high hydrogen permeability and selectivity [10]. Zhang et al. [11] studied the hydrogen permeation behavior of dense palladium membranes prepared by microfabrication technique. According to their study, this technique offers high durability to membrane for operation at elevated temperatures. The application of other metals has also been examined. For example, Ernst et al. [8] successfully fabricated a nickel/ceramic composite membrane which possessed high permeability and selectivity to hydrogen. However, inorganic membranes are generally fraught with complexities in fabrication, difficulties in prediction of permeation properties and require high operating costs [12].

On the other hand, the advantageous properties of polymeric membranes like ease of processing and appropriate robustness may dominate the application of organic membranes over inorganic counterparts. However, the main drawback of polymeric membranes for hydrogen separation compared to inorganic is their limitation in operating temperature range. The coincidence of unfavorable diffusivity selectivity and solubility selectivity for selected gas pairs like $H_2$ and $CO_2$ has also restrained the application of polymeric membranes for separation of such gases. This mainly stems from the negligible difference in kinetic diameters of gas molecules. In addition, it is well shown that $CO_2$-induced plasticization severely deteriorates the separation properties of membrane prepared from glassy polymers including polyimides [13]. Therefore, swelling of the interstitial spaces between polymer chains due to penetrant-induced plasticization may also play a part in deteriorating the separation performance based on size exclusion mechanism [14].

The presence of challenges has resulted in limited number of reports on the development of polymeric membranes for hydrogen separation. In a recent research study by our group [15] polymeric membranes were successfully fabricated with high selectivity for $H_2/CO_2$. It was observed that chemical surface modification of 6FDA-durene offers membranes with gas selectivity of over 100 for $H_2/CO_2$ in pure gas tests and about 42 in mixed gas tests.

The objective of this study is to fabricate high performance polymeric membranes suitable for separation and purification of hydrogen. Dense flat membranes were fabricated by employing the solution blending technique using Matrimid and PBI. Matrimid is a polyimide with high gas permeability and selectivity, high thermal stability and solvent resistance [16,17]. Similarly, PBI is a high performance polymer possessing high glass transition temperature, outstanding thermal stability and chemical resistance that makes it suitable candidate for advanced technologies like fuel cells [18–20]. The gas permeation characteristics of Matrimid/polybenzimidazole (PBI) homogenous blend membranes are evaluated. The effects of composition on miscibility, microstructure and gas separation performance of membranes are also investigated. Gas separation performance of membranes was further ameliorated through chemical cross-linking modification of blend constituents using distinct types of cross-linking agents. To our best knowledge, this is the first study focusing the exploitation of unique properties of blending high performance polymers of Matrimid and PBI for the development of specialty membranes for hydrogen separation and purification.

## 2. Experimental

### 2.1. Materials

The polyimide (Matrimid®5218) (3,3′,4,4′-benzophenone tetracarboxylic dianhydride and diamino-phenylindane) was purchased from Vantico Inc. (Luxemburg) and poly[2,2′-(1,3-phenylene)-5,5′-bibenzimidazole] (PBI) was obtained from Aldrich Chemical Company Inc. (Milwaukee, USA). Both polymer powders were dried overnight at 120 °C under vacuum prior to use. The chemical structure of polymers is shown in Fig. 1. *N*-Methyl-2-pyrolidone (NMP) was supplied by Merck and used as solvent for polymers. Cross-linking agents used in this study were *p*-xylene diamine and *p*-xylene dichloride which were supplied by Merck (Germany) and TCI Inc. (Japan), respectively. Ethanol (analytical grade) and methanol were supplied by Merck and used for density measurements and dissolution of cross-linking agents, respectively.

### 2.2. Preparation of dense flat membranes

Polymer solutions (2 wt.% polymer/98 wt.% NMP) with various compositions of 25/75, 50/50, 75/25 wt.% were prepared from Matrimid and PBI according to the following steps. Firstly, PBI in stipulated quantity was dissolved in

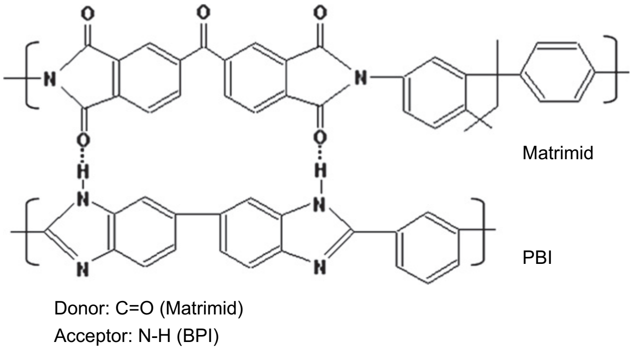

Fig. 1. Schematic representation of the chemical structure of polymers and hydrogen bonding interaction between functional groups of Matrimid and PBI.

NMP at 150 °C using a magnetic stirrer and it took about 2 days to obtain a complete dissolution. The polymer solution was filtered using a 2 μm filter to eliminate any undissolved polymer and dusts. Subsequently, Matrimid powders were added and stirring was continued for few days to allow the complete mixing of blend constituents. After degassing, polymer solutions were poured onto a silicon wafer surrounded by a metal ring. The wafers were placed in a vacuum oven and the temperature of oven was set to 100 °C to allow slow evaporation of NMP. This process was continued for about 5 days. While under vacuum, the temperature was gradually increased at the rate of 20 °C/0.5 h up to 250 °C and membranes were kept at the final temperature for overnight to assure the residual solvent removal. The as-cast membranes were collected after natural cooling.

