Preparation Isotactic Polyropylene Hydrophobic Microporous Flat Sheet via Tips for Membrane Contactor

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Abstract. The membrane technologies nowadays present the membrane to be applied in most gas separation process. Commonly designed for separating CO_2 from flue gas, membrane contactor (MC) is not only able to provide significant advantages required by industries, but also available in Malaysia. Somehow, the membrane technology in Malaysia has many limitations when most of the manufacturers only focus on the application of membrane but not the exploration on membrane fabrication and no production of hydrophobic membrane can be applied in the field of membrane absorption due to high cost, fabrication difficulty and do not meet certain specification required to be applied in specific use in Malaysia. Therefore in this study, the productions of hydrophobic microporous flat sheets were accomplished by using isotactic Polypropylene (iPP) and two type diluents: dipentyl ether and methyl salicylate. The measurement of hyrdophobility of membranes produced was conducted by Contact Angle Instrument. Membranes produced by using TIPS were characterized by SEM and FTIR. All membranes show spherical pores, indicating that membranes were formed via liquid-liquid TIPS and strong bond that formed in the membrane show that the membrane produces is stable and high in strength.

Introduction

The percentage of carbon dioxide (CO_2) gas emission from natural gas, refinery gas or coal gas purification in the world and Malaysia is getting higher year by year [1]. Membrane contractor (MC) has offer a high specific area, higher volumetric mass transfer rate, easier to linear scale up and does not required a large space as the way to minimize the CO_2 gases emission and reduce cost [2,3].

MC is a system consist the combination of the gaseous, liquid absorbent and hydrophobic membrane. It provide a barrier between two phases from dispersion with one another when this two phases being separate through a membrane [4,5,6]. A good membrane properties required for MC are high hydrophobic, high surface porosity, low mass transfer resistance and high resistance to chemicals at the feed streams [7]. A few researchers agree that improving the hydrophobility of membrane can increase the membrane long term performance [8] by providing a high specific surface area, high the selectivity by absorption liquid and increasing the driving force of flux even at a low concentration [9].

Polymeric membrane have characteristic of the polymer material such as polarity and steric are the main effect to the permeation process [10].As for the polymer with higher molecular weight will contribute to small inter-connect structure, researchers commonly use Polypropylene (PP), Polyethylene (PE) and poly (vinylidene fluoride) (PVDF)[10].They have not only lower molecular weight which attribute to the slower phase separation rate but high hydrophobility and low surfaces energies [2,11].Out of these polymers, iPP was chosen for this study due to the low cost, great mechanical properties, thermal stability and chemical resistance polymer [12,13,14].

Isotactic polypropylene (iPP) can not be dissolved in the common solvent at low temperature due to chemical inert properties. It is difficult to be formed into membrane using typical solution casting method thus, liquid-liquid demixing (TIPS)is required to dissolve the polymer [9,15,16]. There are two steps involved in the TIPS, Firstly, is to obtain a polymer –rich continuous matrix and the second steps are a fixation step.

Hydrophobicity is measured by contact angle of a water droplet formed when contacting the surface of solid material [17].Increasing the contact angle surface more than 90^o, wetting membrane phenomena tend to be eliminated [2]. Meanwhile, increasing the hydrophobic membrane to super-hydrophobic membrane contributed to increasing the contact angle from 120^o to greater than 150^o. Both of micro-structure surfaces and low surface energy (also known as surface tension or interface) property are play important rule in the hydrophobic membrane fabrication [18].

Membrane technology in Malaysia has many limitations. Existing membrane are mostly designed only focus on the application of membrane but not the exploration on membrane fabrication and there are no production of hydrophobic membrane can be applied in the field of membrane absorption. Lacking of hydrophobic membrane in local market had eventually increasing the price even, the imported hydrophobic membrane not only expensive but sometimes unable to meet certain specification required for specific uses in Malaysia. Furthermore, the preparation hydrophobic membrane much cheaper compared to others polymeric material.

