Diamine Modified Polysulfone and P-84 Symmetric Membranes for Hydrogen/Carbon Dioxide Separation

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Abstract

The separation1of $H_2/CO_2$1is1technologically crucial to1produce clean and renewable H_2-based energy. There are several established methods used to separate H_2 from CO_2, but membrane-based separation is becoming more prominent due to high energy efficiency and cost effectiveness. However, separation efficiency of existing polymeric membranes is limited due to unfavourable diffusivity and selectivity between H_2 and CO_2. As such, motivated research through investigating the effectiveness of diamine modification towards two different polymeric membrane materials (PSf and P-84) on their performance in H_2/CO_2 separation. The effects of different operating pressures and modification time on the permeance and selectivity are also studied. Comparison of pure and modified membranes will be subsequently undertaken. The fabrication of membranes is done by using controlled evaporation method. Then, the prepared membranes will undergo diamine modification using BuDA for 10 and 30 minutes reaction times. All samples were analyzed by gas permeation test for separation performance and SEM and FTIR for membranes characterization. From SEM analysis, the images show that both polymers have defect-free surfaces and porous cross-section structures. FTIR spectra validate the cross-linking reaction by observing the existence of adsorption peak at 1529 cm^{-1}. This specific characteristic peak implies the occurrence of C-N stretch within the membranes. The gas permeation test shows the respective modification towards P-84 and PSf for 10 and 30 minutes reaction times causes H_2 permeability to increase drastically. Based on the experimental result, P-84 membrane with 30 minutes BuDA-modification reaction time and 5 bar operating pressure gives the best overall H_2/CO_2 saperation performance. By increasing the time to 30 minutes, the H_2/CO_2 selectivity of both polymers were increased to 4.97 and 6.09, respectively compared to its neat membranes.

Keywords: cross-linking, diamine modification, hydrogen, membrane

INTRODUCTION

In general, hydrogen, H_2 is one of the most promising clean energy for fuel cells to generate power or electricity [1]. Hydrogen-based energy present numerous advantages, namely low emissions, environmentally friendly and easy sustainability [2]. Hydrogen could be derived from conventional technologies in refineries and petrochemical industries such as steam methane reforming (SMR) followed by the water-gas shift (WGS) reaction, where enormous amount of mixture of hydrogen, H_2, carbon dioxide, CO_2 and other trace gases are produced [3]. Additionally, the anaerobic digester could also potentially produce bio-hydrogen (bio-H_2) as main gas product by applying dark fermentation at certain specific conditions when treating the organic waste generated in palm oil mills [4]. Based on Mohamad et al., by inoculating a mixed culture bacteria at a temperature of 55 °C and pH value of 5.5, the palm oil mill effluent (POME) digester will produce biogas that consists mainly H_2 and CO_2 gas mixture [5]. Therefore, H_2/CO_2 separation becomes a necessity to capitalize produced hydrogen gas. Consequently, this issue leads to the exploration of different ways to carry out the purification of hydrogen from produced gas mixture.

Usually, energy-intensive conventional methods such as absorption technology using amine scrubbing or hot potassium carbonate aqueous solution, cryogenic distillation or pressure swing adsorption are used to serve for the separation purpose [6, 7]. However, these methods incur high capital cost, complex operation, and large spatial requirements [6, 7]. In order to promote H_2 gas purification economically and holistically, membrane process technology is used as gas separation process due to its promising properties, which are simplicity in operation, low capital cost and spatial requirement, high energy efficiency and more environmentally friendly [8, 9]. Nevertheless, the H_2/CO_2 separation process still confronts some difficulties with the application of polymeric membranes as most polymeric membranes show unfavourable diffusivity selectivity and solubility selectivity towards H_2/CO_2 gaseous mixture. Therefore, it usually gives poor selectivity due to the closeness of kinetic diameters of H_2 and CO_2, which are 2.89 A ° and 3.30 A °, respectively [10].