### 2.3. Chemical modification of membranes

Round-cut pieces of membranes underwent cross-linking using a simple dipping method. A 10 wt.% solution of *p*-xylene diamine in methanol was prepared which was aimed for cross-linking of the polyimide. On the other hand, a solution composed of 2 wt.% *p*-xylene dichloride in methanol was used to cross-link PBI components. Membranes were immersed in the solutions for stipulated periods of 5 and 10 days. After taking out, membranes were immersed in fresh methanol to wash out unreacted molecules followed by drying in vacuum oven at 120 °C overnight.

### 2.4. Characterization techniques

The miscibility of membrane constituents was examined using differential scanning calorimetry (DSC). Glass transition temperature ($T_g$) of polymer films was evaluated on a Perkin–Elmer, DSC-Pyris 1 calorimeter. Approximately 5–10 mg of membrane was put in aluminum pans. Two consecutive scans from 50 to 450 °C at the heating rate 10 °C/min were performed for each sample. The $T_g$ of samples was determined as mid-point transition temperature of the second scan.

A standard displacement technique was employed to measure the density of blend films [21]. Round pieces of films were punched and weighed in air ($w_{air}$) and then in ethanol ($w_{EtOH}$). The density of polymer film was calculated using the following equation:

$$\rho_{polymer} = \frac{w_{air}}{w_{air} - w_{EtOH}} \rho_{EtOH} \tag{1}$$

where $\rho_{EtOH}$ is the density of ethanol. Five pieces of films were prepared for each sample.

The structural properties and inter-chain spacing of membranes were analyzed qualitatively on an X'Pert PRO-MRD wide-angle X-ray diffractometer (XRD) from PANalytical. The measurements were carried out by using Cu K$\alpha$ radiation with a wavelength of $\lambda = 1.54$ Å at room temperature. The scan range was from 4° to 70° with a step increment of 0.04°/s. Average *d*-spacing was determined based on Bragg's law, viz.

$$n\lambda = 2d \sin\theta \tag{2}$$

where $n$ is an integral number (1, 2, 3,...), $\lambda$ denotes the X-ray wavelength, $d$ stands for the intersegmental spacing between two polymer chains and $\theta$ indicates the diffraction angle.

Molecular simulation was performed using the Amorphous Cell procedure developed by Material Studio™ software packages, Accelrys Inc. The most stable energy-minimized configurations of polymer chains were simulated to qualitatively examine the possible chain morphology after cross-linking.

### 2.5. Gas permeability measurements

The gas permeation properties of membranes were determined by a variable-pressure constant-volume method. Detailed experimental design and procedures can be found elsewhere [22]. The rate of pressure increase ($dp/dt$) at steady state was used for the calculation of gas permeability with the following relationship:

$$P = \frac{273.15 \times 10^{10} Vl}{760AT((P_0 \times 76)/14.7)} \left(\frac{dp}{dt}\right) \tag{3}$$

where $P$ is the gas permeability of a membrane in Barrer (1 Barrer = $1 \times 10^{-10}$ cm$^3$(STP) cm/cm$^2$ s cmHg), $V$ is the volume of the down-stream chamber (cm$^3$), $A$ refers to effective area of the membrane (cm$^2$), $l$ is the membrane thickness (cm), $T$ is the operating temperature (K) and the feed gas pressure in the up-stream is given by $P_0$ in psia.

The pure gas permeability was obtained in a sequence of $H_2$, $N_2$, $CH_4$ and $CO_2$ at 35 °C for each piece of membrane. The $H_2$ permeability test was conducted at 3.5 atm, while the testing pressure for other gases was 10 atm. The ideal selectivity of a membrane for gas A to gas B was evaluated as follows:

$$\alpha_{A/B} = \frac{P_A}{P_B} \tag{4}$$

The apparent diffusion coefficient ($D_{app}$) was obtained by using time-lag ($\theta$) method as follows:

$$D_{app} = \frac{L^2}{6\theta} \tag{5}$$

where $\theta$ is the diffusion time-lag. The apparent solubility coefficient ($S_{app}$) was subsequently calculated through the following expression:

$$S_{app} = \frac{P}{D_{app}} \tag{6}$$

## 3. Results and discussion

### 3.1. The miscibility and other characteristics of blends

Extensive studies have given countenance to the marked role of constituents' compatibility on the phase morphology and consequently gas separation performance of blend membranes

[23]. Hence, it is well accepted that miscibility analysis should be set as a prerequisite in the design of superior gas separation membranes. The miscibility of polyimides and PBI has been the subject of few studies [18,24–26]. All these reports unanimously corroborate the miscibility of these polymer pairs. However, referring to those reports, either the analyses have been carried out in a limited range or the grade of materials is found to be different from what was used in this study. Therefore, the miscibility of as-cast blend membranes was examined over the various ranges of compositions. Obtaining clear and transparent films and the presence of a single $T_g$ in calorimetry thermograms have been verified to be appropriate indicatives of miscibility in the molecular level. All the films prepared from the blends of Matrimid and PBI were transparent and homogenous and no symptom of phase separation was detected by visual observation. The DSC thermograms of the blend membranes with various compositions are depicted in Fig. 2. These results also confirm the miscibility of blends by showing the presence of composition dependent single $T_g$ that all fall in the midst of each individual components' $T_g$ value. In addition, a positive shift in $T_g$ was observed with an increase in PBI composition which was in fact due to the higher $T_g$ of PBI. The glass transition temperature of polymer blends was calculated theoretically by using the Fox equation which is expressed as follows:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}} \tag{7}$$

where $T_{g1}$ and $T_{g2}$ are glass transition temperatures (K) of individual polymers while $W_1$ and $W_2$ indicate mass fractions of each component in the blend.

