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THE EFFECTS OF ADIPIC ACID ON THE HYDROPHOBICITY IPP MEMBRANES PREPARED USING DPE VIA TIPS

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ABSTRACT

Over the past few decades, global expansions of industrial activities significantly has increased the concentrations of some gases in the atmosphere, such as Carbon Dioxide (CO_2) from flue gas, which tend to warm the earth's surface. One of the technology is gas separation using membrane can remove the CO_2 from flue gas to prevent the danger of global warming. However, in the flue gas, there is water vapour content that causes the membrane to swell.Thus, for this study, in order to increase the durability and performance of membrane for CO_2/N_2 separation, the hydropobic membrane is purposed. This study focuses on the effect of the addition of adipic acid on the hydrobicity of the isotactic Polypropylene (iPP) membranes. The results show that membrane prepared without addition of adipic acid produces highest contact angle, CO_2 permeability and selectivity which are 112°, 22.01 GPU and 1.59 respectively. For morphology by using Scanning Electron Microscopy (SEM), observation on the increasing adipic acid shows increasing in pore size and the pore size distribution.

Keywords: thermally induced phase separation, isotactic polypropylene, dipenyl ether, hydrophobic membrane, gas separation.

INTRODUCTION

Typically, the compositions of the flue gas are 71.8 % of Nitrogen (N_2), 13.6 % of CO_2, 11.2 % of water vapor (H_2O), and 3.4 % of Oxygen (O_2) (World Bank. 2008). The sources of flue gas emission mainly are from natural gas, refinery gas or coal gas purification (Brunetti *et al.* 2010). Gas separation membranes have been applied commercially to separate gas. One of the significant challenges in gas separation systems is the presence of water vapor from flue gas. The permeability of gases showed a significant decrease in the presence of the water vapor .Water vapor is usually considered as a minor component but, it can affect significantly the membrane gas transport properties (Chen *et al.* 2011). An ideal membrane for membrane contactor application should have high hydrophobic, high surface porosity, low mass transfer resistance and high resistance to chemicals at the feed streams (Tang *et al.* 2010) .

Hydrophobicity of a surface can be determined by measuring the contact angle of a water droplet with the contacting surface of a solid material (Sun, 2010). Increasing the value of the contact angle (more than 90º) implies high hydrophobic whereby a surface with a contact angle of below 90° can be considered a hydrophilic (Dindore *et al.* 2004). By increasing the hydrophobicity of a membrane, the performance and durability of the membrane can be improved (Mansourizadeh and Ismail, 2010). Usually, to improve hydrophobicity in a membrane, the polymeric membrane materials were chosen because of their properties, which are high in molecular weight, and low energy surfaces (Dindore *et al.* 2004 and Matsuyama, *et al.*2002). High molecular weight will contribute to small inter-connect structure (Mansourizadeh and Ismail, 2010), while low surface tension material lead to higher hydrophobicity on the polymer material surfaces.

Isotactic Polypropylene (iPP) is the most outstanding membrane materials because its low cost, offers attractive properties such as rigidity, low molecular weight, thermal and chemical stability. iPP also is excellent resistance to acids, alkalis and organic solvents. The iPP cannot be dissolved in the common solvent at low temperature due to chemically inert properties. It is difficult to be formed into membrane using the typical solution casting method. Therefore, liquid-liquid demixing by Thermally Induced Phase Separation (TIPS) is required to dissolve the polymer (Abedini and Nezhadmoghadam, 2010; Matsuyama *et al.* 2000 and Roach *et al.* 2008).