Based on relevant reported work in the literature, cross-linking diamine modification was reported as one of the promising approaches to improve separation properties as it is able to give a substantial increment in crosslinking density [10]. Shao et al. discovered the effectiveness of linear aliphatic cross-linking agent, ethylenediamine (EDA) towards 6-FDA-durene polyimide (PI) membrane after thermal treatment [11]. Chung et al. also extended the study by using butane-1,4-diamine (BuDA), which enables the formation of three-dimensional cross-linked/network structures in the PI membrane to optimize the interstitial space suitable for H_2 and CO_2 separation, to introduce hydrogen bonds in a cross-linked/network structure, and to alter the chemical environments of the PI membrane by partially transferring the imide group into an amide group [10]. It was discovered that novel diamino-modified polyimides could produce ideal H_2/CO_2 selectivities, which were far superior to other polymeric membranes and were well above the Robeson's upper bound curve, in pure gas tests [10, 12]. The resultant PIs of 6-FDA-durene with 5 minutes BuDA-modification reaction time could give higher H_2/CO_2 selectivity with lower permeability compared to that with same EDA-modification reaction time [10]. This was because EDA, which has the shorter molecular length (about 5.5 Å) compared to BuDA (about 8 Å), is able to trigger the mutual influence between the two NH_2 groups, which in turn thermodynamically restrains the cross-linking reaction [10]. Herein, the determination of the suitable immersion time and operating pressure that could enhance the H_2-selective separation performance of the best polymer type will be carried out. Similarly, Tin et al. discovered that when Matrimid (a thermoplastic polyimide based on a proprietary diamine) cross-linking reaction time increases, the permeabilities for helium (He), oxygen (O_2), nitrogen (N_2), methane (CH_4) and CO_2 tend to decrease, but the selectivities of He/ N_2, O_2/ N_2, CO_2/ CH_4 and CO_2/ N_2 will increase up to a certain extent and then decrease [13]. Moreover, Moradihamedani et al. found that PSf prepared with coagulant bath could give fluctuating CH_4 permeance while the pressure increases from 1 to 7 bar [14].

The aim of this work is to explore the significance of cross-linking of diamine with different polymer membrane materials to produce different characterizations and its effects on the enhancement of gas performance. With easy process ability, versatility, chemical resistance and good mechanical properties, PI has emerged as a crucial membrane material for H_2-selective membranes, but it is highly susceptible to the CO_2-induced plasticization when the pressure is high, which can lead to the destruction of polymer structure [15-17]. Moreover, polysulfone (PSf) has good film forming ability and high plasticization resistance over an operating pressure of 30 bar although it has moderate gas separation performance [18-20]. Since diamine has never been applied as reactive agent towards PSf and polyimide P-84 type (P-84) for gas transport study, so the effect of different diamine reaction times and pressures on the H_2-selective separation performance of pure and modified P-84 and PSf membranes will be studied and compared. The fabricated membranes were characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) and tested with pure

gas permeation test at different pressures, which are 3, 4 and 5 bars, to determine the membrane that could give the best separation performance. The findings will facilitate development of polymeric materials with improved gas separation performance and plasticization resistance properties, which would improve hydrogen gas recovery in a cost-effective manner.

MATERIALS AND METHODS

MATERIALS

PSf in granule form was obtained from Solvay Ltd., whereas P-84 polymer was acquired from Goodfellow Ltd. in fibre form. Both polymers would be pre-dried in oven for 24 hours to remove the moisture. CO_2 and H_2 gases with 99.99 % purity are prepared. BuDA was purchased from Merck, whereas n-methyl-2-pyrrolidone (NMP), tetrahydrofuran (THF) and methanol were purchased from Merck KGaA..

