Preparation and Characterization of PVC-PEG Hollow Fiber Membrane of Biogas Separation

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A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Environmental Management

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ABSTRACT

Flat sheet and hollow fiber membrane were prepared by phase inversion method. Both geometries were studied on physical, permeable, morphological property. Poly (vinyl chloride) (PVC) is the main material; while, Poly (ethylene glycol) (PEG) was the additive used for increasing gas permeation. The resultant flat sheet membranes were fabricated by casting technique. Meanwhile, hollow fiber membranes were spun by dry-jet spinning process. Carboxylated Styrene Butadiene Rubber (XSBR) was used to coat the skin surface of the membranes in order to study membrane performances of the permeation of CO_2, which is one of the main components of biogas. The draw ratio and the air gap distance were investigated in order to consider suitable morphological, permeable and physical properties. Furthermore, the contact angle measurement, dynamic mechanical thermal analysis (DMTA), fourier transform infrared spectroscopy (FT-IR) as well as the tensile strength, viscosity, dielectric measurement and scanning electron microscope (SEM) were examined to verify the properties of appropriate gas separation membranes. The results of the prepared membranes show that the fingers-like substructure may be completely formed at high elongational draws. XSBR rubber was presented as a suitable selective layer for CO_2, N_2, O_2 and mixed gas permeation. The pure gas selectivity experiments indicated that the coated hollow fiber membranes were presented of CO_2/N_2, O_2/N_2 : 12.89, 16.30 and CO_2/CH_4 mixed gas selectivity showed of 1.36 respectively.

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CHAPTER 1
GENERAL INTRODUCTION

1. BACKGROUND

One of the most successful renewable energy development projects in Thailand is the use of beneficial biogas for energy generation. From the past till now, interest in biogas technology has been gradually increasing around the world including Thailand. Due to increase of energy requirements; especially, offers to substitute natural gas and to reduce harmful emissions. Biogas technology offers versatile and case-specific options for tackling all of the above mentioned targets with simultaneous controlled treatment of various organic materials which is essential for biogas fermentation (Luostarinen *et al*., 2011). Usually, biogas can be generated from 3 main sources of industrial wastes comprising of farm wastes, industrial wastes and municipal wastes including landfill, these can be transformed to fuel and electricity such as wastewater from feedstock that can be converted to biogas or bio-methane by anaerobic decomposition (AD) process in which is the main process of biogas generation. These are referred to waste-to-fuel technology which provides certain fuel supply, eco-friendly and sustainable sources.

One of the most advantage keys of biogas technology, it has been continuously admitted in Thailand for over 30 years and is highly consisted of main components like natural gas. Its quality can closely compare to some major fuel gases which can be used for other fuel choices; particularly, fuel for combustion. Due to the basic property of biogas, it can be clarified an important specification to a variety of major fuel gases (see Table 1) because the several properties of biogas similar to natural gas and green gas; therefore, we can use its potential compensate to conventional fuel gases for various applications such as gas heater, kitchen stove, stationary engine (combine heat and power, CHP), vehicle fuel and natural gas grid (Pipatmanomai *et al*., 2009).

The major reason for describing biogas characteristic is that consists mainly of methane (CH_4, 45-70%), carbon dioxide (CO_2, 25-40%), and other elements such as water (H_2O 5-10%), hydrogen sulfide (H_2S, 0.005-2%), siloxanes (0-0.02%), all of these components in biogas are shown in Table 2. However, in order to upgrade biogas quality such like that green gases, natural gas, liquid petroleum gas (LPG) and compressed natural gas (CNG). It is necessary that it can be improved better quality because biogas quality is still unlike CNG or LPG property. Many previous reports informed that the upgraded biogas has been often used a scrubber method which is one of the most admit processes for biogas upgrading in order to achieve better biogas quality. Usually, the biogas quality should be normally contained CH_4 more than 97%, CO_2 less than 3% by volume, H_2S less than 10 ppm and water content should be less than 32 mg/Nm^3 (Najafpour *et al*., 2006).

Table 1 Characteristics of different fuel gases

Parameter	**Unit**	***Biogas**	**Green Gas**	**Natural Gas**
Calorific value	MJ/M^3	21.48	16.1	36.14
Density	Kg/m^3	1.21	0.51	0.82
Wobbe Index (lower)	MJ/m^3	19.5	22.5	39.9
Max. ignition velocity	m/s	0.25	0.70	0.39
Max CO_2-in stack gas	Vol%	17.8	13.1	11.9
Dew point	ºC	60-160	60	59

**Biogas is defined by CH_4 60%, CO_2 38% and H_2S 2%*

Source: IEA (2009)

Table 2 Compositions of biogas, green gas and natural gas

Substance	**Biogas**	**Green gas**	**Natural gas**
Methane	45-70%	94-99%	93-98%
Carbon dioxide	25-40%	0.1-4%	1%
Oxygen	<3%	<3%	1%
Nitrogen	<2%	<1%	-
Hydrogen	Traces	Traces	-
Hydrogen sulfide	<10,000 ppm	<10 ppm	-
Ammonia	Traces	Traces	-
Vapors (H_2O)	5-10%	-	-
Ethane	-	-	<3%
Propane	-	-	<2%

Source: Rasi *et al*. (2007)

Besides the utilized biogas benefit, the increase in global warming during the late 20^{th} century is determined to be caused by anthropogenic changes; especially, the increase in greenhouse gases like CO_2 in the atmosphere. Due to CO_2 emission from using fossil fuel, the reducing in the adversities of climate change can be partially solved by using renewable energy instead of fossil fuel and petroleum products (Phuangpornpitak and Tia, 2013).

Biogas is one of the well-known renewable energy types that it has been gradually interested. Occasionally, it can be purified by separation of CH_4 enrichment or CO_2 elimination. Though the famous method of separating and recovering CO_2 is chemical absorption, it is an expensive and complex to operate process. Therefore, another technology to replace a conventional method is membrane technology interestingly (Iovane *et al*., 2014).

Membrane technology has been being interested in current edge. Since membrane technology have offered high production, convenience to install, reliable system and reducing the operating cost because its lower driving force (pressure). However, many researches may be carried out to study the optimum performance of membrane in order to provide excellent separation properties. While, investigation on

material selection of the based matric is important role to achieve economical material because some materials are expensive such as polymer and ceramic material even rubber material which all mainly materials are used by many researchers (Baker and Lokhandwala, 2008; Faiz and Al-Marzouqi, 2009; Basu *et al*., 2010; Gongping *et al*., 2012; Ozturk and Demirciyeva, 2013). These indicates discovering ways to offer the modified material and the developed preparation are required developments leading to upgrade biogas quality like other fuel gases.

2. LITERATURE REVIEW

2.1 ENVIRONMENTAL ISSUE

2.1.1 Current environmental issue

The environmental issue plays an important role to current global situations which will relate to our life in wide variety scenarios. Because those has unavoidably related to human activities and important sectors (e.g., well-being of human, social and economic requires, genetic diversity). Therefore, we must try to conserve and protect one another. Nowadays, there are plenty of environmental problems which are widely concerned hot issues consisting of climate change (Schmidt, *et al*., 2013), pollution from energy consumptions (Akhmat, *et al*., 2014; James, *et al*., 2015;), the science of public health, hazardous waste, water management, land used, ecosystem and endangered species and food demand (Nejat, *et al*., 2015). Consequently, we need to aware those issues to conserving environment. An environmental problem has rapidly arises which cover around the world. Whenever, there is a changing in the quality or quantity of any environmental conditions both directly and indirectly. There will affect to some environmental impacts and will gravely be destroyed the main construction of ecology and eco-system (Kaygusuz and Bilgen, 2008; Dincer, *et al*., 2013; Werner, *et al*., 2015).

Admittedly, the important challenge of the 21st century is the distributions of weather changes that may lead to effect of socioeconomic and

ecological scenario. One of the most important causes is CO_2 emission from variety activities of human. To solve these impacts of such effects and avoid greenhouse gas (GHG) emissions that they should be more searched an alternative energy and explored novel energy sources for lowering GHG emission from the energy burning. Data revealed that the CO_2 concentration is existed 394 ppm in the atmosphere (IPCC, 2007) and is far over the upper safety limit of 350 ppm. Corresponding with recent energy consumption, many reports expected that the CO_2 concentration in the atmosphere would further increase by 50% to reach 570 ppm in the year of 2010 (Mauna Loa Observatory, 2012). Apart from former information, fossils fuel with 86% is the major energy source consumed in the world (Zhang *et al*., 2006). More than one-third of the CO_2 emissions emit from the combustion of fossil fuel in power plants and human activities (IEA, 2009).

Nowadays, there are still some factors about conserving environment which they can successfully promote our goals. According to many reviews revealed that most of these ways have been used for solving environmental impact which related to scientifically and socially knowledge procedures. They have been brought via various tools along with management knowledge resulting in these problems need to consider in multiple scenarios (Argent, 2004). The increasing of renewable energy proportions will be needed to manage in multiple scenarios consist of awareness of humans, suitable policies from governments, clean technology, considerable operation between cost and energy consumption. Thus, the integration of environmental issue should be concerned about all factors as previously mentioned in order to approach to environmental management and renewable energy management (Mahmoud *et al*., 2009).

2.1.2 Renewable energy management

Since the past decade, human have searched to find an alternative energy to response requirements of human; therefore, a renewable energy has been gradually interested until present day. An issue of renewable energy ought to be more continuously promoted and intentionally emphasized energy conservation. While both natural resources and quantity of energy sources have been decreasing; besides, a number of populations have raised continuously which a half of global populations

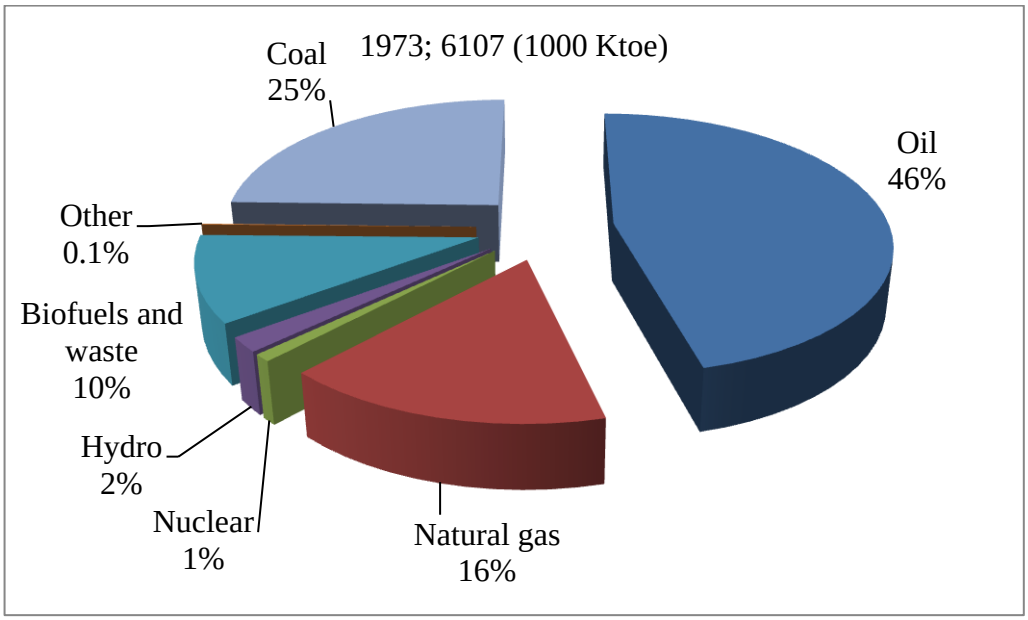
now live in urban areas. For all reasons they mean that the energy demand is much more consumed that it is insufficient use for the related sectors including: industry part, transportation, domestic and agriculture. Additionally, the climate change is one of the great challenges facing us today. Therefore, it is clearly time to change the way to use more renewable energy in order to avoid fossil-fuel price crisis (Rout *et al*., 2008). The encouragement of renewable energy consumptions is useful in terms of both reducing fossil fuel consumption and reducing impact to our environment (Payne, 2010; Omri, 2013; Omri and Nguyen, 2014). Consequently, a renewable energy issues ought to be more earnestly managed along with finding ways to solve any crisis including explored to move forward with implementing climate responsible, environmentally-friendly energy solutions that cover all parts of the sector (Boudghene Stamboul, 2011).

A renewable energy management must be considered in multiple scenarios consisting of energy demand, season, social characteristics, and the potential of renewable energy sources. Because each of areas has specific local energy resources which will be depended on geographical and climatic context that impact on energy demand (Lenzen *et al*., 2008; Calvert and Simandan, 2010). Thus, relevant sectors and local governments should provoke by establishing policies and guiding transition to obtain sustainable energy that relates to conservation energy, saving energy, increase efficient use of energy and advocate the use of renewable energy (Allcott, 2011; Dong *et al*., 2015). In this regard, include solar energy, wind energy, hydro power, wave power and bio-energy. The utilized renewable energy or alternative energy is well accepted as a relatively low environmental impact because they provided with low GHG emissions (Haro *et al*., 2015). Moreover, the potential of local resources both human and renewable energy sources could be supplied to move forward with managing climate-responsible, environmentally-friendly energy solutions, that will become supporting sustainable development (Kaygusuz, 2007). However, renewable energy sources play an important role for offering energy services in a sustainable development that explored the current contribution and potential of renewable energy sources to achieve continuously energy services and security (Adhikari *et al*., 2008; Parnphumeesup and Kerr, 2011).

2.1.3 World renewable energy situation

Historically, development of renewable energy has been increasing rapidly in recent years. Lior (2008) reported that renewable energy sources account for about 3% of the total energy utilizing but about 18% of the total electricity sector, with hydropower accounting for almost 90% of this 18%. In Figure 1 and Figure 2 consisting of fossil fuel supply (oil, natural gas and coal) indicate the main energy use which accounted for more than 80% of total energy use, while renewable energy (nuclear, hydro, bio-fuels and waste) accounted for 18.9%. To date, petroleum products (fossil fuel) still played the greatest proportion supply though renewable energy can be partly shared proportion, the major productivity and energy are still generate from fossil fuel and petroleum products (Phuangpornpitak and Tia, 2013).

However, to be sustainable development, energy must also be met societal needs and be widely distributed sources of energy supply chain which can provide a number of ways to increase the proportion of renewable energy uses (Kamimoto *et al*., 2010) such as improving efficiency of energy conversion, increasing transmission and distribution including combined heat and power, stimulating incentives for projects related to energy conservation, utilizing renewable energy, supporting research and development, encouraging awareness of public and training on efficiency, providing energy policy to meet a number of objectives and planning to prepare scenarios of alternative futures utilizing differing combinations of primary energy, constructing infrastructure networks and markets for renewable energy, developing processes and technologies for renewable energy conversions in order to reduce the cost of processing (Sims *et al.*, 2007; Hass *et al*., 2008).



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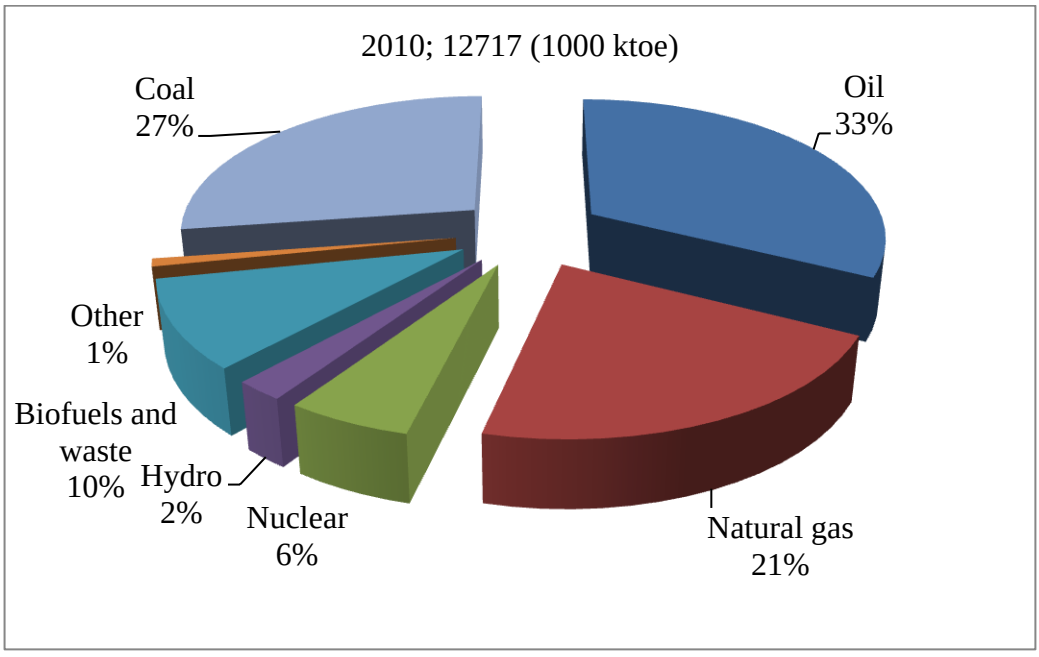
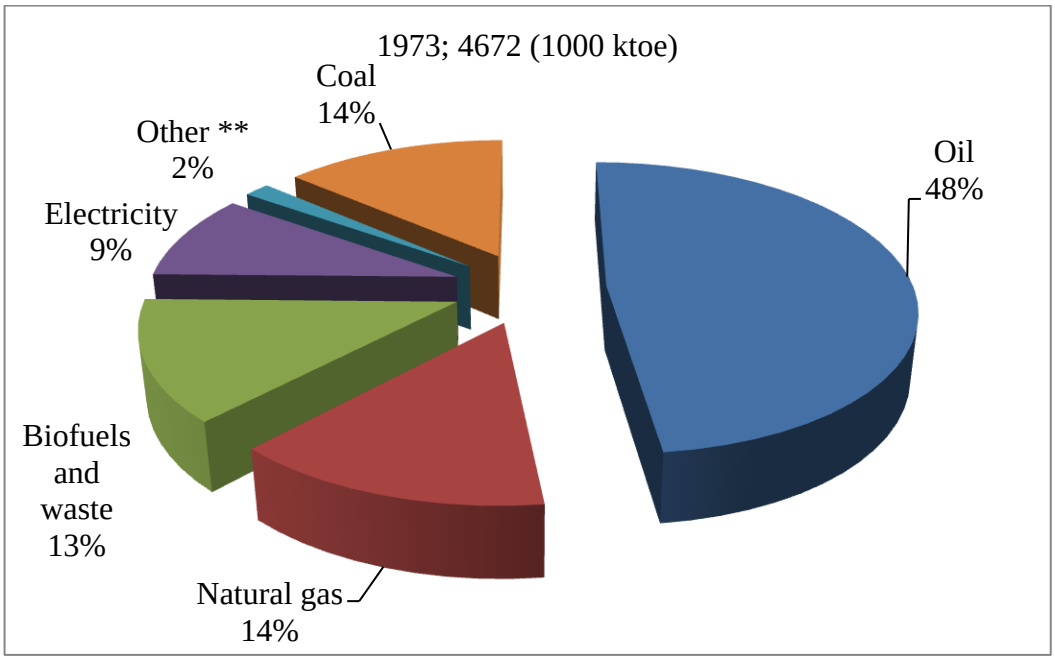


(b)

Figure 1 The world total primary energy supply from 1973(a) to 2010 (b)

Source: IEA (2010)



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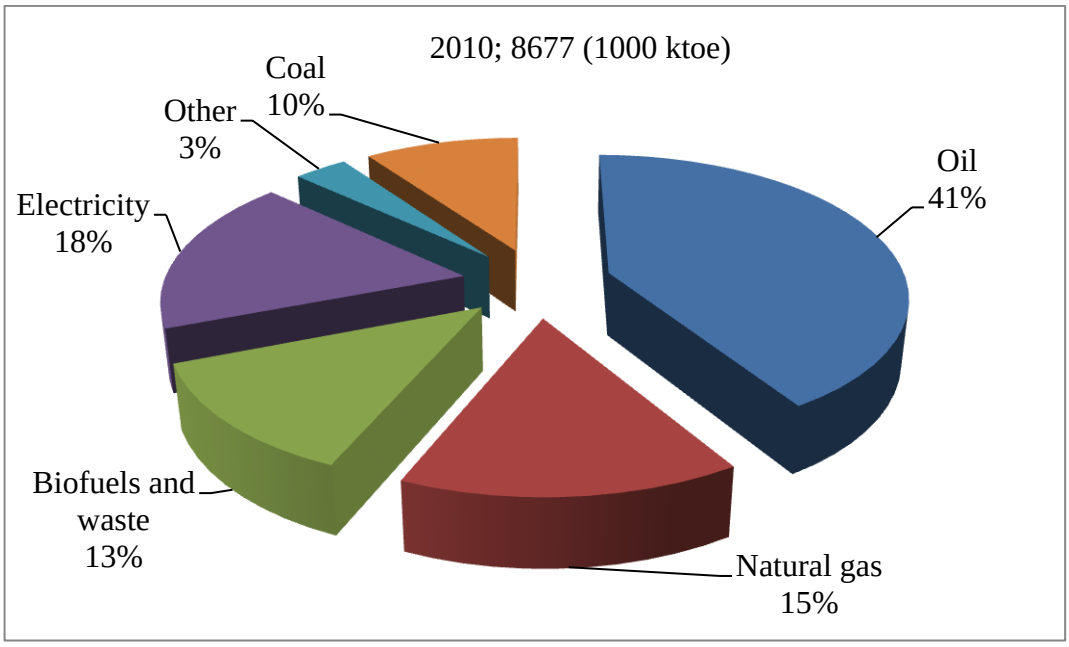


(b)

Figure 2 The world total primary energy consumption from 1971 (a) to 2010 (b)

Source: IEA (2010)

2.1.4 Thailand renewable energy situation

From the past till now, Thailand has been being concerned about energy situation together with renewable energy issue. According to the experience of Thailand development that has been participated in nations outside the Organization for Economic Cooperation and Development (non-OECD countries) (Abdelaziz *et al*., 2011). Since 2012, Thailand's final consumption has reported that the energy consumption increase 3.9% from the previous year whereas final alternative energy consumption grown 7.7% and energy intensity decrease 2.4% (DEDE, 2012a).

In order to confirm relating energy demand with general information to indicate to assert this issue shown that petroleum-produced consumptions are still the large proportion 48% of the total final energy consumption composing of electricity, traditional renewable energy, coal and its products, commercial renewable energy and natural gas shared 18.9%, 10.5, 7.9%, 7.7% and 7.0% respectively, shown in Figure 3.