Nucleation agent, namely adipic acid, benzoic acid and dibenzylidene sorbital act as accelerator for crystallization rate. The polymer crystallization kinetic such as size of pores, porosity, and the pore sizes distribution are also able to be controlled by adding the suitable nucleating agent. It was reported that adding adipic acid on the TIPS process in the solution mixture iPP, the crystallization parameters, namely, dynamic crystallization temperature, spherulite size, crystallization rate, crystallization scope, and crystallinity were changed (Yang *et al.* 2008). A study by McGuire was found that by adding the adipic acid contributed to the smaller spherulites than the membrane prepared without adding nucleating agent (McGuire *et al.* 1993) . A finding by Luo et al, the smaller pore sizes membranes were developed when the additive concentration increased (Luo *et al.* 2006).In this study, adipic acid was used and expected to enhance more nuclei, spherulites pores structures and narrow pores sizes which construct more uniform microporous structure (Kim *et al.* 2002) and thus improve the hydrophobicity (Lv *et al.* 2012).

The hydrophobic membrane commonly has wetting limitations. The wetted incident is very

undesirable for gas-gas separation system. This is due to the exposure of the absorbent to membrane pores during the immersing process. It could affect the membrane to become more resistant and reduce the overall mass transfer coefficient of the membrane (Lv *et al.* 2012). The commercial membranes were manufactured only focusing on in the application but no exploration on the membrane fabrication. Basically, the wetting problem depending on both chemical composition and the geometrical microstructure of the material (Sun, 2010).To minimize the wetting problem, the structure and morphology of the hydrophobic membrane should be controlled during the manufacturing process.

Based on the problems stated, the objectives of this study were to study the effect of adipic acid on the hydrophobicity iPP membranes through several characterizations such as contact angle; Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). In order to obtain high hydrophobic membranes, the TIPS process is believed to be able to control the membrane's pore sizes. The hydrophobic membranes were proposed to minimize the wetting problem in gas-gas separation system.

EXPERIMENTAL

Experiment procedure
The iPP with average molecular weight (Mn) of 250 000 was purchased from Aldrich, as well as adipic acid, Dipenyl Ether (DPE) and methanol. All the diluents purchased from Aldrich were used without further purification. Briefly, the iPP with 20 wt% concentration were mixed with DPE in beakers at desired iPP concentration and adipic acid powder was also added. The experiment design is shown in Table-1.The beaker was placed on 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 poured into the mould. 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. Microporous iPP membranes were obtained by evaporating the diluents in the oven.

Table-1. Experimental.

Bil.	DPE volume	Adipic acid concentration (wt %)
1	80.0	0
2	79.5	0.5
3	79.0	1.0
4	78.5	1.5
5	78.0	2.0
6	77.5	2.5

Gas permeability and selectivity
The performance of polypropylene membrane tested with pure gaseous (CO_2 and N_2) by using permeation test set shows in Figure-1 .The membrane cut into a small circle with diameter 4.8 cm. Then, the circle membrane was pleated and folded around the permeate core. The separation of pure gas across fabricated membrane will be tested at range pressure between 1-2 bars. The permeability is defined as the transport flux of material through the membrane per unit driving force per unit membrane thickness. Meanwhile, the volumetric gas permeation rates were measured with a soap bubble flow meter.
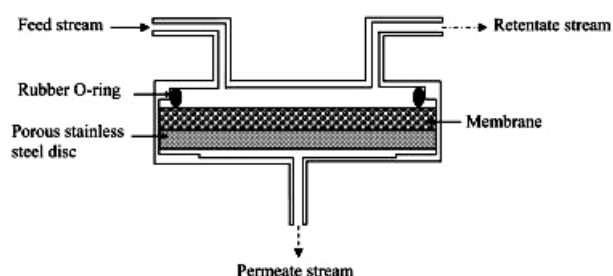

Figure-1. The illustration of the permeation gas (Jawad *et al.* 2014).

Contact angle measurement
Test System of JY-82 Video Contact Instrument was used to measure the contact angle of distilled water on the PP membrane. A droplet of 5 ml distilled water was placed on the membrane surface by a syringe. The contact angles were calculated from a digital video image of the drop on the membrane using an image processing program for the estimation of the contact angle from the height and width of water droplet.

Scanning electron microscopy analysis
The membrane morphology both cross section and surface layer were examined by SEM (Carl Zeiss EVO50). This equipment used for analyzing the membrane surface, examine the morphology, the membrane structure, pore distribution, defects and presence of impurities.

