Fabrication of 6FDA-durene membrane incorporated with zeolite T and aminosilane grafted zeolite T for CO₂/CH₄ separation

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Abstract. In the present work, zeolite T and aminosilane grafted zeolite T are embedded into 6FDA-durene polyimide phase for the fabrication of mixed matrix membranes (MMMs). FESEM images demonstrated that the improvement of interfacial adhesion between zeolite and polymer phases in MMM loaded with aminosilane grafted zeolite T was not significant as compared to zeolite T/6FDA-durene MMM. From the gas permeation test, CO₂/CH₄ selectivity up to 26.4 was achieved using MMM containing aminosilane grafted zeolite T, while MMM loaded with ungrafted zeolite T showed CO₂/CH₄ selectivity of 19.1. In addition, MMM incorporated with aminosilane grafted zeolite T particles successfully lies on Robeson upper bound 2008, which makes it an attractive candidate for CO₂/CH₄ separation.

1. Introduction
Membrane-based technology has received world-wide attention over the past decades for gas separation applications. Among conventional separation techniques such as absorption, adsorption and cryogenic, membrane process is preferable because of its low operating cost and capital investment, low space requirement, energy efficiency and environmental-friendly [1]. Membrane materials can be categorized into polymeric, inorganic and mixed matrix membrane (MMM). Polymeric membrane has been widely used in industrial application due to its advantages such as cheap and easy to fabricate. However, the upper bound curve reported by Robeson demonstrates that the current polymeric membrane has reached a tradeoff between gas permeability and gas pair selectivity [2]. On the other hand, even though inorganic membrane exhibits higher gas separation performance, it is limited due to poor mechanical strength and high fabrication cost. On the other hand, fabrication of MMMs has been identified as one of the emerging strategies for the enhancement of the performance of membrane materials by embedded inorganic fillers into polymer phases. This type of membrane combines the characteristics of polymer material and properties of inorganic fillers [3].

Zeolites have attracted much attention in the fabrication of MMM due to their narrow pore distribution, well-defined repeating pore structures and great molecular sieving property [4]. Zeolite T exhibits a great potential in CO₂/CH₄ separation due to its small pores of 0.36nm x 0.51nm [5]. Hence, zeolite T has been used as the selective fillers in the MMMs fabrication for gaseous and organic/aqueous mixtures separations [6, 7]. Nevertheless, the fabrication of MMMs with minimum defects are normally accompanied with several challenges. Most of the researches confronted difficulties in attaining MMMs with ideal
characteristics such as good compatibility and excellent interfacial adhesion between the filler and polymer. Hereafter, some of the techniques have been proposed to enhance the interfacial properties of filler-polymer. Silane coupling agents are commonly proposed for the modification of the filler surface, which covalently bind the filler and polymer phase and subsequently improve the filler-polymer adhesion properties.

Pechar et al. [8] used 3-aminopropyltrimethoxysilane (APTMS) for the improvement of the compatibility between zeolite ZSM-2 and polyimide phase. They reported that MMM loaded with APTMS-grafted ZSM-2 particles demonstrated the reduction in both gas permeability and gas pair selectivity compared to pristine membrane. The decrement of the separation performance might be due to the partial blockage of zeolite pores by APTMS. Similar results were also obtained by Clarizia et al. [9] when they incorporated silane-grafted NaA zeolite into polyethetherketone (PEEK). On the other hand, Nik et al. [10] reported that the dispersion of particles enhanced when grafted MOF-199 was incorporated into 6FDA-ODA polyimide phase. They also found that CO₂ permeability and CO₂/CH₄ selectivity increased as compared to ungrafted MOF-199/6FDA-ODA MMM. Li et al. [8] grafted zeolite 3A, 4A and 5A using 3-aminopropylmethyldiethoxy (APMDES). The incorporation of grafted zeolites into polymer phase reduced the rigidification of polymer chain and partial pore blockage, which subsequently enhanced both gas permeability and gas pair selectivity of this membrane as compared to MMM loaded with ungrafted zeolite. Overall, silane grafted zeolite has successfully improved the interfacial contact between the filler and polymer phase and thus, the separation properties of MMM.

