

## GAS PERMEATION PERFORMANCE OF POLYSULFONE-ZEOLITE 4A HOLLOW FIBER MIXED MATRIX MEMBRANE USING 3-AMINOPROPYLTRIETHOXSILANE AS SILANE AGENT

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### ABSTRACT

This study investigated the effect of silane treatment on the surface of zeolite 4A molecular sieves that were used as fillers in the production of asymmetric hollow fiber mixed matrix membrane (HFMMM). Polysulfone (PSf) was the continuous phase and the asymmetric HFMMM was spun using a simple dry/wet spinning technique. PSf-zeolite 4A HFMMM with no silane treatment was observed to suffer from severe defects due to poor adhesion between the polymer and filler's surface, rendered the membrane to be totally unselective for O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> separations. The Dynasylan® Ameo or 3-Aminopropyltriethoxysilane was then grafted onto the zeolite 4A so that it could act as a molecular 'bridge', linking the filler to the polymer matrix. The results from the FESEM, DSC, FTIR analysis as well as gas permeation testing confirmed that chemical modification on zeolite surface had taken place. As for PSf-silane treated zeolite 4A HFMMM, the FESEM's cross-section view indicated good compatibility between the polysulfone and zeolite 4A and permeability measurement showed improvement in the O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> selectivities to 2.44 and 7.94 respectively. This paper also calculated the effect of zeolite 4A size on the inter-particle spacing and showed that nano-size particles provide closer inter-particle spacing, lower loading requirement and better inclusion into the active skin layer thickness.

**Key Words:** Gas separation membrane, Hollow fiber, Mixed matrix membrane, Amino silane, Surface modification

### 1.0 INTRODUCTION

Gas phase separation is a major process in chemical industry where its application stretches from feedstock treatment to product purification. From economic consideration, membrane system for gas separation has acquired great significance in industrial scenario [1]. Although polymeric membrane has been accepted as a viable alternative to conventional technology in gas separation, there is a growing interest in the development of gas separation membranes based on alternative materials such as inorganic membranes that provide not only better selectivity, but also improve thermal and chemical stability [2]. Although inorganic membranes are much more expensive than polymeric membrane, they possess advantages in term of superior permeation properties, good temperature and wear resistance, well-defined stable pore structure, and chemical inertness.

Among inorganic membranes, molecular sieving materials such as silica, zeolite and carbon molecular sieve have shown to perform well beyond the current upper boundary of permeability and selectivity trade off curve. However, they are inherently fragile, easily plagued by cracks and difficult to be transformed into a defect free and high surface area module [3]. Inorganic membranes are much more expensive than polymeric membrane. For example, zeolite membrane module would cost around

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## GAS PERMEATION PERFORMANCE OF POLYSULFONE

US\$ 3000/m<sup>2</sup> in comparison to polymeric hollow fiber module that would cost around US\$ 20/m<sup>2</sup> [4].

The limited application of molecular sieve materials due to its inherent fragility may be overcome by mixing molecular sieve particles with the more flexible polymeric material as a continuous matrix. This concept of blending of two different materials enable us to combine the superior gas separation properties of the rigid molecular sieving materials with the ease of processing of the polymers and has the potential to produce a membrane that is far superior than the current commercial polymeric membrane [5]. This membrane is referred to as a mixed matrix membrane.

In spite of numerous researches on conventional polymers in the past four decades, only a few attempts to increase gas separation membrane performance using glassy polymers-zeolite mixed matrix membranes have been reported. Most of them were for dense flat sheet mixed matrix membrane (FSMMM) configurations [6-15].

In 1994, Suer et al. [6] found that the partial incompatibility of PES chains and zeolite 13X particles contributed to the existence of cave-like porous structure around fillers. Mahajan and Koros [10] have similar observation with their Polyimide-zeolite 4A dense FSMMM. Their initial attempt to eliminate this defect was to use silane agent to graft the polymeric phase onto the fillers' surface. Better adhesion was observed but, surprisingly, both O<sub>2</sub>/N<sub>2</sub> selectivity and O<sub>2</sub> permeability were lower than the unsilylated mixed matrix membrane.

Pechar *et al.* [11,16] fabricated dense FSMMM of PI (6FDA-6FpDA-DABA) with silylated ZSM-2 and zeolite-L through the promotion of adhesion by hydrogen bonding. They successfully produced defect free mixed matrix membrane but found no enhancement in permeation performance. They suspected that partial blocking of the zeolite's pores was the cause. Li *et al.* [14], surface-modified zeolite fillers with 3-aminopropyl-diethoxymethyl silane (APDEMS) and reported that better adhesion was observed where no nano-metric voids for penetrant gas to bypass, resulting in improved selectivities. They suggested that the silane coupling with APDEMS reduced the partial pore blockage by the polymer chains.

However, recent works on polymer-zeolite mixed matrix membrane have expanded into the asymmetric hollow fiber mixed matrix membrane (HFMMM) configuration, a preferred structure for industrial application [17-19]. For example, Jiang *et al.* [17] investigated the used of self-synthesized nano-sized zeolite Beta in polyimide matrix to produce single- and dual-layer asymmetric HFMMMs. They found that more works has to be done to overcome serious defects that rendered the produced HFMMM to be too permeable ( $P_{O_2} = 758$  Barrer) and unselective ( $\alpha_{O_2/N_2} = 0.92$ ). Ismail *et al.* [19] has successfully produced HFMMM using polyethersulfone with silane-treated zeolite 4A. The resulting membranes showed selectivity for O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> of 7.26 and 46.28, respectively.

It is clear that research on HFMMM is still at its early stage. More works need to be done in order to find best combination of polymer-filler materials so that the true potential of mixed matrix membrane could be materialized. This work investigated the preparation and performance of HFMMM using polysulfone as the continuous phase with zeolite 4A treated with 3-Aminopropyl-triethoxysilane (H<sub>2</sub>N-(CH<sub>2</sub>)<sub>3</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>) as fillers. To our knowledge, there is no documentation on the use of this silane agent to modify zeolite 4A surface in the production of PSf hollow fiber mixed matrix membrane for gas separation.

