Robustness of PTFE Membrane in The Presence of Impurities and Heavy Hydrocarbons

Fatin Nurathira Binti Mohamad Tawfik, Dr Nur Hidayati Binti Othman

Faculty of Chemical Engineering, Universiti Teknologi Mara

Abstract— **The presence of heavy hydrocarbons such as toluene, and n-hexane are a problem in carbon dioxide separation with loss of flux and selectivity. Moreover, small amounts of condensable heavy hydrocarbons also can cause membrane failure and premature aging. Thus, these impurities and heavy hydrocarbons need to be removed before natural gas undergoes carbon dioxide separation in acid gas removal process. This research aim is to study the effect of such hydrocarbons and impurities to carbon dioxide separation based on chemical and physical characteristic. PTFE hollow fibre membrane was obtained from PETRONAS Research Sdn Bhd. The data is analysed based on membrane characterization such as Fourier Transform Infrared (FTIR) Spectroscopy, Thermogravimetric Analysis (TGA), digital microscope, mercury porosimeter and tensile strength. Based on this study's findings, the exposure of the membrane material to heavy hydrocarbons decreases the thermal, morphology, and mechanical properties of the hollow fibre membrane.**

Keywords— Membrane separation, Hydrocarbon, Carbon dioxide, Toluene, n-hexane, Membrane Contactor, PTFE membrane.

I. INTRODUCTION

Population growth has led to a growing demand for energy worldwide. In addition, the need to tackle environmental effects for example the emission of greenhouse gas is the main concern of the present. For that reasons, researchers have searched and explored the alternatives for potential energy that is more sustainable and environmentally friendly. High quality, economic feasibility, and environmental sustainability energy that can fulfil the global demand has been the world's main concern. Present, natural gas is one of the most vital components of the global energy source that meets the above requirements [1].

Natural gas has characteristics of odourless, shapeless, and colorless in its pure state. Besides, it is a combustible gas and when burned, it releases a significant amount of energy. Natural gas is considered as environmental friendly compared to other fossil fuels such as crude oil and coal [2] because natural gas combustion release lower amount of carbon dioxide and nitrous dioxide compared to others which later helps to reduce problems such as acid rain, and greenhouse gases [3]. However, natural gas in the well contain various contaminants such as acid gases (CO_2 and H_2S), Nitrogen (N_2) and heavies (toluene and heptane). Removal of these gases from natural gas streams are vital in order to meet pipeline specification. Besides, carbon dioxide (CO_2) gas has corrosive property in the presence of water and it is one of the greenhouse gas [1]. Many previous researches using membrane for natural gas purifications has focused on removal acid gases mainly CO_2 [1], [4]–[8] Nevertheless, other contaminants such as heavy hydrocarbons which will give various problems when interacting with membrane also present in natural gas feed. Pre-treatment of the acid gases removes majority of these hydrocarbons but a significant amount of heavy hydrocarbons trace still remain during membrane separation [9].

The existence of heavy, condensable hydrocarbons can become problems for polymeric, asymmetric membranes which can prevail in natural gas streams [10]. Heavy hydrocarbons can affect CO_2 separation with flux and selectivity loss due to its exposure can become damaging to membrane performances. Moreover, small amounts of condensable heavy hydrocarbons also can cause membrane failure and premature aging [10], [11]. Thus, it is significant to evaluate the performance of membrane material under these conditions. It was brought to concern in developing a reliable membrane system for natural gas purification which involves the influence of such heavy hydrocarbons on the membranes. The needs to investigate the characterization of the membrane materials arise in order to understand the impact of such hydrocarbons to the membrane material. Several methods have been used in natural gas purifications of acid gas such as liquid desiccant, solid desiccant, cryogenic distillation, absorption and membrane separation [12] . However, absorption technology is now commonly method used in CO_2 separation from natural gas. Although this process has matured, it still has shortcomings such as high occupancy, high equipment levels, and operational issues for example flooding, channelling, and foaming [13]