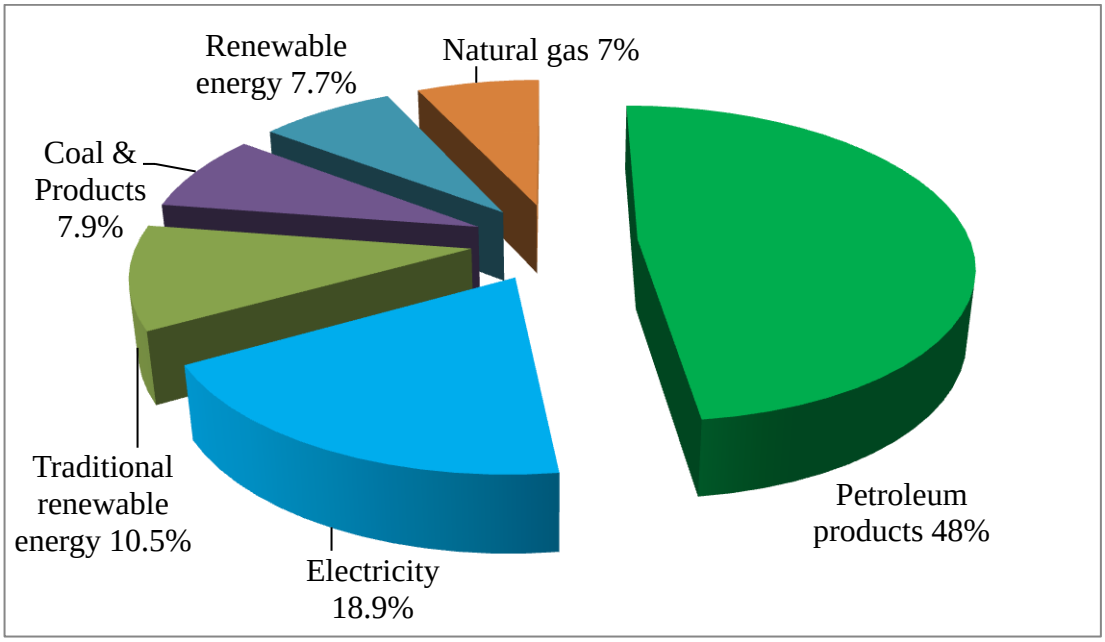
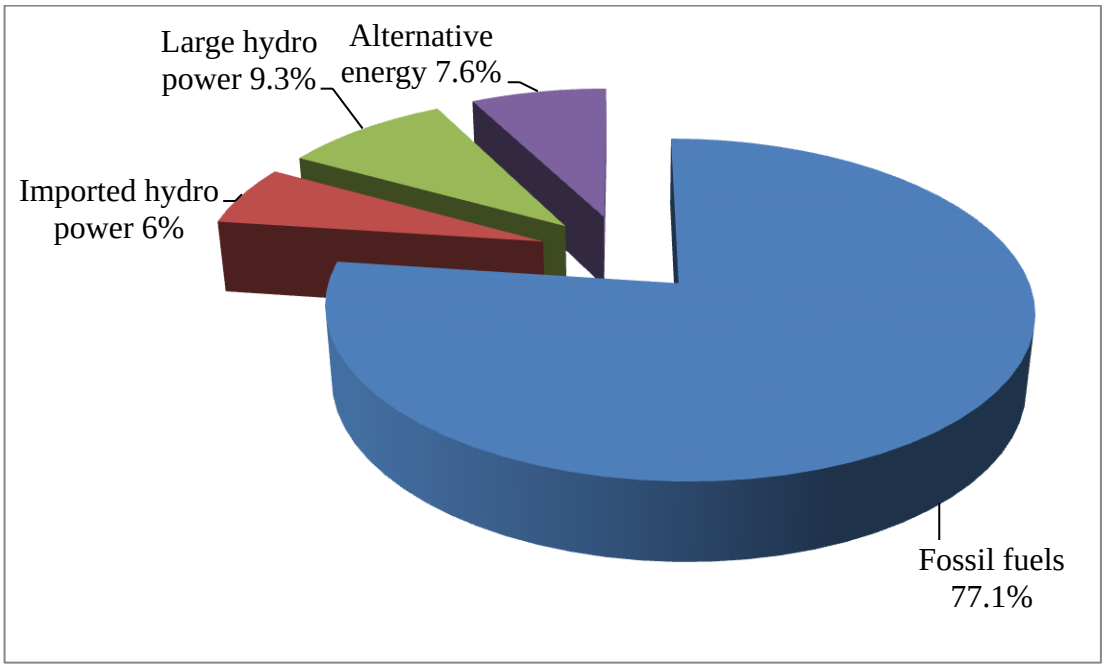


Figure 3 Thailand's final energy consumption in 2012

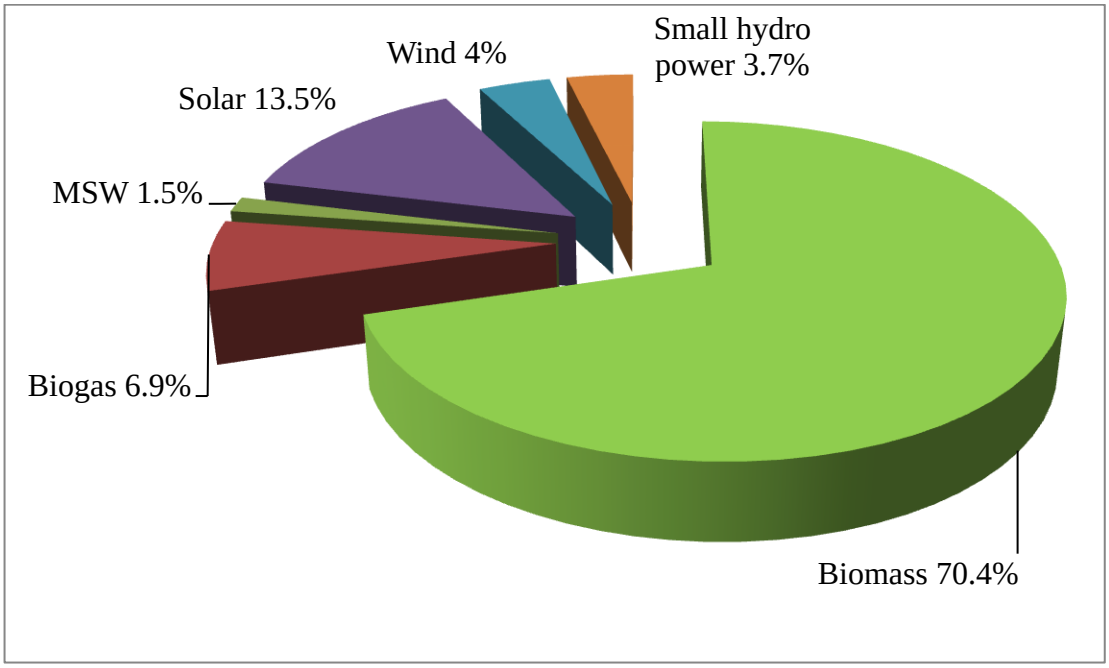
Source: DEDE (2012b)

The indication of this information indicated that Thailand has been being concerned to existing of renewable energy profit. Due to Thailand is one of the countries is facing up to both energy and environment problems (DEDE, 2009); consequently, the relevant agencies should be pushed to participate in their problems. Furthermore, in the past few years found the statistical proportion that more than 60% of primary-commercial energy needs have been imported. For 2012, the most closely related data to the established capacity of renewable energy plants have been constructed 2,786 MW accounting for 7.6% of total power capacity in Thailand and in those proportions can be accounted for almost 77% of the biomass to generate electricity which was the largest proportion of renewable energy utilization (DEDE, 2012a). To extend all energy proportions presented in Figures 4 (a) and (b).

In addition, the total final energy consumption for economic and electrical sectors were the most sectors which comprised of energy consumption in agricultural sector amounted to 3,790 ktoe, industrial sector (including manufacturing, mining and construction) 26,910 ktoe, residential sector 11,083 ktoe, commercial sector 5,303 ktoe and transportation sector 26,230 ktoe respectively (DEDE, 2012b). From this immersed information, it can be initiated to the renewable energy development which avoids depending fossil fuel. Due to Thailand have a great number of agricultural raw materials which are capable of using for multiple sources to produce various kinds of energy including biomass, biogas, bio-diesel and ethanol, and residues from a variety of industries such as the waste/residues that would be used as energy from garbage/ Municipal Solid Waste (MSW). Moreover, Thailand there is able to fetch other energy sources for example: solar energy with its solar radiation averaged at 18.2 MJ/m^2 /day and some parts/regions are with good wind energy potentials. These can lead to increasing potentials that have multiple sources with opportunities to be promoted for energy sources and created for promising energy in the country (DEDE, 2012c).



(a)



(b)

Figure 4 Total capacity energy consumption (a) renewable energy consumption (b)

Source: DEDE (2012a)

2.1.5 Potential of Thailand renewable energy

A particularly interesting, due to Thailand is located on a tropical region that there are a number of natural resources and approval energy sources throughout country (Chingulpitak and Wongwises, 2014; Janjai *et al*., 2014; Aroonrat and Wongwises, 2015). Of particular interest to the development generated renewable energy from agricultural production especially palms-manufactured potential because some byproducts of palm oil industries were used for biomass energy; whereas, wastewater from manufacturing can be generated to produce biogas which is an acceptable renewable energy interestingly (Machado *et al*., 2009; Bidart *et al*., 2013). Corresponding to over the last decades ago, Thailand has been gradually emerged a utilizing of various bio-energies with resources in country (Basri *et al*., 2012; Oswal *et al*., 2012; O-Thong *et al*., 2012). To which information in Table 3 reported that Thailand have a great number of palm oil industries as sources of high organic compositions wastewater which gains from palm oil processes. This information indicated that Thailand have the high feasibility of the producing of biogas tend to be continuously high potential sources of biogas energy.

Table 3 Thailand's Palm oil production and export (kilotons)

Year	**2008**	**2009**	**2010**	**2011**	**2012**	**2013**
Production	1,050	1,540	1,345	1,288	1,546	1,700
Exports	360	114	130	382	500	520

Source: Pleanjai and Shabbir (2009)

In addition, Thailand has variety choices that are generated for energy and electrical sector for example, biogas power plants, biomass power plants, hydro power plants, wind power plants, solar power plants and solar roof top, MSW power plants and geothermal power plants. These can generate to electricity accounting for 4,871 MW as showed information in Table 4 which divided the plan of Ministry of Energy Target into three periods; 2008-2011, 2012-2016 and 2017-2022 (DEDE, 2012a).

Table 4 Renewable energy power plants in Thailand

Power plant types	**Capacity (MW)**
Biogas power plant	146
Biomass power plant	751
Mini Hydro power plant	81
Large Hydro power plant	3,406
Wind power plant	95
Solar power plant and solar roof top	374
Municipal waste power plant	18
Geothermal	-

Source: DEDE (2012a)

In the case of biogas energy, the different types of biogas substrates can be generated from various waste sources which mostly afford from agricultural industry including wastewater from community. They mean that the substrates must be composed of organic matters to generate biogas by anaerobic digestion. Because natural substrates especially biomass or natural fiber consist of a carbon: nitrogen ratio between 20 and 30 due to a vital indispensable nutrient for anaerobic decomposition (Neves *et al*., 2009) which provides mixed gas products. Although, the main aim of utilizing is to be the gas fuel that it can be upgraded become to better clean and valuable fuel such as it is called “bio-methane” and “compressed biogas” by using various upgrading technologies (Aggarangsi *et al*, 2013).

2.2 ANAEROBIC DECOMPOSITION

Biogas production from different sources is a vital issue that entrepreneurs and organizations have become increasingly important by transforming crisis into opportunity. For example, in the case of palm oil industry’s owners that established wastewater from palm oil mill effluent (POME) and turned into biogas

energy (Prasertsan and Prasertsan, 1996; Najafpour *et al*., 2006; Sumathi *et al*., 2008) because there is appropriate potential for both the capacity and the quality of wastewater to enter anaerobic process. Because it provides a chemical oxygen demand (COD) more than 10,000 mg/L which is the highest values when compared to other sources as shown precious collective information in Table 5. Therefore, the quality of wastewater is a very necessary factor to describe before decided treatment (Wu *et al*., 2010; Lam and Lee, 2011).

Table 5 The COD from many types of industrial wastewater

Type of factory	**COD (mg/L)**
Alcoholic industry	30,000-50,000
Palm oil industry	10,000-100,000
Paper industry	8,000-10,000
Noodle industry	≈20,000
Tapioca starch industry	1,500-15,000
Soya industry	≈50,000
Coconut industry	4,000-8,000

Source: Notification of Ministry of Science, Technology and Environment (1996)

With the typical importance of biogas potential described earlier, the biogas can be appropriately generated with Anaerobic Digestion (AD) process in term of metabolic interactions among various groups of microorganisms (Lyberatos and Skiadas, 1999; Diaz *et al*., 2011;; De Vrieze *et al*., 2012). It is important that its conditions of wastewater treatment related to various factors for example the process is reacted in digester that is carried out at temperatures ranging from 30 ºC to 65 ºC (Tippayawong and Thanompongchart, 2012). To obtain successfully, many factors will involve with other parameters that must be accurately controlled due to consisting of a few of steps during procedure (Lyberatos and Skiadas, 1999).

Understandingly, biogas is generated by microorganisms in AD process. Due to all of these sources consist of organic matters which are useful for

microorganisms; therefore, during an anaerobic digestion process, microorganisms will use the organic matter as nutrients for fermentation process (Lee *et al*., 2009). Afterward, the end products of fermentation process are mainly mixing gases; thus, the overall conversion processes of organic matter into gas mixture can be divided in 4 steps as shown pathway in Figure 5 which composed of (1) Hydrolysis, (2) Acidification, (3) Acetogenesis and (4) Methanogenesis (Lyberatos and Skiadas, 1999; Basu *et al*., 2010; Mao *et al*., 2015). These are all anaerobic digestions which are a vital fermentation process by which almost any organic waste can be divided by 4 steps (Appels *et al*., 2011). The main activity within process is a complexity process which requires specific environmental conditions and different bacterial types. By means of microorganisms degraded organic compounds by different kinds of bacteria, the organic wastes carry out as following:

1. In the hydrolysis process consists of proteins like as a macromolecules, polysaccharides and fats all of these have been degraded and converted into small molecules that have been solved in water. This process has been carried out by exo-enzymes excreted by fermentative bacteria. Most bacteria have been metabolized macromolecules such as fat-decomposing microorganism, cellulose-decomposing microorganism and protein-decomposing microorganism. Chemical equation can be written as follows (Siegert and Banks, 2005; Ferry, *et al*., 2008; Lee *et al*., 2009):

   Carbohydrate ⟶ Simple sugar + Alcohol

   Proteins ⟶ Peptide + Amino acid

   Fats ⟶ Glycerol + Fatty acid

2. The second step is an acidogenesis or acidification, a process that the results obtained from hydrolysis process in simple molecules with a low molecular weight such as volatile fatty acid (acetic acid, propinoic acid and butyric acid), alcohols, aldehydes and gases like CO_2, H_2, and NH_3. This process is affected by strictly anaerobic bacteria; moreover, during this step at pH 6.0, the major bacterial specie is *Clostridium butyricum*; whereas, at pH 8, the relevant

bacterial microorganism specie is *Propionibacterium* (Shimizu *et al*., 1999; Lee *et al*., 2009; Basu *et al*., 2010).

3. The third step is an acetogenesis, the products of second step are converted into acetic acid and the amount of matter by non-methanogenic microorganisms. Among the three steps, organic matters are usually clustered together as acid fermentation. This is not removed from among process as a result; it is transformed into suitable form as substrate for methanogesis step. Chemical equation can be written as following (Basu *et al*., 2010; Rotaru *et al*., 2013):

   Complex organics ⟶ Organic acid + CO_2

4. The final step is a methanogenesis, the products from acetogenesis are converted into CO_2 and CH_4 by Methanogenic microorganisms (Deublein and Steinhauser, 2008; Basu *et al*., 2010). Chemical equation can be written as follows:

   $CH_3COOH \longrightarrow CH_4 + CO_2$

   $2CH_3CH_2OH \longrightarrow CH_4 + 2CH_3COOH$

   $CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$

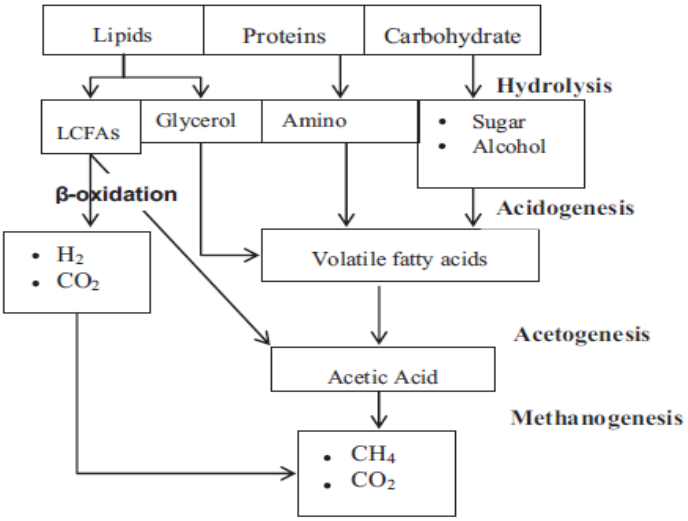


Figure 5 Pathway diagram of anaerobic digestion process

Source: Kuang *et al.* 2002

2.3 BIOGAS UPGRADING TECHNOLOGY

The main treatment of raw biogas is the cleaning contaminates within mixing gases and enriching methane concentration to achieve its property that suitable for using in wide scale applications (Wellinger and Lindberg, 2003). Because mixing gas is contaminated with water vapor and contains trace gas which can be reacted with metal ion and can be formed into acid matter which can damage with piping and motors as summarized the effects of impure biogas in Table 6. Thus, the raw biogas should be operated to cleaning prior to use and should be upgraded providing suitable gas for fuel or other applications. The upgrading biogas can be divided into 4 steps as show in Table 7.

Table 6 Biogas impurities and their consequences

Impurity	Possible Impact
Water	Corrosion in compressors, gas storage tanks and engines due to reaction with H_2S, NH_3 and CO_2 to form acid
Dust	Clogging due to deposition in compressors, gas storage tanks
H_2S	Corrosion in compressors, gas storage tanks and engines Toxic concentrations of H_2S (5 cm^3) remain in the biogas SO_2 and SO_3 are formed due to combustion, which are more toxic than H_2S and cause corrosion with water
CO_2	Low calorific value
Siloxanes	Formation of SO_2 and microcrystalline quartz due to combustion; deposition at spark plugs, valves and cylinder heads abrading the surface
Hydrocarbon	Corrosion in engines due to combustion
NH_3	Corrosion when dissolved in water
O_2/air	Explosive mixtures due to high concentrations of O_2 in biogas

Sources: Hagen *et al*. 2001; Wheless and Pierce (2004); Krich *et al*. 2005; Wellinger and Lindberg (2005); Person and Wellinger (2006).

Table 7 Biogas upgrading steps

Biogas Upgrading Steps	**Function**
Preconditioning/pretreatment	Removal of particles, NH_3, air
Biogas de-sulphurization	Removal of H_2S
Biogas upgrading	Separation of CO_2 and H_2O
Final conditioning	Adjustment of heating value

Source: Harasek (2011)

Preconditioning/pretreatment

The aim of pretreatment step involve with the increase in productivity by degradation rates, increasing biogas yield, increasing process stability and degradation hard substances (Dewil *et al*., 2006). Usually, there are many techniques to use in this step such as absorption with organic solvents, absorption on silica gel and absorption on activated carbon (Ryckbosch *et al*., 2011).

Biogas de-sulphurization

Due to there are available H_2S content in biogas, it is main causes of the corrosion to metal devices. Thus, it is important to remove in an early state of all biogas upgrading process. This contaminant gas will significantly react with a metal ion to form an insoluble metal sulfide (Persson, 2003). To prevent corrosion and avoid toxic H_2S compound even if emitting SO_2/SO_3 compound which is more toxic than H_2S during burning process. It is necessary that should be removed by several methods consist of: $FeCl_3/FeCl_2/FeSO_4$, absorption in water, adsorption on activated carbon, chemical absorption and membrane technology (Hagen *et al*., 2001; Persson, 2003; Wheless and Pierce, 2004; Wellinger and Lindberg, 2005)

Water removal

Several methods for water removal are based on separation of condensed water by using gas drying. According to biogas is usually saturated with water depended on temperature. Consequently, the simplest method is the through

refrigeration. To achieve higher removing the gas should be compressed before cooling. Water removal prevents water contact with devices like compressors, pipes and other parts that cause of corrosion. In addition to other techniques can be described as follows (Schomaker *et al*., 2000; Persson and Wellingger, 2006; Ryckbosch *et al*., 2011):

(1) Demisters in which liquid particles are separated with a wired mesh (micro pores 0.5-2 nm). A dew point of 2-20 ºC (atmosphere pressure) can be reached.

(2) Cyclone separators in which water droplets are separated using centrifugal forces.

(3) Moisture traps in which the condensation takes place by expansion, causing a low temperature that condenses the water.

(4) Water taps in the biogas pipe from which condensed water can be removed.

Removal of CO_2

Upgraded biogas has to be cleaned gas by multiple step procedures. After removal water and H_2S from raw biogas, the removal of CO_2 is important in order to obtain a suitable quality gas according to meets the high CH_4 concentration. The CO_2 gas is removed to decrease the density and increase the caloric value. Therefore, it is necessary to clean raw biogas to obtain high CH_4 concentration before it can come to reach high purity. Most of techniques can be used for removing CO_2 from biogas as follows (IEA, 1999):

(1) Water scrubbing technique has been used for removing not only CO_2 but also H_2S from biogas due to these gases are more soluble in water than methane.

(2) Polyethylene glycol scrubbing is like water scrubbing a physical absorption process. Selexol is one of the trade names used for a solvent. In this solvent, like in water, both carbon dioxide and hydrogen sulphide are more soluble than methane (Freni *et al*., 2006).

(3) Pressure swing adsorption (PSA) uses a filled column with a molecular sieve, activated carbon, silica gel, alumina or zeolite, for different adsorption of the gases CO_2 and H_2O, letting CH_4 pass through (Krich *et al*., 2005; Borque, 2006). Those molecules are adsorbed loosely in the cavities of the molecular sieves and not irreversible bound (Wellinger and Lindberg, 2005).

(4) Membrane separation is based on the selective permeability property of membranes. Two basic systems exist: gas-gas separation with a gas phase at both sides of the membrane and gas-liquid absorption separation with a liquid absorbing the diffused molecules (Ismail and Yacob, 2006).

To obtain the suitable purity, the CH_4 content must be cleaned to equivalent or higher than natural gas (> 81%) (Persson *et al*., 2003; Lester *et al*., 2013). However, an amount of CO_2 content exists in different quantities dependent upon biogas sources. Hence, an adaptable amount of research is offered to the development of suitable techniques in order that techniques are more efficient technology to upgrade biogas to bio-methane. Former gas capture or gas separation techniques like pressure swing adsorption and chemical absorption are vital techniques but at the expense of large carbon footprints and at the energy requirements are higher values for both techniques (Khoo and Tan, 2006). Consequently, it is necessary that affordable separation techniques are interested in membrane technology (Aaron *et al.*, 2009; Hezrog *et al*., 2009).

2.4 ADVANTAGE OF MEMBRANE TECHNOLOGY

Membrane is a thin semi permeable layer like barrier that selectively separates some matter from others. Membrane principles are driven by differences in driving force such as the pressure or concentration of the components across the membrane. Therefore, these concepts can be applied to many processes particularly, gas separation process. Obviously, membrane technology has been proven an established technology for CO_2 removal which was used for the co-removal of H_2S also. As previously mentioned, the multiple benefits of membrane technology have

been admitted in a wide applications resulting in they are installed in many locations around the world. Therefore, the principles of membrane technology in natural gas treatment are able to apply for biogas separation or bio-methane enrichment also. Such this technology is already selected to receive many advantages more than other technologies, taking into account the attractive opportunity, the summarized can be described a number of benefits as follow (Mat Isa and Akkil Azhar, 2009):

(1) Membrane technology requires lower energy to operate than chemical absorption process leading to saving in one or more equipment units.

(2) Membrane technology has less rotating equipment resulting in less manning and maintenance requirement.

(3) The treated gas from membranes is dehydrated and can be exported directly into the sales gas pipeline. Amine treated gas is water saturate and requires additional equipment for drying the gas. Membrane treated gas is very dry with no risk of corrosion in the gas export pipeline.

(4) There is no solvent and chemical make-up that will require additional space on platform or working place for chemical handling and storage. The need to replenish solvent and chemicals will add to logistics and transportation costs.

(5) Membrane units are simple to operate with low operation intervention and have no foaming and corrosion problems.

(6) Membrane system occupy less working place than amine systems resulting in significant cost saving.

(7) Membrane system avoids the need to have a fire source on the working place which is a potential source of ignition in a hazardous situation involving the release of hydrocarbon gases.

(8) Environmentally friendly: membranes systems do not release the periodic removal and handling of spent solvents or adsorbents. Permeate gases can be flared, used as fuel, or re-injected into the module.

(9) Ideal for remote locations: many of the factors mentioned above make membrane systems a highly desirable technology for remote locations.

Admittedly, the advantage of membrane technology has been accepted to install on many locations. According to previous reports (Makarruk *et al*., 2010), the natural gas is often treated by variety methods that were utilized on pressurized water scrubbing, pressure swing adsorption, amine scrubbing, scrubbing with organic solvents and membrane permeation. However, the membrane technology has been gradually interested in gas treatment rather than other methods as show information in Figure 6 which presents the selection factors rating (0-5) and the competition of natural gas technology for CO_2 removal in many methods (Mat Isa and Akkil Azhar, 2009); obviously, shown that the membrane technology is the optimized acceptable technology for CO_2 removal especially in offshore plants.