The $T_g$–composition curve of the blend system is shown in Fig. 3. It can be seen that the connection of experimental data points forms a sigmoidal curve. The comparison of experimental and theoretical results indicates that the Fox equation can almost successfully predict the $T_g$ values for the blends rich in Matrimid. However, the trend is followed by a negative deviation in prediction of $T_g$ as the composition of PBI is further increased. Interestingly, the deviation turns to the positive prediction once the composition of PBI in the blend system exceeds 65 wt.%. It should be noted that deviation from the theoretical results is a common phenomenon which is seen in behavior of majority of polymer blends and is generally a reflection of the specific interactions between the components. The nature of miscibility of Matrimid/PBI is believed to be the intense hydrogen bonding between N–H group of PBI and C=O group of Matrimid which provides a specific interaction for intermolecular compatibility [18,24,25]. This strong interaction has been confirmed by various techniques including FTIR through which Karasz et al. [27] observed shifts in N–H bond of PBI and carbonyl group of Matrimid. The schematic representation of this interaction is shown using dotted lines in Fig. 1.

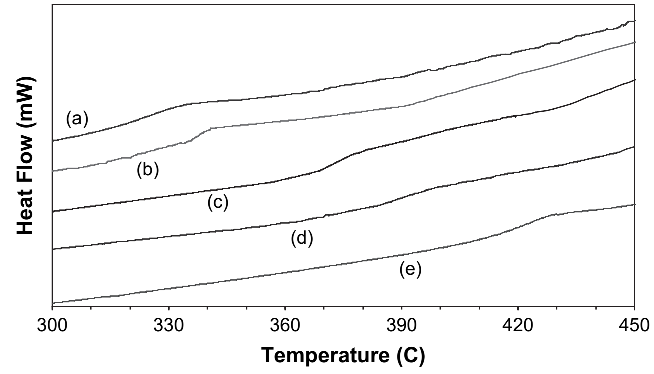

Fig. 2. DSC thermograms of the polymer blend membranes and individual constituents: (a) 0, (b) 25, (c) 50, (d) 75, and (e) 100 wt.% PBI composition.

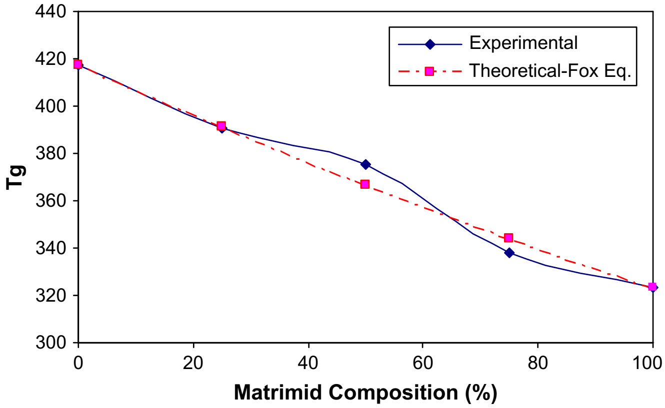

Fig. 3. Composition dependency of $T_g$ and comparison with theoretical values predicted by Fox equation.

## 3.2. Gas separation characteristics of blend membranes

Basically, potential use of polymeric blends for the transport and separation of gaseous systems entails a dexterous control over the phase morphology and interfacial interaction of blend components [28,29]. The confirmed miscibility may satisfy this prerequisite criterion for the use of Matrimid/PBI blends for gas separation. Table 1 provides the results of gas permeability measurements and ideal selectivity of blend membranes. The results denote a general decline in gas permeability with an increase in PBI concentration. It can be found that the decrease in gas permeability of membranes commensurate with kinetic diameter of gas molecules. In other words, gases with larger kinetic diameter experience more decrease in permeability with the increase of PBI content. The instrumental consequence of this behavior was the melioration in selectivity of selected gas pairs. For example, data in Table 1 show that the selectivity of $H_2/CO_2$ and $H_2/N_2$ increases by about 1.5-fold and reaches to about 9.43 and 260.47, respectively. Interestingly, quite similar improving trend was observed in the selectivity of $CO_2/CH_4$ in which there is a minor difference in size of these molecules and ideal selectivity of this gas pair reached to about 60. It is worthwhile to mention that the separation of this gas pair is of paramount importance in processing of natural gas. Thus considering the large amount of production, any small improvement in separation efficiency could result in substantial cost reduction in processing of natural gas.