Membranes have been used in large quantities for removal of CO_2, but have the disadvantages of high hydrocarbons loss and irreversible degradation as a result of CO_2-induced plasticization or physical aging [7]. Membrane is a discrete, thin interface which act as a selective barrier that control the permeation of chemical species interact with it. Recently, membrane contactor, a technology that combines the membrane process with traditional absorption has emerge as a potential technology for purification of natural gas [1], [14]. Membrane contactor technology has been used in natural gas purification because it has an independent control of gas and absorbent flows, compact modular structure that offers the flexibility to scale up or down, and higher packing density compare to the traditional absorption process [1]. In addition, the microporous membrane functions as a nonselective barrier that allows the liquid and gases to interact without, however, spreading one phase into the other, thus can prevent the occurrence of foaming or flooding problems. Their packaging in hollow-fibre membrane modules provides a higher mass transfer area compared to traditional packed columns, which gives membrane contactor a high intensification potential [15]

Heavy hydrocarbons such as pentane, toluene and hexane are the main impurities in natural gas and is believed to be one of the reason of membrane failures and detrimental performance loss [10], [16]. It was brought to concern in developing a reliable membrane system for natural gas purification which involves the influence of such heavy hydrocarbons on the membranes. The needs to investigate the characterization of the membrane materials arise in order to understand the impact of such hydrocarbons to the membrane material. The objectives for this study are to investigate the effect of hydrocarbon and impurities towards physical and chemical the properties of membrane and to investigate the effect of operating conditions (temperature) toward the robustness of membrane. This study will focus on effect of toluene and n-hexane exposure to the membrane and the effect of different temperature of the hydrocarbons toward the PTFE hollow fibre membrane.

II. METHODOLOGY

A. Materials

The commercialized PTFE hollow fibre (porosity > 40%) membranes were cut into small pieces (~5g), and then were exposed to solvents by immersing it into different type of hydrocarbon chemicals; toluene, C_7H_8 (R&M., purity > 99%) and n-hexane, C_6H_{14} (Merck, purity > 99%) up to six weeks. The membrane also been exposed to the hydrocarbon solvent at temperature of 70°C, 80°C and 90°C for toluene and 50°C, 60°C and 70°C for n-hexane for at least 8 hours.

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B. Characterizations

1) Fourier transform infrared (FTIR) spectroscopy

Fourier-Transform infrared (FTIR) spectra of before and after solvent exposure were determined with a Perkin Elmer Spectrum One spectrometer to study the composition and functional group of the membrane samples. The samples were examined in transmittance mode from 500-4000 cm^{-1} [17].

2) Thermogravimetric analysis (TGA)

Thermogravimetric Analysis was conducted to study the degradation temperature of the membrane and a weight loss curve (with respect to temperature). A membrane sample of 2-3 g was loaded into an alumina crucible. TGA test runs were performed under N_2 using a heating rate of 10 °C /min from 50 – 800°C with heating rate of 10°C/min [12].

3) Microscope

A digital microscope (Olympus BX41PDP72) was used to analyze the morphology of the hollow fiber membrane. The membrane sample is glued to the slide by using plasticine.

4) Mercury porosimeter

The membrane pore structure was characterized using the mercury porosimetry method (Micrometrics Auto Pore IV 9500, Kromtek Sdn Bhd.). After the PTFE hollow fibre membrane was placed in the mercury porosimeter chamber, the operating pressure was increased to fill the pores of the fibre with mercury. The pore size and porosity were determined from the volume change of mercury as a function of the operating pressure. The pressure range between 0-33,000 psia.

5) Tensile strength

The mechanical properties of the membranes were evaluated using a tensile testing machine (Universal Testing Machine, Tinius Olsen) with a tensile speed of 50 mm/min, and a load cell of 10 kN. The Young's modulus, tensile strength and strain at break were determined.