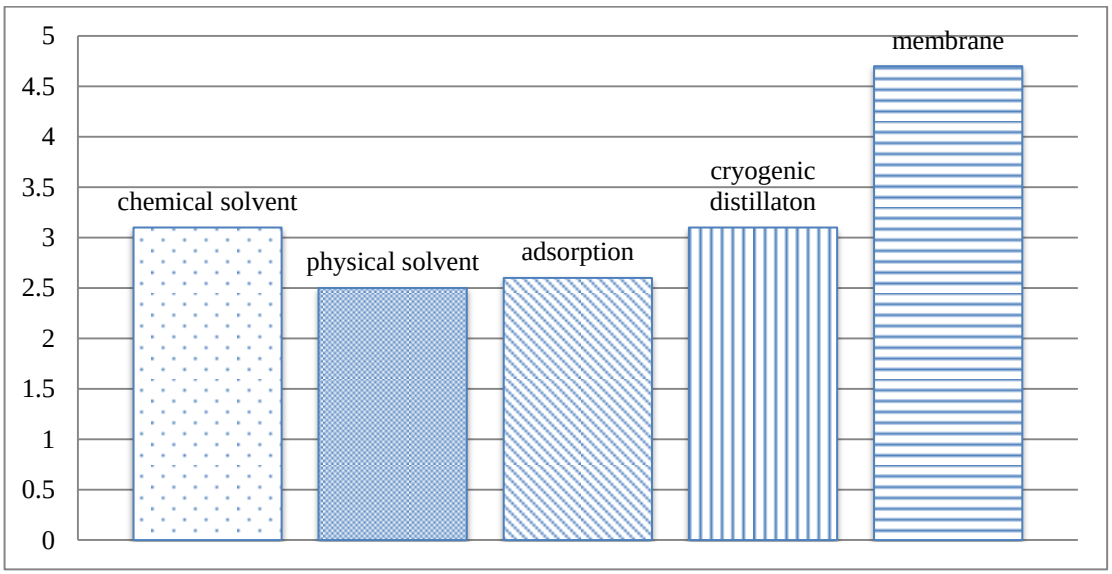


Figure 6 Various screening technologies for CO_2 removal
Source: Mat Isa and Akkil Azhar (2009)

2.5 MECHANISM OF GAS TRANSPORT TROUGH MEMBRANE

The first foundation for gas separation was discovered by Thomas Graham in 1829. He recorded experiment on the transport of gases and vapors in polymeric membranes then in 1866, he provided concepts for gas permeation in term of a solution-diffusion mechanism (Graham, 1866). In 1855, Fick offered a

quantitative description of material transport through boundary layers (Fick, 1855). Resulting in these two concepts has been contributed admittedly to the describing of gas-diffusion phenomena across membranes.

Therefore, the major concept of membrane technology for gas permeation is the transported selectivity via the solution-diffusion model which dissolves in membrane material then diffuses through membrane from feed side to permeate side that means the permeation is separated by solubility of materials in membrane phase with permeation in feed side (Meares, 1966Yasuda and Peterlin, 1973). Moreover, another mechanism of gas transport is the mass transfer of gas through porous membrane which depended on the basic property of the pore structure and the solid. There are main four different mechanisms for describing the gas separation through both porous and dense membrane consisting of different mechanism as follow (Baker, 1995; Pandey and Chauhan, 2001):

(1) Convective flow is the gas separation mechanism, if the pores are large from 0.1-10 μm, which gasses flow through membrane by convection flow.

(2) Knudsen diffusion is the diffusion mechanism, if the pores are smaller than 0.1 μm, then the pore diameter is the same size as or smaller than the mean free path of the gas molecules. Significantly, this mechanism is based on the differences in the molecular weights of the components of a gas mixture. The low-molecular weight gas rapidly moves mare than larger molecular weight because it attaches the wall more frequently.

(3) Surface diffusion or molecular sieve is the transportation of gas flow gasses, if the pores membrane is extremely small of the order 5-20 Å. Transport through this mechanism is complex and includes both diffusion and the gas phase and diffusion of adsorbed species on the surface of the pores. It means that, this mechanism occurs when the adsorbed component diffuses faster than the other non-adsorbed components such as the separation in gas mixture (natural gas and biogas).

(4) Solution diffusion is the selective adsorption of the more strongly adsorbed components of biogas or natural gas (gas mixed) onto the pore surface. It means that, the diffusion of component passes on the asymmetric polymeric hollow fiber membranes happen in free space holes created by thermal motion of polymer chains (Koros, 1995).

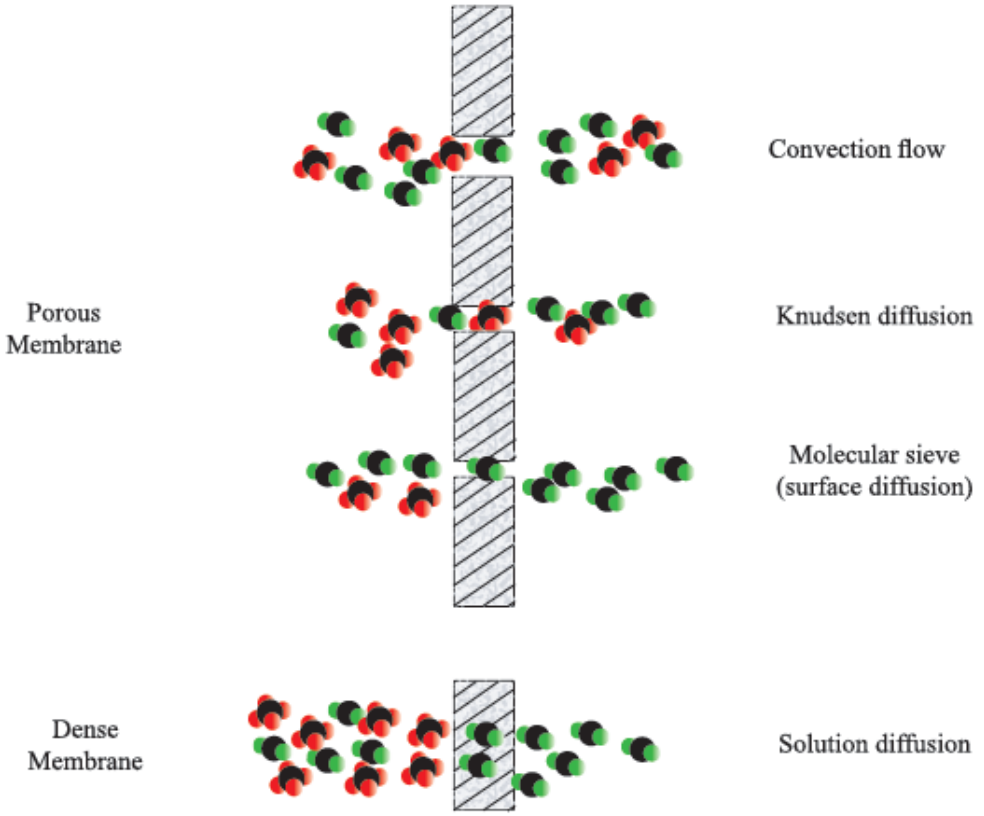


Figure 7 Schematic presentations of mechanisms for permeation of gases through membrane

Source: Baker (1995)

In the case of biogas or natural-gas separation, likes the theoretical background of gas separation of both porous and dense membrane, can be described by the selective gas separation concept in three stages (Stern *et al*., 1994). Initially, the gas molecules must be dissolved in membrane material then the gas molecules diffuse across the membrane and finally, the gas must be released to another side (Lui, 2008).

With a synthetic membrane that it has different transport abilities, it can transport under a variety of diving forces including pressure, concentration and electrical potential across the membrane (Pandey and Chauhan, 2001). Because of the difference of mechanism between the solution-diffusion model and the pore-flow model which are related to size and permanence of the pores, free volume (pores) in the dense membrane are small spaces between polymer chains motivated by thermal motion or chain entanglement when dissolved in solvent. From these parameters,

solution diffusion provides the most flexible and attractive choice for the descriptive separation, selectivity is determined by the preferential adsorption of certain components of the mixed gas on the surface of the membrane pores as well as by the diffusion of the adsorbed molecules.

In addition, Table 8 shown a diameter size of element particles in many ranges, these are evidences to corroborate the different selectivity performances that cause the allowing selective removal of fast gases (CO_2, H_2, He, H_2S and water vapor) rather than slow gases (CO, N_2, CH_4, C_2H_6 and other hydrocarbons) when considered the pore sizes larger than fast gas particles (Bondar *et al*., 2000; Bondar *et al*., 1999). Resulting in it could easily separate methane from biogas components by both rubbery and glassy membrane materials.

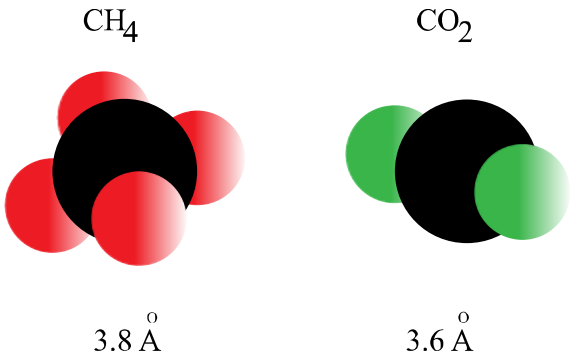


Figure 8 Schematic representations of CO_2 and CH_4 molecules
Source: Mulder (1996)

However, the CO_2 particles are used suitable for separation by glassy membranes (utilizing size selectivity) (Parro, 1985; Schell *et al*., 1989), whereas, the H_2S particles which is larger and more condensable than CO_2, are used suitable for separation by rubbery membranes (utilizing sorption selectivity) (Chatterjee *et al*., 1997). Therefore, accordance with the solution-diffusion model is also widely used to describe the transport mechanism for the polymeric membranes which is mainly covered by relative penetrant motilities (Koros and Mahajan, 2000; Kim and Park,

2011) and by structural factors such as polymer chain entanglement and inter-action between polymer packing.

Table 8 The physical properties of gases

Parameter	CO_2	CH_4	N_2	H_2
Molecular weight	44.01	16.04	28.01	2.02
Kinetic diameter, A	3.30	3.80	3.64	2.89
Quadruple ($erg^{1/2}\,cm^{5/2}.10^{26}$)	-4.3	0	-1.5	0.66
Density, gas at 0 ºC, 1 atm, g/l	1.977	0.72	1.250[a]	0.0899
Specific gravity, gas at 0 ºC	1.521	0.5549[b]	-	0.0695
Critical temperature, ºC	31.0	-82.1	-147.1	-240.2
Critical pressure, atm	72.9	45.8	33.5	12.8
Critical density, g/ml	0.468	0.162	0.311	0.031
Viscosity, gas at 70 ºF, 1 atm, cp	0.0148	0.0106[c]	0.0170[d]	0.0087[e]
Solubility in water at 25 ºC	759	-	23	19

[a]at 20 ºC, [b]60 ºF, [c]4.4 ºC, [e]15 ºC

Source: Braker and Mossman (1971); Weh *et al*. (2002)

Transport through dense membranes

According to Fick's law, gas diffusion through non-porous or dense polymer membranes can be extended by Mulder (1996).

$$J = -D\frac{dc}{dx} \quad (1)$$

Where *J* is the gas flux through the membrane (cm^3 (STP)/cm^2.s), *D* is the diffusion coefficient (cm^2/s) and *dc/cx* is the driving force, or the concentration gradient over the membrane. Assuming steady-state conditions, Equation 1 can be integrated and results in the following Equation:

$$J = \frac{D_i(C_{i,f} - C_{i,p})}{l} \quad (2)$$

Where D_i is the diffusion coefficient (cm^2/s) of component i, $C_{i,f}$ and $C_{i,p}$ are the concentrations (mol/cm^3) of component i on the feed and permeate side of the membrane, respectively and l equals the thickness (cm) of the membrane. According Henry's law the concentration of component i (C_i) is linearly related to its partial pressure (p_i):

$$C_i = S_i \ . p_i \quad (3)$$

Where S_i is the solubility coefficient of component i (cm^3 (STP)/cm^3.cmHg). Combining Equation 2 and 3 and by talking into account that the product of solubility (S) and diffusion (D) equals the permeability (P), this results in Equation 4:

$$J = \frac{P_i\,(p_{i,f} - p_{i,p})}{l} \quad (4)$$

Where P_i is the permeability of component i (cm^3 (STP)/cm^3.s.cmHg), $p_{i,f}$ and $p_{i,p}$ are the partial pressure of component i at the feed and at the permeate side, respectively and l equals the thickness (cm) of the membranes.

Generally, the equation $P = D.S$ is understood as the solution-diffusion model for gases through dense polymeric membranes (Wijmans and Baker, 1995). The solubility can reflect the number of molecules dissolved in the membranes material (Mulder, 2004). More particularly for the separation of CO_2 from CH_4, CO_2 is more condensable and more polar than CH_4 and a higher CO_2 solubility in the polymer membrane can be expected; while, the diffusivity is a kinetic parameter that is influenced by the size of the gas molecules. Usually, the diffusion coefficient decreases with increasing kinetic diameter of the gas (Mulder, 1996). Therefore, the main factor to extend the performance of a membrane is its separation ability, called the selectivity (α). The ideal selectivity often using pure gases is gained by the ratio of

the permeability coefficients (P_i), when assuming solution-diffusion to occur, composed of a diffusivity selectivity term (D_{CO2}/D_{CH4}) and a solubility selectivity term (S_{CO2}/S_{CH4}):

$$\alpha = \frac{P_{CO_2}}{P_{CH_4}} = \frac{D_{CO_2}}{D_{CH_4}} . \frac{S_{CO_2}}{S_{CH_4}} \quad (5)$$

2.6 TYPES OF MEMBRANE MATERIALS FOR GAS SEPARATION

The different types of membrane materials include inorganic and polymeric as well as ceramic and metal films with symmetric or asymmetric structure. The inorganic membranes contain both porous and dense which are mainly produced from alumina, carbon, glass, silica, titania, zeolite and zirconia (Hsieh, 1996). Whereas, the polymer membranes are most widely produced both lab-scale and commercial membrane for gas separation. The two main types of polymer are glassy and rubbery polymer which glassy polymers are rigid and operate below their glass transition (T_g) temperatures. Furthermore, glassy polymers have low chain-entangle mobility and long relaxation times in contrary, rubbery polymers express the opposite characteristics (Stern, 1994). Usually, penetrant diffusion in glassy polymers is relatively slower but the involving of the rate to the size of the penetrant molecules is much greater resulting almost all commercial membranes for gas separation have been interested glassy polymer because their high gas selectivity and good mechanical properties.

The example of glassy polymer membrane in previously reported (Shieh and Chung, 2000) that investigated cellulose nitrate (CN)-based composite hollow fiber membrane for gas separation. They was found that the effects of coating solution (CN) to reduce defects of the surface on PSF substrate which was prepared on the different solvent for dissolving cellulose nitrate, surely affected the selectivity property of the multilayer composite membrane. This effect might be occurred by the formation of different morphology. The other glassy polymer membranes comprises of Polyimide/Poly (ether sulfone) (Lui *et al*., 2003), Polyimide (Wind *et al*., 2003),

Poly (vinylidene fluoride-*co*-hexafluoropropylene) (Reverchon and Cardea, 2006) or Poly (ether-ether ketone) (Cardea *et al*., 2006) for instance.

Polymeric membrane for gas permeation

Over the last few decades, inorganic, polymeric and composite membranes have been used widely for gas separation, due to their low manufacturing cost compared to inorganic materials (Baker, 2001). To achieve economical fluxes of gas separation that will be required high membrane performance and can be made by various kinds of sources. Consequently, the major materials have been used for membranes and have been resulted the concepts that related to membrane fabrications as follows:

(1) Membrane materials: Organic polymer, Ceramics, Metals, Mixed matrix or composite materials.

(2) Membrane cross section: Symmetric or asymmetric, Bi-or multilayer, Thin-layer or mixed matrix composite.

(3) Precipitation methods: Phase inversion, Sol-gel process, Interface reaction, Stretching, Extrusion, and Track-etching.

(4) Membrane configurations: Flat sheet, Hollow fiber and Spiral wound (Scholz *et al.*, 2011).

Asymmetric polymeric membranes are most commonly prepared by a dry/wet phase inversion (immersion precipitation) process. This process involves the phase separation of polymer solution in polymer rich and polymer lean phases which is obtained by the immersion-precipitation technique. Accordingly, phase inversion occurs by combination of the wet spinning and dry spinning method. Usually, homogenous spinning solution in phase inversion method was considered in fast and delayed demixing of forming membrane which relates to evaporation time and immersion-precipitation processes. Iqbal and co-workers (2008) reported that fast demixing of casting solution forms a highly porous membrane with the existing of macrovoids whereas delayed demixing approaches to less porous and macrovoids-free substructure of a membrane. In summary of forming membrane by phase inversion

method is to get a thin integral defect-free skin and porous substructure devoid of macropores.

Besides, the notices of using polymer membranes are good process abilities, inexpensive production and low operating cost. In previously researched, the utilization of polymer materials for gas separation membrane such as cellulose acetate (Matsuyama *et al*., 2002), polycarbonate (Kim and Lee, 2004), poly (vinylidene fluoride) (Huang *et al*., 2007). In this regard, former studies showed that the efficiency of membranes is still improved particularly, the permeability and the selectivity. However, it is well known that the plasticization effect can occur during high partial pressure for gas separation process, due to sorption of gas molecules especially CO_2 molecules in polymer base matrix, translating to enhanced polymer chain mobility (Bos *et al*., 1999; Visser et al., 2005; Kanehashi et al., 2007). Accordingly, the mass transfer for all gas molecules is increased.

2.7 POLY VINYL CHLORIDE MEMBRANE

Over the past 20 years, membrane materials have developed from simple polymers, like CA (Donohue *et al*., 1989), PSF (Henis and Tripodi, 1981), etc., to obtain suitable polymers. However, they have been limited some properties such as thermally rearranged polymers and gradually increased costs therefore, it is necessary that they be found other materials. Poly (vinyl chloride, PVC) has been used in a wide variety of applications consist of engineering plastics, household products including membrane products. Because PVC material has a properties and performances suitable for a wide range temperature utilizing, acid/base duration and resist to high pressure. Earlier work found that PVC material is able to instead of other materials due to its property has exhibited chlorine atoms of the functional molecules (Jia *et al*., 1997) which their basic structure can be induced a polar gas such as CO_2 more diffuses through membrane than non-polar gas such as CH_4 and N_2 that means the increasing of CO_2 gas permeability (Ghosal *et al*., 1995; Raymond and Paul, 1990). Accordingly, the main reason of PVC using as membrane for gas separation besides all properties previously mentioned is the polar groups of the polymer which they may have dipolar

interactions with the polarizable CO_2 molecules (Bos *et al*., 1999). Furthermore, PVC is a flexible and durable polymer with suitable biological and chemical resistance. PVC is a good mechanical support (tough plastic) of glassy polymers, hardness and low cost (Wiks, 2001).

Poly vinyl chloride blends Poly ethylene glycol

In previously considered, the gas transports across polymeric membranes can summarize as the permeation process relating the sorption and diffusion step, and the extent of sorption of the gas molecules depending on the interaction of the penetrant and the polymer structure. As a result, the conceptual theory approach to fabricate CO_2-selective polymeric membranes is to integrate high CO_2-affanity moieties like ether oxygen or siloxane into polymer matrices. Because CO_2 molecules are acidic in nature and can interact with polar molecules such as ether oxygen via dipole-quadrapolar interactions. Thus, more CO_2 molecules permeate across the polar polymeric membrane when compared to other gas molecules consist of H_2, N_2 and CH_4 (Lin and Freeman, 2005 and Dzielawa *et al*., 2008).

The use of membrane technology for CO_2 separation from light gases obtains increasing consider because development of membranes with high polar/non-polar selectivity which based on differences in solubility instead of size (Bondar *et al*., 1999 Bondar *et al*., 2000). In addition, PEG is still compatible with various polymer materials and can be used as a proton selective layer. Therefore, this modification can be improved to achieve the high solubility selectivity of polar gases molecules via addition of PEG, due to the strong interaction between CO_2 and PEG phase. Moreover, there was an increased affinity between PEG and CO_2 molecules also. The main reason of using PEG because it is often used as additive to improve more permeability and increase porosity of membrane including increase efficiency of separation of CO_2 from non-polar gases (Ren *et al*., 2012) because PEG comprises of an ether linkage structure indicated as $HO\text{-}(CH_2\text{-}O\text{-}CH_2)_n\text{-}OH$ which formed as liquids or low melting waxes like solids. Furthermore, the repeating unit of PEG structure contains the “-O- atoms” in ethylene oxide or ether oxygen units which can build hydrogen bonds (H-bonds) with an H atom in CHCl group of PVC back bone (Kuehne

and Friedlander, 1980; Lin and Freeman, 2004). Another supported feasibility of PEG using as additive is the polarity of gas molecule is divided by two types are non-polar gases consists of H_2, N_2 and CH_4, followed by quadruple CO_2 is a much higher solubility in polar membranes. To sum up of all reasons above mentioned are the polar membranes which are usually combine ethylene oxide (EO) units or containing hydrogen bond units (-O-H) in molecular structure (Bondar *et al*., 1999; Bondar *et al*., 2000; Lin and Freeman, 2004).

As formerly researched regarding PVC blended PEG has been shown in many reports such as Sadeghi and co-worker (2008) reported the effect of the addition the different molecular weight of PEG on the effectiveness of gas permeability and selectivity of a blended membranes between PVC 10 wt% PVC (K-value of 67) blended PEG in several molecular weight 400 and 4000 Dalton in many ratio as following 10wt%, 20wt% and 30wt%, and di-methyl formamide (DMF) which is as solvent. From this research, it was found that the blended membranes having PEG with 4000 Da showed higher values of CO_2 permeability. Moreover, the gas permeability of PVC/PEG membrane rapidly increased with an increase in PEG concentration. As a result, the PVC blended PEG 4000 containing 10, 20, 30wt% shown the permeability of CO_2 equal to 0.84, 2.38, and 5.82 Barrer respectively. Furthermore, still showed a pair gasses selectivity between CO_2/N_2 were 49, 70, and 109 respectively. While CO_2/CH_4 selectivity increased from 46.47 (PEG 4000 content 10%) to 84 (PEG 4000 content 30%). The other example is reported by Ji and co-workers (1998), they prepared the poly (ethylene glycol) blended with cellulose acetate (CA) to produce film membranes. The membranes have been reported CO_2 permeability (P_{CO2}) 6-7 Barrer and P_{CO2}/P_{N2} = 31-36 at 35 ºC. However, PEG has a strong tendency to crystallize structure and this reason tends to decrease CO_2 permeability. Accordingly, various methods have been offered to limit crystalline-state property of using PEG in membranes such as using PEG with low molecular weight (Brunetti *et al*., 2010).

3. OBJECTIVES

(1) To study the preparation of asymmetric PVC blends PEG via phase inversion technique.
(2) To indicate the hydrophobic/hydrophilic property of different PVC K-values and different PEG molecular weights.
(3) To study the fabrication of flat sheet membrane and hollow fiber membrane preparation via dry/wet phase inversion and spinning process.
(4) To investigate the property of flat sheet and hollow fiber membrane via single gas and mixed gas permeation properties, physical and chemical properties.
(5) To optimize the efficiency of spinning system that can fabricate dense skin layer both shell-side layer and lumen-side layer
(6) To study the performance of the XSBR coating on PVC blends PEG.
(7) To measure single gas and mixed gas selection of both flat sheet membranes and hollow fiber membranes.

4. SCOPE OF WORK

(1) This research employed PVC as support membrane that used in K-value 580, 610 and 710.
(2) PEG is an additive for increasing flexibility property of PVC matrix that was used in 2 grades: 400 Da and 4000 Da.
(3) The fabrication of flat sheet membranes and hollow fiber membranes were prepared via dry/wet phase inversion method.
(4) XSBR acts as skin layer and selective layer of the resultant membranes that were coated on PVC-PEG supporting membranes via dipping method.