## 2.0 EXPERIMENTAL

### 2.1 Material selection

The industrial grade polysulfone was supplied by BP Amoco under the trade name Udel® P-1700. It is an amorphous and a hydrophobic material and is considered a high performance engineering thermoplastic that resist degradation. It has high CO<sub>2</sub> plasticization pressure and excellent thermal and chemical stability as well as good mechanical properties. The molecular sieve filler was zeolite 4A or sodium aluminosilicate available from SIGMA®. This is a zeolite Type A containing sodium cations with 8-member ring pore opening. It is a free flowing white powder molecular sieve with particle size of 2-3 microns and nominal pore diameter of 4Å.

### 2.2 Chemical modification method of zeolite surface

In order to improve polymer zeolite adhesion, surface treatment of zeolite filler was carried out with 3-Aminopropyltriethoxysilane. This treatment enabled the polysulfone chains to adhere to the surface of zeolite 4A fillers via silane molecules. Thus silane acts as a molecular 'bridge' for strong and stable bonding. Successful modification of filler's surface with silane would also result in many other attractive properties inclusive of an improved mechanical strength and a better filler dispersion.

3-Aminopropyl-triethoxysilane is a colorless to slightly yellowish low-viscosity liquid with amine-like odor and is commercially available as Dynasytan® Ameo from Degussa AG. It is a bifunctional silane possessing a reactive primary amino group and hydrolyzable ethoxysilyl groups. The dual nature of its reactivity allows it to bind chemically to both inorganic materials (such as glass fibers, metals, mineral fillers) and organic polymers (thermosets, thermoplastics and elastomers) thus functioning as an adhesion promoter, crosslinkers and/or surface modifiers.

In this experiment, the application of silane was according to method shown by Lee *et al.* [20]. During silane treatment, 1 wt% of Dynasytan® Ameo (relative to the zeolite 4A) was hydrolyzed by mixing with a mixture of ethanol/water with weight ratio of 95/5 for 15 minutes at room temperature. The zeolite 4A was then added and stirred to the hydrolyzed solution for 30 minutes at 50°C. The mixture was transferred to a mortar and placed in an oven at 85°C in order to vaporize and remove any by-product and solvent. It was further oven dried for another 24 hours at 120°C to remove the water. The dried silane-treated zeolite 4A was ground and stored in a desiccator. The sample was later analyzed with FTIR spectroscopy.

### 2.3 Dope preparation of asymmetric mixed matrix hollow fiber membrane

Three types of polysulfone-zeolite 4A HFMMM at 10% (w/w) loading were produced namely PSf-Z4A (PSf-zeolite 4A), PSf-Z4Ap (primed PSf-zeolite 4A) and PSf-Z4As (silane treated PSf-zeolite 4A). The optimized four-component dope solution proposed by Pesek and Koros [21] was used. The dope preparation for HFMMM was generally similar to the preparation of unfilled dope solution with the exception of the addition of filler particles. The round-bottom flask was filled with 57.82 grams of Dimethylacetamide and 28.91 grams of Tetrahydrofuran (THF). The rest of THF (28.91 grams) was kept aside for pre-wetting of the filler particles. Dried polysulfone pellets (40 grams) were added to the cold solvent mixture via a funnel and stirred. A quantity of zeolite 4A that is equivalent to 10%(w/w) loading was dispersed in the leftover THF

## GAS PERMEATION PERFORMANCE OF POLYSULFONE

solvent and was thoroughly stirred to break up aggregates of particles and then carefully poured into the mixture. The mixture was agitated thoroughly and continuously using the mechanical stirrer to dissolve the polymer. The quantity of the fillers and the amount of polymer used will determine the loading (or solid particles concentration). Prior usage, the zeolite powders were heated to 105°C for at least overnight to remove moisture that may have been absorbed during storage.

### 2.4 Hollow fiber Spinning

The asymmetric hollow fiber membranes were spun using 4 meters long dry-wet phase inversion spinning machine with forced convection in the dry gap. The details of the spinning conditions and parameters were summarized in Table 1. For the production of HFMMM, the dope solution was spun as soon as possible to minimize gravity settling of the suspended filler particles in the dope solution.

Both the bore fluid and the dope were extruded simultaneously through the hollow spinneret needle that has the inside diameter and outside diameter of 229  $\mu\text{m}$  and 635  $\mu\text{m}$ , respectively. Once spinning was completed, the as-spun fibers were cut from the drum and placed in the distilled water for 2 days to remove the remaining solvents. Following this, they were then placed in methanol for another 2 days to remove all traces of water. The fibers were left to dry in air for three days to allow the methanol to completely evaporate.

**Table 1** General spinning conditions

Spinning conditions	Value
Spinning dope temperature	20 $\pm$ 2°C
Spinneret dimensions	OD 635 $\mu\text{m}$ and ID 229 $\mu\text{m}$
Gear pump throwing capacity	0.3 cm <sup>3</sup> /revolution
Internal coagulant composition	20% (w/w) potassium acetate in water
Internal coagulant temperature	20 $\pm$ 2°C
Dope extrusion rate (DER)	4.5 cm <sup>3</sup> /min
DER: Internal coagulant injection rate	3:1
Forced convection gas	Nitrogen
Forced convection chamber height/diameter	15 cm/5 cm
Forced convection residence time	0.55 s
Forced convection rate	4 l/min
Forced convection temperature	20 $\pm$ 2°C
External bath composition	Water
External bath temperature	14 $\pm$ 0.5°C
Jet stretch ratio	1:1
Collection drum diameter	16 cm

### 2.5 Characterization of asymmetric mixed matrix hollow fiber membrane

Characterization of HFMMM was very important in order to investigate the structure of membrane in relation to its performance. Fourier transform infrared spectroscopy (FTIR) analyzer was used to identify functional group in order to confirm successful grafting of silane molecules on the zeolite's surface. The performance of membrane was measured using gas permeation apparatus while the morphology of the membrane was observed using the image from field emission scanning electron micrograph (FESEM).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to measure the glass transition temperature and the thermal stability of the membranes respectively.