III. RESULTS AND DISCUSSION

A. *Effects of Solvent Exposure Toward Chemical Stability of PTFE Hollow Fiber Membrane*

Fourier-Transform infrared (FTIR) spectrophotometer is used to study the composition and functional group of the membrane sample. The samples were examined in transmittance mode between 500-4000cm^{-1}. Fig 1 and Fig 2 show the infrared bands for the PTFE membrane samples before and after been exposed to toluene and n-hexane up to six weeks respectively. Based on the figures below, a broad peak can be observed at around 1203 and 1149 cm^{-1} that can be indicated as the presence of amine compound with C—N bonds [12]. The peaks are also caused by CF_2 and CF_3 stretching as mentioned by Hunke, Soin, Shah et al. and Mihaly', Sterkel, Ortner et al. [18], [19]. A very weak band at approximately 1365 cm^{-1} can be traced which belong to aliphatic hydrocarbon as a result of surface reaction or adsorption [19]. The peaks at 2920 and 2850 cm^{-1} show the stretching of aliphatic C—H. Similar findings have also been found from and Mihaly', Sterkel, Ortner et al. where in this study the aliphatic C—H stretching can be found at peaks of 2853, 2927, and 2960 cm^{-1} [19] Furthermore, these findings also supported by a recent study that found the C—H stretching at peak of 2796, 2851, and 2920 cm^{-1} [12]. Peaks at 624 and 637 cm^{-1} show the CF stretching vibration and bending modes. This also can be supported as Mihaly', Sterkel, Ortner et al. in their studies also stated that the CF stretching vibrations can be found at peaks of 640 and 630 cm^{-1} [19]. CF_2 bending can be found at peak 553 cm^{-1} [19]. From both graphs, we can deduce that there are no significant changes on chemical stability of the PTFE membrane before and after exposure with different types of hydrocarbons namely toluene and n-hexane.

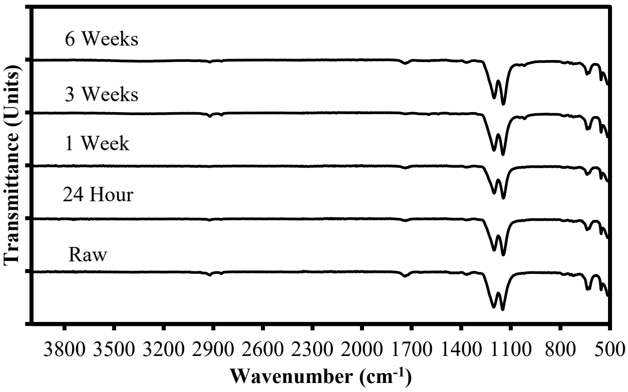

Fig 1: IR Spectra of toluene-exposed membrane at different period of exposure

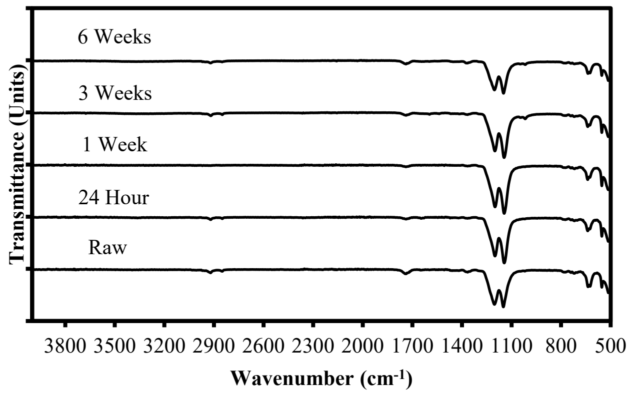

Fig 2: IR Spectra of n-hexane-exposed membrane at different period of exposure

B. Effect of Solvent Exposure Towards Thermal Stability of PTFE Hollow Fiber Membrane

The thermal analyses of the membrane were performed using TGA to determine the decomposition temperature and the weight loss of the membrane sample as a function of temperature [20]. This analysis was performed on the PTFE hollow fiber membrane samples with different solvent exposure. The samples were heated from 50°C until 800°C at 10°C/min.

Fig 3 and Fig 4 show the weight percent changes as a function of temperature for toluene and n-hexane exposure respectively. From both graphs, it shows that as the temperature increases, the weight loss percent of the membrane decreases. Based on Fig 3, at temperature between 50 to 500°C, the membranes show a slow decrement, this situation may be due to moisture content trapped in the membrane is eliminated [20]. The TGA data decreased dramatically at temperatures above 500 °C, indicating a change to the crystalline phase and has begun to decompose as stated by Husaini et al. [21]. The materials were damaged at temperatures above 640 °C. It is also observed that as the period of solvent exposure increases, the weight loss of the membranes increases. For toluene exposure, the weight percent of the membrane after 24 hours of exposure is higher than the membrane before exposure.