Based on the problems stated, the objectives of this study are to optimize the formulation of iPP membrane Preparation of iPP membrane using TIPS method with manipulating two different type of diluents dipentyl ether (DPE) and methyl salicylate (MS). Times of immersion in methanol were manipulated. The best parameters are identified for optimum membrane preparation condition and characterized.

Experimental

The iPP with average molecular weight (Mn) of 250 000 was purchased from Aldrich. DPE and MS were used as diluents for membrane preparation. Methanol was used to extract the DPE from polymer. All the diluents purchased from Aldrich were used without further purification.

Briefly, the were mixed with diluents MS or DPE in beakers at desired iPP concentration (20wt %).The beaker was placed in a hot plate until a homogeneous solution formed. A stainless steel mould was pre-heated on the hot plate. A little portion of homogeneous solution was pour into the mould. It was then reheated on the hot stage at 453K for another 5 minutes. The entire assembly was then quenched in water bath to induce phase separation in the sample.

Then, membranes were immersed in methanol to exact the remaining diluents in membranes. The immersion time were varied. Microporous iPP membranes were obtained by evaporated the extraction reagent in the oven at 333K (60°C) for about half hour.

Result and Discussion

Effect of Immersion Time to the Hydrophobility

A hydrophobility membrane can be achieved when the contact angle of the water droplet on the membrane is higher than 120°.Thus, both side of the membranes were tested to determine the best side to be applied in membrane contactor. It can be see from the Fig.1, that both of the contact angle on the membrane surface fluctuated over the time. The hydrophobility of membranes somehow higher for the membranes that use DPE as diluents compared to the MS diluents. At 3 hours immersion time, the highest contact angle for MS diluents was obtained for 103.270°. Whereby, the MS's highest peak is 103.040°. Figure 2(a) show the droplet waters having the highest contact angle with the top surfaces membrane for using MS.

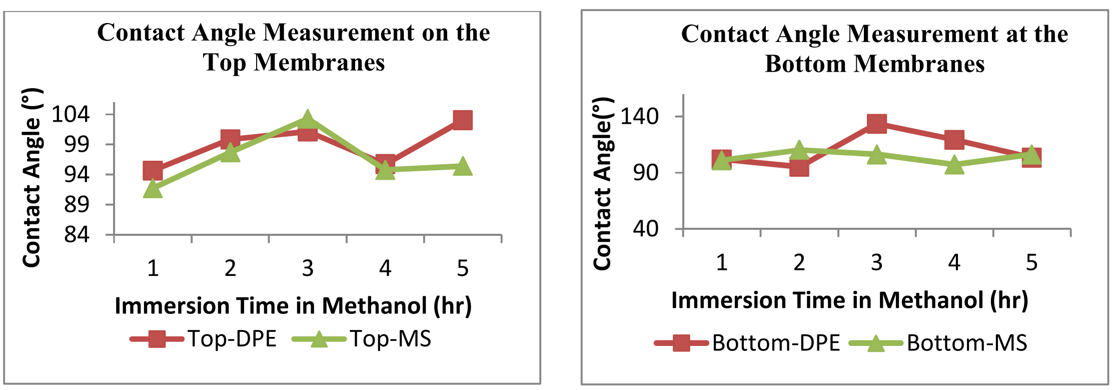


Figure 1. The graph of the contact angle on membrane top (left side) and bottom (right side) using two types of diluents versus immersion time in methanol

From graph of contact angle measurement at bottom, it can be observed that the both of diluents graph are showing opposite changes over time. The contact angles at the membrane bottom of DPE diluent mostly show higher hydrophobility than MS diluent. The highest peak of the graph shows the membrane contact angle of 133.440° at immersion time in 3hrs show in Fig. 2(b) which is ideally fulfill the standard for a hydrophobic membrane.