RESULT AND DISCUSSION

Effect of adipic acid on the hydrophobocity membrane
A hydrophobic membrane can be achieved when the contact angle of the water droplet on the membrane was higher than 90°. Lower than 90°, the membrane turns to a hydrophilic membrane (Dindore *et al.* 2004). The effect of additives was also observed and compared with the membrane prepared without the additive by contact angle measurement. Figure-2 demonstrates the effect of additive concentration on the contact angle measurement of PP-DPE. The highest value of contact angle obtained from bottom side of membranes prepared were ~112° for DPE. Increasing the additive concentration, the

hydrophobicity of the membrane also increase from 0.5 wt% until reach 1.5 wt% before the hydrophobicity gradually decrease when additive was added until 2.5 wt%. This shows that increasing the nucleation agent (0.5 to 1.5 wt% of adipic acid) also decreasing the space for the pore growth and thus produces the narrow pore sizes's membrane (Kim *et al.* 2002). The smaller pore diameter was expected to resist the wetting problem better than larger pore diameter membranes. However, if the pores were too small (2.0 to 2.5 wt% of adipic acid in homogeneous solution) would lead the pores to trap some alcohol and prevents the solvent from evaporating, thus wet the pores and reduce the hydrophobicity of the membranes. A few of large error bars can be observed in the figure indicates the large standard deviation. This result may due to drying process and surface roughness (Yave *et al.* 2005). But the membranes prepared without additive, give the highest contact angle.
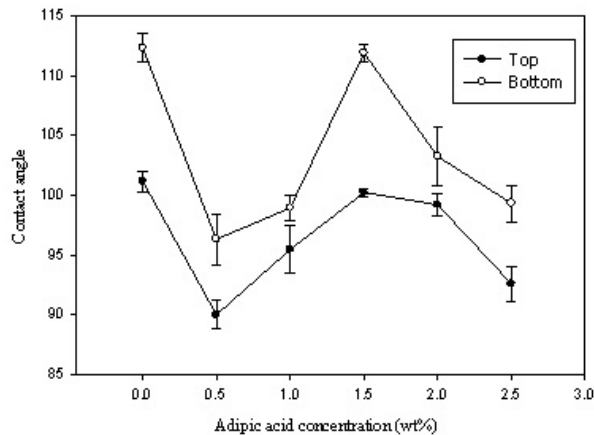

Figure-2. The effect of additive concentration on the contact angle measurement on membrane surfaces using diluents DPE.

It was obvious that the bottom sides of the membranes were better than the top side of the membrane. It was may associate with the smaller pore size on the bottom side. Small pore sizes were attributed by a very fast cooling rate (McGuire,1993). The small pore sizes also distributed to the higher hydrophobicity measurement (Mansourizadeh and Ismail, 2010).

Effect of adipic acid on membrane's permeability and selectivity

Membrane separation is a technology which selectively separates (fraction) materials via pore and minute gaps in a molecular arrangement of a continuous structure. Membrane separations are classified by pore size and by the separation driving force (Ismail *et al.* 2015).Permeability is the rate of molecular gases will pass through a membrane. The lower the number of permeability, the less the molecule gases will come through the membrane. The thickness of the membranes prepared to be ~0.025cm (250μm) where according to

Albrecht *et al.* the range pore size between 10-300 μm would posses high porosity microfiltration properties (Albrecht *et al.* 2005). The pressures applied at 1.0 bar, 1.5 bars and 2.0 bars compare the permeation rate of CO_2 and N_2 of the developed membrane