(5) CO_2, O_2 and N_2 are single gas that was filtrated through flat sheet membranes; then, the permeability and selectivity factors were investigated.

(6) Mixing gas between CO_2 and CH_4 of 40:60 proportions was separated by the coated XSBR PVC-PEG hollow fiber via contactor module.

(7) The hollow fiber membranes were fabricated by spinning process that produced in laboratory room.

(8) The effects of three main parameters, initial dope extrusion rate, bore extrusion rate and draw ratio were studied.

5. DISSERTATION ORGANIZATION

This dissertation is organized into two main parts. The first part is **Chapter 1** General Introduction. This chapter presents the background of the environmental issues, the potential of renewable energy in Thailand, the importance of membrane technology for biogas upgrading, literature reviews and the purpose of this research. The second part is Chapter 2 and 3 predominantly focus on process technological and material design resulting in membrane formation; particularly, the focus of Chapter 2 is primarily on the experiment of suitable process that relates to the material design, process design and improvement design.

In **Chapter 2** the different grades of PVC flat sheet membranes are studied and investigated the influence of the type of difference K-values. Besides, the commonly used the two molecular weights of PEG are added in PVC-based polymer matrix. Three types of commercially available PVC grade are fabricated via phase inversion technique that account for solvent solubility, compatibility, miscible ability and viscosity of solution, all of these factors will cause of different effective membranes. Furthermore, in this work that XSBR is used as coated skin in order to improve better CO_2 absorption effectively. Therefore, the chosen membrane types on the overall investigation are indicated by the permeation of CO_2, O_2, N_2, and mixing gas, the physical properties and chemical properties to concentrate on development

into hollow fiber membrane that is alternative aspect for the increase in gas permeation due to significantly increase surface area as studying in Chapter 3.

In **Chapter 3** the investigations of hollow fiber membrane fabrication are prepared by dry/wet phase inversion spinning technique that uses PVC as based matrix polymer and PEG as an additive with two molecular weights. The spinning dope solution is extruded into coagulant bath that acts as precipitated solution. The apparatus of spinning system is built in the laboratory. Process experiments are involved with many factors that consist of air gap between coagulant bath and head spinneret, drawing ratio between dope extrusion rate and wind-up rate, feed pressure and dope viscosity for instance. The results of this experiment can be observed by various instruments such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectrometry (FTIR) and Dynamic Mechanical Thermal Analysis (DMTA). Next to the influence of those factors, the differences of fabricated hollow fiber membranes are determined. However, the future works of these fibers can be developed into contactor module that will enhance surface area for exact application such as gas separation or CO_2 absorption.

In **Chapter 4**, the hollow fiber membrane that obtained from the suitable characters in chapter 3 were coated with XSBR and then packed into contactor module. This module was tested with CO_2, O_2, N_2 and mixing gas permeation. The permeability and selectivity were measured by gas permeation testing unit in laboratory room. In addition, the percentage of CO_2 and CH_4 within mixing gas was measured by gas chromatography (GC).

In **Chapter 5** summarized the main conclusions of the work and suggests directions for future research in order to develop the hollow fiber membrane for biogas upgrading.

CHAPTER 2
GAS PERMEABILITY OF XSBR COATED PVC-PEG MEMBRANE

ABSTRACT

The polymeric membrane composed of a blend of poly vinyl chloride (PVC) with poly ethylene glycol (PEG) as a supporting membrane, carboxylated styrene butadiene rubber (XSBR) as the coated layer was prepared as flat sheet configuration. The supporting membrane was prepared by using phase inversion technique and established by casting method. The morphology of cross-section images from scanning electron microscope (SEM) showed finger-like sponge structure after adding higher contents of PEG with averaged molecular weight 400 g/mol. The dense polymeric film was coated with XSBR rubber that atced as selective layer. The mechanical properties of polymeric membrane was improved after coating with XSBR as well as gas selectivity. The mechanical properties of the membrane were investigated using dynamic mechanical thermal analyzer (DMTA). The permeation of the two single gases consisting of CO_2 O_2 and N_2, through the membranes were measured by VAC-V1 LabThink gas testing unit and ideal gas selectivity was computed.

1. INTRODUCTION

1.1 Background

The progress in the field of CO_2 removal by membrane technology has been very rapid interesting. It has expanded from early diffusion property, through the

simple concepts of diffusion and permeation, to economically accepted products. Besides, polymeric membranes have been well-known for their excellent transport properties, high process ability and their high adaptable performance. However, a limit in the unbalance between permeability and selectivity has been considered by improvement in economical permeability and high selectivity (Xiao *et al*., 2009). In addition, inorganic membranes such as zeolite membrane are used for gas separation. Though their superior thermal, mechanical, and chemical stability are accepted, their high costs of manufacturing and utilizing issues (Sridhar *et al*., 2007).

To more explanation for polymeric membrane property, gas separation membranes approach to be highly permeable of one gas; whereas, significantly obstructing the other components resulting in the considering material selection. There are various membrane materials having been studied; however, they have been shown the normal performance that the permeable polymers possess low selectivity. Especially glassy polymers, because their properties are based on T_g that is one of the most important properties of polymer materials, at the below glass-transition temperature, the polymer chains are importantly packed; the polymer is a rigid, tough, glassy material and the effect of the differences in size of gas molecules on their relative mobility is large. If the polymer is used above its glass-transition temperature, mobility of the polymer chains is possible. Whereas, rubbery polymeric membranes should operate above the glass-transition temperature due to polymer chains, the membranes are able to rearrange on a meaningful timescale and are often in thermodynamic equilibrium (Nunes and Peinemann, 2006). Thus, the ability of gas permeability in glassy polymers is determined by the gas kinetic diameter, whereas in rubbery polymers the order is determined by gas condensability (Baker and Lokhandwala, 2008). Therefore, material selection plays an important role for the desirable membrane applications.

1.2 Poly vinyl chloride membrane

PVC is an important commercial thermoplastic. PVC is a hard and stiff material which can be immensely modified with plasticizer for flexibility (*da* Silva *et*

al., 2011). Using of the PVC for membrane fabrication which acts as glassy polymers, mostly preferred as membrane material because it was highly durable material and ease to fabricate in many aspects. However, this glassy polymer is always met problems as plasticization behavior occuring from dissolution of gas molecules into micro-void inside polymer phases resulting in the plasticization that can be changed the performance of membranes. In addition, PVC can be probably prepared dense and supporting membrane material because of its suitable properties that consist of low cost, excellent chemical resistance and physical properties, acid and alkaline resistance, as well as mechanical properties (Tiemblo *et al*., 2001; Tiemblo *et al*., 2002; Xu and Xu, 2002; Bierbrauer *et al*., 2010). Besides, PVC has many advantages over other types of plastic such as Poly ethylene (PE), Poly propylene (PP) and Poly styrene (PS) because it can be improved for various property requirements (soft and hard) and can also be recycled because of the thermoplastic type.

However, PVC still has low gas permeability due to the nature properties such as slightly crystalline, poor hydrophilic, poor flexibility and glassy polymer that presents more densely packed molecular chains; therefore, improvement of approach high permeability membrane should be found out to develop suitable membrane. For more densely packed molecular chains of glassy polymers, hydrophilic, flexibility and more porosity are mainly needed by adding the additive or pore former into PVC matrix. Therefore, membrane modification is considered. The modifying of polymeric membranes can be improved by blending with additive used extensively for receiving high-performance membrane; at the same time, it is the most multipurpose method of achieving materials with new desirable properties (Paul and Newman, 1978). Therefore, a pure PVC membrane modified by blending with other polymers should be considered.

1.3 Poly ethylene glycol addition

Membrane modifications can be considered with PEG mainly involved additives and pore former with conventional membrane system such as ultrafiltration, microfiltration and reverse osmosis. In addition PEG has been reported as a pore

former to increase the permeation properties (Park *et al*., 2007; Arthanareeswaran *et al*., 2009; Khayet *et al*., 2010). Nowadays, new membrane applications such as fuel cells and gas separation have been considered due to theirs the structure of membranes often necessary to select the transport of charged species and polar molecules (such as CO_2 and H_2S gases molecules). Therefore, this membrane modification consists of the addition of poly (ethylene glycol) that the reasons to choose PEG are related to the possibility of the transport ions and polar molecules across the membranes. In addition, PEG is still compatible with many organic materials and can be used as a proton selective layer. Therefore, membrane modification can be improved in order to achieve the high solubility selectivity of polar gases molecules via the addition of PEG into polymer matrix due to the strong interaction between CO_2 and PEG phase. Moreover, there was an increased affinity between PEG and CO_2 gases molecules. As the former reported, Xu and Xu (2002) prepared ultrafiltration PVC hollow fiber membranes that they investigated hollow fiber fabrication by dry/wet spinning technique from dope solutions which consist of PVP and PEG as additives. The affecting of these additives agent were also increased the PVC hollow fiber porosity, enhanced the permeation flux in contrast, decreased in the protein separation.

Furthermore, Sadeghi and co-workers (2008) investigated the effect of different molecular weights of PEG on the effectiveness of gas permeability and selectivity of resultant membranes among PVC, PEG, and DMF which acts as a solvent. By mixing a several molecular weights of PEG as following ranged from 400 to 4000 Da. It was found that the blended membranes having PEO with 4000 Dalton showed higher values of CO_2 permeability. Moreover, the gas permeability of PVC/PEG rapidly increased with an increase in PEG concentration. The ratios of PVC/PEG blending comprising 10 wt% PVC (K-value of 67) was dissolved in DMF and added 10, 20, and 30 wt% of PEG 4000, as a result the permeability equal to 0.84, 2.38, and 5.82 Barrer (1 Barrer = 10^{-10}cm^3 (STP) cm/cm^{2}s cmHg), respectively. Furthermore, showed a pair gasses selectivity between CO_2/N_2 were 49, 70, and 109, respectively. These results and comparisons of pure PVC, due to polyethylene glycol molecular structures have some –OH bonds $(CH_2\text{-}O\text{-}CH_2)_n$-OH and can be caused interaction with CO_2, therefore, the preparing of some PVC/PEG blended membranes indicated that the gas solubility is dominant in the CO_2 permeation. Sanchez and co-

workers (2002) reported that the gas permeation properties can be observed according to the ethylene oxide/epichlorhydrin ratio in the copolymer. The gas permeability characteristics of poly (ethylene oxide-co-epichlorohydrin) films were determined by using the constant volume and pressure-increase method. Permeation measurements reveal that a wide range of gas transport properties can be obtained according to the ethylene oxide/epichlorhydrin ratio in the copolymer. The copolymers show very high permeability (up to 105 Barrer) and selectivity for CO_2 respect to N_2 and CH_4 (CO_2/N_2 = 63 and CO_2/CH_4 = 17).

However, blending membrane might not meet the suitable demand of gas separation property because the compatibility of polymer-polymer blend during the blended solution that are immiscible thermodynamically or conditionally compatible (Qian *et al*., 2002). Therefore, the improvement of the membrane material performances should be chosen from commercially affordable simple polymers without complicated synthesis. Thus, other surface or skin layer modifications are considered. Coating with rubbery materials is one of the most modified materials because the coating method is a simple fabrication; meanwhile, the rubbery materials express flexible and dense properties. The coated membranes have been developed in various processes such as coating with elastomer materials; for example, silicone rubber, Feng and co-workers (2002) investigated that gas permeation of poly dimethyl siloxane (PDMS) coated PSF hollow fiber composite membrane acts as supporting layer. Moreover, the field of commercially industrial rubber products contains many types of rubbers interestingly considerable utilization such as styrene butadiene rubber (SBR), carboxylated styrene butadiene rubber (XSBR) and natural rubber (NR).

1.4 Carboxylated Styrene Butadiene Rubber (XSBR)

XSBR is generally used in a wide range of application in contact with hydrocarbon liquids, oils or greases (Stephen *et al*., 2006). XSBR is copolymers of butadiene, styrene and one more unsaturated acid such as acrylic acid which prepared by emulsion polymerization (Du *et al*., 2008). Due to the basic property of XSBR latex is higher than NR and is attributed to the polarity of XSBR latex (Stephen *et al*.,

2006). As a consequence, it would be modified to surface improvements in order to achieve more polar gases permeability such as CO_2 than unmodified surface. Unfortunately, XSBR rubber has not been applied in membrane modifications, but other elastomers have been used for membrane modification. In previous researches regarding increases high gases permeability by modifying with elastomer materials for example (Rajabi *et al*., 2013), this study was to investigate on PVC/multi wall carbon nanotubes (MWCNTs) and PVC/SBR/MWCNTs blend MMMs for CO_2/CH_4, CO_2/N_2 and N_2/CH_4 gas separation. PVC was used as base polymer membrane due to its various interesting such as low cost, suitable biological and chemical resistance, easy process ability and recyclability. The researcher claimed CO_2/CH_4 selectivity was increased from 39.21 to 52.18 at 2 bar pressure meanwhile; the modified membranes have been blended with SBR showed 63.52 and 34.70 CO_2/CH_4 and CO_2/N_2 selectivity respectively.

These modified membranes as previous matter as a result from adding polar groups in theses membranes as a result of increase solubility especially; CO_2/CH_4 due to CO_2 permeability in these membranes has been induced more than other test gases. Researchers aim to prepare membrane blending from cellulose acetate (CA) blend with various materials as follow: multi wall carbon-nano tube (MWCNTs), polyethylene glycol (PEG) and styrene butadiene rubber (SBR) respectively. Results showed that addition of C-MWCNT instead of R-MWCNTs in modified membrane has better CO_2/CH_4 and CO_2/N_2 selectivity reach to 21.81 and 13.74 from 13.41 and 9.33. As a result from the effect of PEG and SBR on the gas transport showed the highest CO_2/CH_4 at 2 bar pressure was reached to 53.98 for CA/PEG/C-MWCNT blend MMMs (Moghadassi *et al*., 2014). Reijerkerk and co-workers (2010) presented the performance of membrane made from commercially available PEBAX® MH 1657 consisting of PDMS 20 wt% in order that membranes obtained high permeability and PEG 80 wt% to achieved high selectivity. From these experiments, they were found that the pure gas CO_2 permeability increased when membrane also contained the PEG at 50 wt%, the CO_2/CH_4 selectivity of PDMS-PEG membranes decreased slightly with PDMS-PEG loading and pressure (0-25 bar). The PEG loading in PDMS-PEG indicated that the increase in amorphous PEG contents leads to a modest increase in CO_2 solubility.

2. MATERIALS AND METHODS

2.1 Membrane casting by dry/wet phase inversion method

Dry/wet phase inversion method is generally processed for flat sheet membrane fabrication approaching to ultrathin and defect-free asymmetric membrane. The main mechanism of forming is using forced-convective evaporation including phase separation in the outermost regions of nascent flat sheet membranes. With selective loss of the volatile solvent, the solvent causes destabilization in the outermost region of nascent membranes; therefore, this step is dry/wet separation that the entire phase separation process occurs by the diffusion exchange of solvent and non-solvent in the coagulant bath (Pesek and Koros, 1993; Widjojo *et al*., 2008; Guillen *et al*., 2011; Garcia-Ivars *et al*., 2014).

The purpose of casting membrane method was prepared from casting solutions containing PVC, PEG and DMF. PVC was supplied by Thai Plastic and Chemical Co., Ltd by varying K-Value 580, 610 and 710, DMF (99.8% grade) bought from Ajax Finechem Pty Ltd., as solvent, PEG 400 and 4000 Dalton bought from Honam Petrochemical, Co., Ltd., by varying concentration of PEG from 1.0% to 20.0% by weight., respectively. The mixed solution between PVC and PEG solution was homogenized by using hot plate magnetic stirrer of VS-130SH from Vision Scientific Co., Ltd and these solutions were heated at temperature 60 ºC approximately 24 hr to ensure that polymer membrane completely dissolved homogeneous solution. Then, the mixed solution was cast on glass plate. The cast membranes were suddenly immersed into coagulant water bath for 24 hr. after casting. To ensure complete solvent evaporation, the prepared membranes were dried at room temperature (25 ºC) for 24 hr**.** The liquid XSBR was poured on the dried flat sheet membrane laid on the glass plate; after that, casts XSBR suddenly and brings it to oven vacuum in order to remove water content and dry moisture at 60 ºC for 24 hr. In summarize, membrane products were called as multilayers membrane composed of PVC blend PEG acting as support layer and XSBR coating acts as skin layer.

2.2 Morphological measurement

The geometrical characteristics and morphology of polymeric membranes were studied using scanning electron microscope (SEM). The samples of membranes were frozen by liquid nitrogen before testing in order to break samples, and then mounted on sample stubs with double-side tape. The preparing samples were sputtered with thin layer gold. The study of morphology with SEM can be observed cross-section, surface and pore size of membranes. In this research, the investigated morphology of the prepared membranes was observed with scanning electron microscopy, Quanta-5800. The surface and cross section can be shown different aspects as a result from different components in dope solution and fabricated membranes (Xu and Xu, 2002; Widjojo *et al*., 2008; Basu *et al*., 2010).

2.3 Contact angle measurement

The contact angle (θ) is the angle at which a liquid/vapor interface meets a certain solid surface. This technique was determined by the hydrophobic and hydrophilic properties of membrane, when the molecules of a liquid are strongly attracted to the membrane surface as a result of a drop of liquid that will completely spread out on membrane surface, corresponding to a contact angle of 0º. While the membrane surface is hydrophobic, the contact angle will be larger than 90º. Therefore, the morphology of membranes can be indicated that the hydrophobic property is $\theta >$ 90º and the hydrophilic is $\theta <$ 90º (Palacio *et al*., 1999; Khayet *et al*., 2010; Ghadimi *et al*., 2014; Rajabzadeh *et al*., 2015).

2.4 Fourier transforms infrared spectroscopy (FTIR)

FTIR was used to investigate the functional groups of components compared within the bulk of membrane. This technique is obtained an infrared spectrum data and provides information about chemical bonding or molecular of

materials both organic and inorganics. A molecular structure is absorbed to infrared spectrums which are characteristic to clearly verify the incorporation of PEG into the PVC backbone and detect characterization of specific inter-molecular interactions among the groups in different composition of polymer. In these researches will be involved main materials which need to observe by FT-IR Bruker EQUINOX-55 Spectro-photometer (Balakrishnan and Jayakrishnan, 2005; Mei *et al*., 2011; Rajabzadeh *et al*., 2015).

2.5 Dynamic Mechanical Thermal Analysis Measurements

The dynamic mechanical properties of the fabricated membrane were measured using DMTA (dynamic mechanical thermal analyzer, Model-V, supplied by Rheometric Scientific). The cantilever mode of the deformed sample was carried under the test temperature ranging from 0 °C to 500 °C, and the tested frequency is 1 Hz. The cooling process was gained through liquid nitrogen. The terms of this method were presented in terms of loss tangent (*tan* δ) and glass transition temperature (T_g). In this investigation, the loss tangent was the ratio of loss modulus (*E"*) to storage modulus (*E'*) meanwhile T_g was perceived from the loss modulus peak (Mondal and Hu, 2006; Coelho *et al*., 2012; Ghadimi *et al*., 2014;).

2.6 Tensile stress and elongation at break measurements

Tensile strength (TS) and percentage tensile elongation at break (E) of the film membranes were tested at room temperature using a Universal Testing Machine follow by ASTM D412 Die C. The tensile strength was shown as the maximum force at break divided by the initial cross-section area of the film membrane and the elongation at break as a percentage of the origin of the original length.

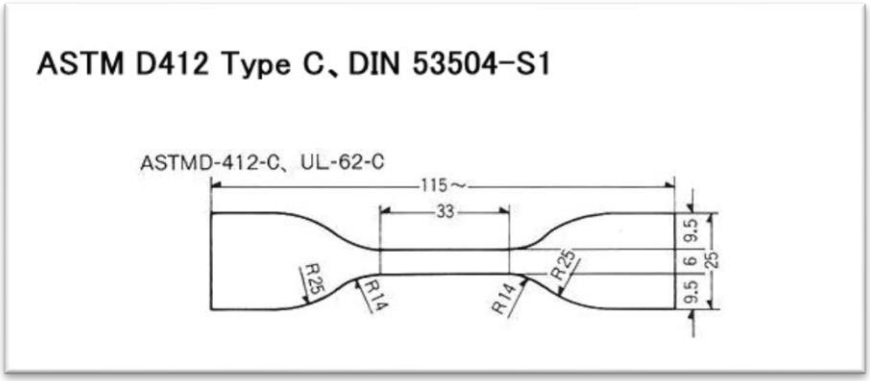


Figure 1 Laboratory apparatus for ASTM D412 standardized test to determine membrane Young' Modulus

Source: ASTM (2002)

Data from ASTM D-412 test were converted to stress and strains by using Equation:

$$\text{Tensile strength (MPa)}, \delta = \frac{F}{A} \quad (1)$$

Where, F is the force (Newton) and A is the cross section area of specimen (m^2).

$$\text{Elongation at break (\%)}, \varepsilon = \frac{L - L_0}{L_0} \quad (2)$$

Where, L is the elongation at break (mm) and L_0 is the initial length of specimen (mm). Therefore, the values of tensile strength at break, Young's modulus and elongation at break are observed (Xu and Xu, 2002; Yu and Selvadurai, 2005; Chen *et al*., 2011).

2.7 Gas permeation measurements

The flat sheet membranes were measured gas permeation property by using pure CO_2, N_2 and O_2 gases which were tested at room temperature. The gas permeation property of the prepared flat sheet membranes was calculated as follows:

$$P = \frac{QL}{A\Delta p} 10^{-10} \quad (3)$$

Where Q is the steady-state permeation rate [cm^3 (STP)/s], L is the membrane thickness (cm), A is the permeation area of the membrane (cm^2), and Δp is the pressure difference across the membrane (cmHg).

Moreover, the gas selectivity of membrane can be represented in the ability of a membrane is defined as (Baker, 1995; Sanchez *et al*., 2002; Sadeghi *et al*., 2008):

$$\alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} \quad (4)$$

For considerable gas permeation, the membranes were tested by VAC-V1 Gas permeability tester which was the instrument of Labthink Instruments Co., Ltd. The test instrument conforms to the ASTM (2009) 1434-82 standards. Practically, permeability measurements of both gases were performed by VAC-V1 tester at room temperature using an experimental setup with the method described in ASTM 1434-82. The results of gas permeability tests can be presented in the permeability coefficient (cm^3 (STP) cm/ (cm^2 s cmHg)) and the selectivity coefficient as presented in Equation 3 and 4 respectively.

3. SCOPE OF THIS RESEACH

The aims of this research are the preparation of three-grade PVC flat sheet membranes blending with PEG in different molecular weights via casting dry/wet method due to blending. It is a convenient method to improve a high hydrophilicity membrane. The PVC-PEG blending membranes act as supporter layers of entire asymmetric membranes; after that, the surface improvement can be developed by XSBR coating. To confirm the performance of membranes, they were investigated that many instruments are used in order to study consisting of physical and chemical properties, gas permeation of CO_2, O_2 and N_2 gas.

4. RESULTS AND DISCUSSIONS

Scanning Electron Microscopy

The picture of PVC flat sheet membranes obtained from SEM shows the morphological variation depending on PVC concentration and casting conditions as illustrated in Figures 2, 3 and 4. The surface instabilities induced by fist allowing the evaporation of the solvent in a casting membrane; after that, creating the porous support by solvent/non-solvent exchange during a precipitation step (in coagulant bath).

In Figure 2, the dominant structures are classified by the different molecular weights of PVC grades of which PVC580 contains the lowest molecular weight; 610 and 710. Obiviously, lower molecular weight expresses as higher chain mobility; therefore, it seems that the enhancement of phase-separation is to more rapid-liquid demixing resulting in larger finger-likes structure and offers the membranes with more defect-free structure. On the other hand, this indicated that the higher molecular weight relating to viscosity increment could not expand finger-like structures in the depth of the sub-layer structure because it is difficult to be formed. During slow precipitation of solution, the wall between small droplets is difficult to be

constant structure; therefore, many small droplets agglomerate to form larger droplets transforming into drop shape cavities or macro-voids structures; particularly, they are appeared near the below surface.