For membranes that have been exposed to n-hexane solvent, the same decreasing pattern as the membranes that have been exposed to toluene is observed. As shown in Fig 4, the resistance to temperature changes of the PTFE membrane was retained up to 520 °C due to the elimination of moisture [20]. The membranes were gradually decrease at temperature above 520°C due to crystallization and degraded at temperatures above 600°C.

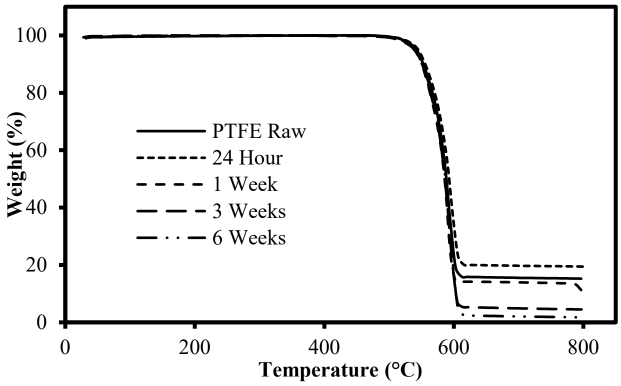

Fig 3: TGA analysis of membrane with toluene exposure at different period

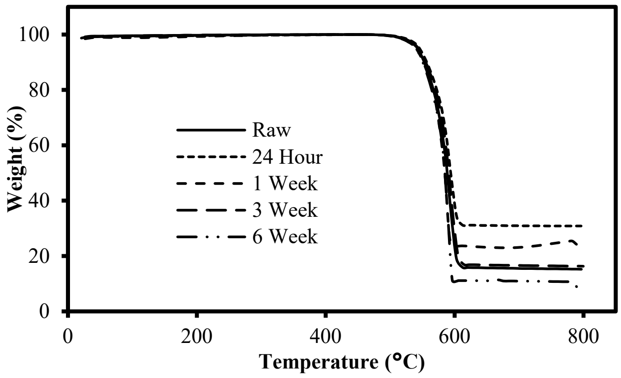

Fig 4: TGA analysis of membrane with n-hexane exposure at different period

C. Effect of Solvent Exposure Towards Morphology of PTFE Hollow Fiber Membrane

Digital geology microscope is used to observe the morphology of the membrane samples. Fig 5 and Fig 6 show the image of the cross-section and surface of the membrane samples under microscope at 200µ magnification before and after been exposed to toluene and hexane for different period of exposure respectively. As shown in the figure, the wall thickness of the membrane has reduced slightly over time when compared with raw membrane before exposed. These findings are similar to Hodgkies, Hanburry, Law et al. where the exposure of the membrane to the hexane causes the membrane suffered damage which will reduce the flux of the membrane [22]. As can be observed, the membrane that has been exposed with toluene has bigger reducing in terms of wall thickness compare to membrane exposed to n-hexane. As mentioned by Scholes, Stevens, and Kentish, the possible explanation for this finding is toluene has a greater diffusion coefficient in polymeric membrane because of its smaller critical volume compared to hexane which allows it to more easily penetrate into the membrane morphology [23].

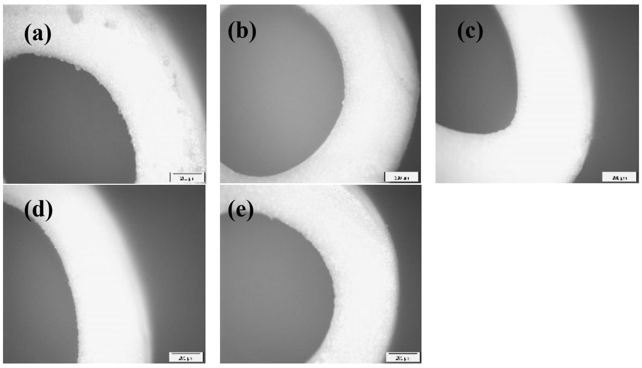

Fig 5: The image of membrane samples exposed with toluene under microscope. (a) raw membrane, (b) 24 hours, (c) 1 week, (d) 3 weeks, (e) 6 weeks