MEMBRANE FABRICATION

The synthesis of polymeric membrane was performed by slightly modifying the composition set by [21]. The dense symmetric PSf membrane was prepared in a conical flask according to Table 1. The flask was then covered with plastic paraffin film, together with aluminium coat and stirred for half day to produce clear solution [22], followed by sonification of membrane solution for 10 minutes for degassing purpose [22]. Subsequently, the solution would be poured onto the casting plate to produce an even film of each polymeric solution across a flat glass plate. The thickness was adjusted to 50 μm using a casting knife. It would be placed in the oven for half day for the evaporation of highly volatile THF [23]. The dry membrane was then readily available and could be scrapped off. Water could aid the scrapping of the membrane and another one day was needed for it to dry in the oven. Same technique was applied to fabricate neat P-84 membrane (solution composition in Table 1), but the dissolution of PI into both solvents would take longer time.

Table 1. Mass percentage composition of the chemicals in the synthesized membranes.

Polymer	Mass Composition (%)			
	PSf	P-84	THF	NMP
PSf	-	7.5	67.5	25.0
P-84	7.5	-	67.5	25.0

CHARACTERIZATION AND GAS PERMEATION TEST

The characterization of fabricated membranes was conducted by SEM and FTIR using Phenom Pro-X imaging desktop SEM and Perkin-Elmer Spectrum 400 FT-IR Spectrometer to investigate its surface and cross-section morphology as well as validate the degree of cross-linking reactions respectively. Pure gas permeabilities of both H_2 and CO_2 with purity more

than 99% were determined using gas permeation module as shown in Fig. 1 through a constant pressure system [24], in which the upstream pressure was adjusted to 3, 4 and 5 bars whereas the downstream pressure was set at atmospheric. Flat sheet membrane discs with a diameter of 4 cm and effective membrane area of 12.6 cm^2 were tested. The soap bubble flow meter was used to measure the volumetric flow rate of permeate. The experimental data will be recorded and calculated by using the formula as shown below and the unit for gas permeability is barrer, where 1 barrer is equal to 10^{-10} cm3 (STP). cm /cm^2 s cmHg.

$$P_i = \frac{Q_i \times L}{A \times \Delta p_i}$$

where

P_i : Permeability of a particular gas

L : Thickness of membrane

Q_i : Volumetric flow rate of particular gas at permeate outlet at standard temperature and pressure

A : Effective area of the membrane

Δp_i : Transmembrane pressure difference

The ideal selectivity, α of both membranes for the H_2/CO_2 will be estimated via the ratio of both gases' permeance through the equation (2) as shown below:-
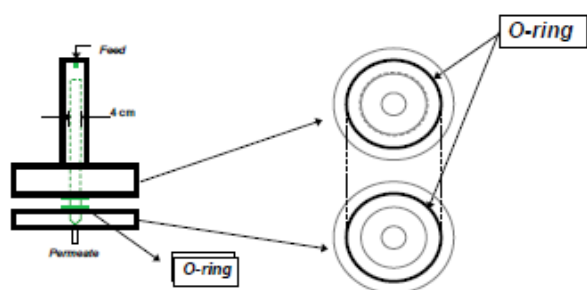
$$\alpha_{H_2/CO_2} = \frac{P_{H_2}}{P_{CO_2}}$$

Figure 1 – Schematic representation of gas permeation module [24].

DIAMINE MODIFICATION OF MEMBRANE

Fabricated PSf and P-84 membranes were undergone diamine modification according to Chung et al. [10]. A crosslinking solution with the concentration of 1.65 mol.L^{-1} was prepared by dissolving BuDA in the non-solvent, methanol. The membranes were immersed into the cross-linking solution for 10 and 30 minutes. After removal from the reagent solution, the modified film was washed with fresh methanol immediately for 3 times to clear off the residual solution. The step was then followed by drying in oven at 85 °C for 1 day. The PSf with 10 and 30 minutes BuDA modification were known as M-PSf-10 and M-PSf-30 respectively, while for P-84, M-P-84-10 and M-P-84-30 were named in accordance

with the reaction times. The modified membrane will then undergo similar characterization analysis as their neat membrane for comparison purpose.