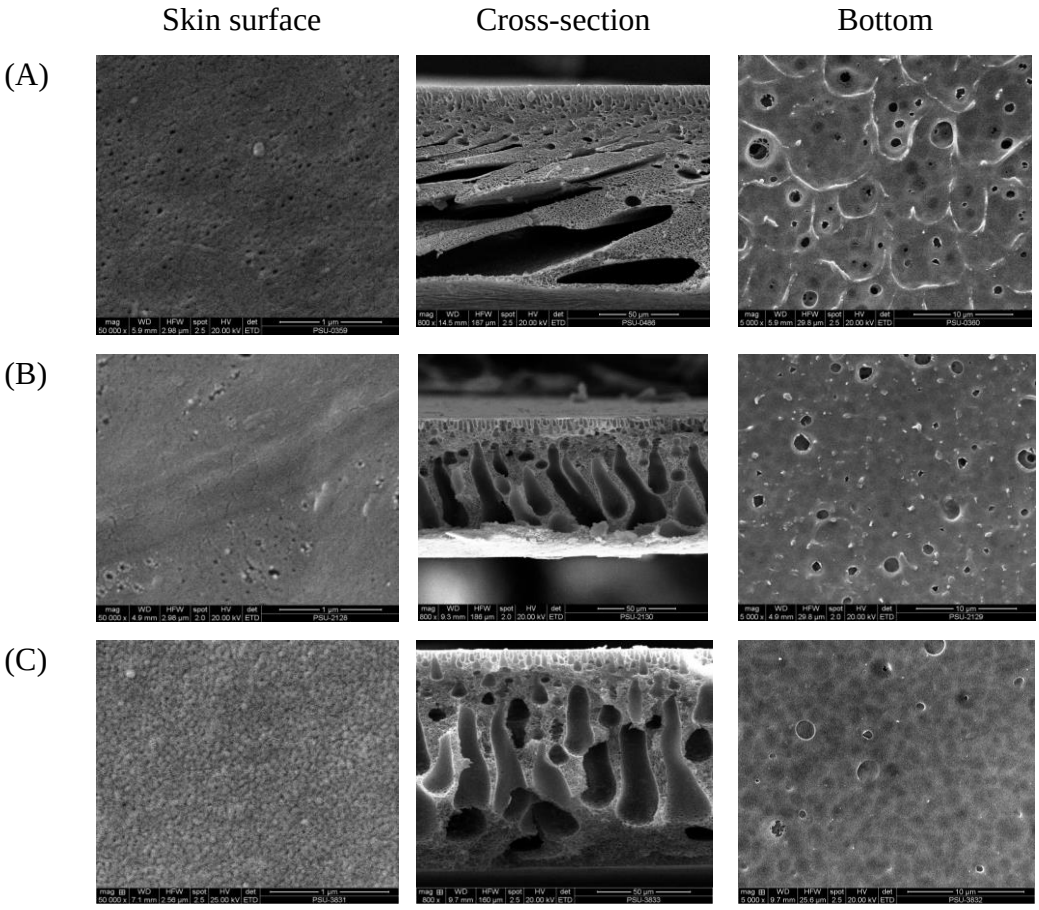


Figure 2 SEM images of 16 % by weight of: (A) PVC580; (B) PVC610; and (C) PVC 710

In Figure 3, it is interesting to notice that different PEG-400 contents and different molecular weights are affected to skin and sub-layer structure of membranes. Because PEG is water-soluble, it is also soluble in coagulant bath. Therefore, it can be formed as a pore former to enhance the permeation. The skin surfaces are found that the porosity remained almost unchanged when the PEG contents increased from 5wt% to 10 wt% while it increased with increasing PEG

contents from 10 wt% to 15 wt%. The poor miscibility of the casting solution is one of the main factors affected to skin surface and sub-layer structure. While, the effect of the increase in PEG molecular weight is provided with longer PEG molecular chains resulting in stronger macromolecule chain entanglement, which may produce larger macro-void and larger pore structures. They can be attributed by slow solidification from the coagulant bath and relatively higher viscosity; whereas, the dense or selective skin in Figure 3 (A) occurred by the solvent outflows from the casting solution causes the phase separation; at the same time, the porous structure is transformed by the liquid-liquid demixing and nucleation growth of the polymer lean phase. At the same time, the effect of increase in PEG molecular weight like PEG-4000 can be described as the enhancement of viscosity casting solution due to decrease chain movement, entalgle conformation and tighter intermolecular chain displacement resulting in the slow solovent and non-solvent exchanging. This slow exchanging is caused by large pores within substructure and porous skin like Figures 3 (D) and (E) that their skin layers are usually highly porous. These membranes were not provide satisfactory gas separation properties.

With the general flat sheet membranes for gas separation, the skin layer should show good permeability and selectivity; therefore, the observation of all membranes in Figures 2 and 3 might not be acted as suitable membrane for gas applications because their morphology shown large defects on skin layer. The defects on skin layer might show high all gas permeation but cannot show high gas selectivity. Consequently, XSBR rubber is used for skin layer by coating on PVC-PEG membranes acting as supporting membrane like Figure 4.

Although the membrane adds porous additives like PEG was found that the finger-like structures that might show high gas permeability; however, it will minimize gas selectivity. Therefore, the casting membranes were modified by coating with XSBR which acts as skin layer and blended PVC which acts as support layer. In Figure 4, the image is the coated membranes for developing selectivity. They can be clearly seen that the XSBR skin is denser than supporter layer which is provided non-defect skin; therefore, it was determined that this coated membranes can be achieved gas selectivity.

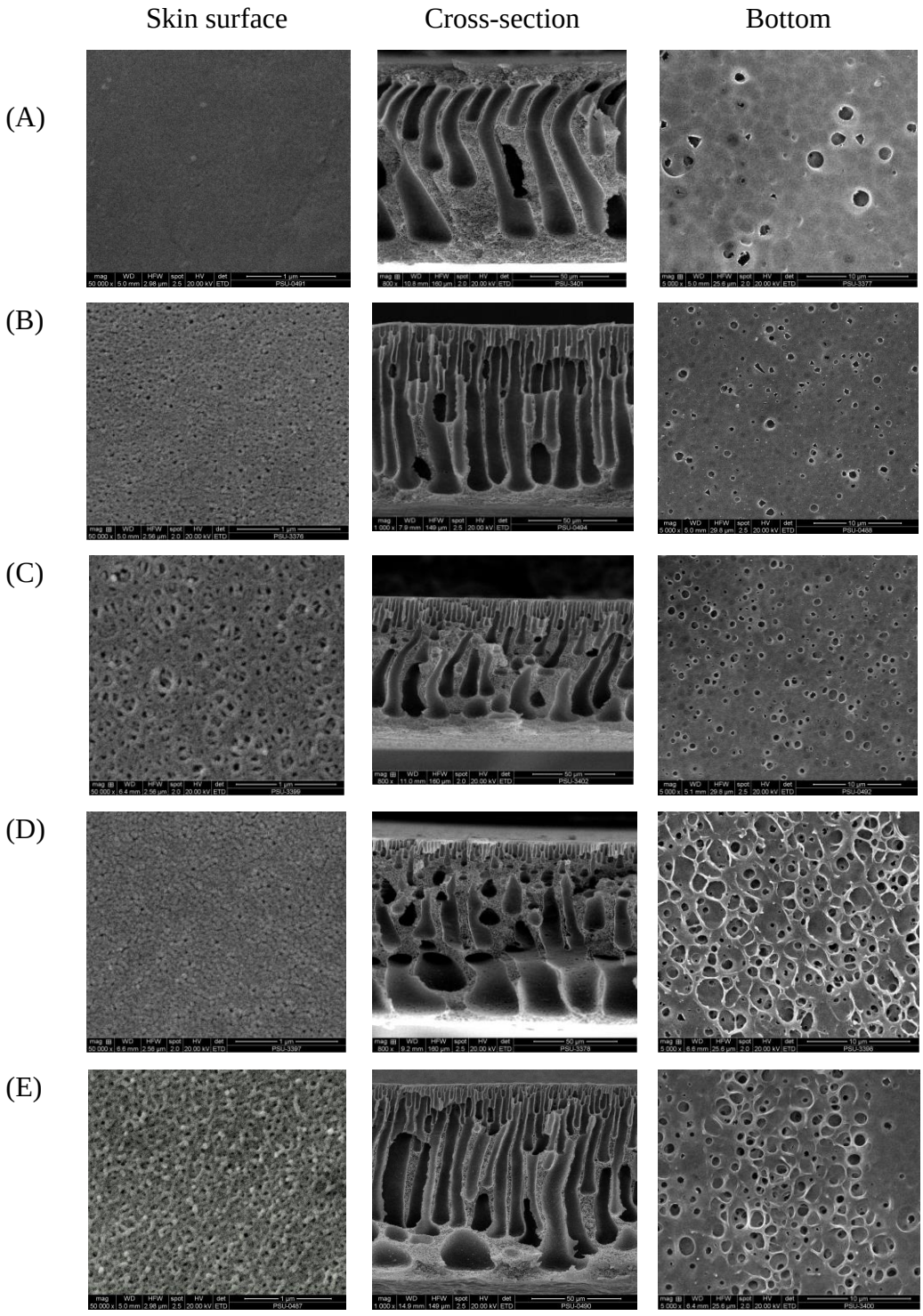


Figure 3 SEM images of: (A) PVC580-PEG-400 5wt%; (B) PVC580- PEG-400 10wt%; (C) PVC580-PEG-400 15 wt%; (D) PVC580-PEG-4000 5wt%; and (E) PVC580-PEG-4000 10wt%

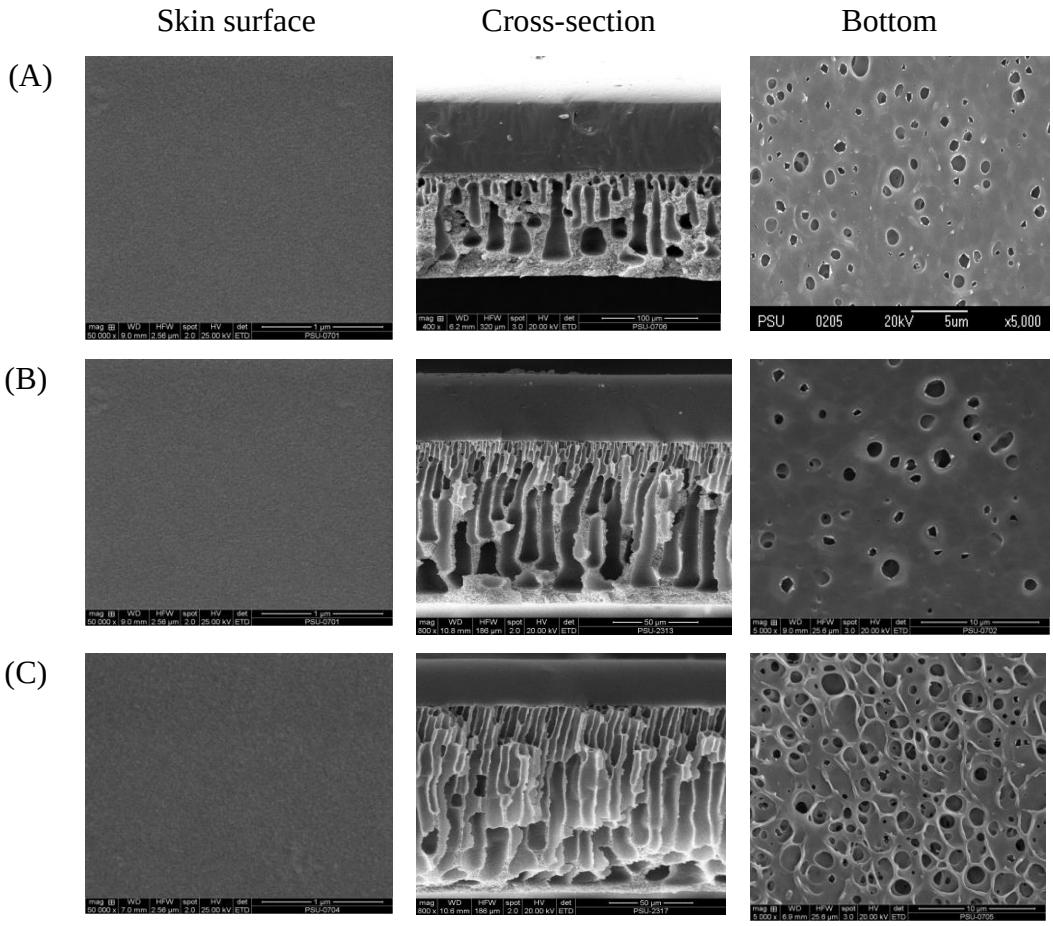


Figure 4 SEM images of XSBR coated: (A) PVC580; (B) PVC580-PEG-400 5wt%; and (C) PVC580-PEG-400 10wt%

Contact angle results

The contact angle for membrane characterizations was found to be significantly less than 90º suggesting that the more hydrophilic the membranes is, the informed data reported in Table 1. It was noted that smoother surface and the highest hydrophilic property showed on the PVC-580-G400 (10%)-coated XSBR (40.63 ± 27). According to presented data, it was found that the hydrophilic property can be determined by the increase in PEG contents; at the same time, to comparing among PVC grades that can be summarized that low molecular weight showed more hydrophilic material than high molecular weight that showed surface roughness in SEM images.

Table 1 Contact angle results of flat sheet membranes

Membrane	**(θ)**
PVC-580-Pure	88.28 ± 22
PVC-580-G400 (5%)	87.62 ± 32
PVC-580-G400 (10%)	88.34 ± 21
PVC-580-G400 (15%)	80.76 ± 26
PVC-580-G400 (5%) coated XSBR	41.22 ± 31
PVC-580-G400 (10%) coated XSBR	40.63 ± 27
PVC-610-Pure	89.36 ± 08
PVC-710-Pure	91.22± 63

Fourier transforms infrared spectroscopy (FTIR) results

According to PEG containing polar moiety, such as ether groups, has an affinity for CO_2 due to dipole–dipole interaction. This affinity may be induced to more permeability CO_2 than light gases. In this research, to verify that PVC and PEG miscibility which is the main matrix polymer; in Figure 5, the PEG is the absorptions material due to comprise stretching and bending vibrations restricted to C-C stretch, C-O stretch, C-H stretch (methylene absorptions) and C-H bending. The O-H stretching vibration is observed in the region 3378 cm^{-1}. In the case of PEG exhibits absorptions which comprise of stretching and bending vibrations restricted to C-C stretch, C-O stretch, C-H stretch (methylene absorptions) and the C-H bending. The O-H stretching vibration is observed in the region 3378 cm^{-1} exhibiting hydrogen bonded nature. The methylene group of PEG has been found to vibrate in the stretching mode around 2803 cm^{-1}. The absorption around 1474 cm^{-1} is due to bending vibration of $–CH_2$. As in the case of primary alcohol, the C-O stretching vibration, a strong band around 1362 cm^{-1} and 1287 cm^{-1} is also observed (Subban and Arof, 2004; Balakrishnan and Jayakrishnan, 2005; Polu and Kumar, 2010). All of these observations, they are an important evidence to ensure that the blended membranes can induce polar gases through membranes by blending with PEG.

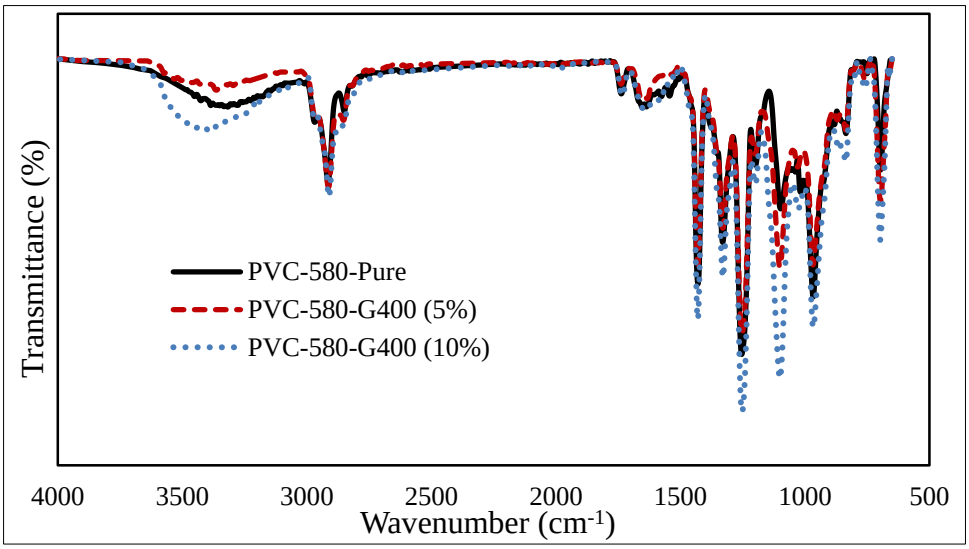


Figure 5 The FT-IR of PVC-Pure membrane and PVC blend PEG membrane

Table 2 Wavenumber of PVC and PEG structure

PVC		**PEG**	
Wavenumber (cm^{-1})	Vibration	Wavenumber (cm^{-1})	Vibration
638	C-Cl stretching	3378	O-H stretching
2974	C-H of CHCl	2803	$-CH_3$ stretching
2912	C-H of $-CH_2$	962	-CH stretching
961, 1064	C-C stretching	1362, 1287	C-O stretching

Thermal properties

The changes in storage modulus (E') of PVC casting membranes on heating are shown in Figure 6. The moduli will drop with temperature as the chain movements within the molecular structures. The glassy state modulus of PVC 580 is much higher than the other casting membranes resulting from thermal property because of the massive interaction among the molecular chains due to the crystallize state that the T_g of PVC 580 without adding PEG is approximately 100-110 ºC as showed by *tan* δ in Figure 6. In the case of adding PEG, the effect of the increase in PEG contents gradually decreases the T_g. This phenomenon can be determined by the present of flexible PEG segments which would decrease T_g.

The ratio of *E´´/E´* is the loss tangent (*tan δ*). Usually, the peak of either loss modulus curve or the peaks of the *tan δ* curves are always used to define the T_g. Consequently, we defined as the peak of the *tan δ* curve. T_g of adding PEG was decreased due to presence of flexibility PEG segment that increases the chain motions.

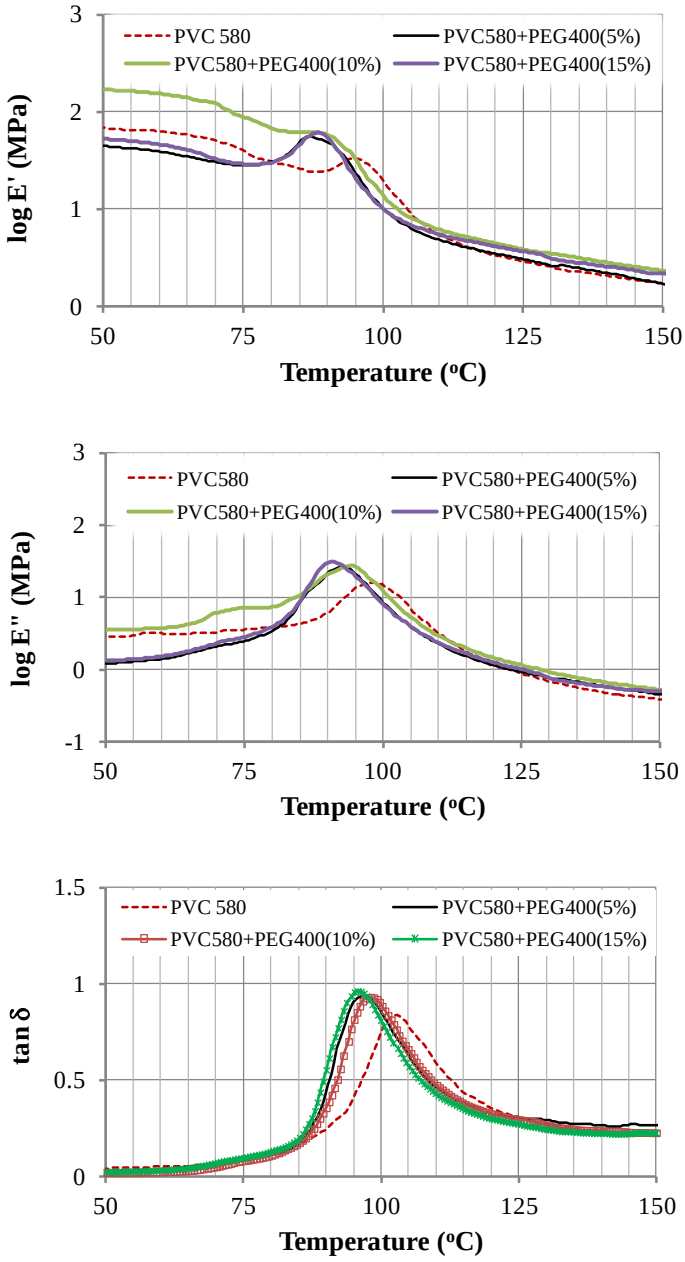


Figure 6 DMTA thermogram of membrane prepared from PVC580 and their blends

Tensile properties

The results of tensile testing are presented in Table 3. Tensile strength and elongation are based on the effect of hard and soft segment. The general behavior observed is that the modulus property was only enhanced with the flexibility of the PEG segment contents up to 5 wt%. Interestingly enough, the modulus property of coated XSBR was enhanced more than two-fold upon the elastic property of XSBR. For the non-blended PEG of casting membranes, Young's modulus of PVC-610 and PVC-710 was lower than the PVC-580. Those are described by the effect of the increase in molecular weight resulting in a high crystallize structures and on the other hand the tensile strength slightly increased that may be due to the presence of polymer chains are entangled and interconnected network structure.

Table 3 Tensile stress and elongation at break results

Membrane	**Thickness (mm)**	**Strength (N/mm^2)**	**Elongation @ break**	**Modulus (N/mm^2)**
PVC580-Pure	0.10	3.27	29.0	10.12
PVC580-G400 (5%)	0.12	2.55	25.0	10.19
PVC580-G400 (10%)	0.12	3.45	35.0	9.85
PVC580-G400 (15%)	0.13	3.95	55.5	7.11
PVC580-G400 (5%)-XSBR	0.15	8.31	51.0	16.29
PVC610-Pure	0.15	5.13	55.5	9.25
PVC710-Pure	0.17	4.15	51.0	8.14

Gas permeation results

The gas permeation test of this study was carried on 1 bar and investigated to the XSBR coated PVC-PEG blending membranes that can be explained into two parts due to including of two layers consisting of XSBR layer and PVC supported layer. The first reason is the present of XSBR layer because consists of carboxyl group that can adsorb polar gas like O_2 and CO_2 more than inert gas like

N_2; thus, the polar gas permeability can show high permeability presented in Figure 7. Besides, the CO_2 gas molecule is more permeable than N_2 and CH_4 due to the larger condensability, indicated by the critical temperature (T_c), e.g. $T_{c,CO2}$ = 304 K, $T_{c,\,CH4}$ = 191 K (Lin and Freeman, 2004). Another effect is the results of the addition PEG within PVC membrane that is to study of effect on gas permeation property. The high contents of -OH functional group within blending membrane reported as FT-IR curve of -OH peak in Figure 5, increased in high gas permeation concluded by O_2, CO_2 and N_2. The values for the apparent permeability coefficient are shown in many researches. It can be seen that, as usual, O_2 and CO_2 are the gas with higher permeability than N_2, this characteristic can be estimated in two reasons.

The first reason, the increase in amorphous PEG concentration comprises O-H bonds in PEG chains. They contain in PVC rich phase known to have good affinity with O_2 and CO_2 molecules; consequently, resulting in high permeability and selectivity. Second, and more significant, the addition of the highly flexible of PEG provides a “high diffuse” through the high content of amorphous phase for the gas permeation.