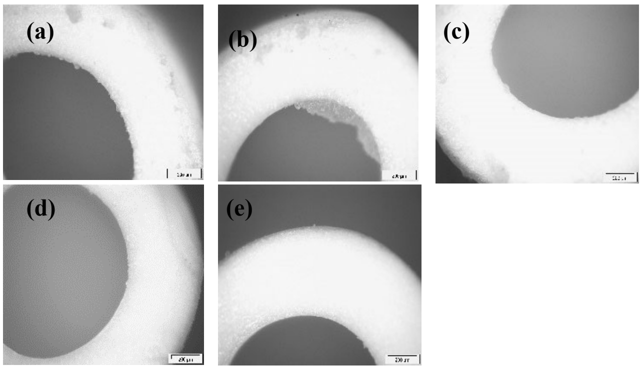

Fig 6: The image of membrane samples exposed with n-hexane under microscope. (a) raw membrane, (b) 24 hours, (c) 1 week, (d) 3 weeks, (e) 6 weeks

D. Effect of Solvent Exposure Towards Porosity of PTFE Hollow Fiber Membrane

A mercury porosimeter is used to determine the pore size of the membrane samples. Table 1 shows the porosity of the membrane samples after been exposed to toluene and n-hexane solvent for different period of exposure. It was found that such exposure caused significant decreases in membrane that has been expose to toluene but moderate decreases in n-hexane. The porosity reduced from 57.76% to 36.23% after has been exposed for 24 hours. It then later decreased to 35.5%, 32.77% and 31.31% at exposure time of 1 week, 3 week, and 6 weeks respectively. On the other hand, the porosity of the membrane reduced from 57.76% to 44.51%, 35.19 and 30.82% when the immersing time increases to 24-hour, 1 week and 3 weeks respectively. After 3 weeks, the membrane porosity has no significant changes where it decreases gradually from 30.82% to 30.75%. Nogalska et al mentioned that a high porosity in membrane is good for the flux [24] and gives a high interfacial area between phases available for the mass transport [25] unfortunately they can contribute to the membrane wetting which are a major concern in membrane process [24]. Furthermore, a study conducted by Khaisri et al. on the effects of membrane porosity in two different modules with porosity of 23% and 40% for desorption performance found that the module with high membrane porosity (40%) produced a high desorption rate however after it was carried out at long hour operation, the performance of the membrane reduced which is due to the wetting problem [26]. Lu et al, also stated in their study high porosity membrane encourages pore wetting significantly compares to a lower porosity membrane [27]. Thus, increasing the time for exposure will decrease the porosity of the membrane which in turn will reduced the performance of the membrane. The reduced in porosity of the membrane can best be explained based on the thinning of the walls of the hollow fiber membrane.

Table 1: Porosity of membrane sample at different period of exposure

Sample	Toluene	n-Hexane
	Porosity	Porosity
Raw	57.76	57.76
24 Hour	36.23	44.51
1 Week	35.50	35.19
3 Weeks	32.77	30.82
6 Weeks	31.31	30.75

E. Effect of Solvent Exposure Towards Mechanical Strength of PTFE Hollow Fiber Membrane

Tensile strength is used to measure the membranes ability to withstand a stress applied to it. Table 2 shows the mechanical properties of the membrane after has been exposed in toluene and n-hexane for a different period. It was found that as the solvent exposure time increases, the tensile strength and the initial Young's modulus decrease. The tensile strength decreases from 24.1 MPa to 15.1 and 8.33 MPa when exposed to toluene at 24 hours and 1 week respectively. Furthermore, for membrane that has been exposed to n-Hexane, the tensile strength shows a similar result as with toluene where it decreases with the increasing of the solvent exposure time. The tensile strength reduced from 24.1 MPa before exposure to 17.8 MPa after 24 hours exposure and reduced greatly to 5.63 MPa after 1 week of exposure. The decreasing of tensile strength may be due to the weaker interaction within membrane molecules where the increase in solvent exposure time, making more solvent penetrate into the membrane pores causing the intermolecular interaction between PTFE molecules weaker thus decreasing the membrane mechanical strength [28]. Besides, the alteration of membrane morphology as can be seen in Section C where the thickness of the membrane wall decreasing causing the tensile strength to decrease as well. These results are similar to the study done by Tsai, Huang, Ruaan, et al., [29]