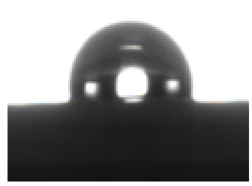
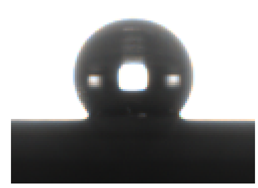
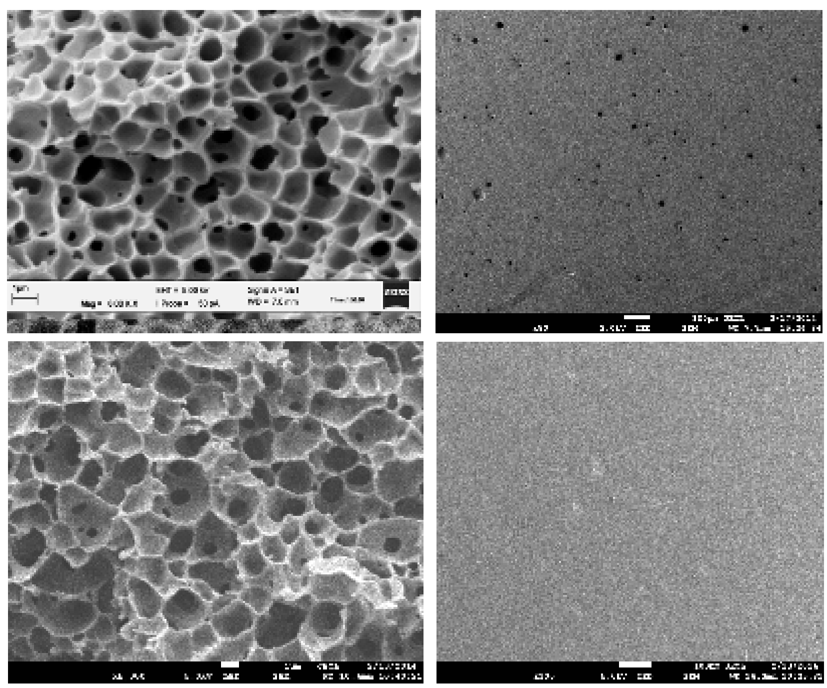
a.  b. 

Figure 2. The picture of the highest contact angle of the water droplet on the membrane a) top surface using MS and b) bottom surface using DPE

The data collected highlights all membrane show the contact angle bigger than 90° which able to limited wetting phenomena. The hydrophobic membrane that suit to be applied in the membrane contractor is at the bottom side by using DPE which was immersed in methanol for exactly 3 hour.

Morphology and Pores Structure of the Membrane

The highest contact angle value samples were picked to be observing their morphology and pores structure. Previous studies showed that the optimal polymer concentration for membrane concentration is 20wt%, which is because membranes with high porosity are obtained [12].



a.

b.

Figure 3. Final morphology of the cross sections (left side) and surfaces (right side) of membranes prepared from 20wt% of iPP: (a) 3h using DPE and (b) 2hr using MS

Fig.3 presents the resulting morphology of the membranes prepared with 3 and 2hour of immersion time in methanol. The internal pore sizes could be estimated being between 1.0 ~ 1.2µm for membrane prepared by DPE. The larger internal pore sizes can be detected for MS diluents compared to the DPE diluents. The internal pore sizes could be estimated being between 1.35~ 2.17µm for MS diluents. Membranes structure is considered similar and show spherical pores, indicating that membranes were formed via liquid-liquid TIPS [19].

However, marked differences have been observed for the outer surfaces where pores are detected for 3 hour immersion for DPE solvent. This could lead to anisotropic pore structure near to the membrane surfaces, since cooling rate in the surface is faster than inside the membrane. As the mould was used for membrane formation, the interfaces between polymer solution and stainless steel mould may have an influence.

Chemical Composition of the Membrane

The graph in Fig.4 presents the raw iPP which is before under going the TIPS process. The frequencies detected for the raw iPP are 2953.73, 2920.71 and 1456.44 cm^{-1}.At both 2953.73 and 2920.71cm^{-1}, wavelengths shows membrane having the stretching of C-H bonds which indicated a strong intensity. Wavelength 1456.44cm^{-1} shown the C-H bend put it at a variable intensity.