The permeability of the gas CO_2 was measured using different pressure from 1.0 to 2 bars for PP-DPE shown in the Figure-3. The non-additive starts the graph with a high permeability for 1.0, 1.5 and 2.0 bar respectively, but when adding more additive from 0.5 to 2.0 wt %, the permeability was increased gradually. Meanwhile, the permeability of N_2 is shown in Figure.4 by the membrane prepared by DPE diluents. As it can be observed, the permeate flux and permeability of CO_2 are lower than N_2 for permeation test using membranes prepared. Since permeability, lower for N_2 compared with CO_2 gas, the N_2 and CO_2 molecule permeation through the membrane were by kinetic diameters difference. Membranes prepared without the additives obtain the highest CO_2 and N_2 permeate flux which is 22.0 GPU and 15.5 GPU respectively. The similar work of CO_2/N_2 separation performance, revealed the CO_2 permeance greater than 10 GPU which demonstrated the similar result (Merkel *et al.*2010). As examined in the SEM micrograph, the membranes prepared without adding adipic acid had smaller pore size compared to the membranes prepared by adding adipic acid. Thus, it became one of the factors to promote a high permeability for the membrane without the additive. The permeability obtained might attribute by the larger average pore size. The high permeability might due to the membrane large free volume (Pandey and Chauhan, 2001). As the pore size decreases, the porosity also decreases, resulting in a lower gas flow through the membrane. Both average pore sizes and pore size distribution must be balanced in order to fabricate a good membrane, thus increase the flux of the membrane (Abedini and Nezhadmoghadam, 2010 and Kim *et al.* 2002).

The relative contributions of the different mechanism are depending on the properties of the membranes and the gases, as well as on operating conditions like temperature and pressure (Pandey and Chauhan, 2001) .Theoretically, as pressure increases, the permeate flux and permeability also must increase. The permeability increased linearly with the increase in pressure show that the graph follows the laminar flow and also obeys the Darcy's law (Yave *et al.* 2005).However, in Figure-3 and 4 show that increasing the pressure from 1 to 2 bars, the permeate flux the gases were reduced . The highest permeability obtained when 1 bar pressure was applied. It can be concluded that permeate flux and permeability decreases when increasing the pressure from 1 to 2 bars. At 1.5 bars, the permeate flux and permeability decreases because the membrane may be starting to cloak or damage. Cloaking can reduce the pore size and thus cause a drastic reduction in the efficiency of a membrane separation property (Yu *et al.* 2005).
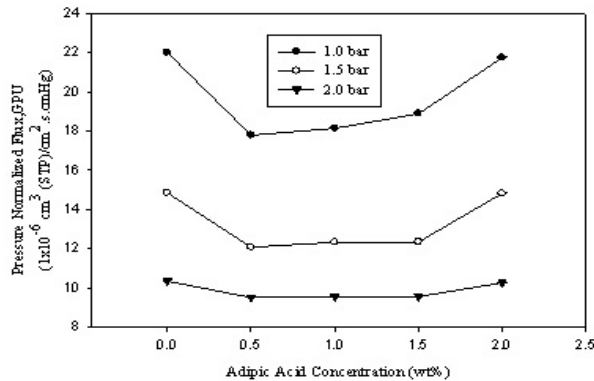
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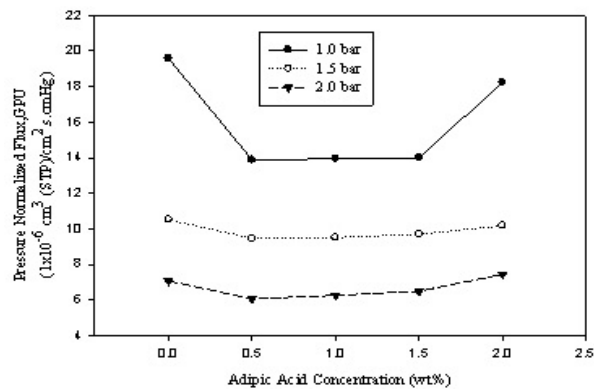**Figure-3.** CO_2 permeability of membrane prepared using DPE.

Figure-4. N_2 Permeability graph of membrane prepared using DPE.