RESULTS AND DISCUSSION

CHARACTERIZATION ANALYSIS

The surface and cross-section morphologies of both symmetric PSf and P-84 types are displayed in Fig. 2 (a) and (b) respectively. According to the SEM images, the PSf type is less dense than the P-84 type because it is observed that PSf type has high distribution of spongy-like pores, which can be clarified with the previous literature whereas P-84 type only has little amount of pores [25]. Hence, PSf type is deduced able to give higher H_2 permeance as compared to P-84 type. However, both types have same defect-free skin surface, which represents the actual selective barrier [26].
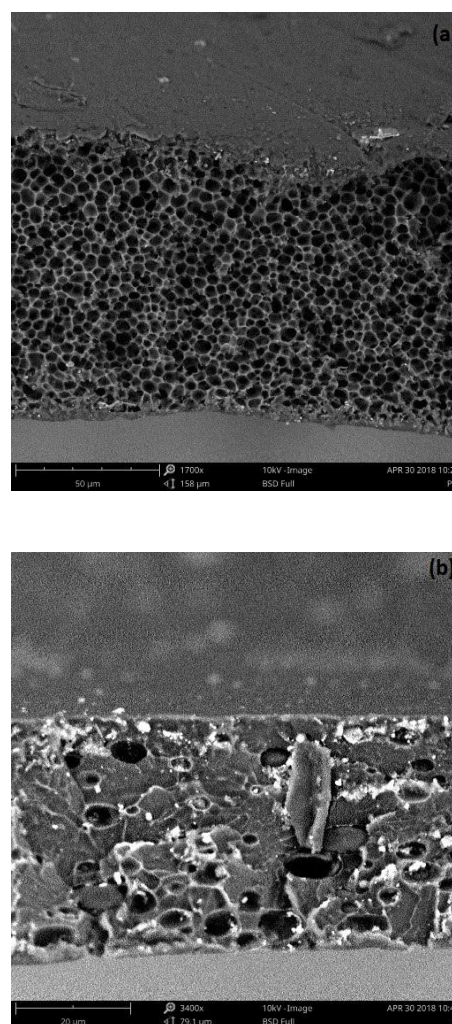

Figure 2 – Cross-section SEM photograph of (a) PSf membrane; (b) P-84 membrane.

The FTIR spectra of these three membranes are shown in Fig. 3. The FTIR spectra of pure PSf membrane displayed bands at

1295 cm^{-1} and 1323 cm^{-1}, representing the presence of O=S=O stretching vibration [27]. The FTIR spectrum of C=C stretching conjugation of benzene rings is characterized by the bands of 1585 cm^{-1} [27]. The adsorption peaks at 2968 cm^{-1} and 1364 cm^{-1} are corresponded to C-H stretching and bending vibrations respectively [27]. Likewise, the C-O-C stretching is detected at 1242 cm^{-1} and is set as reference peak to quantitively determine the reaction progress as C-O-C group is inert to the BuDA cross-linking [28]. The similar trend of FTIR spectra of pure PSf can be seen in M-PSf-10. It shows no proof of cross-linking between the BuDA molecules with any functional group of PSf. It can be explained by referring to Chung et al., BuDA has the longest molecular length (around 8 Å), which may restrict its diffusion into PSf membrane, thus reducing reaction rate [10]. Thus, longer time is required for BuDA to react with PSf to allow the cross-linking to occur. However, the FTIR spectra of M-PSf-30 show successful reaction of BuDA with PSf. This can be proven with the uprising adsorption peak at 1530 cm^{-1} and minimal decrement in the intensity of C=C stretching peak, which imply the existence of C-N bond after one of the double bonds shared between the carbon atoms is broken [29].
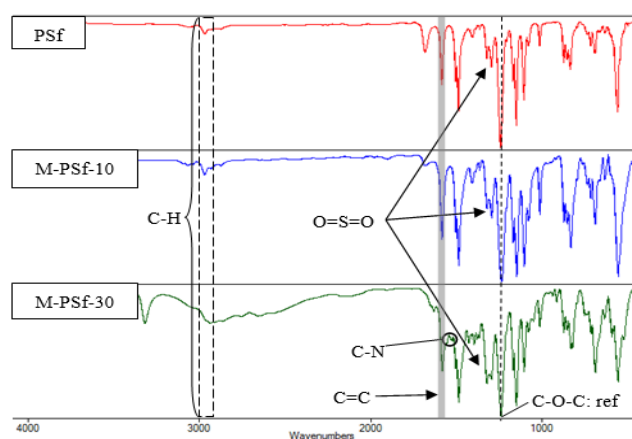