On top of that, it was found that the initial Young's modulus also decreased with an increase of solvent exposure time. Young's modulus is a measure of the stiffness of a material, and it is defined as the ratio of stress to strain. For toluene-exposed membrane, the Young's modulus reduced gradually from 306 MPa to 193 and 151 MPa after 24 hour and 1 week of exposure respectively. Also, for membrane that has been exposed to n-hexane, the same trend can be seen where the Young's modulus decreased from 306 MPa before exposure to 217 and 169 MPa after exposure for 24 hour and 1 week respectively. As stated by Mohamed, Hasbullah, Jamian et al., the possible reason for the decreasing of the initial Young's modulus is because the membrane elasticity increases and thus decrease its brittleness [28].

Table 2: Mechanical strength of membrane samples after has been exposed to toluene and n-hexane at different period

Sample		Toluene		n-Hexane	
	Raw	24 Hour	1 Week	24 Hour	1 Week
Tensile Strength (MPa)	24.1	15.1	8.33	17.8	5.63
Strain at Break (%)	52.2	43.3	32.9	26.6	16.3
Young's Modulus (MPa)	306	193	151	217	169

F. Effect of Temperature Towards Chemical Stability of PTFE Hollow Fiber Membrane

Fig 7 show the IR Spectra of the membrane before and after been exposed with toluene and n-hexane at different temperature. Each sample have been exposed to the solvent at different temperature for a minimum of 8 hours. Based on the figure below, a similar trend as in section A has been observed. A broad peak can be observed at around 1203 and 1149 cm^{-1} that can be indicated as the presence of amine compound with C—N bonds [12]. The peaks are also caused by CF_2 and CF_3 stretching as mentioned by Hunke, Soin, Shah et al. and Mihaly', Sterkel, Ortner et al. [18], [19]. A very weak band at approximately 1365 cm^{-1} can be traced which belong to aliphatic hydrocarbon as a result of surface reaction or adsorption [19].

The peaks at 2920 and 2850 cm^{-1} show the stretching of aliphatic C—H. Similar findings have also been found from and Mihaly', Sterkel, Ortner et al. where in this study the aliphatic C—H stretching can be found at peaks of 2853, 2927, and 2960 cm^{-1} [19] Furthermore, these findings also supported by a recent study that found the C—H stretching at peak of 2796, 2851, and 2920 cm^{-1} [12]. Peaks at 624 and 637 cm^{-1} show the CF stretching vibration and bending modes. This also can be supported as Mihaly', Sterkel, Ortner et al. in their studies also stated that the CF stretching vibrations can be found at peaks of 640 and 630 cm^{-1} [19]. CF_2 bending can be found at peak 553 cm^{-1} [19]. From both graph, it can be seen that exposure to hydrocarbons at different temperature did not have significant change on the chemical stability of the membrane.

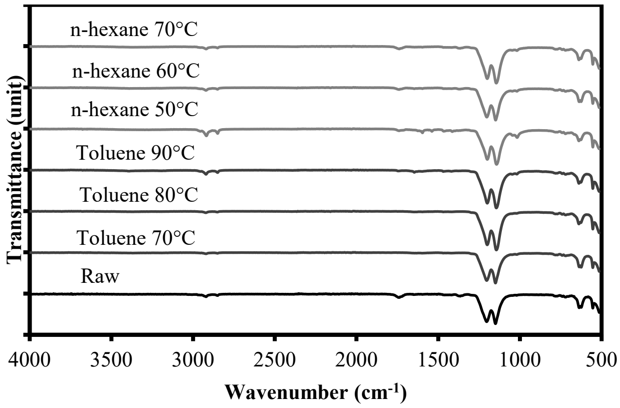

Fig 7: IR Spectra of membrane with toluene and n-hexane exposure at different temperature

G. Effect of Temperature Towards Thermal Stability of PTFE Hollow Fiber Membrane

Fig 8 and Fig 9 show the weight percent changes as a function of temperature for toluene and n-hexane exposure at different temperature respectively. From both graphs, it shows that as the temperature increases, the weight loss percent of the membrane decreases. As shown in Fig 8, the membrane shows a slow decrement at temperature of 50°C to 520°C, which the reasoning behind this is the same as in Section B of this paper where it is due to the elimination of the trapped moisture content in the membrane [20], [30] and reduced promptly at temperature above 520°C due to the change in crystallinity phase [21]. The membranes were damaged at temperature of 620°C.