The range of selectivity of CO_2 to N_2 obtained was 1.13 to 1.59 for iPP-DPE shown in Figure-5. Membranes prepared without the additive shows the highest selectivity, whereby adding additive 1.0 and 0.5 wt% shows the lowest selectivity for iPP-DPE membrane. In a study by Merkel *et al.* CO_2/N_2 selectivity of 20 - 100 were obtained using a pressure ratio of 5 -10 bars using Poly (ethylene oxide) (PEO) (Merkel *et al.* 2010).
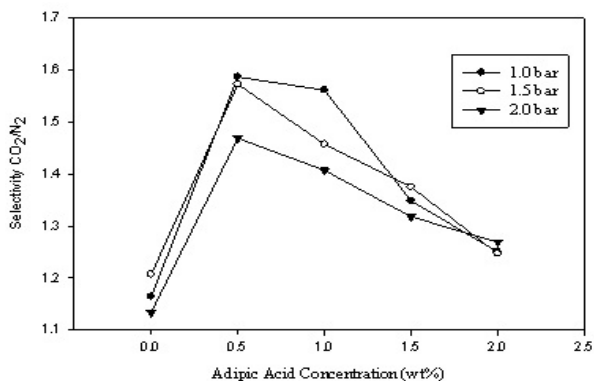
Figure-5. The relationship between the additive concentration with the selectivity of CO_2 and N_2 gas by membrane prepared by DPE.

The permeate flux and the permeability of the CO_2 gas through membranes without the additive were higher than membranes prepared with various additive concentrations. The pore size and the pore size distribution affected the viscous and diffuse flow differently (Iversen *et al.* 1997). Viscous flow would allow small molecules to pass through while diffuse flow happens due to the diffusion of selective molecular gas through the membrane. In gas separation, it is normal for membrane to have higher in permeability, but eventually lower in selectivity (Pandey and Chauhan *et al.* 2001).

The separation of common gas pairs is typically accomplished by a size selective sieving mechanism (Robeson *et al.* 2008).From the result, it shows that the selectivity of nitrogen was less than CO_2. The differences between these two gases were due to the kinetic diameter size (Å) of the gaseous molecules (Kentish *et al.* 2008). As CO_2 has a smaller kinetic diameter than N_2 which 3.30 and 3.64 Å respectively, CO_2 selectivity was found larger than N_2. As according to Baker, the permeability increases with increasing permeate size and larger molecules permeate preferably (Baker, 2004).N_2 has the largest kinetic diameter and lower critical temperature, which accounts for its relatively low permeability in polymer membranes (Low *et al.* 2013).

**Morphological characterization of membranes by SEM**

The morphology of the fabricated membranes is resulting from the thermal separation process reflects the thermodynamics and phase separation kinetics of the polymer-diluent system. Thermodynamic involved the growth period of the pores which depends on the cooling rate and the temperature difference between binodal and crystallization curves in the phase diagram. On the other hand, the separation kinetics depend on the viscosity of the polymer system (Yave *et al.* 2005). The highest contact angle value samples were picked to be observing their morphology and pore structure. Previous studies showed that the optimal polymer concentration for membrane concentration was 20 wt%, which was because membranes with high porosity are obtained (Yave *et al.* 2005 and Matsuyama *et al.* 1999).

The polymer crystallization kinetic such as size of pores, porosity, and the pore sizes distribution is also able to be controlled by adding the suitable nucleating agent (Yang *et al.* 2008 and Luo *et al.* 2006). There were few researchers found that adipic acid being the preferable nucleating agent in the iPP membrane preparation (Tang *et al.* 2010 and Kim *et al.* 2002). By adding a nucleating agent, more nuclei enhanced, spherulites pore structures and narrow pores sizes expected to be accomplished. Researchers believed that smaller pores attributed to higher hydrophobicity on the membrane surfaces (Lv *et al.* 2012).