## **2.6 Module fabrication and gas permeation experiment**

A hollow fiber membrane was prepared into a module so that it could be placed in stainless steel housing for the permeability measurement. A dried fiber was cut into 38 cm of length and treaded carefully through the tube sheet and silicone tubing. It was essential that the hollow fiber membrane be handled very carefully so as not to damage the delicate active layer skin. One end of the fiber was placed in the hollow end-cap while the other end was placed in the tube sheet. The potting material was injected into the end-cap and then via the silicon tubing into the tube sheet. The final length of the fiber for the module was carefully recorded for use in the permeability calculation. A total of six hollow fiber modules were prepared for each type of membrane and each module was individually tested for gas permeation properties.

The HFMMM was then left to dry after it had been dip-coated with a dilute coating solution that was made using a clear liquid silicone elastomer (Slygard 184 from Dow Corning) that came with a curing agent to make 3 % w/w in n-hexane solvent.

Pressure-normalized flux (or permeance) and selectivity are the two most important properties of an asymmetric hollow fiber membrane in gas separation application. This measurement was carried out using gas permeation test apparatus. The HFMMM module was loaded inside stainless steel housing and all the fittings were subsequently tightened. The pressure-normalized flux of the fiber was measured for O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub> and CH<sub>4</sub> at 25°C and at a trans-membrane pressure drop of 5 bars. The permeance was determined from a bubble flow meter measurement.

The intrinsic selectivity of polysulfone for an oxygen-nitrogen system is 6.2. The corresponding intrinsic selectivity for carbon dioxide-methane is 28.1. These values assume that the membrane is defect free and that the governing transport mechanism is solution-diffusion [22,23].

## **3.0 RESULTS AND DISCUSSION**

### **3.1 Performance evaluation and structural properties of PSf-Z4A HFMMM**

To calculate the flux, we first need to measure the actual diameter of the fiber as this was different from the outside diameter of the spinneret. As the fiber was emerging from the spinneret, it was stretched as it descended towards the coagulation bath. In this case, the actual outside diameter of the fiber was smaller than the value of the spinneret's outside diameter. The actual diameter was measured using optical microscope. The reading was calibrated using a 0.64 mm needle that gave reading of 7.4. The outside diameter of the fiber produced was found to be 0.54 mm.

The permeability and selectivity values were calculated for all modules and average values were determined along with the standard deviations. The results are listed in Table,2 and the discussion on these results is presented in the following sections.

## GAS PERMEATION PERFORMANCE OF POLYSULFONE

**Table 2** Average permeability and selectivity of membrane produced

HFMMM Type	P <sub>O2</sub> (GPU)	P <sub>N2</sub> (GPU)	P <sub>O2</sub> / P <sub>N2</sub>	Std. Dev.	P <sub>CO2</sub> (GPU)	P <sub>CH4</sub> (GPU)	P <sub>CO2</sub> / P <sub>CH4</sub>	Std. Dev.
PSf-Z4A (10%)	100.26	94.65	1.06	0.2	138.73	135.39	1.02	0.3
PSf-Z4Ap (10%)	77.82	70.51	1.10	0.8	-	-	-	-
PSf-Z4As (10%)	17.86	7.33	2.44	0.6	80.01	10.08	7.94	2.8

For the HFMMM filled with untreated zeolite 4A fillers (PSf-Z4A (10%)), the selectivities were 1.06 and 1.02 for O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> respectively. The permeabilities were high for all gases while the selectivities were very low and in fact very close to unity. These were clearly indicative of the pore flow behavior resulting in the membranes' inability to discriminate the gas penetrants [24]. This implied the existence of severe defects. An attempt to double coat the membrane to enhance the selectivity was also unsuccessful as the defects were too large to be sealed or repaired with silicone coating.

Images from electron microscopy are shown in Figure 1. The earlier suspicion was confirmed upon closer inspection on the FESEM images, there appeared to be a poor bonding between the cubic-like shape of zeolite 4A particles and the polysulfone matrix as manifested by the delaminating effect. These severe defects were primarily due to poor adhesion between zeolite 4A fillers and the polysulfone matrix, creating voids or gaps at the interphases surrounding the fillers. These gaps are so severe that they introduced a resistant-free path for the gas to bypass the filler particles, hence cancelling the intended role of the fillers. In their experiment with polyimide-zeolite 4A dense FSM, Mahajan and Koros [25] also observed delamination. They suspected this to occur when solvent leave the polymer during membrane formation process. They also described this phenomenon as "sieve in a cage" referring to the gap surrounding the sieve [10].

At 20000x resolution, we can clearly see the ruptures on the fibers' outer surface. The present of relatively large size cubic-like zeolite 4A particles with edges plus the poor adhesion with the polymer matrix were likely to cause surface ruptures in some areas of the active layer. The defects were so severe that all effort to seal with double coating were also failed. As expected, an attempt to prime the untreated zeolite 4A (PSf-Z4Ap (10%)) was also failed to improve the adhesion between filler and the matrix. There was reduction in the permeability for both O<sub>2</sub> and N<sub>2</sub>, but no significant difference in the membrane selectivity. It was obviously unnecessary to continue with permeability measurement for CO<sub>2</sub>/CH<sub>4</sub>.