Table 1
The permeability and ideal gas selectivity of polymer blend membranes with various compositions

| Membrane constituents | Permeability (Barrer) | | | | Ideal selectivity | | |
|---|---|---|---|---|---|---|---|
| | $H_2$ | $N_2$ | $CH_4$ | $CO_2$ | $H_2/N_2$ | $H_2/CO_2$ | $CO_2/CH_4$ |
| Matrimid®5218 | 27.16 | 0.280 | 0.210 | 7.00 | 97.00 | 3.88 | 33.33 |
| Matrimid/PBI (75/25 wt.%) | 19.72 | 0.163 | 0.130 | 4.19 | 120.98 | 4.07 | 32.23 |
| Matrimid/PBI (50/50 wt.%) | 13.06 | 0.072 | 0.045 | 2.16 | 181.38 | 6.05 | 48.00 |
| Matrimid/PBI (25/75 wt.%) | 5.47 | 0.021 | 0.0097 | 0.58 | 260.47 | 9.43 | 59.79 |
| PBI[a] | 0.6 | 0.0048 | 0.0018 | 0.16 | 125 | 3.75 | 88.88 |

1 Barrer = $1 \times 10^{-10}$ $cm^3$(STP) cm/$cm^2$ s cmHg; testing temperature: 35 °C.
[a] From Ref. [34].

The gas selectivity of a membrane for a gas pair is the ratio of their individual permeability coefficients, while the gas permeability ($P$) is a product of solubility ($S$) and diffusivity ($D$) coefficients which are highly dependent on the nature of penetrant and the membrane material and morphology. These coefficients jointly control the overall permeability of a membrane. Table 2 provides the calculated values of the diffusivity and solubility coefficients of the membranes developed in this study. It seems that the interrelation between the size of gas molecules and changes in permeability as well as the presence of interaction between the components fortify the idea that the possible reason for changes in transport properties of membranes might have been the effect of PBI on membranes' morphology in a molecular level. Based on the solution-diffusion mechanism, the present experimental results imply that the incorporation of PBI results in the enhanced stiffness and decreased spacing between polymer chains with little changes in solubility selectivity. In addition, it is well documented that free volume is a determining factor in gas transport properties of a membrane [30,31]. Therefore, the free volume analysis was performed in order to investigate the effect of incorporation of PBI on microstructure and how the strong interaction between blend components can alter the transport properties of membranes.

The fractional free volume (FFV) calculations were based on the following equations:

$$\mathrm{FFV} = \frac{V_{\mathrm{sp}} - V_0}{V_{\mathrm{sp}}} \tag{8}$$

$$V_0 = 1.3V_{\mathrm{W}} \tag{9}$$

$$V_{\mathrm{sp}} = 1/\rho \tag{10}$$

where $V_{\mathrm{sp}}$ is the specific volume of polymer film ($cm^3$/g) and $V_0$ is the volume occupied by the chains ($cm^3$/g). The values of Van der Waals volumes ($V_{\mathrm{W}}$) for individual polymers were obtained by applying group contribution method [32]. According to Bondi [33], Eq. (9) provides a good approximation for the evaluation of $V_0$ based on the Van der Waals volume. Moreover, $\rho$ represents the density (g/$cm^3$) of polymer films which was measured experimentally. The corresponding values of $V_{\mathrm{W}}$ and $M$ for blends were calculated using the mixing rules.

The results of measurements and calculations are shown in Table 3. Data in this table indicate that Matrimid and PBI possess the maximum (0.268) and the minimum (0.116) fractional free volumes, respectively. These values are in good agreement with other reports [13,34]. The difference in FFV of these materials possibly stems from the difference in chemical structure [30]. It can be seen from Fig. 1 that Matrimid and PBI are quite similar in structure of backbone and repeating units. However, it is expected that the presence of few side oxygen groups as well as large methyl groups in the structure of Matrimid does not allow the polymer chains to come closer. Furthermore, molecular simulation is found to be a very useful tool in analysis of the properties of membranes [35]. Application of molecular simulation study on the configuration and conformations of polymer chains corroborated our hypothesis. As it is presented in Fig. 4, clearly a better chain packing can be observed between the PBI macromolecules. However, in contrast to PBI, there exists a relatively larger free volume formed in the structure of Matrimid chains which mainly occurs in the junction of two repeating units where the bulky methyl groups provide spatial hindrance against well chain packing. It should be noted this hindrance is large enough

Table 2
Gas diffusion coefficients and solubility coefficients of polyimide, blend membranes and modified blend membranes

| Membrane constituents | $D$ ($\times 10^{-8}$ $cm^2$/s) | | | | $S$ ($\times 10^{-2}$ $cm^3$(STP)/$cm^3$ cmHg) | | | |
|---|---|---|---|---|---|---|---|---|
| | $H_2$ | $N_2$ | $CH_4$ | $CO_2$ | $H_2$ | $N_2$ | $CH_4$ | $CO_2$ |
| Matrimid®5218 | 174.0 | 0.413 | 0.093 | 0.897 | 0.16 | 0.68 | 2.26 | 7.80 |
| Matrimid/PBI (75/25 wt.%) | 136.0 | 0.312 | 0.061 | 0.572 | 0.15 | 0.52 | 2.12 | 7.32 |
| Matrimid/PBI (50/50 wt.%) | 94.0 | 0.144 | 0.022 | 0.311 | 0.14 | 0.50 | 2.03 | 6.95 |
| Matrimid/PBI (25/75 wt.%) | 44.5 | 0.044 | 0.005 | 0.088 | 0.12 | 0.48 | 1.85 | 6.62 |
| Matrimid/PBI (25/75 wt.%) − 5 days PXDC | 43.8 | 0.040 | 0.009 | 0.070 | 0.12 | 0.47 | 1.87 | 6.50 |
| Matrimid/PBI (25/75 wt.%) − 10 days PXDC | 33.9 | 0.030 | 0.008 | 0.048 | 0.12 | 0.46 | 1.86 | 6.41 |
| Matrimid/PBI (25/75 wt.%) − 5 days PXDA | 34.4 | 0.032 | 0.003 | 0.034 | 0.12 | 0.47 | 1.82 | 6.13 |
| Matrimid/PBI (25/75 wt.%) − 10 days PXDA | 32.1 | 0.029 | 0.002 | 0.023 | 0.11 | 0.46 | 1.81 | 6.22 |