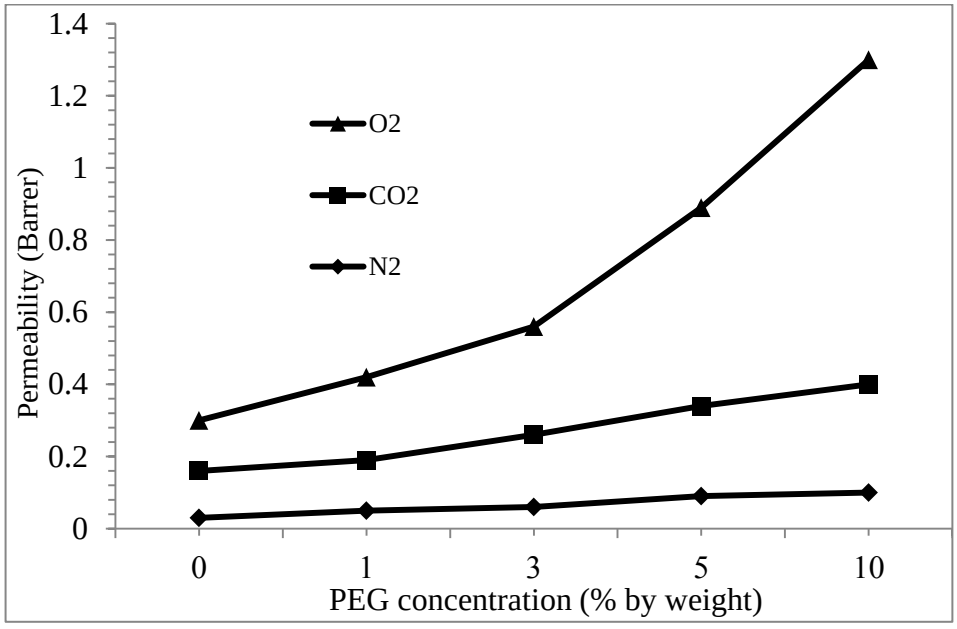


Figure 7 Effect of PEG concentrations on gas permeability of XSBR coated PVC-PEG membrane

However, the gas selectivity of single gas is one of the important parameter of membrane performance because its ability of penetrated gas can show the difference of membrane performances. According to ideal gas selectivity data in Figure 8, the selectivity of O_2/N_2 relatively presented the highest degree of gas selectivity resulting from the difference of polar and non-polar gas adsorption with XSBR skin layer. At the same time, the CO_2/N_2 selectivity shows lower pair-gas selectivity corresponding with lower permeability.

From all information above, they might assume that the combination of ability of coating XSBR and high porous supporting membrane can provide the feasible gas separation membrane and might adapt to several gas separation or other applications.

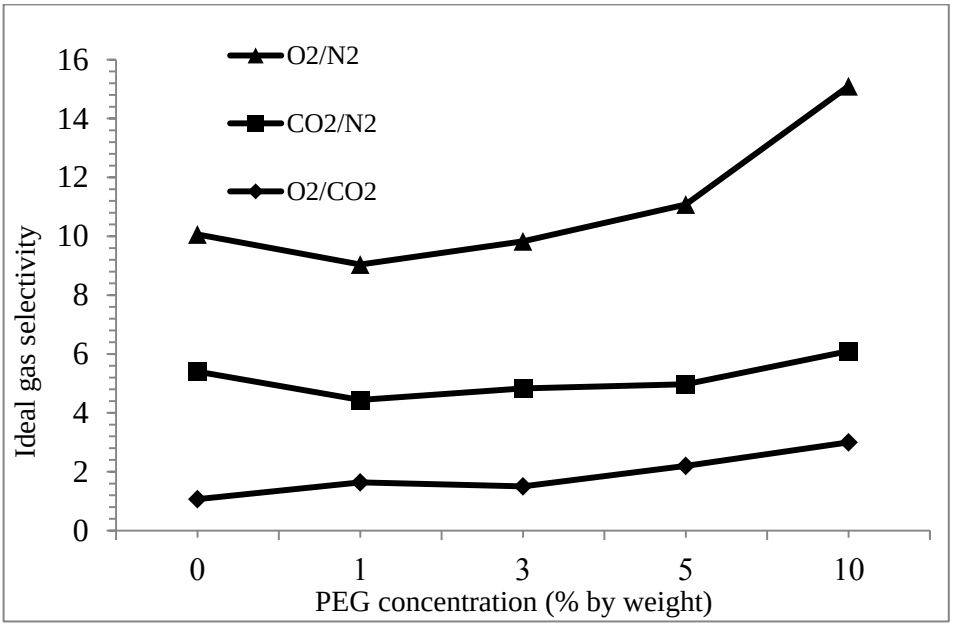


Figure 8 Effect of PEG concentrations on ideal gas selectivity of XSBR coated PVC-PEG membrane

CONCLUSIONS

This study showed that the blending PVC-PEG membranes were successfully prepared by casting method and the choosing high concentration of PVC grades were mixed solvent in DMF. The blended PEG with PVC membranes should show finger-like substructures and dense skin layer that are the appropriate morphology for gas separation membrane, but the high molecular weight of PEG is affected to high porous structure that does not satisfy for gas separation. While the high molecular weight of PVC promoted the high viscosity casting solution resulting in the difficulty of solvent and non-solvent exchanging during membrane formation. Therefore, the combination of both effects was considered in order to promote the formation of skin layer required to ensure suitable gas permeability and selectivity performance. Though its ability shows good permeability of gases, offered low gas selectivity; consequently, XSBR rubber is used for acting as skin layer or selective layer. It was observed that the gas permeability was significantly decreased when compared with uncoated XSBR while the selectivity was enhanced with increased in PEG contents and coated XSBR. This was attributed to induce the polar gas due to XSBR contains carboxyl group that is a polar structure; at the same time, this membrane does not adsorb a non-polar gas like N_2 resulting in the high gas selectivity of CO_2/N_2.

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CHAPTER 3
PREPAREATION OF PVC HOLLOW FIBER MEMBRANES

ABSTRACT

This work aimed to prepare PEG blended PVC with different grades-580, 610 and 710 in order to produce hollow fiber membrane via dry/wet spinning process that was operated under different conditions. The considered conditions were desired in various factors consisting of air gap, wind-up speed, dope extrusion rate, bore extrusion rate; besides, the different lengths of center tube which acted as inner-side fiber diameter were studied. Due to all of these factors are influenced on the forming hollow fiber membrane resulting in the different fiber properties, this research investigated morphological property, dielectric property and dynamic mechanical thermal property by observation to study suitable preparation hollow fiber membranes for feasible applications, especially hollow fiber membrane for CO_2 removal. The observed morphology from PVC-580 blended PEG-400 5wt% hollow fiber membrane presented an appropriate dope viscosity and showed a dense skin both inner and outer fiber surface. Moreover, it offers finger-like substructures that could provide high applicable feed-stream permeability and selectivity. At the controlled center tube length of 0.3 cm, finger-like substructures existed among near inner fiber surface more than center tube of 1 cm which was resulted from more rapid exchanging of solvent and non-solvent within lumen tube than exchanging of solvent and non-solvent within coagulant bath. The effect of wind-up speed during spinning process was a significantly influenced affordable hollow fiber that can be indicated by draw ratio (λ). It was found that the draw ratio of 3.3 showed the thickness thinner than 2.6 and 2.0 respectively. In conclusion, a studied preparation was achieved by controlling an appropriate dope viscosity, wind-up speed and agglomerated period importantly.

1. INTRODUCTION

In the last 40 years, hollow fiber membranes have been interested as a favorable apparatus for gas filtration because of their high separation efficiency, self-mechanical support, good flexibility and easy handling during fabrication (Chung *et al*., 1997). However, the preparation of hollow fiber membranes consisting of permeability and selectivity is often found a challenge due to confronting the complexity of spinning process. This is a main problem of the membrane scientists, how to fabricate hollow fiber membrane with adapted structure to obtain high pressure application, plasticization and suitable morphology. A defect-free hollow fiber membrane and an ultra-thin dense-selective layer are to be the desirable configuration because these geometrics are led to be greatly increased gas permeability. An ultra-thin dense-selective layer can reduce transport resistance and leads to enhance the gas selectivity. Besides, the sub-layer within membrane seems to be the plasticization effect that can eliminate the membrane performance (Peng and Chung, 2008). As a consequence, the preparation of hollow fiber membrane needs to consider many factors that involve during processes in order to succeed desirable requirements.

1.1 Hollow fiber membrane

Hollow fiber membranes were first presented in a series of patents by Mahon in 1966 assigned to the Dow Chemical Company (McKelvey *et al*., 1997). Indeed, the development of hollow fiber membrane technology has been dramatically accepted by intensive research regarding reverse-osmosis membrane during 1960s via solution spinning and phase inversion techniques. Recently, hollow fiber has been remarkably used in a large number of commercial benefits consisting medical devices, water reclamation, pervaporation and gas filtration due to its good mass transfer properties and high ratio of membrane area per volume (Mulder, 2003).

Generally, the different types of tubular membranes can be classified into 3 aspects that consisted of hollow fiber membrane (inner diameter < 0.5 mm),

capillary membrane (inner diameter 0.5 - 5) and tubular membrane (inner diameter > 5 mm) (Mulder, 1991). Besides, hollow fiber membranes can be divided into 2 functions: open hollow fiber and loaded hollow fiber. In case of open hollow, the feed flow of lumen medium is not restricted. In contrast, lumen of the loaded fiber is filled with feeds (Moch, 1997).

Many different methods to prepare synthetic membranes have been produced by the several important methods that are sintering, track-etching, phase inversion and coating. With all various methods, phase inversion method is a simply applied in fabrication of available membranes. At the same time, phase inversion method is divided into four broad categories (Koros and Fleming, 1993): wet/wet phase inversion, dry/wet phase inversion, dry/dry phase inversion and dry/dry-wet phase inversion. The difference between dry and wet process is referred to whether using the outlet of the spinneret or casting knife that exposes the dope solution from a closed coagulant bath and exposed to air or immerged directly in a non-solvent coagulation bath due to using for precipitation process (Yamasaki *et al*., 1997; Ismail *et al*., 1999; Wang *et al*., 2002; Sukitpaneenit and Chung, 2009). Accordingly, those methods can be used for a phase inversion process; moreover, during process that exchanging of solvent and non-solvent, evaporating of solvent, forming by thermal precipitation, and cooling by immersion in non-solvent bath are occurred (Pesek and Koros, 1993). Furthermore, the precipitation process is important to casting or spinning of polymer solution because it involves with immersion in a non-solvent coagulation bath; consequently, it means that the membrane is formed by combination of mass transfer and phase separation.

1.2 Spinning process

A satisfactory spinning process must offer fibers for many applications that need to be considered several abilities concluding permeability, surface pore size and stability under long-term pressure. Normally, the principle factors during spinning process are dope composition, dope viscosity, temperature, dope pumping rate, bore solution, bore pumping rates coagulation temperature and fiber draw rates, for

instances. Besides, a spinning process contains 4 conventional spinning methods: melt spinning; wet spinning; dry spinning and dry/wet spinning. However, dry/wet spinning is the most common commercial leading to produce gas separation membranes (Koros and Fleming, 1993) due to provide simultaneously ultra-thin and defect-free asymmetric membrane that is formed by forced-convection evaporation. In typical dope spinning and phase inversion method, spinneret is the most vital part in a spinning process. Generally, there are three types of spinnerets that are used for the hollow fiber spinning method consisting of the segmental-arc design, plug-in-orifice design, tube-in-orifice jet design and multi-annular design (Moch, 1997).

In general, polymeric hollow fiber membranes have been prepared by the well favorite dry/wet spinning process using tube-in-orifice spinnerets (Mulder, 1991). Due to this process involved that the polymer solution or dope solution is extruded from the outer orifice of the spinneret and the non-solvent or bore solution is extruded from the center tube of the spinneret, respectively. There has been considerable attention to the development of several hollow fiber membranes with very small outer/inner diameter of ≈ 0.25/0.14 mm that were completely prepared using this conventional spinning process (Peng and Chung, 2008). From this process, there is an air gap between the spinneret and the coagulant bath which plays an important role for membrane forming; at the same time, the size and the length of tube-in-orifice influence to membrane forming both within lumen side of and outside hollow fiber membrane. Usually, a dense-selective layer or defect-free skin layer on surface asymmetric hollow fiber membranes may result from packing of kinked polymer chains (Datta *et al*., 1992; Ismail and Yean, 2003) that gains the influence from the controlled parameter during spinning process.

As a consequence, this work concentrated on the importance of an internal spinneret design and annulus dimension because they play an important influence on membrane forming that results from not only the chain mobility, chain packing, morphological structure, but also the ability of membrane separation, is influenced to morphological structure of hollow fiber membrane.

1.3 Advantages of hollow fiber membrane

Several applications of hollow fiber membranes were reported in the previous studies such as hollow fiber membrane for gas separation was reported by Mansourizadeh and Ismail (2011), they used polyvinylidene fluoride (PVDF) hollow fiber membrane for CO_2 absorption. Jones and co-workers (2011) produced PVC hollow fiber membrane to obtain the ultimate quest to produce the reliable separating of oxygen and ozone gas mixtures. Hasbullah and co-workers (2011) prepared polyaniline (PAni) hollow fiber membrane via dry-jet wet spinning to investigate gas separation performance. These are partly available evidences of favorable membrane configuration that can be expanded the advantages as below:

- Due to high packing density and large surface area, hollow fiber membranes provide higher productivity per unit volume (Moch, 1997; Van't Hof *et al*., 1992) as a suitable configuration for various applications as shown in Table 1.
- Hollow fiber membrane can be operated under high pressure condition; therefore, simplify the hardware for preparation of membrane permeator (Moch, 1997).
- High recovery in individual units.
- Low cost (Wang *et al*., 2000).

However, the hollow fiber membrane contains few disadvantages; for instances, its sensitivity to fouling and plugging by some feed matter due to a relatively low free cavity between fibers (Moch, 1997). But in case of gas separation, feed stream in gas are rather clean. Besides, pressure drop is significant with gas flow through the membranes (Puri, 1990).

In addition to all mentions above, the applications of hollow fiber membrane are considered to the direction of feed flow, permeate flow and retentate flow that are vital factors for using membrane to obtain an optimum performance. Consequently, the flow configuration of hollow fiber membrane should consider.

Table 1 Different module for different process

Process	Plate and frame	Spiral would	Disc-tube	Tubular	Capillary	Hollow fiber	TFM
MF	+			++	+		++
UF	+	+	+	++	++		++
NF	+	++	+	++	++	+	+
RO	+	++	+	+		++	
GS		++	+		+	++	+
PV	++	+	+		+		
ED	++						
DL	+				++	++	

++: Best suited to given process

+: Suited under certain circumstance

Source: Franken (1998)

1.4 Hollow fiber flow configuration

Normally, the hollow fiber module flow configuration can be designed for different industry applications that the first type of hollow fiber module is the countercurrent flow with the feed enters outside the fiber (Shell-side feed). The fibers in this type of unit are open at both ends, and the feed fluid is circulated through the bore of the fibers (Figure 1). This flow configuration has been usually used for reverse osmosis and ultrafiltration application. Another type is countercurrent flow with the feed flows in the fiber bore and permeate is moved through outside the fibers (Bore-side feed). The last type is the cross flow with shell side feed that was generally used for microfiltration applications (Figure 2) (Baker, 2004).

According to the difference of flow configuration, the selective layer of hollow fiber membrane can be designed during the spinning process by establishing the tube-in-orifice spinneret and center tube in several sizes to obtain several kinds of hollow fiber membranes.

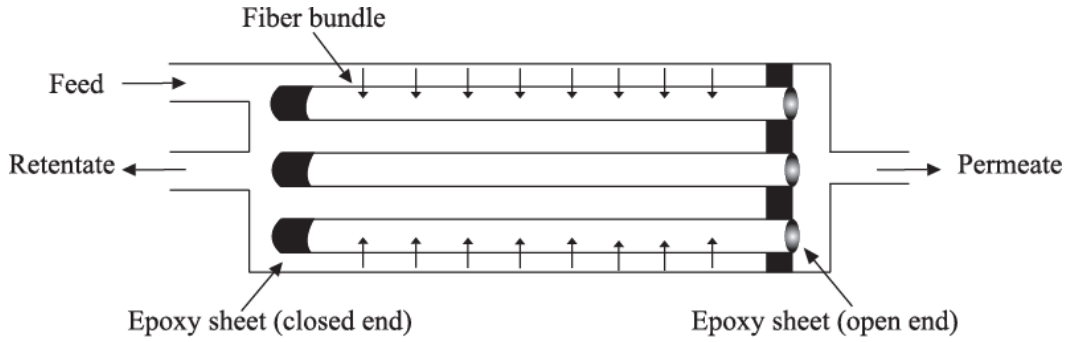


Figure 1 Schematic of shell-side feed configuration
Source: Baker (2004)

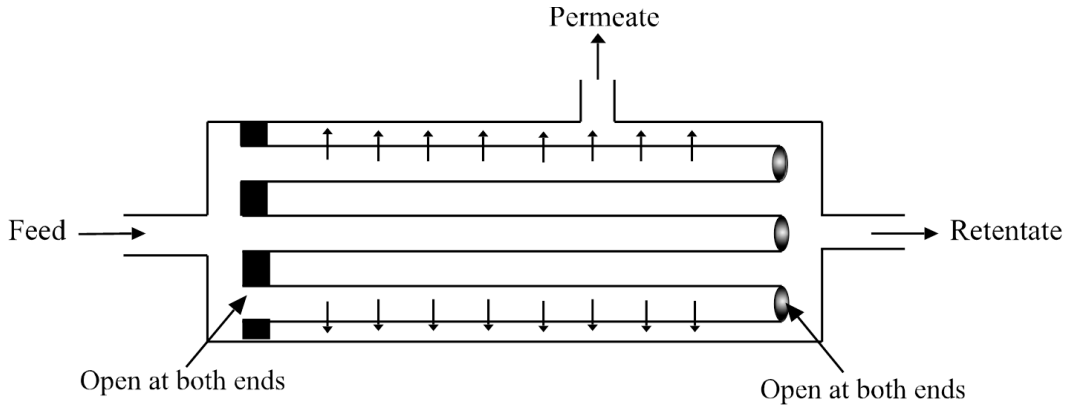


Figure 2 Schematic of bore-side feed configuration
Source: Baker (2004)

1.5 PVC hollow fiber membrane

The using PVC for membrane fabrication which acts as semi-glassy polymer type, mostly preferred as membrane material because it was highly durable material and ease to fabricate in many aspects. However, glassy polymers are always meet problems as plasticization behavior that occurs from dissolution of gas molecules into micro-void inside polymer phases which these characters are smaller than the gas molecule diameter as a result of damages to the polymer matrix and leads to larger

inter-chain spacing in the polymer matrix, resulting in plasticization can be changed the performance of membranes. PVC can be probably prepared as dense membrane material because of its suitable properties that consist of low cost, excellent chemical and physical properties, acid and alkaline resistance, as well as mechanical properties (Tiemblo *et al*., 2001; Tiemblo *et al*., 2002; Bierbrauer *et al*., 2010). In addition PVC has many advantages over other types of plastic such as Poly ethylene (PE), Poly propylene (PP) and Poly styrene (PS) since it can be improved for various property requirements (soft and hard) and can also be recycled because of the thermoplastic type. Thus, it can save numerous of energy and reduce amount of plastic not to overflow the world as well (Xu and Xu, 2002). However, PVC still has low gas permeability due to nature properties such as slightly crystalline and glassy polymer therefore, in order to improve to approach high permeability that should be found out the improvements to develop a high efficient membrane.

1.5.1 The effect of PEG additives

The addition of PEG contents is a remarkable method because it is often used as an additive to improve more permeability and increase porosity of membrane because PEG comprises a molecular structure indicated as HO-(CH_2-O-CH_2)$_n$-OH which is formed as liquids or low melting wax like solids (Kuehne and Friedlander, 1980). The repeating unit of PEG structure contains the O atoms in ethylene oxide units which stained the hydrogen bonds (H-bonds) with the H atoms in CH-Cl group of PVC back bone (Lin and Freeman, 2004; Car *et al*., 2008). In addition, PEG is water-soluble polymers that effects of additional PEG were focused on the PVC dope solutions, membrane structure, and separation performance. In former researches regarding PVC blended PEG, many reports have been shown. Sadeghi and co-workers (2008) reported the effect of the addition the different molecular weight of PEG on the effectiveness of gas permeability and selectivity of a blended membranes between PVC 10 wt% PVC (K-value of 67) blended PEG in several molecular weight 400 and 4000 Dalton in many ratio as following 10wt%, 20wt% and 30wt%, and DMF which is as solvent. From this research, it was found that the blended membranes having PEG with 4000 Da showed higher values of CO_2 permeability. Moreover, the gas permeability of PVC/PEG membrane rapidly

increased with an increase in PEG concentration. In addition, a concentrated polymer solution with additives between PVC and PEG was investigated by reports of Neiro and Castro (Neiro *et al*., 2000; Castro *et al*., 2003). They explained that the electron-rich O atoms in PEO may act as donors and have attractive interactions with the electron-deficient Cl atoms in PVC structure. Thus, these reasons can be modified membrane for gas separation to CH_4 enrichment from mixed gases such as natural gas and biogas.

Remarkably, the effect of the different PEG molecular weights is often available experiment that has been used to study the improvement of membrane performance by many researches. Kim and Lee (1998) reported that when the molecular weight of PEG additive was added from 600 to 2000 and 6000 Da in PSF matrix, pure water flux increased and solute rejection decreased; meanwhile, with an enhance in the ratio of PEG-600 contents to solvent, water flux increased and solute rejection decreased. These are the evidences that PEG additive act as pore former of membrane. Moreover, Chakrabarty and co-workers (2008) also reported the properties of PSF membrane that they used PEG-400, PEG-6000 and PEG-2000 as additives. They studied that the porosity remained almost invariable morphology when increasing PEG molecular weight from 400 to 6000 Da; at the same time, increasing with PEG molecular weight from 6000 to 20000 Da. The increases in of PEG molecular weight are influenced of the poor miscibility of the dope solution.

1.5.2 Preparation of PVC hollow fiber membrane

One of the most favor membrane aspects is the hollow fiber membranes which have been gradually interested for many sectors such as gas separations, food industry even medical applications (Bierbrauer *et al*., 2010). In the past few decades, it is well-known that hollow fiber membranes have been significantly prepared by polymer materials via wet spinning process. In typical concentrated solution spinning and phase inversion method, a hollow fiber membrane is fabricated by extruding capillary spinneret along with wind-up stretching fiber whereas non-solvent solution acts as bore liquid that is extruded through the internal capillary. During processes, both external coagulant and internal coagulant are necessary for aggregation and formation of polymer structure (Guillen *et al*., 2011; Jones *et al*., 2011; Liu *et al*.,

2011; Mansourizadeh *et al*., 2010; Mansourizadeh *et al*., 2011; Mansourizadeh *et al*., 2011). The diameter and wall thickness of fibers are controlled by the inner/outer diameter capillary which is quite limited in the changing capillary diameters.

According to capillary diameters, these factors can be resulted in different efficiency separation (Ward *et al*., 1980). Significantly, it is a practical challenge to adapt the size of hollow fiber membranes by using a blunt needle. In previously reported, Yao and his co-workers (Yao *et al*., 2012) demonstrated that they use a single orifice spinneret to fabricate ultrafine hollow fiber membranes which was extruded by blunt needle. It was found that this method is much simpler than the conventional spinning process.