Figure-6, 7 and 8, present the resulting morphology of the membranes prepared without additive and by adding an additive respectively. All the sample structures were considered similar and show spherical pores, indicating that membranes were formed via liquid-

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liquid TIPS (Matsuyama *et al.* 2002). The thinner wall and higher interconnectivity between cellular pores can be observed throughout the iPP-DPE membranes with additive while, thicker wall and less interconnectivity additive structure in the membrane without adding the additive. The more time required for the membrane without adipic acid in order for pores to grow and the interconnectivity between the pores to increase. Higher hydrophobocity of the iPP-DPE diluents may contribute not only by the smaller pores sizes membrane, but also the interconnectivity between the pores. According to Mansourizadeh and Ismail, more uniform microporous structure constructs would improve the hydrophobicity (Mansourizadeh and Ismail, 2010).Not only smaller pore diameter and pore size distribution were able to develop better hydrophobicity on the membranes, but also uniform structure were counted as well.
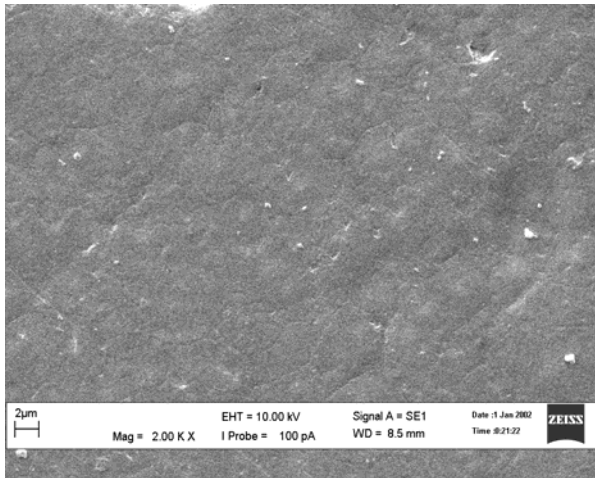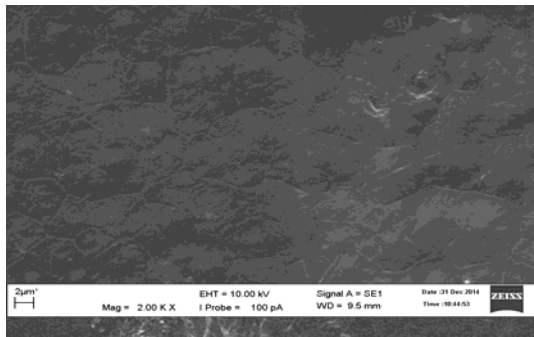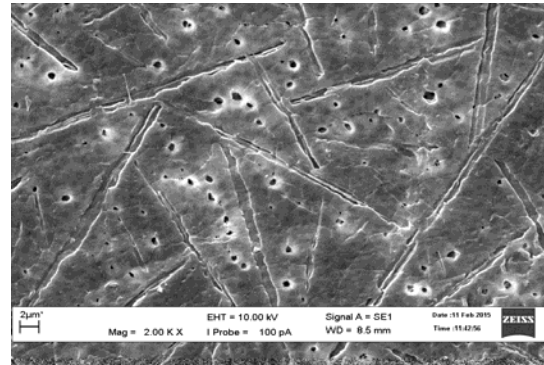

(a)
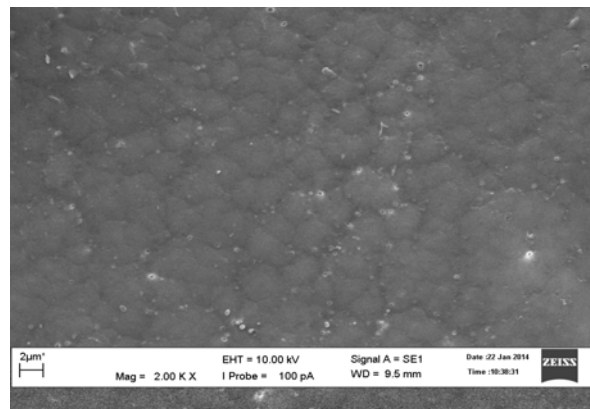
(b)
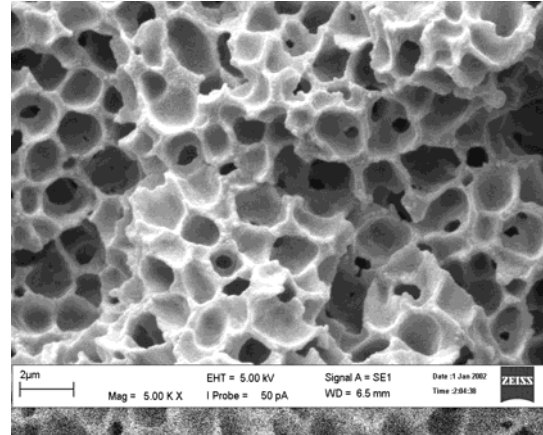
(c)

Figure-6. Final morphologies and structure of PP-DPE membranes without additive. Where a: top surface, b: bottom surface and c:cross section (5000 x).