Table 3
The effect of blend composition on the physical properties and fraction of free volume of membranes

| Membrane constituents | $M$ (g/mol) | $\rho$ (g/cm$^3$) | $V_w$ (cm$^3$/mol) | $V_0$ (cm$^3$/g) | $V_{sp}$ (cm$^3$/g) | FFV |
|---|---|---|---|---|---|---|
| Matrimid®5218 | 568.6 | 1.172 | 273.1 | 0.624 | 0.853 | 0.268 |
| Matrimid/PBI (75/25 wt.%) | 469.5 | 1.192 | 229.9 | 0.637 | 0.839 | 0.241 |
| Matrimid/PBI (50/50 wt.%) | 399.6 | 1.244 | 199.6 | 0.649 | 0.804 | 0.193 |
| Matrimid/PBI (25/75 wt.%) | 347.9 | 1.274 | 177.1 | 0.662 | 0.785 | 0.157 |
| PBI | 308 | 1.311 | 159.8 | 0.674 | 0.763 | 0.116 |

that results in the chain conformational rotation at the junction of repeating units of Matrimid.

Therefore, in consistence with data shown in Table 1, the FFV of membrane films undergoes a stepwise decline by an increase in PBI composition. It should be noted that in addition to this phenomenon, the formation of strong hydrogen bonding between blend components which was not present in any of the individual polymers may also contribute to the diminishment of FFV by keeping the distinct polymer chains in the minimum interstitial distances. This hydrogen bonding also restrains the polymer chain from free rotation and mobility. The augmentation of glass transition temperature by increasing the PBI composition is a sign of enhancing chain stiffness. The increase in density as a result of increase in the PBI content in the blend membrane can be considered as another evidence for amplified polymer chain packing throughout the microstructure of resultant membranes.

The XRD analysis was performed in order to obtain further information about the effect of blending on microstructure and $d$-spacing of membranes. As shown in Fig. 5, the indicative peak of Matrimid is a merger of two amorphous peaks with $d$-spacings of 3.86 and 5.53 Å. An increase in PBI concentration gradually vanishes the peak of Matrimid at 5.53 Å and finally the sample containing 75 wt.% PBI possesses almost a mere peak at 3.86 Å. The shift in $d$-spacing indicates a shift of interstitial chain–chain distance and free volume distribution toward a tighter and narrower structure.

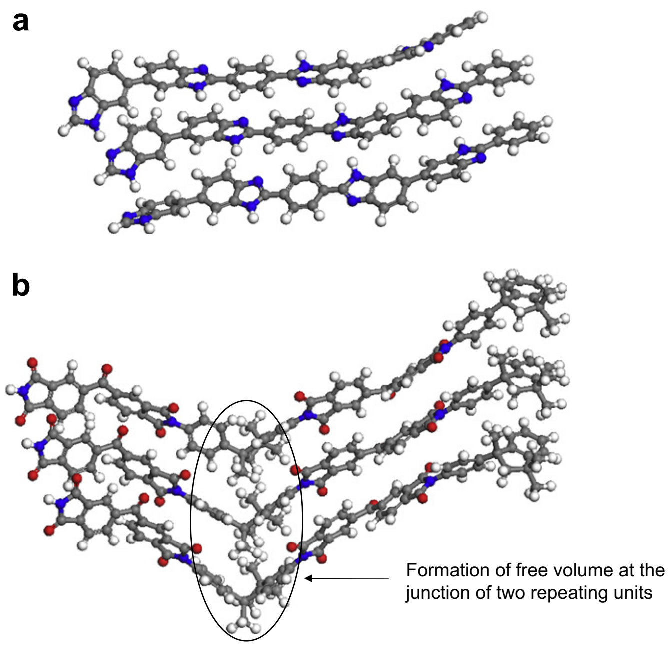

Fig. 4. Analysis and comparison of the status of free volume in the structure of (a) PBI and (b) Matrimid membranes using molecular simulation.

The results of microstructural analysis of polymer blends indicate that the decrease in permeability and enhancement in gas separation performance can be attributed to the contribution of reduction in fractional free volumes and $d$-spacings, restrictions in mobility of polymer chains and increase in chain packing density. These changes highly affect the diffusivity selectivity and stabilize the membrane structure against $CO_2$-induced swelling phenomena and consequently result in significant increment in selectivity for $H_2/CO_2$, $H_2/N_2$, and $CO_2/CH_4$ separations. In fact, one of the main advantages of developed blend membranes in this study is exploiting benign properties of PBI for gas separation that otherwise could not be fabricated as a free-standing membrane due to its poor processibility and high degree of brittleness.