To our best knowledge, there is no research work reporting on the fabrication of MMM loaded with aminosilane–grafted zeolite T particles for CO₂/CH₄ separation. Therefore, in the present work, zeolite T has been grafted with AAPTMS silane coupling agent before incorporated into 6FDA-durene polyimide phase for the formation of MMM. The structure and physicochemical properties of the resultant membranes were investigated by using different analytical tools. In addition, the permeation properties of MMM incorporated with aminosilane grafted zeolite T particles was assessed and compared with ungrafted zeolite T incorporated MMM.

2. Methodology

2.1. Chemicals and gases
6FDA-durene polymer and zeolite T particles were synthesized from our laboratory. For the preparation of aminosilane grafted zeolite T particles, N-(2aminoethy1)-3-aminopropyltrimethoxysilane (AAPTMS, C₆H₂3N₂O₃Si, ≥ 97% purity, Merck) and toluene (C₆H₅CH₃, 99.8% purity, Sigma Aldrich) were used as received. For the fabrication of MMM, dichloromethane (DCM, ≥ 99.8% purity) were purchased from Sigma Aldrich and used without further purification. In addition, the purified methane and carbon dioxide gases (purity of 99.9995%) used for gas permeation testing were obtained from Gas Walker Sdn Bhd and used as received.

2.2. Synthesis of zeolite T and aminosilane grafted zeolite T particles
Zeolite T particles was synthesized via sonochemical-assisted hydrothermal growth method at molar composition of SiO₂ : 0.04Al₂O₃ : 0.26Na₂O : 0.09K₂O : 14H₂O as reported in our previous work[5]. Meanwhile, aminosilane grafted zeolite T was prepared using the method reported by Li et al. [8]. Zeolite T particles, AAPTMS silane coupling agent and toluene were mixed and stirred for 24 h at room temperature under nitrogen purge. The aminosilane grafted zeolite T particles were then recovered by centrifugation and washed with methanol before dried in an oven at 110°C for 24 h.

2.3. Fabrication of pristine 6FDA-durene and MMs
Pristine 6FDA-durene membrane was fabricated based on the method reported in our previous work [5]. 2% w/v 6FDA-durene polymer solution was cast on Petri dish prior to dry and thermal anneal at
250°C in the vacuum oven. On the other hand, MMMs contained 1 wt% of zeolite T particles (ungrafted and grafted) in 6FDA-durene polymer phase were fabricated by solution blending method [7]. 6FDA-durene polymer solution was added into zeolite T suspension before casted on Petri dish. The cast film was then dried and annealed in the vacuum oven for 24 h.

2.4. Characterization of particles and membranes
The functional groups presence in ungrafted and aminosilane grafted zeolite T particles were observed using Fourier transform infrared spectrometer (Perkin Elmer Spectrum One). The spectrum of the particles was obtained using KBr method from the acquisition of 50 scans in the wavelength range of 450-4000 cm\(^{-1}\) under the transmission mode.

Subsequently, the resultant membranes were characterized using FESEM, EDX and DSC. The morphology of membrane was attained using field emission scanning electron microscope (FESEM, Zeiss Supra 55 VP) operated at 10 kV under vacuum condition. In addition, the distribution of the particles in the polymer matrix was investigated using Oxford Instrument Inca energy dispersion X-ray (EDX) mapping. The glass transition temperature (\(T_g\)) of the membrane samples was analyzed using differential scanning calorimetry (DSC), Thermal Analysis (TA) instruments DSC Q2000. The \(T_g\) of samples were determined using the midpoint temperature of the transition region in the second heating cycle.

2.5. Gas Permeation Measurements
Single gas permeation properties were measured using custom-built gas permeation test rig at pressure of 3.5 bar and temperature of 30°C for pure gases of CO\(_2\) and CH\(_4\). The detailed explanation on the testing setup and procedure were described elsewhere [1]. The permeability of CO\(_2\) and CH\(_4\) was determined using equation (1) as follows:

\[
P = \frac{V_p t}{A_m(p_f - p_i)}
\]

where \(P\) refers to the membrane permeability (Barrer), \(V_p\) is the permeate flow rate \((\text{cm}^3(\text{STP})/\text{s})\), \(t\) is the thickness of membrane (cm), \(A_m\) refers to the membrane area \((\text{cm}^2)\), \(p_f\) and \(p_i\) are the pressure in feed side and permeate side, respectively \((\text{cmHg})\). The gas permeability of the membrane is defined in the unit of Barrer \((1 \text{ Barrer}=1\times10^{-10}\text{cm}^3(\text{STP}).\text{cm}/\text{s}.\text{cm}^2.\text{cmHg})\).