Figure 3 – FTIR spectra of pure PSf, M-PSf-10 and M-PSf-30 membranes.

Fig. 4 depicts the FTIR spectra of the pure P-84, M-P-84-10 and M-P-84-30 membranes. The imide group is characterized by the bands at 1778 cm^{-1} (C=O asymmetric stretch), 1717 cm^{-1} (C=O symmetric stretch) and 1366 cm^{-1} (C-N stretch) [29]. But, when the comparison is made among the FTIR spectra of the pure P-84, M-P-84-10 and M-P-84-30, the difference is more distinct than that in modified P-84 membranes. With increased reaction time, the intensities of these imide characteristics peaks at 1778, 1717 and 1366 cm^{-1} have gradually disappeared. The thermodynamic cross-linking between the BuDA and P-84 can be characterized by the appearance of amide characteristics peaks at 1653 cm^{-1} and 1529 cm^{-1}, which represent C=O and C-N stretching of the O=C-N-H group for M-P-84-10 as well as 1653 cm^{-1} and 1529 cm^{-1} for M-P-84-30 [29]. The possible cross-linking mechanism between the P-84 and BuDA illustrated in Fig. 5 is similar with the previous literature [29].
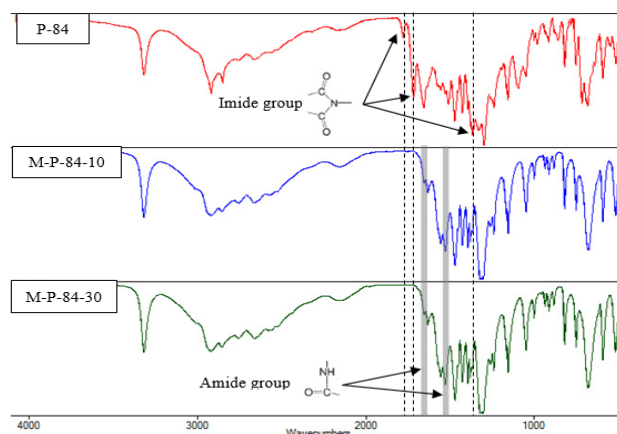

Figure 4 – FTIR spectra of pure P-84, M-P-84-10 and M-P-84-30 membranes.