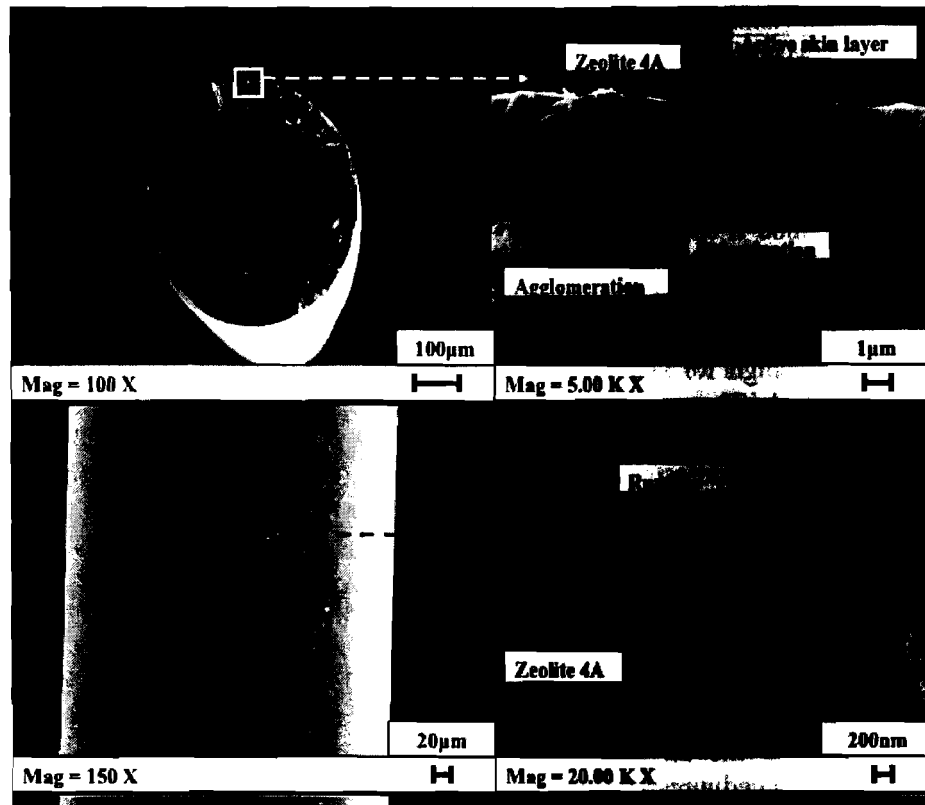


Figure 1 FESEM images: PSf-Z4A (10%) HFMMM

All of the above suggest the importance of **ensuring proper** polymer-filler adhesion in the production of MMM. This was also **consistent with** the findings by researchers who have worked on dense FSMMM such as Mahajan [8]. However, for the asymmetric HFMMM, the gas molecule not only can **bypass the filler** through the voids or cages surrounding the fillers but more seriously **through the surface defects** (large pores/ruptures) resulting from poor filler-polymer interaction **particularly near at the skin layer** of the asymmetric membrane.

### 3.2. Performance Evaluation and structural properties of PSf-Z4As HFMMM

The permeability result, as shown in Table 2, showed that **there was an improvement** of the selectivity for silane treated (PSf-Z4As (10%)) as **compare to the untreated** HFMMM. This therefore suggested that a better filler polymer **contact was achieved**. The selectivities were 2.44 and 7.94 for  $O_2/N_2$  and  $CO_2/CH_4$  **respectively**. These improved selectivities were, however, still lower compare to **intrinsic selectivity** of polysulfone membrane and were largely due to higher permeabilities of **slow gases** namely  $N_2$  and  $CH_4$ . Compare to untreated PSf-Z4A HFMMM, the **improvement was obvious** but insignificant. The silane treatment appeared to **enhance the adhesion** but this improvement somehow did not completely **eliminate the defects**. This was similarly encountered by Mahajan and Koros [10] when they studied the **silane-treated Polyimide-Z4A dense MMM**. They believed that there were still **defects** due to non-selective “leakages” from the existence of nano-metric region of **disturbed packing** at the polymer filler inter-phase.

3.3. Effect of chemical modification of zeolite surface

The images for silane treated zeolite 4A filled HFMMM are shown in Figure 2. The adhesion between the particles and polymer was improved where delaminating and ruptures were significantly suppressed compare to previous untreated PSf-Z4A HFMMM. Similar observation was achieved when Ismail et al. [19] produced HFMMM using polyethersulfone and silane-treated zeolite 4A fillers.

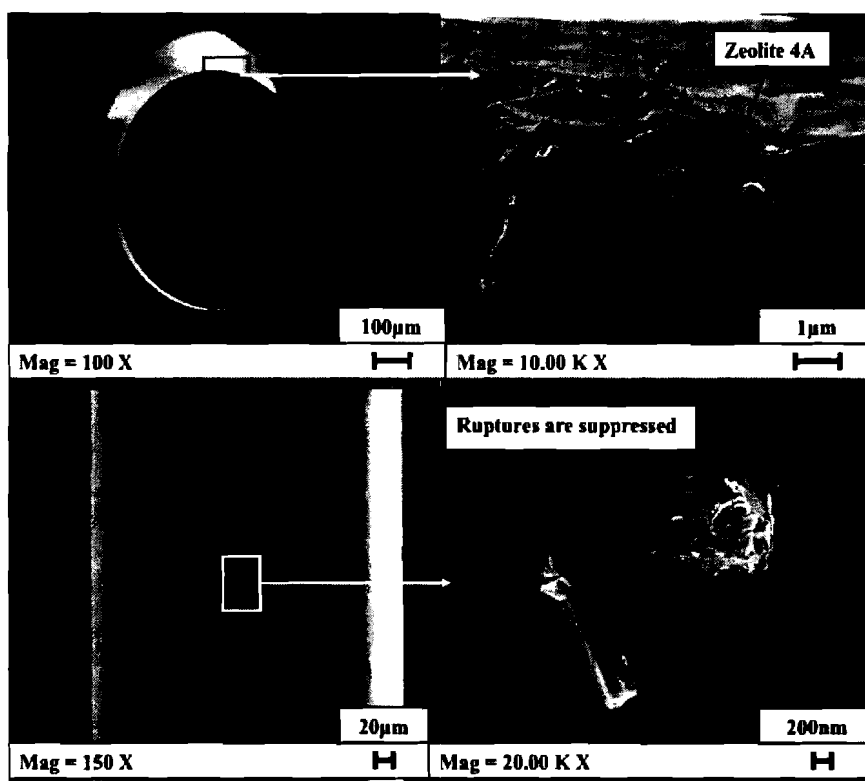


Figure 2: FESEM images: PSf-Z4As (10%) HFMMM

This improvement shows the ability of 3-Aminopropyl-triethoxysilane to act as the molecular 'bridge' between zeolite 4A and polysulfone. The silane molecular 'bridge' also gave the adhesion energy required to tolerate larger stresses during membrane formation, hence avoiding delamination [26]. The silicon at the center is connected to two different functional groups; the organophilic amino group (H<sub>2</sub>N) and the ethoxy group (OCH<sub>2</sub>CH<sub>3</sub>). In the presence of water, the ethoxy groups hydrolyzed and formed reactive silanol (Si-OH) groups and ethanol was released as byproduct, as shown in Figure 3.