The ideal selectivity of the membrane was calculated using equation (2) as follows:

\[
\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}}
\]

where \(\alpha\) represents the ideal selectivity of membrane.

3. Results and Discussion

3.1. Characterization of ungrafted and aminosilane grafted zeolite T particles
Figure 1 shows the FTIR spectra of ungrafted and aminosilane grafted zeolite T crystals. Based on Figure 1 (a), both of the zeolite T particles comprise the characteristic peaks at 465 cm\(^{-1}\), 575-615 cm\(^{-1}\), 720-775 cm\(^{-1}\) and 1040-1150 cm\(^{-1}\), which were consistent with those FTIR result reported in the literature for zeolite T structure [11]. The T-O bend in zeolite T topology is characterized by the peaks at 465 cm\(^{-1}\). The absorbance peaks in the range from 575 cm\(^{-1}\) and 615 cm\(^{-1}\) is attributed to the secondary building units of single 6-ring of zeolite T structure [12]. In addition, the symmetric and asymmetric stretching vibrations of double ring for zeolite T structure is characterized by the absorption bands in the region of 720-775 cm\(^{-1}\) and 1040-1150 cm\(^{-1}\), respectively.
On the other hand, it can be observed that the aminosilane grafted zeolite T demonstrates N-H bending and NH$_2$ scissoring at the characteristic peaks of 1470 cm$^{-1}$ and in the region of 1620-1650 cm$^{-1}$, respectively [13, 14]. Furthermore, based on Figure 1(b), the detection of absorption peak at 3250 cm$^{-1}$ and 3450 cm$^{-1}$ are contributed from the presence of N-H stretch and O-H stretch of the hydrogen bonded silanol group [15, 16]. The grafted zeolite T particles also demonstrates two N-H absorption bands in the region of 3300-3500 cm$^{-1}$ due to the presence of amine primary group in the chemical structure (-NH$_2$) [17]. Overall, the presence of N-H bonds in aminosilane grafted zeolite T particles confirms that the AAPTMS were successfully attached on the zeolite T surface.

![Figure 1: FTIR spectrum of ungrafted and aminosilane grafted zeolite T particles at a) lower wavenumber ((450 – 2000 cm$^{-1}$) and b) higher wavenumber ((2800-4000 cm$^{-1}$)](image)

3.2. Characterization of membranes
Figures 2 and 3 demonstrate the morphology and the dispersion of particles (ungrafted and aminosilane grafted) in the polymer phase, respectively. Based on Figure 2 (b) and (c), it can be observed that both of the membranes exhibit a good dispersion of zeolite T particles in polymer phase with no significant interfacial voids between the particle and polymer phase. The good distribution of zeolite T particles in MMM loaded with ungrafted and aminosilane grafted zeolite T particles are further verified by the homogenous dispersion of Si element in EDX mapping shown in Figure 3(a) and (b), respectively. Overall, the incorporation of aminosilane grafted zeolite T particles into 6FDA-durene polymer phase did not contribute to a significant effect on the improvement of the interfacial adhesion between the particles and polymer matrix.
Figure 2: FESEM images of a) pristine 6FDA-durene and MMMs incorporated with b) ungrafted zeolite T c) aminosilane grafted zeolite T particles

Figure 3: EDX-mapping images for MMM incorporated with a) ungrafted zeolite T and b) aminosilane grafted zeolite T particles

The glass transition temperatures ($T_g$) of the pristine 6FDA-durene and MMMs are displayed in Table 1. Referring to Table 1, the pristine 6FDA-durene and MMM loaded with ungrafted and aminosilane grafted zeolite T demonstrate glass transition temperature of 410.06°C, 425.22 °C and 426.01 °C, respectively. The enhancement of $T_g$ shown by aminosilane grafted zeolite T/6FDA-durene MMM demonstrates that the incorporation of aminosilane grafted zeolite T in the polymer matrix alters the polymer packing structure of the membrane by restricting the movement of polymer chains. In addition, the increment of $T_g$ might also be attributed to the polymer matrix rigidification.