### 3.3. Effect of chemical modification on performance of membranes

Abundance of reports [16,36–38] on the successful improvement of gas separation performance of chemically modified polymeric membranes initiated the idea of applying this technique in this study. The presence of five carboxyl group in repeating unit of Matrimid and two N–H groups in repeating unit of PBI provides a great potential that these polymers get involved in any modification reactions. Thus, Matrimid/PBI blend membranes with composition of 25/75 wt.% which exhibited the superior performance to other compositions were chemically modified using two different cross-linking agents. The proposed mechanisms for cross-linking process are shown

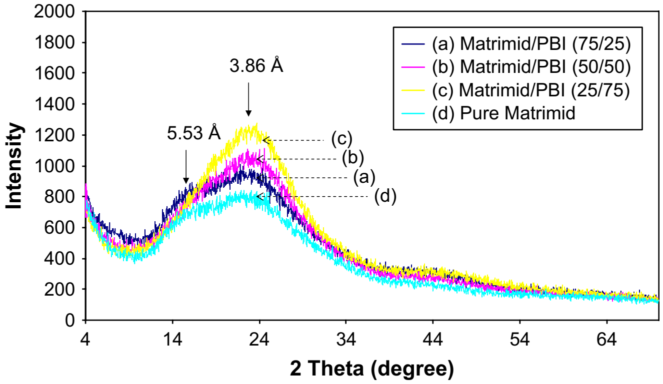

Fig. 5. The XRD spectra of blends depicting the effect of composition on microstructure of membranes.

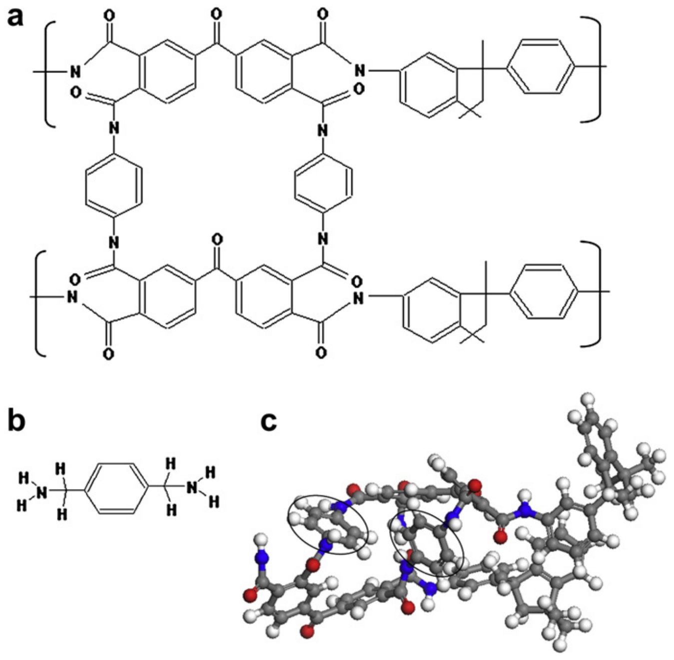

Fig. 6. (a) Proposed mechanism for the chemical cross-linking modification of Matrimid component of blend using *p*-xylene diamine. (b) Chemical structure of *p*-xylene diamine and (c) possible chain morphology and configuration of *p*-xylene diamine cross-linked Matrimid (cross-linking agents are specified by ovals).

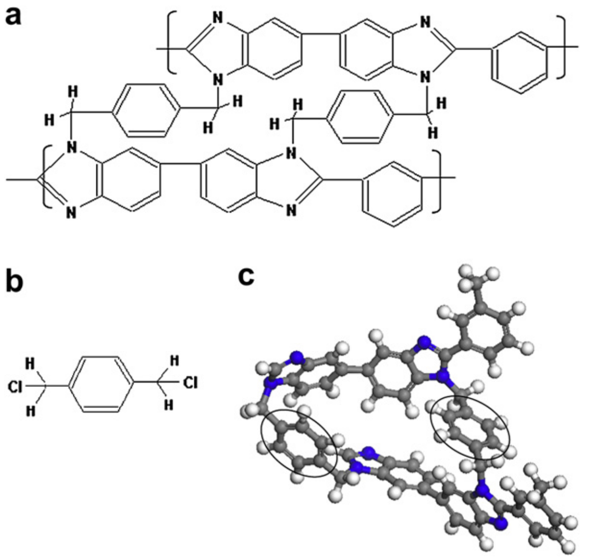

Fig. 7. (a) Proposed mechanism for the chemical cross-linking modification of PBI component of blend using *p*-xylene dichloride. (b) Chemical structure of *p*-xylene dichloride and (c) possible chain morphology and configuration of *p*-xylene dichloride cross-linked PBI (cross-linking agents are specified by ovals).

in Figs. 6 and 7. The most stable energy-minimized configurations for cross-linked PBI and Matrimid are also illustrated in these figures. According to these schematics, in the course of chemical modification, *p*-xylene dichloride molecules attack at the N—H groups of PBI and *p*-xylene diamine molecules react with amide groups of Matrimid. Obviously, it seems that the chemical structure of Matrimid contains a polar bond (ether groups) which may result in lesser linearity of the polymer backbone as well as a lesser degree of molecular packing compared to PBI.