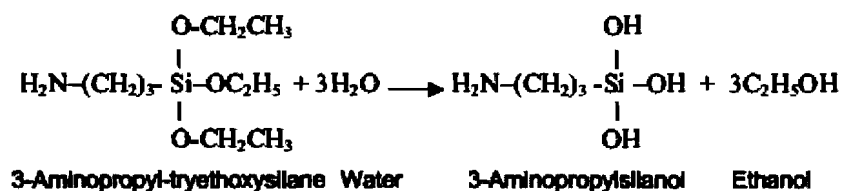
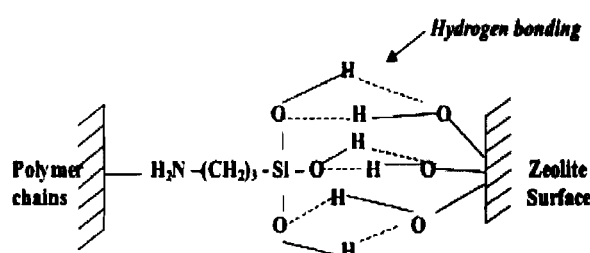


Figure 3: Hydrolysis reaction of 3-Aminopropyltriethoxysilane



This reactive silanol groups could bond to filler's surface provided that the surface was receptive to the silanol. In the case of zeolite 4A fillers, stable Si-O-filler bonds were formed through the bonding between the silanol and the hydroxyl groups on the zeolite surface. For each of OH group, the oxygen atom is an electronegative atom and act as hydrogen bond acceptor, whereas the hydrogen itself will be the hydrogen bond donor [27]. The hydrogen atom on silanol will be attracted to oxygen atom of the hydroxyl group on the zeolite surface. Similarly, the hydrogen atom of the hydroxyl group on the zeolite surface will also be attracted to oxygen atom of the silanol, forming a strong network of dipole-dipole attraction known as hydrogen bonding [28]. This process is shown in Figure 4. The organophilic amino group, on the other hand, reacted/linked with the polymer chain to complete the role of silane as a molecular 'bridge' between the filler and polymer [1].



**Figure 4:** Silane molecular 'bridge' and hydrogen bonding

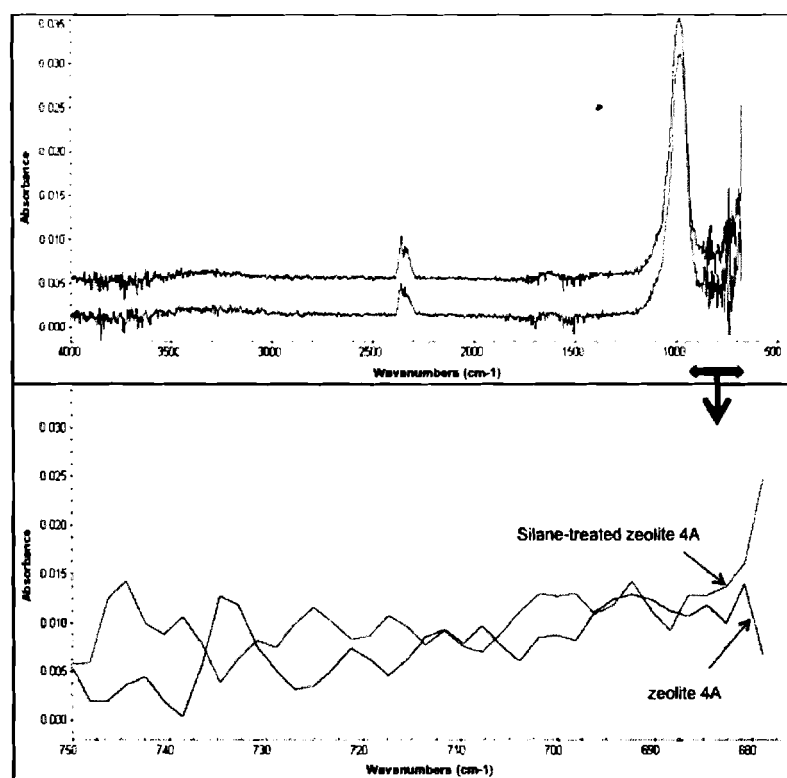
The FTIR spectra for untreated as well as silane treated zeolite 4A are shown in Figure 5. The top figure shows the strongest vibrations in the range of 900-1200  $\text{cm}^{-1}$  that represent internal tetrahedron symmetric stretch of Si(or Al)-O in the zeolite structure. Lee et al. [20] also observed similar peaks on a natural zeolite. If the spectra of zeolite 4A and silane-treated zeolite 4A are overlapped and zoom in within the range of 750 to 680  $\text{cm}^{-1}$ , the increase in the intensity of peaks for silane-treated zeolite 4A is clearly observed. These peaks were due to the various rotations and vibrations of bonds within  $-(\text{CH}_2)_3-$  group. This confirmed that silane had been successfully grafted onto the zeolite 4A surface as the  $-(\text{CH}_2)_3-$  group was part of 3-aminopropyltriethoxysilane molecular structure.