Table 1: Glass transition temperature of the membranes fabricated in this work

| Membranes                        | Glass transition temperature, $T_g$ (°C) |
|----------------------------------|----------------------------------------|
| Pristine 6FDA-durene             | 410.06                                 |
| Ungrafted zeolite T/6FDA-durene MMM | 425.22                                |
| Aminosilane grafted zeolite T/6FDA-durene MMM | 426.01                                |
3.3. Gas separation performance
The performance of the resultant membranes was determined by using CO₂ and CH₄ single gases permeation testing. The permeability of CO₂ and CH₄ and CO₂/CH₄ selectivity of the membranes are displayed in Figure 4. Referring to Figure 4, both MMMs demonstrate higher CO₂ permeability and CO₂/CH₄ selectivity compared to pristine 6FDA-durene membrane. On the other hand, CH₄ permeability of the MMMs are lower compared to the pristine 6FDA-durene membrane.

![Figure 4: Permeabilities of CO₂ and CH₄ and CO₂/CH₄ selectivity of the membranes fabricated in the present research](image)

The increment of gas separation performance of MMMs as compared to the pristine 6FDA-durene membrane might be contributed to the presence of zeolite T particles in the polymer phase which may interrupts the interaction between the polymer chain packing and enhances the free volume in the membrane. Furthermore, the tremendous improvement of CO₂/CH₄ selectivity upon the addition of zeolite T particles (ungrafted and aminosilane grafted) might be due to the contribution of sieving and adsorption effects of zeolite T particles. Moreover, strong interaction of CO₂ with the zeolite T framework may also assist the penetration of gases through the membrane [18, 19].

Besides, as compared to ungrafted zeolite T/6FDA-durene MMM (CO₂ permeability of 844 Barrer and CO₂/CH₄ selectivity of 19.1), MMM incorporated with aminosilane grafted zeolite T particles exhibits a 2.7% decrement in CO₂ permeability with the enhancement of CO₂/CH₄ selectivity up to 38%. The improvement of separation performance of aminosilane grafted zeolite T/6FDA-durene MMM might be due to the good dispersion of zeolite T particles in the polymer phase as demonstrated in FESEM and EDX-mapping images in Figures 2 and 3, respectively. Besides, as revealed in Table 1, the increment of Tₚ of this membrane as compared to zeolite T/6FDA-durene MMM also supports its higher separation performance. In addition, the improvement of the separation performance might be also contributed from the ability of aminosilane grafted zeolite T in minimizing the transportation of gases via the unselective voids and consequently increases the selectivity of the membrane [20].

3.4 Performance Comparison with Robeson Upper Bound
Figure 5 demonstrates the Robeson plot for CO₂/CH₄ separation and the position of the data point for the membranes fabricated in the present research. Based on Figure 5, the pristine 6FDA-durene membrane lies below Robeson upperbound line 1991. Meanwhile, all the MMMs are able to surpass tradeoff curve limit 1991, where MMMs incorporated with aminosilane grafted zeolite T successfully lies on Robeson upperline 2008.
Figure 5: Gas separation performance of the membranes fabricated in the present work compared with \( \text{CO}_2/\text{CH}_4 \) Robeson’s upperbound

4. Conclusion
In the present research, zeolite-T and aminosilane grafted zeolite T particles have been incorporated into 6FDA-durene for the formation of MMM. The FTIR spectrum demonstrated that the aminosilane group was successfully grafted onto the zeolite T structure. The FESEM images showed that the grafted zeolite T/6FDA-durene MMM exhibited no significant improvement on the interfacial adhesion between particles and polymer matrix as compared to MMM loaded with ungrafted zeolite T particles. From the permeation results, the incorporation of grafted zeolite T successfully increased \( \text{CO}_2/\text{CH}_4 \) selectivity up to 38% as compared to ungrafted zeolite T/6FDA-durene MMM and subsequently successfully lies on Robeson upper bound limit 2008.

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