Meanwhile, marked differences have been observed for the outer surfaces where pores were detected at the bottom membrane and not at the top membranes. This is defined that both membranes had a very weak surface porosity. The pore structure near to the membrane surfaces are smaller since the cooling rate on the surface was faster than inside the membrane (Matsuyama *et al.* 1998). As the mold was used for membrane formation, the interfaces between polymer solution and stainless steel mold may have an influence. Apparently, there were some defects are detected on the surfaces. This may attribute to the decreasing the membrane permeability as well as selectivity performance, but minor and negligible effect to be applied in liquid separation. Defect on the outer surfaces might occur due to the entrapment of the air bubbles when cooling processes act quickly on the outer side, and dust particle (Robeson, 2008).
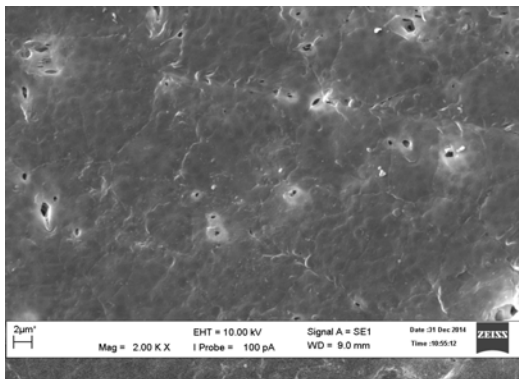
At the bottom surface, a few pores were detected. This phenomenon is similar to the membrane without the additive. Somehow, the gaps between the pores in this membrane were larger compared to the membranes prepared without adding the additive (pore size distribution). The pores sizes on top side of membrane of 1.5 wt% additive were larger compared to the membrane samples prepared by 0.5 wt%. There were also white stain on the bottom surface, possibly on the membrane with additive because of the faster crystallization process, due to the shift from the cloud point to dynamic crystallization curves when quench in water bath. The crystallization also may contribute by the nucleating agent in the homogeneous solution. The membranes did not show any pores on the top surfaces, but there were some defects were detected.
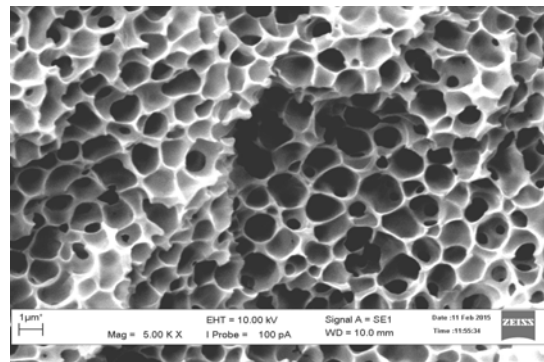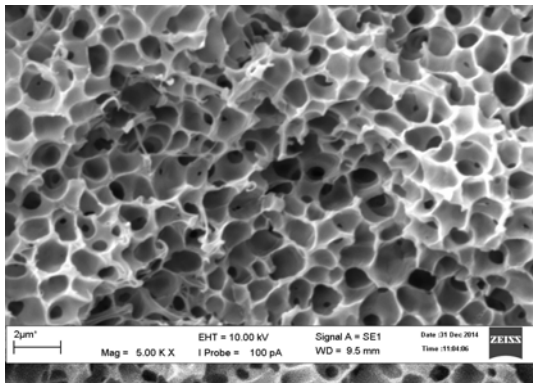
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(a)

(b)