EFFECT OF DIAMINE REACTION TIME ON THE H$_2$-SELECTIVE SEPARATION PERFORMANCE

Table 2 summarizes the H$_2$/CO$_2$ separation performance through pure and modified PSf and P-84 membranes. One can observe that at three different operating pressures, the H$_2$ permeability of PSf reveals a minor reduction by not more than 20% when the cross-linking period is increased to 10 minutes. This is because based on the FTIR result, the cross-linking between BuDA and PSf is absent, giving no improvement in H$_2$ permeability. Conversely, PSf might not be properly dried before undergoing gas permeation test. Since PSf is easily susceptible to high degree of moisture swelling, it will cause contraction in membrane pores, which could lead to the reduction in the H$_2$ permeability and increase in the H$_2$/CO$_2$ selectivity by 20% [30]. When the cross-linking period is up to 30 minutes, the cross-linking of BuDA to PSf successfully occurs. At this cross-linking period, the H$_2$ permeability of PSf tends to increase dramatically within the range of 11 to 24% because the electronegative nitrogen of cross-linked BuDA could have formed hydrogen bonds with H$_2$, which enable the attraction of larger amount of hydrogen penetrating through the membrane, causing the H$_2$ permeance to surge drastically. In terms of H$_2$/CO$_2$ selectivity, PSf membrane modified by 30 minutes BuDA reaction time showed good increment of selectivity (~44 %) at 3 bar operating pressure. The increment trend of H$_2$/CO$_2$ selectivity is recorded when the operation pressure is increase (58 % at 4 bar, and 67 % at 5 bar) by comparing with neat membrane at respective operating pressure.

Under same circumstances, the H$_2$ permeability of P-84 encounters the opposite trend undergone by PSf, in which it increases by 320.59 % when 10 minutes of BuDA reaction time applied and reduces up to 25% when it is 30 minutes. In previous literature, the diamine cross-linking is able to enhance the H$_2$/CO$_2$ selectivity achieved by the modified 6DFA-durene PI membrane with its reduced permeability [10]. However, when the diamine reaction time is increased to 10 minutes, the attractive hydrogen bond between BuDA and

Table 2. Gas permeability and selectivity through pure and modified PSf and P-84.

| Sample | Estimated Thickness (μm) | P_{H2} (×10^3 barrer) | | | P_{CO2} (×10^3 barrer) | | | $\alpha_{H2/CO2}$ | | |
| | | Pressure (bar) | | | Pressure (bar) | | | Pressure (bar) | | |
		3	4	5	3	4	5	3	4	5
PSf	50.0	82.3 ± 18	89.9 ± 10	105.0 ± 24	24.1± 15	31.5± 21	42.2 ± 25	3.41	2.86	2.49
M-PSf-10	63.3	68.6 ± 1	81.0 ± 1	84.8 ± 0.2	17.1± 0.5	21.4± 0.4	23.1 ± 0.6	4.01	3.79	3.67
M-PSf-30	50.0	91.5 ± 2	104.7 ± 4	129.9 ± 4	19.6± 1	23.2± 2	31.1 ± 4	4.66	4.51	4.17
P84	56.6	132.5± 21	151.6 ± 51	191.2 ± 94	25.8± 0.2	28.1± 7.0	35.0 ± 10	5.11	5.40	5.31
M-P84-10	63.3	778.1± 53	804.1 ± 49	804.1 ± 61	193.0± 4	175.6± 2	206.8 ±25	4.03	4.58	3.90
M-P84-30	56.6	594.8± 27	602.7 ± 27	654.3 ± 40	101.0± 5	103.5± 2	107.3 ± 2	5.88	5.82	6.09