Table 3 showed the DSC measurement of glass transition temperature ( $T_g$ ) where there was a slight increased in  $T_g$  of the PSf-Z4A HFMMM as compare to the neat polysulfone HF membrane. An increase of almost 2°C was observed for the HFMMM with silane-treated zeolite 4A as fillers. This may indicate that silane treatment increased the polymer matrix rigidification at the interphase region. This is important as polymer chain rigidification would reduce the free volume, hence lower interphase permeability as compare to bulk polymer matrix, hence could starve the filler of gas penetrants [28]. In this study, however, the lower overall performance of the PSf-Z4As HFMMM was largely influenced by the interphase leakages due to nanometric defects as explained earlier. Ismail et al. [19] also observed an increase in  $T_g$  in the range of 3 to 5°C as the loading increase from 10 to 20 wt% for their PES-silane treated zeolite 4A HFMMM.

**Table 3:** Glass transition temperature

Membrane type	Glass transition temperature (°C)
Neat PSf HF	183.81
PSf-Z4A (10%) HFMMM	184.23
PSf-Z4As (10%) HFMMM	185.35

## GAS PERMEATION PERFORMANCE OF POLYSULFONE



**Figure 5** FTIR spectrum for zeolite 4A and silane-treated zeolite 4A

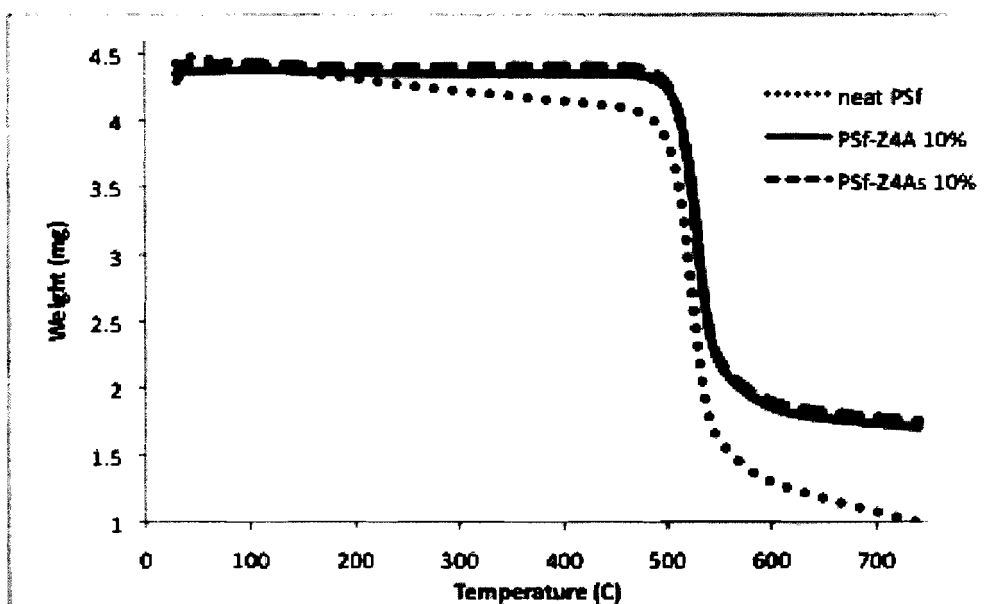
In the case of dense FSMMM where the dense layer is thick, the nanometric defect surrounding the filler is a closed system or 'cage' encapsulated within the thickness of the dense layer. These defects acted as paths of less resistance and would actually help to increase the membrane permeability as was found by Mahajan and Koros [10]. The nanometric defects could be said to reduce the effective thickness of the dense FSMMM, hence resulting in higher permeability.

For this experiment, there were two possible locations of defects that were not totally eliminated by silane treatment. The first one was within the active skin layer where nano-sized voids or cages still existed in spite of the improved adhesion. The second one was at the outer surface of the hollow fiber. With incomplete adhesion, the present of large size zeolite 4A with uneven edges at the surface contributed to surface defects or pores that cannot be completely sealed with coating. For asymmetric HFMMM where the thickness of the dense active skin layer is much less than  $1000\text{\AA}$ , these cages of nanometric defect surrounded the large size zeolite 4A particles ( $2.5\ \mu\text{m}$  or  $25000\text{\AA}$ ) were no longer 'closed' but would be exposed or opened to the membrane outer surface. So there was a combined effect of nanometric channels and surface defects for gas penetrants to bypass. As shown in Table 4, the permeability of fast gases ( $\text{O}_2$  and  $\text{CO}_2$ ) increased slightly compare to the neat polysulfone HF, but on the contrary, the increase in the permeability for the slower gases ( $\text{N}_2$  and  $\text{NH}_4$ ) was as high as 300%. It could be said that the channels created by these defects seemed to favour the flow of slower gases, hence leading to poor overall selectivity. This implied that the permeability and selectivity were also influenced by the interaction between silane-treated zeolite 4A particles and gas penetrants.

**Table 4** Comparison gas permeance between PSf HF versus PSf-Z4As HFMMM

Membrane Type	P <sub>O2</sub> (GPU)	Std. Dev.	P <sub>N2</sub> (GPU)	Std. Dev.	P <sub>CO2</sub> (GPU)	Std. Dev.	P <sub>CH4</sub> (GPU)	Std. Dev.
Neat PSf HF	14.8	0.9	2.3	0.2	78.1	5.5	2.5	0.3
PSf-4As (10%) HFMMM	17.9	1.2	7.3	2.1	80.0	4.6	10.1	3.0
% Increase	21		217		2.4		304	

Figure 6 shows the TGA plots of weight loss versus temperature for the three hollow fiber membranes (neat HF PSf, PSf-Z4A and PSf-Z4As). All membranes show similar decomposition's temperature of around 500°C. Unlike neat HF PSf membrane, the HFMMMs (PSf-Z4A and PSf-Z4As) feature no significant losses of less volatile components prior the decomposition's temperature. The plots also indicated that HFMMM with silane-treated zeolite (PSf-Z4As) has a slightly lower percentage weight loss as compare to the untreated zeolite. The high reduction in percentage of weight losses reaffirmed that the overall effect of the addition of zeolite fillers were to increase the overall thermal stability of HFMMM as compare to the neat HF PSf membrane.