(b)

(c)

Figure-8. Final morphologies and structures of PP-DPE membranes with 1.5 wt% of additive. Where a: top surface, b: bottom surface and c:cross section (5000 x).
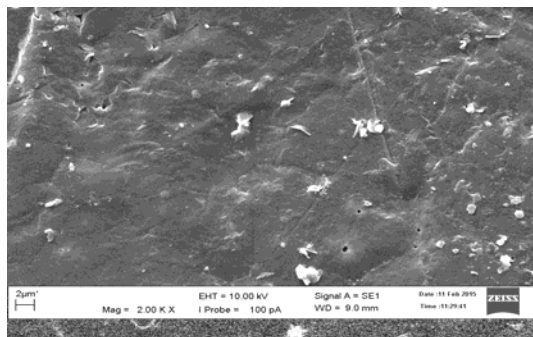

(c)

Figure-7. Final morphologies and structures of PP-DPE membranes with 0.5wt% of additive. Where a: top surface, b: bottom surface and c:cross section (5000 x).

(a)

The higher pore distribution can be observed by membranes prepared by adding adipic acid as nucleating agents. The internal pore sizes could be estimated to be between ~0.6 to ~ 1.9 μm for non additive membranes, whereby ~0.44 to ~2.22 μm and ~0.78 to ~1.78 μm 0.55 ~ 1.27μm for 0.5 and 1.5 wt% additive in the membranes respectively shown in Table-2. The internal pore sizes in the membranes were found with 0.5 wt% additive smaller than can be detected in the PP-DPE system without adding additive. However, adding more nucleating agent from 0.5 to 1.5 wt% in the homogeneous solution, the larger pore sizes were formed. The results show that the permeability and selectivity of fabricated membranes were increased when pore sizes increased. Larger pore would allow the gases to pass through easily and faster compared to smaller pore size membranes might because of the viscous flow (Pandey and Chauhan, 2001).

Table-2. The average pore size and pore size distribution.

	Pore size distribution	Average pore size
iPP-DPE	0.60 - 1.90 μm	1.10 μm
iPP-DPE (0.5wt% of Adipic Acid)	0.44 - 2.22 μm	1.09 μm
iPP-DPE (1.5wt% of Adipic Acid)	0.78 - 1.78 μm	1.17 μm

CONCLUSIONS

The membranes prepared without additive were able to produce higher contact angle measurement compared to the membrane that using additive. The highest contact angle value obtained of membranes prepared was ~112°. While the highest contact angle obtained by the membranes prepared with the adipic acid, concentrated of 1.5 wt% which was ~111 °. The hydrophobicity on the membranes prepared were observed higher with the increasing the pore size. The hydrophobocity at the bottom sides of the membranes were better than the top side of the membrane. There was no significant effect on hydrophobicity discover by adding the adipic acid compared to membrane prepared without adding adipic acid, which also shows that adipic acid contribute less effect on the nucleation. It can be concluded that adipic acid was not a good nucleating agent for iPP-DPE system.

Increasing the adipic acid into polymer solution, develop higher the permeate flux of the CO_2 and N_2 gaseous, however adding more than 1.5 wt% would lead the permeability and selectivity to decrease. The highest membranes in term of membrane porosity and flux performance were able to achieve by adding 2.0 wt% adipic acid. However, the highest permeability and selectivity performance was generated by membrane samples without adding additive. CO_2 selectivity was found larger than N_2. This condition was considered that gaseous permeate through the membrane by molecular sieving mechanism where the larger pore sizes membranes would allow higher permeability and selectivity. It was found that, maximum CO_2/N_2 selectivity of 1.58 and a CO_2 permeance of 22.00 GPU were obtained without adding the adipic acid.

There were smaller pore sizes established by the membranes with 0.5 wt% for the fabricated membranes. At the top surface of the membranes show the dense, thin layer was formed which explained the hydrophobicity were weak on this side. Somehow, cross sections depict those membranes structures were similar and show spherical pores, indicating that membranes were formed via liquid-liquid TIPS.

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