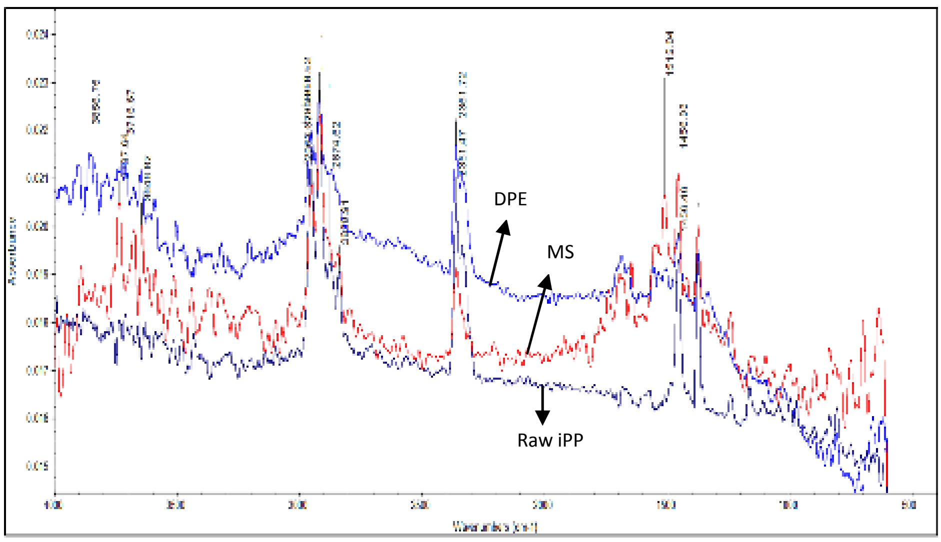


Figure 4. IR spectra of raw membrane and membrane produce through TIPS

The C-H bonds are stretching or fairly abiquistous with each others can be point out from the frequency 2953.68 cm $^{-1}$ for iPP-DPE. The spectrum's frequency is at 1456.46 cm $^{-1}$ which picturing the C-H bends. The wavelengths for iPP-MS are also show the similarity to the one obtained for iPP-DPE. The highest peak shown in range of 2918.99 cm^{-1}. There is also a frequency of 2953.05^{-1} detected. The frequencies range indicated alkanes C-H bonds are stretching. Whereby, C-H bend are detected at the wavelength 1455.44 cm^{-1}.

All the wavelengths for all membrane contain relatively peaks demonstrating a strong C-H bond. This medium bond that formed in the membrane show that the membrane produces is stable and high in strength. The membrane shows that the membrane has high selectivity and permeability. The raw iPP and the membrane IR spectra graph were show that TIPS does not change the chemical composition in iPP through out the membrane preparation process.

Conclusion

Immerse membranes in methanol for 1 to 5hours for both diluents produce membranes that resist wetting problem. Furthermore, hydrophobic membranes were able to fabricate for 3hr immersion time by using DPE. Further immersion in methanol may reduce the liquid resistant on the membrane surface. Overall, the bottoms of the membranes were able to constrain water droplet better than top membrane. It is due to the bottom membrane had smaller pores size since cooling rate at the bottom is faster than the top and inside the membrane.

Analysis by SEM shows that all membranes produced spherical pores which indicating that membranes were formed via liquid-liquid TIPS. The pores sizes of iPP-MS membrane were found larger compared to iPP-DPE pair due to the lower viscosity. The membrane produced were anisotropic membrane as cooling rate slightly different from top to bottom.

The chemical compositions in membrane before and after TIPS process were also analyzed. It was found that there are no changes for iPP composition that through out TIPS process. All the wavelengths for all membranes produce contain relatively peaks demonstrating a strong C-H bond. This strong bond that formed in the membrane show that the membrane produces is stable and high in strength and estimated to have a high selectivity and permeability.

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