**Figure 6:** TGA plot of weight loss vs. temperature

### 3.4. Calculation of fillers' inter-particle spacing

Apart from good polymer and molecular sieve adhesion, the success of asymmetric HFMMM will also depend on the optimum particle size. Particle size could affect the particle distribution in the matrix phase and particularly its inclusion into the thin-active skin layer of the asymmetric HFMMM. This study also investigated the relationship between particle size and the inter-particle spacing. By assuming an ideal and uniform dispersion, an inter-particle spacing can be calculated using simple geometry based on isotropic fillers arrangement within a unit cubic space. The number of particle on each

## GAS PERMEATION PERFORMAMANCE OF POLYSULFONE

edge of the cube is cubic root of the total particle number. The distance between two particles on the edge side is then calculated as follows,

$$d = \frac{1}{(n_{\text{particle}})^{1/3} - 1} \quad \dots(1)$$

Where  $d$  is the inter-particle spacing and  $n$  is the number of particle. For many particles presence in a cubic space, the above equation is reduced to the following simple equation,

$$d = \frac{1}{(n_{\text{particle}})^{1/3}} \quad \dots(2)$$

The inter-particle spacing can then be compared to the diameter of filler particle in order to gauge the proximity of the fillers in the polymer matrix. Table 5 shows the calculation of number of particle and inter-particle spacing for 10% w/w loading for various particle sizes. The calculation is based on the physical property of zeolite 4A. For comparison, the size of polysulfone molecule is 70 nm as was approximated by Bhardwaj et al. [29].

**Table 5** Inter-particle spacing for zeolite 4A

Filler Particle Size (nm)	Number of Particles per m <sup>3</sup>	Inter-particle Spacing (nm)
2500	6.3844x10 <sup>15</sup>	3267
1000	4.4790x10 <sup>17</sup>	3306
500	3.5832x10 <sup>18</sup>	653
100	4.4790x10 <sup>20</sup>	130
50	3.5832x10 <sup>21</sup>	65

The presence of relatively large particles, was translated into a smaller total number of particles; hence the average inter-particle spacing was farther apart. Even if we could somehow achieve ideal polymer-filler adhesion and homogenous filler dispersion, we should expect that the polymer matrix to govern the overall permeability properties of the HFMMM instead of the molecular sieve particles. This inter-particle calculation highlighted the importance of the role of smaller size molecular sieve particles. The smaller the particle, the higher the number of particle for the same loading, hence the proximity of filler particles to one another is increased. Application of smaller particle size could also reduce the loading requirement of a more expensive high performance molecular sieve fillers.

Based on the approximate size of polysulfone, the size of molecular sieve from inter-particle spacing point of view should be less than 100 nm. Furthermore placing molecular sieve particle in the active skin layer of asymmetric HFMMM demand smaller particles with this nano-size dimension. An investigation on the usage of nano-sized zeolite as filler in the skin layer of hollow fiber was carried out by Jiang et al. [17]. Their work provided some fundamental understanding of the mixed matrix hollow fiber spinning with special emphasize on the effect of particle loadings and the mechanisms of nano-particle dispersion during the membrane formation. They found that the outer layer

has a defective skin and proposed to investigate at various ways to **eliminate** the defects particularly on the use of various post-treatments.

#### 4.0 CONCLUSION

This study highlighted important issues of PSf-zeolite 4A **interactions at the molecular level** on the performance of polysulfone-zeolite 4A HFMMM with the following conclusions,

- It was shown that without silane treatment, the **zeolite filled asymmetric HFMMM** showed severe defects due to poor contact/**adhesion with PSf matrix** and rendered the HFMMM to be totally unselective toward **all the gases**.
- The results have shown that improved macroscopic **adhesion was observed** after the zeolite 4A had been treated with 3-aminopropyl-triethoxysilane. The delamination and surface ruptures were suppressed.
- The PSf-silane treated zeolite 4A HFMMM showed **limited improvement** in permeability properties that could be due to the **combined effect** of interphase nanometric channels and surface defects creating **path of less resistance** for gas penetrants to flow.
- It was also shown that the permeability was influenced by **the interaction** between mixed matrix materials and gas penetrant. The presence of **nanometric defects** seemed to favour the flow of slow gases (**CH<sub>4</sub> and N<sub>2</sub>**), hence making the HFMMM less selective for **CO<sub>2</sub>/CH<sub>2</sub> and O<sub>2</sub>/N<sub>2</sub> separation** than the unfilled hollow fiber membrane.
- Inter-particle spacing calculations showed that the **size of the molecular sieve particles** influence the proximity of particles to one **another, and that molecular sieve of nanosize dimension** should be considered for **asymmetric HFMMM configuration**.

#### ACKNOWLEDGEMENT

The authors would like to thank Universiti Teknologi Malaysia for **financial support** for this research and the Commonwealth Scholarship Commission for **their support** during one-year attachment at Chemical and Process Engineering **Department**, University of Strathclyde.

#### REFERENCES

- [1] Chung T.S., S.K. Teoh, and X. Hu. 1997. **Formation Of Ultrathin High Performance Polyethersulfone Hollow Fiber Membranes**, *J. Membrane Science*. 133: 161-175
- [2] Fuertes A.B. and T.A. Centeno. 1998. **Preparation Of Supported Asymmetric Carbon Molecular Sieve Membranes**, *J. Membrane Science*. 144:105-111
- [3] Libby B., W.H. Smyrl and E.L. Cussler. 2003. **Polymer-Zeolite Composite Membranes For Direct Methanol Fuel Cells**, *AICHE J. April*: 991-1001
- [4] Vu D.Q., W.J. Koros and S.J. Miller. 2003. **Mixed Matrix Membranes Using Carbon Molecular Sieves I. Preparation And Experimental Result**, *J. Membrane Science*. 211:311-334