The chemical modification of polyimides [36,37] and specifically Matrimid [16] using *p*-xylene diamine has been extensively investigated and verified. Similarly, the successfulness of chemical modification of PBI with *p*-xylene dichloride through this mechanism was previously confirmed by our group where Wang et al. [39] employed FTIR and XPS techniques and confirmed the cross-linking of PBI membranes post-treated for up to 24 h. Therefore, it is anticipated that the reaction starts with the modification of functional groups at the outermost surface of membranes which are easily accessible to the cross-linking agents. In the meantime, swelling of membrane structure by the carrier (i.e., methanol) provides the opportunity for the transport of the cross-linking agents to penetrate inside the membranes and access the functional groups of polymers within the membrane structure. The process of cross-linking at the internal structure of membrane is expected to decline with the progress of superficial modification which seems to impede further inward penetration of agents.

Gas permeability and ideal gas selectivity of modified membranes with *p*-xylene dichloride and *p*-xylene diamine are presented in Tables 4 and 5, respectively. It can be seen from the results that chemical modification of membranes clearly affects the gas permeability of membranes and a gradual decline in gas permeability was resulted by prolonging the immersion time. Interestingly, the extent of depletion in permeability follows the similar trend of dependence to the size of gas molecules as it was observed in permeability of blend films. Consequently, this characteristic phenomenon results in variation in selectivity performance of membranes. According to Table 4, slight improvements were achieved in selectivity of $H_2/N_2$ and $H_2/CO_2$ after cross-linking of PBI, but the selectivity of $CO_2/CH_4$ underwent a slight decrease. On the other hand, as shown in Table 5, a similar declining trend is observed for the membranes upon cross-linking of Matrimid phase. Considering the structural models in Figs. 6 and 7 and the results in Table 2, the opposite trends in selectivity of gas pairs upon cross-linking can be attributed to the combinatory effects the configuration changes in the polymeric structure of membranes as well as the inherent molecular size difference of gas molecules.

A comparison of the results shown in Tables 4 and 5 for the corresponding chemically modified membranes reveals the fact that treatment with *p*-xylene diamine has spelled greater effect on the transport properties of membranes which was noticed from the level of changes in permeability values. As a result, the $H_2/CO_2$ selectivity of the resultant membrane has reached up to about 26 after 10 days modification with *p*-xylene diamine which is considerably higher than that of other samples and the corresponding individual components.

The effect of chemical cross-linking on gas permeability decay of membranes is probably due to the tighter interstitial spaces among the chains and restriction in vibration and mobility of polymer chains and side groups attached to the backbone.

Table 4
The effect of chemical modification using *p*-xylene dichloride on gas permeability and selectivity of blend membranes

| Membrane constituents | Permeability (Barrer) | | | | Ideal selectivity | | |
|---|---|---|---|---|---|---|---|
| | $H_2$ | $N_2$ | $CH_4$ | $CO_2$ | $H_2/N_2$ | $H_2/CO_2$ | $CO_2/CH_4$ |
| Matrimid®5218 | 27.16 | 0.280 | 0.210 | 7.00 | 97.00 | 3.88 | 33.33 |
| Matrimid/PBI (25/75 wt.%) | 5.47 | 0.021 | 0.0097 | 0.580 | 260.47 | 9.43 | 59.79 |
| Matrimid/PBI (25/75 wt.%); duration = 5 days | 5.34 | 0.019 | 0.0175 | 0.453 | 281.05 | 11.79 | 31.03 |
| Matrimid/PBI (25/75 wt.%); duration = 10 days | 4.04 | 0.014 | 0.0158 | 0.306 | 288.57 | 13.02 | 19.36 |

1 Barrer = $1 \times 10^{-10}$ $cm^3$(STP) cm/$cm^2$ s cmHg; testing temperature: 35 °C.

Table 5
The effect of chemical modification using *p*-xylene diamine on gas permeability and selectivity of blend membranes

| Membrane constituents | Permeability (Barrer) | | | | Ideal selectivity | | |
|---|---|---|---|---|---|---|---|
| | $H_2$ | $N_2$ | $CH_4$ | $CO_2$ | $H_2/N_2$ | $H_2/CO_2$ | $CO_2/CH_4$ |
| Matrimid®5218 | 27.16 | 0.280 | 0.210 | 7.00 | 97.00 | 3.88 | 33.33 |
| Matrimid/PBI (25/75 wt.%) | 5.47 | 0.021 | 0.0097 | 0.580 | 260.47 | 9.43 | 59.79 |
| Matrimid/PBI (25/75 wt.%); duration = 5 days | 4.09 | 0.0152 | 0.0046 | 0.209 | 269.1 | 19.56 | 45.43 |
| Matrimid/PBI (25/75 wt.%); duration = 10 days | 3.60 | 0.0132 | 0.0031 | 0.138 | 271.2 | 26.09 | 44.51 |