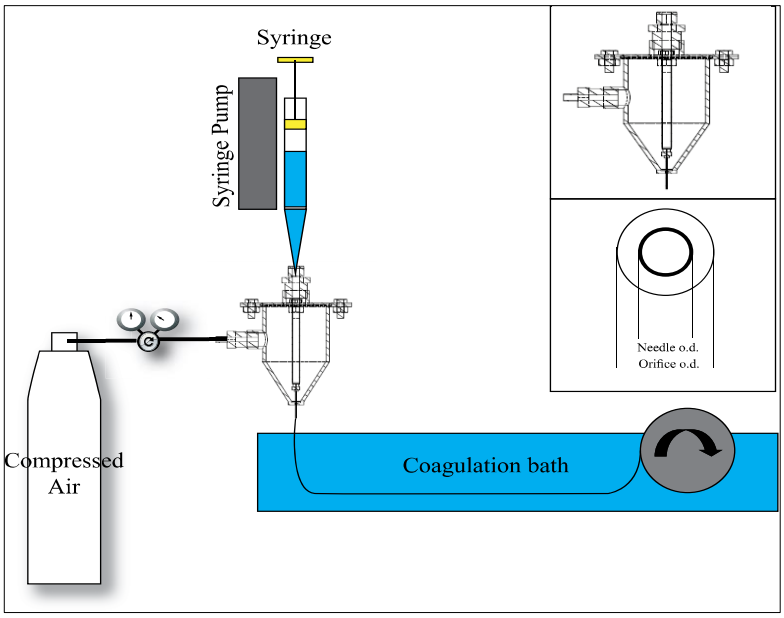


Figure 3 Schematic diagram of dry/wet phase inversion spinning of PVC hollow fiber membranes through the tube-in-orifice spinneret

As previously mentioned above, one of the alternative methods, to eliminate some limitations, is creating a novel apparatus to be a simple equipment and an uncomplicated spinneret dimension adjustment by using center tube (metal needle) acts as inner capillary which is used for the extruding bore fluid (Figure 3). Not only its process is to be adaptable instrument but also the final product has to be high

efficient fabrication like conventional apparatus. Besides, the dominate advantage of this spinneret is that it can avoid using mixing solvent within bore fluid by increasing in center-tube length instead of utilizing mix bore fluid.

Since mix bore fluid can control internal surface as porous surface, especially shell-side feed direction. As the former researches, Wang and co-workers (2004) fabricated asymmetric hollow fiber membrane from PES and injected mix solvent NMP/water: 86/14 into lumen side of hollow fiber membrane, Widjojo and co-workers (2007) prepared mix matrix hollow fiber membrane and used NMP/water: 95/5wt% as internal coagulant solution; Peng and Chung (2008) used mix solvent NMP/DI water: 90/10wt% as bore fluid. These bore fluids are influenced on the forming-retardant precipitation of internal surface resulting in porous surface that can eliminate pressure during separation process.

2. MATERIALS AND METHODS

2.1 Membrane materials and chemicals

PVC was kindly supplied from Thai Plastic and Chemicals Co., Ltd, K-value 580, 610 and 710. The solvent DMF (99.8%) was purchased from Ajax Finechem Pty Ltd. PEG 400 and 4000 Dalton were purchased from Honam Petrochemical, Co., Ltd. Dope solution was prepared by dissolving PEG in DMF and stirred for several minutes. Then, PVC was subsequently added with continuous stirring and heating at 60 °C until the solution is completely dissolved and homogeneous. The resultant dope solution was continuously kept at 60 °C before spinning process.

2.2 Dope viscosity measurement

To prepare dope spinning solutions, dope temperature was maintained at about 60 °C until all components were entirely dissolved. The homogeneous

solution of PVC and PVC blended PEG was measured using a Brookfield Viscometer (Model 5XHBTCP). The experiments were carried out using spindle number 4. The flux times were recorded every 30 s. Measurements were performed at a constant temperature at 25 °C (Sukitpaneenit and Chung, 2009; Yong *et al*., 2013).

2.3 Fabrication of PVC hollow fiber membrane

The mixed solution or dope solution between PVC and PEG was homogenized by using hot plate magnetic stirrer of VS-130SH from Vision Scientific Co., Ltd. The mixed solution can be completely dissolved in form homogeneous solution at temperature 60 °C approximately 24 hr. Then mixed solution was poured into in-situ extruder which had been already installed with blunt needle. During the spinning process, phase separation and stretching process, the mixed solution which is insoluble in water is pushed into the coagulant bath and toward fiber to wind-up drum which is controlled the collective speed by Overhead stirrer IKA RW 20 digital. Then, the fibers are immerged in water at 25 °C for 2 days to ensure releasing solvent. The detailed conditions of hollow fiber spinning are presented in Table 2.

Table 2 Spinning conditions of the fabricated PVC hollow fiber membranes

Dope extrusion rate (ml/min)	5
Feed pressure (bar)	1
Bore fluid composition	Tab water
Bore fluid flow rate (ml/min)	0.5
Center tube o.d. (cm)	0.1
Orifice o.d. (cm)	0.3
External coagulant	Tab water
Air gap distance (cm)	1
Coagulant temperature (°C)	25
Room relative humidity (%)	60-70
Wind-up drum speed (rpm)	30, 40, 50

2.4 Dielectric property measurements

According to improving PVC-HF membrane with additive PEG, the blended membranes have defected a structure and provided a free volume. Besides, they are still contained an O-H group as functional group of PEG backbone structure (Kalakkunnath *et al*., 2007). Consequently, the comparison of the dielectric properties of the PVC-pure and PVC blended PEG membrane in various contents can be provided by alternative indication on their structural polarity of the polymer materials (Kreuer, 2001). Normally, the polymer materials have a high dielectric constant which they are able to highly retain a charge and not to be a good conductivity of electricity. It is evident that due to important differences in charge mobility across layer of distinct phases, alternative accumulation and dissipation of the charge will occur at these interfaces under oscillation of the electric field (Serguei *et al*., 2014). Dielectric measurements were carried out in the frequency range 1 MHz up to 300 MHz by using precision LCR meter (Agilent 4285A).

2.5 Dynamic Mechanical Thermal Analysis Measurements

The dynamic mechanical properties of the fabricated membrane were measured using DMTA (dynamic mechanical thermal analyzer, Model-V, supplied by Rheometric Scientific). The cantilever mode of the deformed sample was carried under the test temperature range from 0 °C to 500 °C, the test frequency being 1 Hz. The cooling process was gained through liquid nitrogen. The terms of this method were presented in terms of loss tangent ($tan\ \delta$) and glass transition temperature (T_g). In this investigation, loss tangent was the ratio of loss modulus (E'') to storage modulus (E'); meanwhile, T_g was perceived from the loss modulus peak (Mondal and Hu, 2006; Coeho *et al*., 2012; Touaiti *et al*., 2012).

2.6 The draw ratio measurement

The remarkable research regarding the draw ratio is the study of Cao and co-workers (2004). They investigated the gas separation performance of PES hollow fiber membranes. They discovered that their selectivity and permeability were caused by the draw ratio and shear rate during spinning process. They described that elongation field stimulates the uncoiling motif of molecular chains; as a consequence, they were compacted packing in the skin layer. In addition, they found that the effect of draw ratio is affected to improving the membrane structure during spinning process due to the elongation arranged molecular orientation which accelerates polymer chains to provide more regular packing and more mono-disperse space (Jiang *et al*., 2006; Widijojo *et al*., 2006). Besides, it is believed that the increasing air gap distance and wind-up speed may play an important role on membrane morphology because the elongation stress is eliminated, retarded chain relaxation and orientation. The draw ratio (λ) during the spinning process is presented as equation 1 (Yu *et al*., 2006):

$$\lambda = \frac{V}{V_0} \tag{1}$$

Where V_0 is the extrusion speed and V is the wind-up speed

2.7 Morphological measurement

The geometrical characteristics and morphology of polymeric membranes were studied using scanning electron microscope (SEM). The samples of membranes were frozen by liquid nitrogen before being tested to brake up samples, and then mounted on sample stubs with double-side tape. The preparing samples were sputtered with thin layer gold. The study of morphology with SEM can be observed cross-section, surface and pore size of membranes. In this research, the investigated morphology of the prepared membranes was observed with scanning electron microscopy, Quanta-5800. The surface and cross section can be shown different

aspects as a result from different components in dope solution and fabricated membranes.

3. SCOPE OF THIS RESEACH

The purpose of this work is to explore the feasibility of achieving via an alternative instrument for preparing hollow fiber membranes on how to fabricate defect-free hollow fiber membranes with ultra-thin dense-selective layers from a novel apparatus. To support the efficiency of this new instrument, here we investigated the morphological and physical properties such as a thickness, skin surface both inner and outer surfaces, repeating unit on backbone structure to substantiate existing of an additives and hydrophobic/hydrophilic properties. In addition, the effects of the diameter of orifice and different length of center tube still involved membrane forming (solid phase).

Aside from the designed spinneret header, the wind-up speed, the speed is influenced to different morphological properties. The beginning of fabrication hollow fiber membranes were prepared from spinning process by unemployed center tube that acting as lumen capillary tube in order to ensure the ability of novel spinneret system. Then, the used center tube was investigated to study the different morphology resulting from the effect of center-tube length, the effect of rapid and low formation of hollow fiber membranes due to controlling different wind-up speed. To sum up, we aim to study the feasible performance of a novel spinneret apparatus that can provide a defect-free skin layers and ultra-thin layers hollow fiber membranes like gas separation hollow fiber membrane resulting from conventional spinning process.

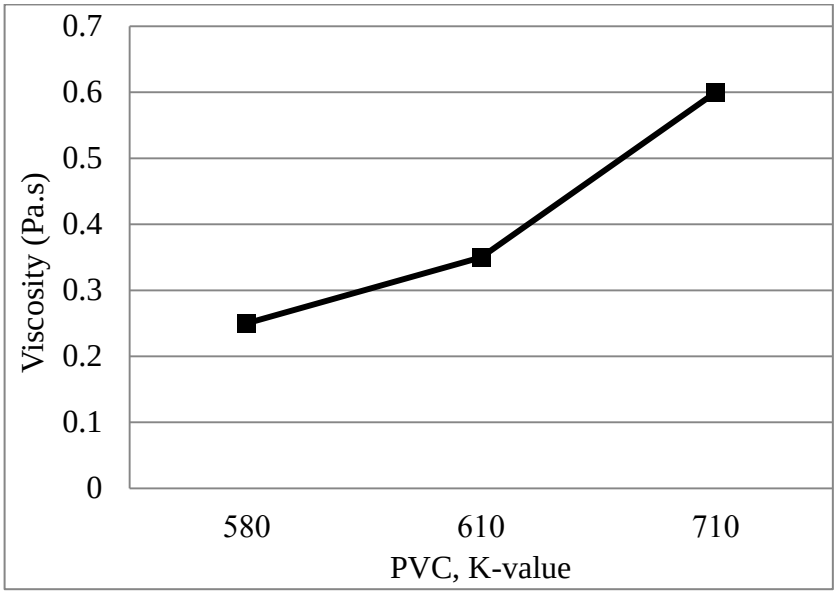
4. RESULTS AND DISCUSSIONS

Viscosity results

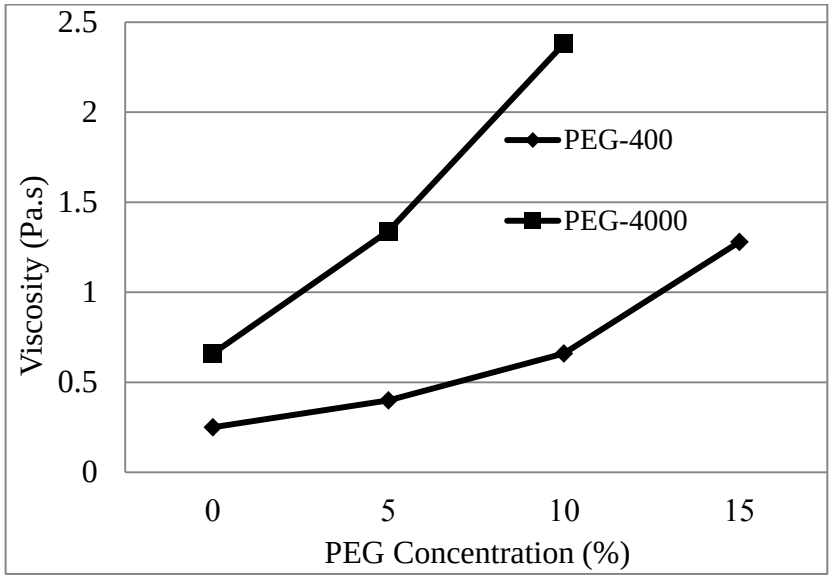
The rheological behavior of polymer dope solutions is another vital parameter that involves in elongation flow during spinning process. The results of this effect must be considered because the elongation viscosity of dope solution is induced by the gravity of the nascent fibers in the air gap distance (Cao *et al*., 2004). To have a better understanding of the blend dope rheology and decreasing surface defects of fabricated membranes for better gas separation, the suitable concentrations of PVC-PEG spinning dope solutions were pre-determined before fabrication (Chung *et al*., 1997). Many experiments and theatrical methods have been used to investigate polymer-compatible efficiency. Viscosity measurement is a vital method because of its simplicity and reliable (Kulshreshtha *et al*., 1988). Theoretically, absorptive interaction among the chain mobility of polymers in solution may induce expanding of the high viscosity cause of the shrinking of chain mobility similar to tendency in Figure 4(a) which showed the viscosity of the three K-value of PVC 14% in DMF without PEG concentrations resulting from the increase in different degree of polymerization. It is observed that different K-value has a significant influence on viscosity of spinning solution resulting in different morphological efficiency.

The effect of PEG additive on dope rheology was significantly considered because the viscosity of the dope solution is an important parameter relating the kinetics of the phase inversion in membrane fabrication. In Figure 4(b), given the tendency of viscosity containing PVC-580 blended with 5 wt%, 10 wt% and 15 wt% of PEG-400 and PEG-4000, both different PEG contents and PEG molecular weights present distinctive effects on dope viscosity. Longer PEG chain segments for the PEG with a higher molecular weight may grow into denser macromolecule chain entanglement, which may be chargeable for the viscosity increase (Ohya *et al*., 2009). In contrast, the minimized viscosity may be due to the relatively poor interaction between PEG and DMF resulting in viscosity decrease. Significantly, the segments of a PEG chains tend to attract each other in a poor solvent, because DMF is a poor

solvent of PEG, resulting in the shrinkage of PEG chain segments participates in single polymer coils (Flory, 1953).



(a)



(b)

Figure 4 Viscosity results of (a) the different K-values of PVC, (b) the different PEG 400 and 4000 concentrations

Aside from previous mentioned, since viscosity of these dope solutions from different K-values and PEG molecular weights are low, it seems that increasing of phase-inversion due to rapid liquid-liquid demixing overcomes the kinetic effect (Manosurizadeh and Ismail, 2011). This effect resulted in the large finger-likes and induced the membranes with open structure that can be expected to increase gas permeability because their structure contains high porosity within bulk structure (Park *et al*., 2007).

Morphology of PVC hollow fiber membranes with unemployed center tube: air gap 1.0 cm

In this preliminary experiment regarding hollow fiber spinning process, a variety of dense PVC-based membranes were prepared via a phase inversion method, and then fabricated by a dry/wet spinning process without bore fluid respectively. The two different molecular weights of additive-PEG were introduced into the spinning dope to develop the membrane morphology for CO_2 absorption. Significantly, the beginning of fabrication is a dope spinning by in-situ spinning with unemployed metal needle to study a basic morphology of fiber membrane with controlling air gap distance at 1 cm and wind-up speed at 50 rpm. The cross section, cut-cleaved section, outer surface and skin layer were examined through SEM. There are morphologies in Figure 5 showing that the morphology of and can be described as follow:

- P-0 membrane was prepared by the lowest viscous solution, due to without blending PEG which plays a vital role for improving membrane efficiency. In this sample, the exchanging of solvent (DMF in dope solution) and non-solvent (water in coagulant bath) rapidly transferred as well because of its high soluble efficiency between DMF and water. This occurrence promotes the nuclei growth due to its solvent power decreases resulting in the chain entanglement of PVC molecules tend to align themselves pack less closely (Mansourizadeh *et al*., 2011). Specifically, the medium finger-like structures are occurred.

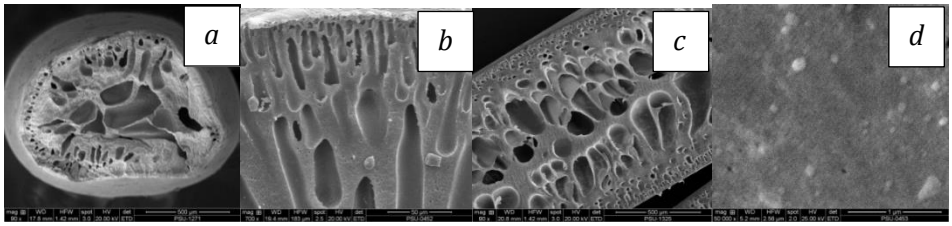
- P-G4-5 and P-G4-10 morphology increase longer finger-like structure, obliviously presented in P-G4-5, P-G4-10, P-G4K-5 and P-G4K-10. To more understand the formed behavior, in the previous research has been explained the

vicious fingering concept which has been used for studying the formation of finger-like, sponge-like and macro-void structure. Specifically, the behaviors of PEG with an increase in PEG molecular weight shown more holes or another word is macro-void structure within substructure because the high mass might be trapped inside the dope during the phase inversion process (Wongchitphimon *et al*., 2011). While the high PEG concentration can be explained by when the dope solution is contacted with water in coagulant bath, the instantaneous de-mixing occurs at the skin surface which is the first agglomeration. Another explanation is during precipitation process; water diffuses into the polymer-lean phase with linearly unstable condition and initiates the agglomeration of sponge-like pores by osmotic pressure. When the rate of viscous fingering is faster than that of the phase inversion, a finger-like structure will be gained.

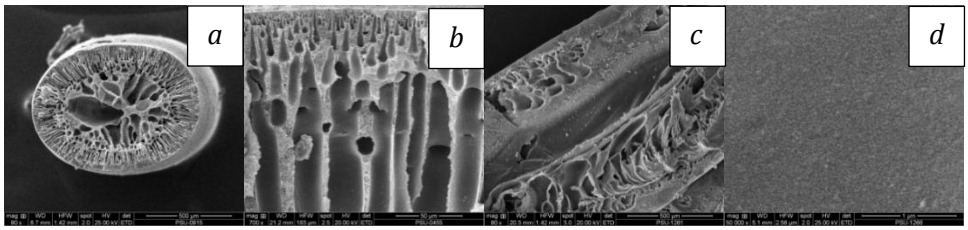
Consequently, it can be summarized that the membrane morphology with various structures can form finger-like structure via exchanging solvent and non-solvent during process which is depended on the viscosity of dope solution, whereas some macro-void structures can estimate when the rate of the phase inversion is faster than that of the viscous fingering. Another supporting reason is the formed surface is already transformed into solid phase before sub layer resulting in the exchanging between solvent. Also, non-solvent through skin surface is difficult that relates to the molecular chains among sub layer continually movement till transform into solid phase. These behaviors can be determined by a variety of structures which should be selected the proper structure of membrane to further develop to CO_2 adsorption.

Practically, the increase in macro-void substructures like high contents and concentration PEG leads to decrease of the effective thickness of the dense layer due to macro-voids existing in the substructure layer. However, as it can be seen in Figure 5, the PVC-G400-5% (P-G4-5) membrane quite appropriate to developing the CO_2 adsorption membrane because its many suitable properties consist of the polar structure of PVC and PEG contents, the finger-like substructure, the dense skin layer and sponge-likes structure provides a high degree of touristy and a high wall surface areas (Mansourizadeh *et al*., 2011).

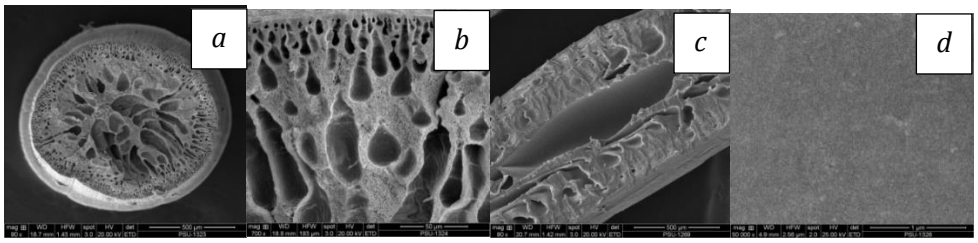
PVC-Pure (P-0)



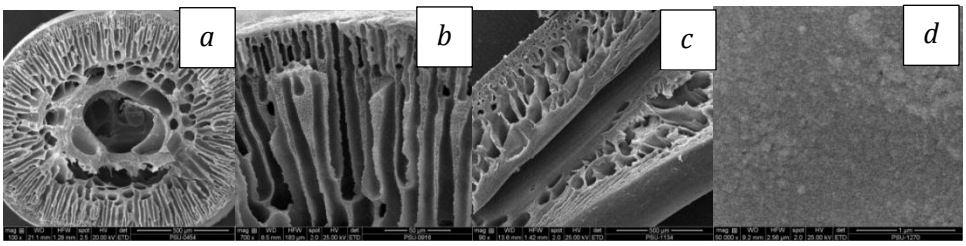
PVC-G400-5% (P-G4-5)



PVC-G400-10% (P-G4-10)



PVC-G4000-5% (P-G4K-5)



PVC-G4000-10% (P-G4K-10)

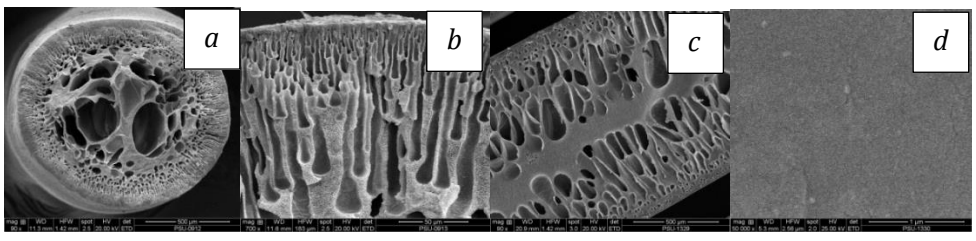


Figure 5 SEM images of PVC fiber membrane with unemployed center tube: (a) cross section, (b) edge of cross section, (c) cut-cleaved section and (d) skin surface

Effects of center-tube length

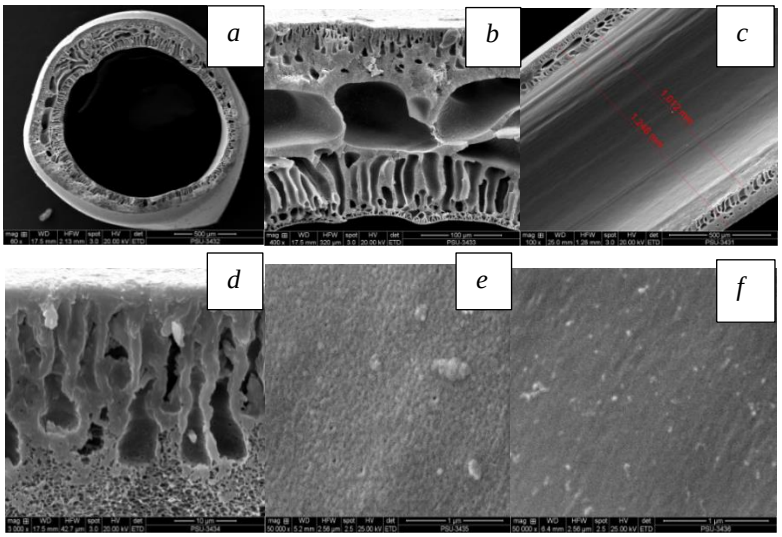
This research investigates the different morphology by using polymeric hollow fibers which are prepared by the well-established dry/wet process using tube-in-orifice spinneret. In this research polymer solution is extruded from the outer orifice of the spinneret and non-solvent is extruded from the center tube or metal needle of the spinneret as the phase inversion solution. Since the effect of the different metal needle lengths which act as controlling bore fluid was greatly influenced on forming morphology. It can be expected that morphology of the forming membrane occurs dense skin on inner surface which leads to the novel effect. According to the rapid liquid-liquid demixing between solvent in dope solution and water in metal needle resulting in the inner surface rapidly formed into solid phase faster than outer surface. As shown in Figure 6A, the SEM images of the PVC hollow fiber membranes were prepared by 0.3 cm metal needle length and controlled air gap of 1 cm. It was found that the effect of the metal needle length affects dramatically the morphology near the inner surface of hollow fiber: finger like structures were clearly seen with 0.3 cm needle length, whereas the macro-void structure in a middle area became bigger than with 1 cm center-tube length (Figure 6B).