On the other hand, for the membrane that has been exposed to n-hexane, the resistance to temperature changes of the PTFE membrane was retained up to 500 °C due to the elimination of moisture [20] as shown in Fig 9. The membranes were gradually decrease at temperature above 500°C due to crystallization and degraded at temperatures above 600°C. It was found that as the temperature of exposure increases, the weight percent decreases which similar to previous study [30].

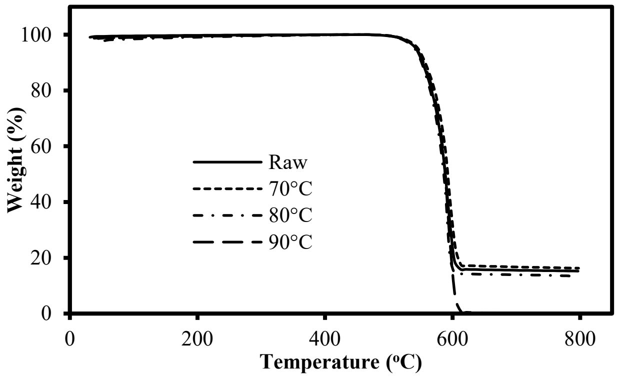

Fig 8: TGA analysis of membrane with toluene exposure at different temperature

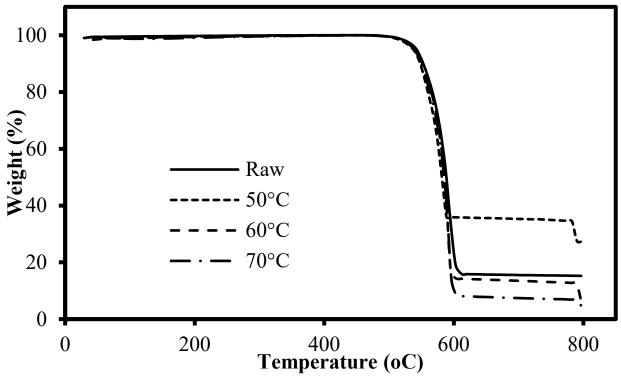

Fig 9: TGA analysis of membrane with toluene exposure at different temperature

H. Effect of Temperature Towards Morphology of PTFE Hollow Fiber Membrane

Fig 10 shows the image of the cross-section and surface of the membrane samples under microscope at 500µ magnification before and after been exposed to toluene and hexane at different temperature of exposure. As shown in the figure, there is no significant changes on the thickness of the membrane wall or the diameter of the membrane samples. The same result can be found from Hodgkiess et al. where no clear evidence of the mechanisms of damage brought about by exposure to the hydrocarbon were obtained [22]. This may be due to the exposure time of the membrane at different temperature is too short for the solvent to absorbed into the membrane structure.

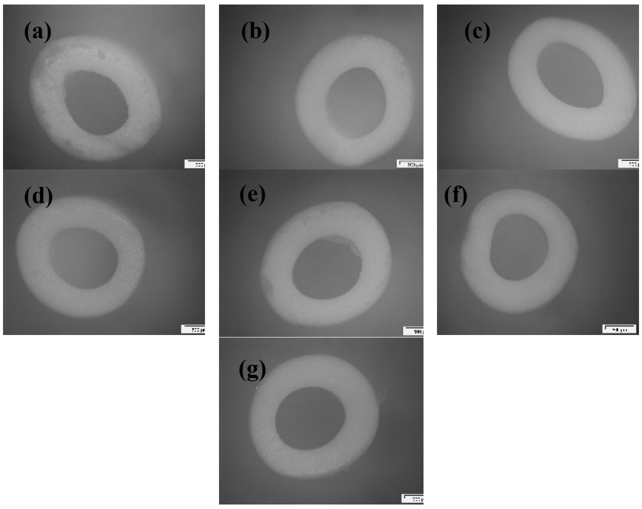

Fig 10: The image of membrane samples exposed with hydrocarbons under microscope. (a) raw membrane, (b) 70°C toluene, (c) 80°C toluene, (d) 90°C toluene, (e) 50°C n-hexane, (f) 60°C n-hexane, (g) 70°C n-hexane,