1 Barrer = $1 \times 10^{-10}$ $cm^3$(STP) cm/$cm^2$ s cmHg; testing temperature: 35 °C.

As a result, diffusion of penetrant gas molecules through the membrane is hindered and gas permeability decreases. Therefore, in agreement with a similar report [37], the enhanced selectivity performance of membranes is mainly achieved by the diffusivity selectivity of membranes. This was confirmed by examination of the *d*-spacing between the polymer chains through XRD analysis. According to Fig. 8, the interstitial space between the polymer chains has shifted from the original value of 3.86 Å down to minimum 3.36 Å after cross-linking with *p*-xylene diamine for 10 days. The order of shift is proportional to the period of modification and it is more pronounced for samples modified with *p*-xylene diamine. Furthermore, the molecular modeling of the systems shows that cross-linking of Matrimid results in relatively more compact structure compared to that of PBI. It seems that bond breaking reaction at the imidazole sites of Matrimid during the cross-linking provides this flexibility for polymer chains to find better configuration. However, this phenomenon is not observed for cross-linking of PBI due to its relatively rigid polymer structure. As a result, the cross-linking agent seems to act as a bridge between the lateral polymer chains.

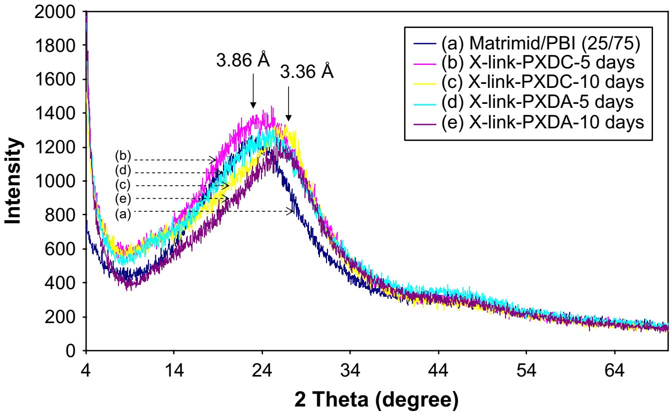

Fig. 8. The XRD spectra of blend membranes cross-linked with *p*-xylene dichloride (PXDC) and *p*-xylene diamine (PXDA) for different periods of time.

Furthermore, it is anticipated that cross-linking of polymer chains offers a special integrity and a structural stability which protect the membrane from $CO_2$-induced swelling and plasticization. One possibility for more intense influence of cross-linking with *p*-xylene diamine compared to *p*-xylene dichloride might be the difference in concentration of the cross-linking agents in the solution. It could also be ascribed to the difference in activity of functional groups of constituents toward corresponding cross-linking agents. In such a case, results may indicate that the cross-linking efficiency of Matrimid is considerably higher than that of PBI.

It seems also worthwhile to consider this issue with respect to the size of the cross-linking agents. Structural analysis of *p*-xylene dichloride and *p*-xylene diamine by molecular simulation denotes the fact that although these chemical agents have

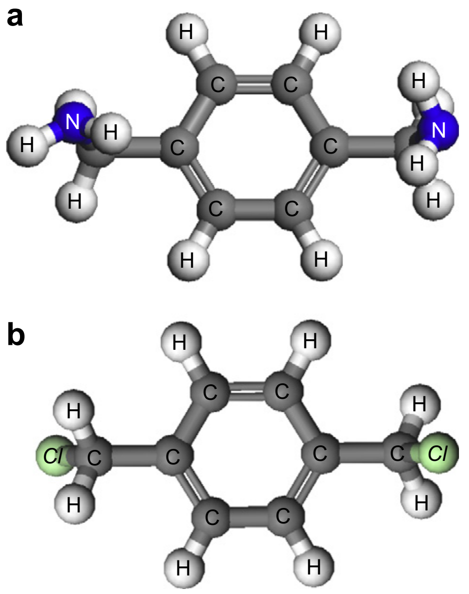

Fig. 9. Molecular simulation analysis of chemical structure of cross-linking agents: (a) *p*-xylene diamine and (b) *p*-xylene dichloride.

similar molecular width (around 3 Å measured by Material Studio software), there is only a minor molecular length different between these two cross-linking agents, (7.9 and 8.0 Å, for *p*-xylene dichloride and *p*-xylene diamine respectively). The structure and configuration of cross-linking agents at the minimum energy are provided in Fig. 9. According to this figure, it can be seen that except the benzene group that both cross-linking agents have in common, the rest of the molecules have not much difference in the spatial configuration. As a result, the difference in the size of these molecules is not large enough to be justified for the difference in penetration rate of cross-linking agents into the membrane structure.

## 4. Conclusions

Blend membranes prepared from Matrimid and PBI are completely miscible in whole ranges of compositions in molecular level. This property is given to the blends by strong hydrogen bonding interaction among the functional groups of components. Therefore, incorporation of PBI resulted in improvements in gas separation performance of Matrimid which was caused by increase in chain packing density and hindrance in segmental mobility of polymer chains and its consequence effects on diffusivity selectivity. This was confirmed by analysis of microstructure of membranes. Chemical modification was found to be an instrumental means for tailoring performance of membranes for separation of selected gas pairs. However, distinguished behaviors were observed for blend membranes toward cross-linking agents. The effect of *p*-xylene diamine in progressive performance of membranes was more pronounced compared to *p*-xylene dichloride. The Matrimid/PBI (25/75 wt.%) blend membrane cross-linked with *p*-xylene diamine exhibits the best performance with $H_2/CO_2$ selectivity of about 26 which was due to high chain packing density and restrictions in segmental mobility of polymer chains.

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