H_2 is seemingly more dominant, leading to steep increase in H_2 permeability and marked decrease in H_2/CO_2 selectivity. But, when the reaction is further extended to 30 minutes, the H_2 permeability is reduced with the slight elevation of H_2/CO_2 selectivity (~15 %). This is due to the formation of tighter infrastructure of cross-linking network, which reduces the interstitial space of the polymer chain at a higher cross-linking density [10,11]. Therefore, the gas separation data of the M-P84-30 consistent with that literature. Based on the H_2 permeability characteristic, it can be deduced that the interaction force of BuDA and membrane in the chemical environment gives more significant impact towards the permeability of the prepared membranes.
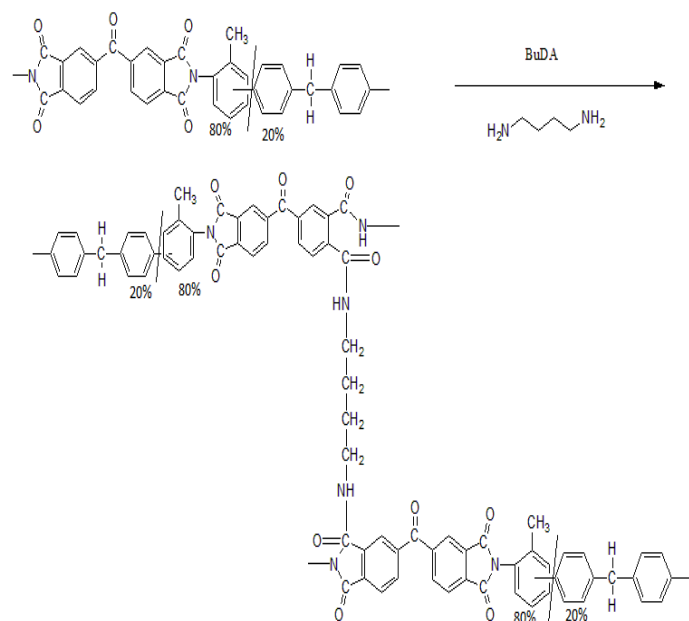
ROBESON'S H_2/CO_2 UPPER BOUND CURVE

The Robeson's upper bound curve represents conventional state of the membrane technology [12]. Therefore, it is important to determine whether the diamine modification towards PSf and P-84 could enhance the H_2/CO_2 gas separation performance so that it could surpass the previous separation performance of membranes. After undergoing BuDA modification of 10 and 30 minutes, the H_2/CO_2 separation performances of PSf and P-84 lie above the Robeson's upper bound curve as shown in Fig. 6 [12]. Hence, it implies that BuDA modified PSf and P-84 membranes are superior than other conventional polymeric membranes, which are situated well below the present upper bound (red dots). It is evident that the proposed modification method can alter the physiochemical structure of both membranes with superior separation performance for H_2 and CO_2 separation.
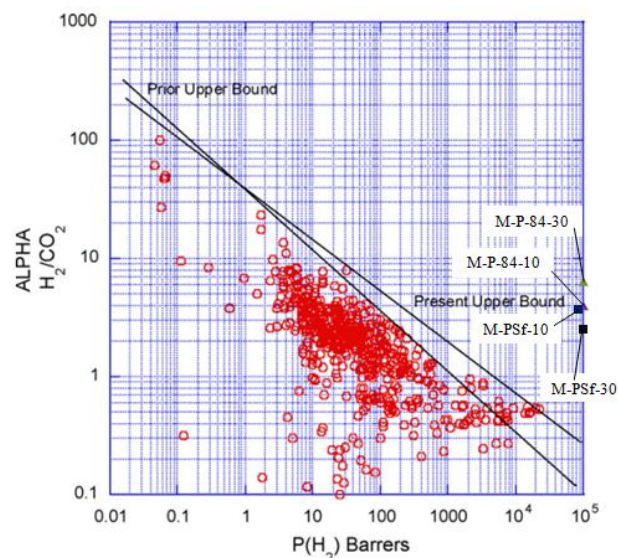

Figure 5 – Possible cross-linking mechanism for P-84 with BuDA.

Figure 6 – H_2/CO_2 separation performance with the Robeson's trade-off line [12].

CONCLUSION

The BuDA modification approach has been conducted for H_2 and CO_2 separation. This research demonstrates the effectiveness of cross-linked BuDA towards the H_2 permeability of PSf and P-84 membranes. From the discussion, the chemical characterization is more dominant than the physical characterization of the membrane as the physical structures of both membranes do not provide significant impact on their gas separation performances. By modifying with BuDA in 10 minutes reaction time and settling the operating pressure at 5 bar, P-84 type provides the best H_2 permeability performance with the permeability increment of 320.59%. By increasing the time to 30 minutes, the H_2/CO_2 selectivity of both polymers were increased to 4.97 and 6.09, respectively compared to its neat membranes.

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