I. Effect of Temperature Towards Porosity of PTFE Hollow Fiber Membrane

The porosity of membrane samples after has been exposed to toluene and n-hexane at different temperatures is shown in Table 3. For membrane that has been exposed to toluene, the porosity of the membrane samples plummet from 57.76% to 33.59% before exposed to toluene and after has been exposed to toluene at 70°C for 8 hours respectively. The porosity did not change significantly when the temperature of the toluene solvent increase to 80°C where it only decreased from 33.59% to 33.58%. At temperature 90°C, a similar trend where minimal changes are observed when the porosity on reduced to 33.24% from 33.58% at 80°C. Thus, the porosity of the membrane samples decreases as the temperature increases for both solvents. According to Feng, Zhong, Wang et al., the heating process melted the membrane surface and thus resulted in a decrease porosity of the membrane [31]. These results were comparable to previous studies by Wang et al. [32].

As for membrane samples that has been exposed to n-hexane, a similar trend can be observed as the membrane exposed to toluene where the porosity of the membrane decreased with the increase of temperature. The porosity drops from 57.76% to 37.14% after has been exposed to n-hexane at 50°C before decrease slightly at temperature of 60°C and 70°C. the reason behind the decreasing of the porosity is the same as has been mentioned earlier [31].

Table 3: Porosity of membrane at different temperature

Sample	Toluene	n-Hexane
	Porosity	Porosity
Raw	57.7630	57.7630
50°C	-	37.1411
60°C	-	36.7403
70°C	33.5933	36.3934
80°C	33.5890	-
90°C	33.2398	-

J. Effect of Temperature Towards Mechanical Strength of PTFE Hollow Fiber Membrane

The mechanical properties of the PTFE membrane samples after has been exposed to toluene and n-hexane at different temperature is shown in Table 4. It was found that the tensile strength of the membrane decreased with an increase of temperature for both toluene and n-hexane exposure. The tensile strength decreases significantly from 24.1 MPa to 8.09 MPa when high temperature is introduced for toluene exposed membrane while it reduced from 24.1 MPa to 8.57 MPa in n-hexane exposed membrane.

These trends are similar as Section E where the membranes are exposed to the solvent at different time of exposure. A similar result can be obtained from Tabatabaei, Carreau, and Ajji [33]. As indicated by Reyna-Valencia, Kaliaguine, and Bousmina in their study, solvent molecules plasticize polymeric chains, increasing their segmental mobility and affecting drastically their mechanical strength [34]. Besides, the Young's modulus also decreases when the temperature increase. The explanation for this finding is the same as mentioned earlier where the increased of membrane elasticity which in turn causing the membrane brittleness to decrease causing the Young's modulus to decrease [28].

Table 4: Mechanical properties of the membrane at different temperature of toluene and n-hexane exposure

Sample	Raw	Toluene			n-Hexane		
		70°C	80°C	90°C	50°C	60°C	70°C
Tensile Strength (MPa)	24.1	17.7	11.5	8.09	16.1	9.83	8.57
Strain at Break (%)	52.2	45.9	23.7	24.0	46.9	23.5	29.3
Young's Modulus (MPa)	306	265	151	98.9	286	222	201

IV. CONCLUSION

The effect of heavy hydrocarbons on chemical stability, thermal stability, morphology, porosity and mechanical strength of the PTFE hollow fiber membrane has been studied under different period of exposure and operating condition (temperature). As the exposure time increases, the chemical stability of the membrane does not show any changes, while the thermal stability increases. The wall thickness of the membrane slightly decreases while tensile strength increases due to the weaker intermolecular interaction between PTFE molecules weaker thus decreasing the membrane mechanical strength. The increase of temperature of the solvent exposure does not bring any changes to chemical stability and morphology of the membrane due to the short time of exposure. On top of that, the thermal, porosity and mechanical strength of the membrane decreases as the temperature of exposure increases.

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