## GAS PERMEATION PERFORMANCE OF POLYSULFONE

- [5] Duval J.M., B. Folkers, M.H.V. Mulder, G. Desgrandchamps and C.A. Smolders, 1993. Adsorbent Filled Membranes For Gas Separation. Part I. Improvement Of The Gas Separation Properties Of Polymeric Membranes By Incorporation Of Microporous Adsorbents, *J. Membrane Science*. 80:189-198
- [6] Suer M.G., N. Bac and L. Yilmaz. 1994. Gas Permeation Characteristics Of Polymer-Zeolite Mixed Matrix Membranes, *J. Membrane Science*. 91: 77-86
- [7] Gur T.M. 1994. Permselectivity Of Zeolite Filled Polysulfone Gas Separation Membranes, *J. Membrane Science*. 93: 283-289
- [8] Mahajan R. 2000. Formation, *Characterization And Modeling Of Mixed Matrix Membrane Materials*, The University of Texas at Austin: PhD Dissertation.
- [9] Yong H.H., H.C. Park, Y.S. Kang, J. Won and W.N. Kim. 2001. Zeolite-Filled Polyimide Membrane Containing 2,4,6-Triaminopyrimidine, *J. Membrane Science*. 188: 151-163
- [10] Mahajan R. and W.J. Koros. 2002. Mixed Matrix Membrane Materials With Glassy Polymers. Part 1, *Polym. Engineering and Sci.* 42: 1420-1431
- [11] Pechar T.W., M. Tsapatsis, E. Marand and R. Davis. 2002. Preparation And Characterization Of A Glassy Fluorinated Polyimide Zeolite-Mixed Matrix Membrane, *Desalination* 146: 3-9
- [12] Ayala D., A.E. Lozano, J. de Abajo, C. García-Perez, J.G. de la Campa, K.-V. Peinemann, B.D. Freeman and R. Prabhakar. 2003. Gas Separation Properties Of Aromatic Polyimides, *J. Membrane Science*. 215: 61.
- [13] Li Y., T.S. Chung, C. Cao and S. Kulprathipanja. 2005. The Effects Of Polymer Chain Rigidification, Zeolite Pore Size And Pore Blockage On Polyethersulfone (PES)-Zeolite: A Mixed Matrix Membranes, *J. Membrane Science*. 260: 45-55
- [14] Li Y., H. Guan, T.S. Chung and S. Kulprathipanja. 2006. Effects Of Novel Silane Modification Of Zeolite Surface On Polymer Chain Rigidification And Partial Pore Blockage In Polyethersulfone (PES)-Zeolite: A Mixed Matrix Membrane, *J. Membrane Science*. 275: 17-28
- [15] Sen D., H. Kalıpcılar and L. Yilmaz. 2007. Development Of Polycarbonate Based Zeolite 4A Filled Mixed Matrix Gas Separation Membranes, *J. Membrane Science*. 303: 194-203
- [16] Pechar T.W., S. Kim, B. Vaughan, E. Marand, M. Tsapatsis, H.K. Jeong and C.J. Cornelius. 2006. Fabrication And Characterization Of Polyimide-Zeolite L Mixed Matrix Membranes For Gas Separation, *J. Membrane Science*. 277: 195-202
- [17] Jiang L.Y., T.S. Chung, C. Cao, Z. Huang and S. Kulprathipanja. 2005. Fundamental Understanding Of Nano-Sized Zeolite Distribution In The Formation Of The Mixed Matrix Single- And Dual-Layer Asymmetric Hollow Fiber Membranes, *J. Membrane Science*. 252: 89-100
- [18] Jiang L.Y., T.S. Chung and S. Kulprathipanja. 2006. An Investigation To Revitalize The Separation Performance Of Hollow Fibers With A Thin Mixed Matrix Composite Skin For Gas Separation, *J. Membrane Science*. 276: 113-123
- [19] Ismail A.F., T.D. Kusworo and A. Mustafa. 2008. Enhanced Gas Permeation Performance Of Polyethersulfone Mixed Matrix Hollow Fiber Membranes Using Novel Dynasylan Amino Silane Agent, *J. Membrane Science*. 319: 306-312
- [20] Lee J.Y., S.H. Lee and S.W. Kim. 2000. Surface Tension Of Silane Treated Natural Zeolite. *Mater. Chem. and Phys.* 63: 251-255
- [21] Pesek S.C. and W.J. Koros. 1993. Aqueous Quenched Asymmetric Polysulfone Membranes. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* 34(2): 1000-1001

- [22] Ismail A.F., I.R. Dunkin, S.L. Gallivan and S.J. Shilton. 1999. Production Of Super Selective Polysulfone Hollow Fiber Membranes For Gas Separation. *Polymer* 40: 6499-6596
- [23] Sharpe I.D., A.F. Ismail and S.J. Shilton. 1999. A Study Of Extrusion Shear And Forced Convection Residence Time In The Spinning Of Polysulfone Hollow Fiber Membranes For Gas Separation, *Separation and Purification Technology*. 17:101-109
- [24] Baker R.W. 2000. *Membrane Technology And Applications*, McGraw Hill, New York.
- [25] Mahajan R. and W.J. Koros. 2000. Factors Controlling Successful Formation Of Mixed-Matrix Gas Separation Materials, *Ind. Eng. Chem. Res.* 39: 2692-2696
- [26] Hillock A.M.W., S.J. Miller and W.J. Koros. 2008. Crosslinked Mixed Matrix Membranes For The Purification Of Natural Gas: Effects Of Sieve Surface Modification, *J. Membrane Science*. 314: 193-199
- [27] Jeffrey G.A. 1997. *An Introduction To Hydrogen Bonding, Physical Chemistry*, Oxford University Press, USA.
- [28] McQuarrie D.A and P.A. Rock. 1987. *General Chemistry*. 2<sup>nd</sup> Edition, W.H. Freeman and Company, New York.
- [29] Bhardwaj V., A. Macintosh, I.D. Sharpe, S.A. Gordeyev and S.J. Shilton. 2003. Polysulfone Hollow Fiber Gas Separation Membranes Filled With Sub-Micron Particles, *New York Academy of Sci.* 984: 1-11