A possible reason to explain the different morphology is that the mass transfer between solvent in dope solution and non-solvent bore fluid in metal needle was transferred immediately after extruding from the metal needle which acts like the rapid precipitation; therefore in the case of 0.3 cm metal needle length, it presented higher an amount of finger like structures at near inner surface than 1 cm that can be explained by Khayet (2003), he explored that at the low air gap length, the hollow fiber was exchanged in between the non-solvent and solvent more rapidly than at higher air gap distance that can be compared to a shorter center-tube length (0.3 cm) resulting in rapid exchanging of solvent and non-solvent at inner surface, which may have less oriented polymeric chains and high free volume. Consequently, it might be appropriated to increase CO_2 permeable flux of the membrane.

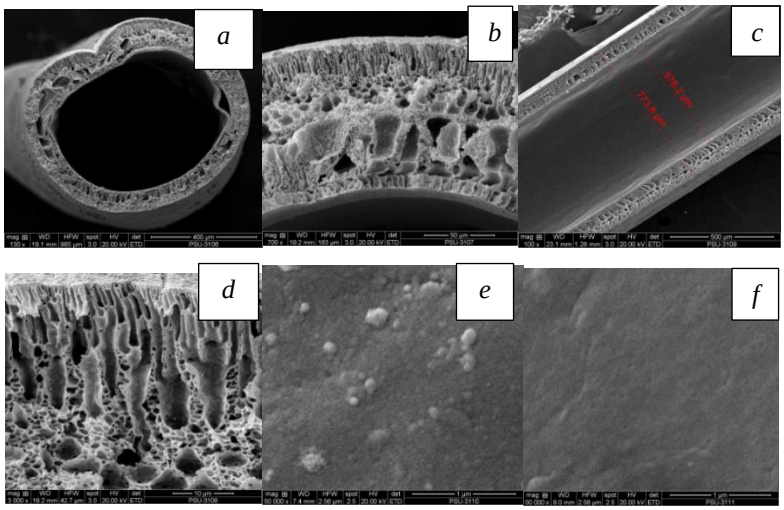
Obliviously, the macro-void structures are rather formed at middle cross-sectional morphology since the transferred solidification of inner surface is not completely formed at the same time the outer surface is being formed into solid phase also resulting in the solvent, as well as non-solvent process is trapped inside the dope

solution. To summarize of utilizing 0.3 cm metal length, this might be influenced by reducing PEG chain mobility, PVC chain alignment, less oriented polymer chains and had caused high free volume. The current study observed that increase and decrease in metal needle length may cause the effects to efficiency significantly. In addition, these effects can estimate to the efficiency of membrane by supporting reports from previous reasonable study; Ismail and co-workers (2006), they discovered that the finger-like structure within structure provided low wetting resistance and high permeability resulting from the molecular chains of the PVC solution tend to align themselves better and pack more closely to each other which approach to a dense skin layer (Mulder, 1996; Hasbullah *et al*., 2011).

Consequently, in the present study, an attempt was made to prepare asymmetric PVC-HF with improving structure turned into more finger-like structure for CO_2 absorption. It was found that the 0.3 cm metal needle length is the most possible structure to CO_2 absorption when it was controlled air gap distance (1 cm) because it consisted of finger-like structure and dense skin both inner and outer surface resulting from the rapid precipitation of spinning dope solution. On the other hand, the sponge-like structure can be formed by the high viscosity of spinning dope solution which leads to decrease of mutual diffusion between solvent and non-solvent resulting in the slow solidification. Therefore, it can be concluded that the membrane with finger-like structure and small pore sizes tend to show high permeability and low wetting resistance which can be developed CO_2 flux of the membrane. At the same time, the sponge-like structure offered high wetting resistance and low permeability (Kim and Park, 2011) as shown the SEM morphology in Figure 6B. In other words, it means that the increasing center-tube needle length is equal to increasing air gap length for inner surface precipitation resulting in hollow fibers with denser skin surface with tighter structure, reducing the finger-like voids length which might be turned into macro-void structure (Wongchitphimon *et al*., 2011).



(A) Condition: 0.3 cm center tube (P-G4-5-0.3)



(B) Condition: 1 cm center tube (P-G4-5-1)

Figure 6 SEM images of PVC-HF membranes, wind-up speed 30 m/min with employing 0.3 and 1 cm center-tube length: (a) cross section (b) edge of hollow fiber membrane; (c) cut-cleaved section; (d) outer edge of outer layer; (e) outer surface; and (f) inner surface

To summarize the effect of the different metal needle lengths, if the non-solvent (water) in the bore fluid contacts with dope solution before outside precipitation, the skin will tend to be formed on the inside surface of the fiber. Since the inner skin layer was precipitated immediately after extruding from the spinneret,

whereas the outer skin layer was formed later when extruding into the coagulant bath resulting in the difference morphology. In contrast, if the outside surfaces are reversed so that the bore fluid contains non-solvent solution and the coagulation bath is water, the skin will tend to be precipitated on the outside surface of the fiber as shown in Figure 7.

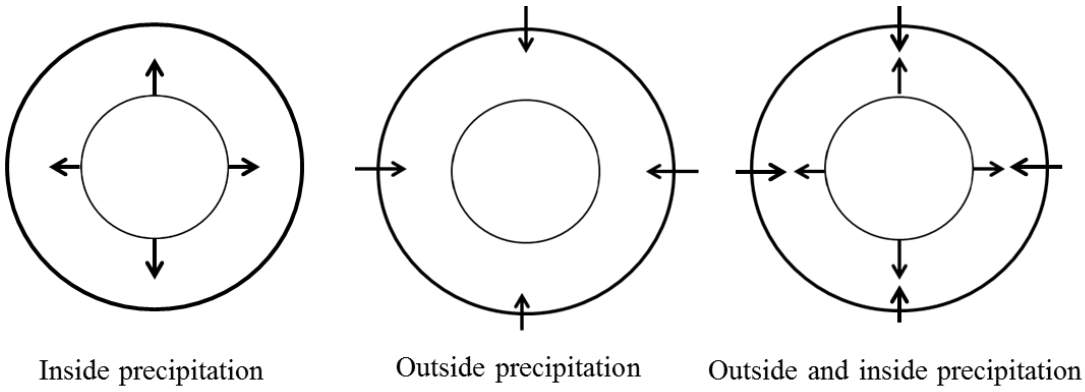


Figure 7 Depending on the bore fluid and the composition of the coagulation bath, the selective skin layer can be formed on the inside, the outside or both sides of the hollow fiber membrane

Source: Baker (2004)

Effects of wind-up speed

The effects of wind-up speed (or Take-up speed) and extrusion rates on the dimensions of the resulting hollow fiber membrane is shown in Table 3. It was found that the outer and inner diameters decreased with the increase of the wind-up speed. This suggests that the morphology of hollow fiber membrane was prepared from air gap 1 cm and center-tube length 0.3 cm became a denser when the hollow fibers were obtained the stress by wind-up speed. In addition, using PEG as additive resulted in an improvement in the precipitation rate of the spinning dope solution resulting in a thin finger-like structure near the outer surface. Therefore, the increase in wind-up speed is directly feasible increasing solidification of spinning dope solution. Moreover, this effect is referred to the previous studies (Wang *et al*., 2009;

Xiao *et al*., 2006) that there should be related to fabricate membranes with macrovoid-free structure by high drawing speed of hollow fiber membrane.

Three causes may be involved with macrovoid-free structure which tends to suitable membrane for gas permeation: (1) the effect of the high drawing ratio may induce large negative normal stresses perpendicular to the skin surface and result in radial outflow, consequently it delays non-solvent diffuse and macrovoid agglomeration; (2) the effect of high shear stresses resulting from smaller annulus gaps that may provide oriented and denser polymer chain packing; thereby the macrovoid forming is hindered (Widijojo and Chung, 2006). With comparing the drawing ratio presented in Figure 8 (A, B and C), the effect of high-speed drawing may stabilize the smooth skin which can prevent non-solvent intrusion to transform into polymer-rich phase resulting in macrovoid-free structure; (3) the effect of high miscibility between the solvent and the coagulant may form finger-like structure as a result of rapid demixing of spinning dope solution (Cheng *et al*., 1996).

Prepare from air gap 1 cm and center-tube length 0.3 cm

Considerably the population of the very small pores and free volumes in the membrane's structure are determined to grow due to the random entanglement and alignment of polymer chains (Sperling, 2001). Another reported (Ismail *et al*., 2006) that the dope extrusion rate increases, better and packs more closely to each other, which approach to a dense skin layer. Therefore, the combination of PEG-blended addition, finger-like structure and high wind-up speed or high drawing ratio (λ) may gain another promising membrane that tends to fabricate a suitable CO_2 adsorption membrane consisting of high CO_2 selectivity and permeability. In Figure 8 (C) shows that the highest stretching, the chain molecules were oriented and in a more ordered arrangement. This may increase the compactness of the structure. When the drawing ratio was increased further hence, the porosity decreases with the increase of the drawing ratio.

Another reason of this effect is the evaporation time of the skin layer formation because it is expected that the DMF volatile solvent will be removed from the fiber surface that results in a skin layer is formed during this dry phase-separated region (Pinnau and Koros, 1993). From this reason, this work involved with the DMF

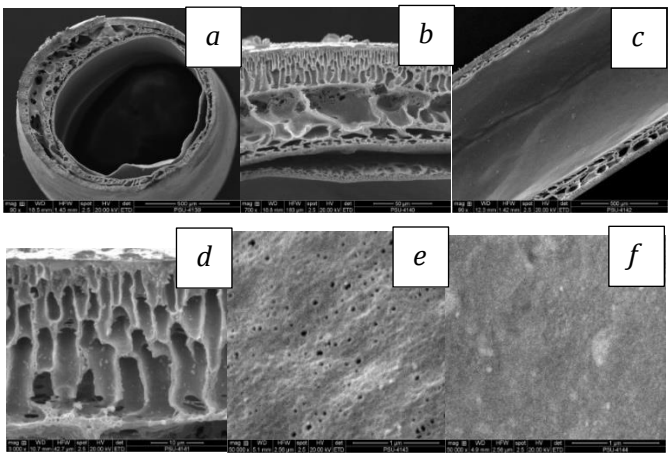
solvent from inner surface and outer surface; therefore, the solvent from 50 rpm is removed faster than 40 and 30 rpm resulting in the exchanging between solvent and non-solvent in coagulant bath occurs suddenly. At the same time, the solvent exchanging of 40 rpm within inner and outer surface is removed simultaneously leading to the morphology of both sides being similar.

In summary, a recent work showed draw ratio data in Table 3 that the draw ratio increment can eliminate the macro-void structure during dry-wet spinning. To more obviously understand regarding the increment of wind-up speed or draw ratio, it might make polymer chains parallel and delay the insertion of external coagulant; as a consequence, the cross-section morphology of high wind-up speed showed the finger-like among bulk structure and dense skin both the inner and external coagulant sides.

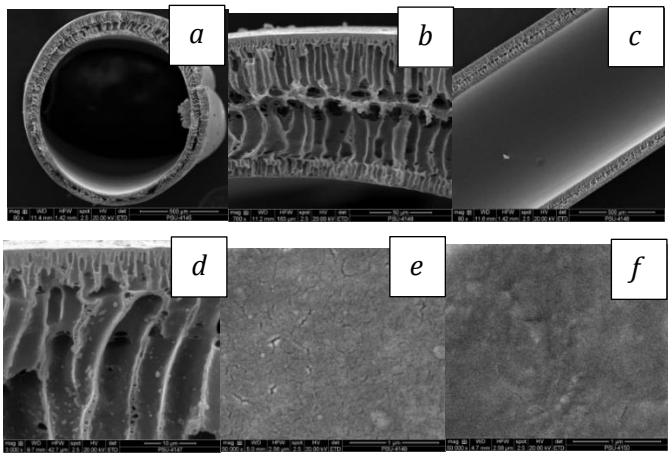
Table 3 The draw ratio on the different wind-up speed of PVC-HF spinning

***Sample**	**Extrusion speed (m/min)**	**Wind-up speed (rpm)**	**Draw ratio (λ)**	**o.d. (μm)**	**i.d. (μm)**	**Thickness (μm)**
A: P-G4-5	15	30	2.0	1200	800	350
B: P-G4-5	15	40	2.6	1100	850	220
C: P-G4-5	15	50	3.3	750	500	170

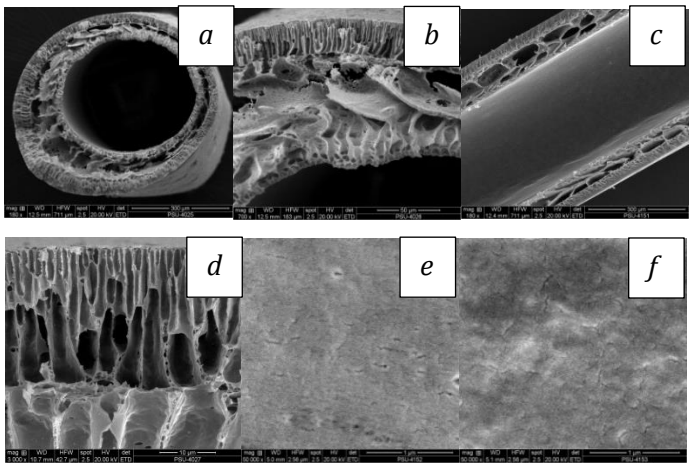
** Prepare from air gap 1 cm and center-tube length 0.3 cm*



(A) Wind-up speed: 30 rpm



(B) Wind-up speed: 40 rpm



(C) Wind-up speed: 50 rpm

Figure 8 SEM images of PVC-G400-5% with 0.3 cm employing center-tube length: (a) cross section; (b) edge of hollow fiber membrane; (c) cut-cleaved section; (d) outer edge of outer layer; (e) outer surface; and (f) inner surface

Contact angle results

The water contact angle is a vital parameter in surface investigation. Although contact angle observations are difficult to exactly proof the character for surface membranes due to capillary forces within the pores, roughness and restructuring of the surface skin (Zhu *et al*., 2009), the morphological study can be easily achieved by water contact angle measurement. From this study, it was found that the PVC-HF membrane had the highest contact angle of 89.0° indicating the lowest hydrophilic. These can be attributed to the membrane structure with high permeability (surface porosity) and low wetting resistance. Therefore, the resultant PVC-HF membranes might be estimated that the blending PEG membranes had the high porosity and increased the CO_2 absorption performance resulting from the existing of high PEG concentration and hydrophilic property.

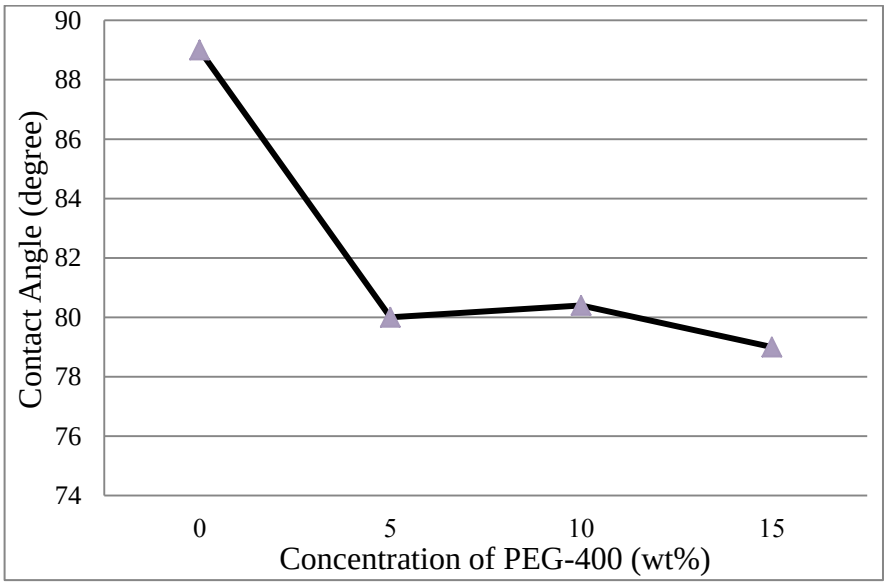


Figure 9 Water contact angle of PVC pure and PVC blended PEG membrane as a function of the PEG-400 concentration of the PVC membrane

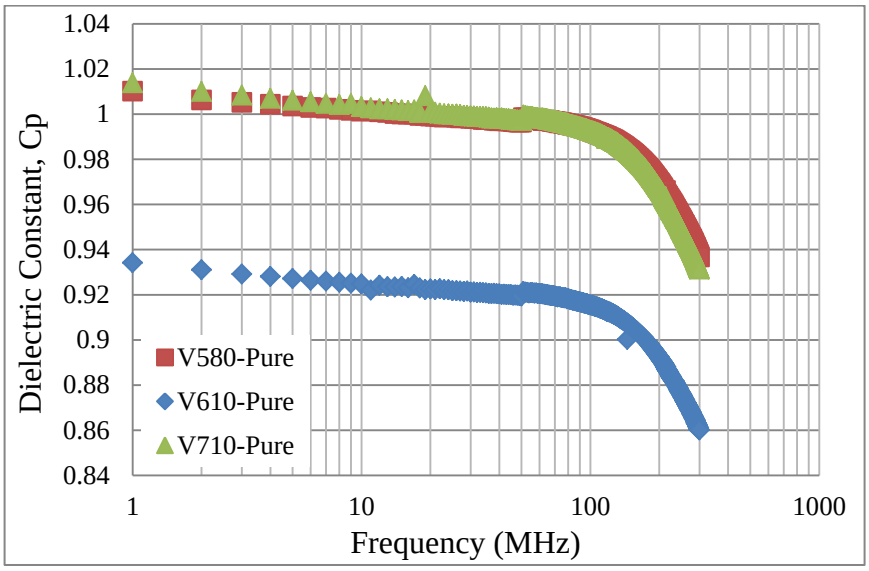
Dielectric property results

It is well known that molecular motions beneath T_g, are appeared in sub-T_g relaxation processes, as identified by dielectric spectroscopy and dynamic

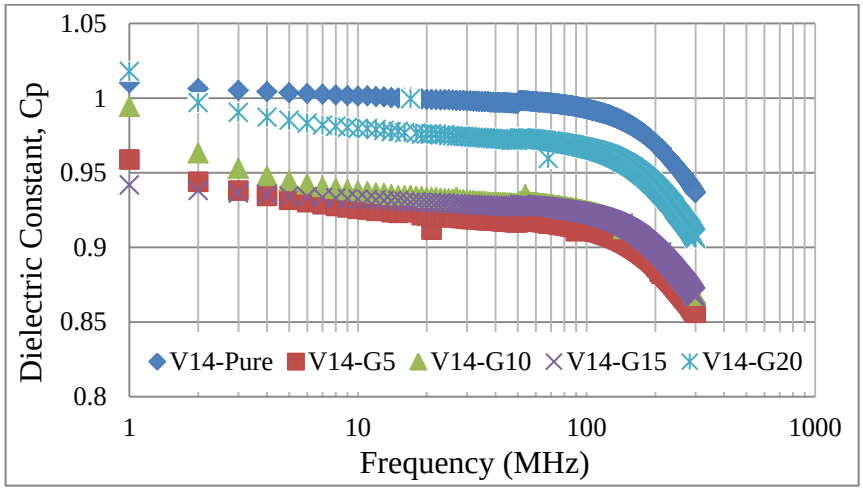
mechanical analysis. The investigation of mechanical sub-T_g relaxations in gas separation membranes has used particular attention to the influence of systematic changes of intra-segmental mobility and chain packing efficiency in permeability and selectivity (Moriola *et al*., 2013).

According to PVC is a main key polymer and its dipole moment is perpendicular and rigidly attached to the main-chain backbone of the macromolecule. Besides, it is strongly polar structure due to the existing of C-Cl bond. In the course of this measurement, it became evident that relatively small changes in the details of the molecular structure of PVC blended with PEG which is tendency to crystalize structure and they could have a significant impact on segmental dynamics and fractional free volume (Sumod *et al*., 2007). Theatrically, during of the drying process the time scale of free volume relaxation may become larger than the timescale of diffusion (Vrentas *et al*., 1975) which is involved with the viscosity and the compatibility of dope solution during spinning process. Most of these effects will be affected on the increase in free volumes which are increased in diffusivity of gases.

The dielectric permittivity or dielectric storage (ε') of non-blended PEG and blended PEG were measured over the frequency range from 1 MHz up to 300 MHz at room temperature. The dielectric results are shown in Figure 10, it can be seen that non-blended PEG membrane exhibits the highest values of permittivity at low frequencies. However, the dielectric permittivity of PVC blended PEG-400 for 20wt% that was increased due to phase separation of PEG from PVC during the demixing and spinning process. At the same time, some of the PEG contents covered the various contents and formed hollow fiber membrane that leads to increase capacitance of material rather than other PEG contents. Especially, the effect of PEG at lower concentration (PEG 5 wt%, 10 wt% and 15 wt%) lowered dielectric constant owning to the better compatible and miscible blending phase of PVC and PEG phase. Besides, the different decrease in dielectric constant in lower frequency range of V14-G5, V14-G10 and V14-G15 is attributed to the decrease in contribution of both interfacial polarization and conductivity.



(a)



(b)

Figure 10 Dielectric property of (a) PCV-Pure and (b) PVC blended PEG hollow fiber membranes

Dynamic Mechanical and Thermal property results

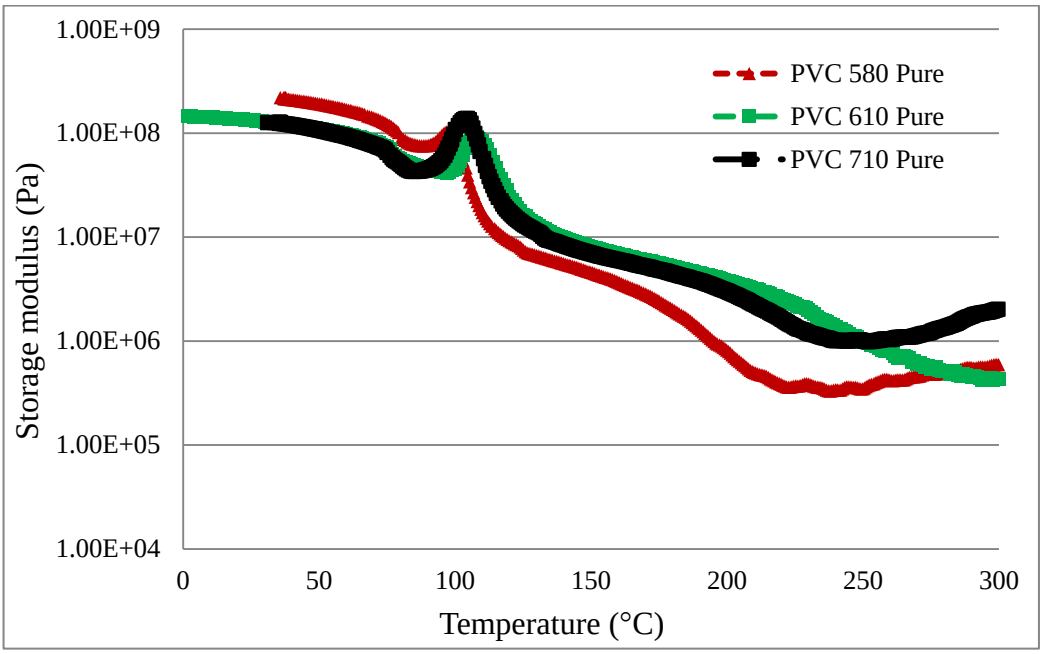
The effects of the blended PEG can be achieved and controlled by incorporation of additives into neat rigid PVC. External PEG-blended can change PVC chain dynamic properties by providing free volume and by softening the intermolecular interactions which are involved with viscoelastic relaxation properties;

consequently, it leads to a decrease in the glass transition temperature (Wypych, 2004). The PVC blended PEG occurs through van der Waals and dipole-dipole interactions that can be established between PVC polar carbon-chlorine bonds (Beltran *et al*., 2001) and the PEG polar which consists of ether oxide units on backbone structure, and thus most of these effects could be considered to observe variable properties of the blended membrane.

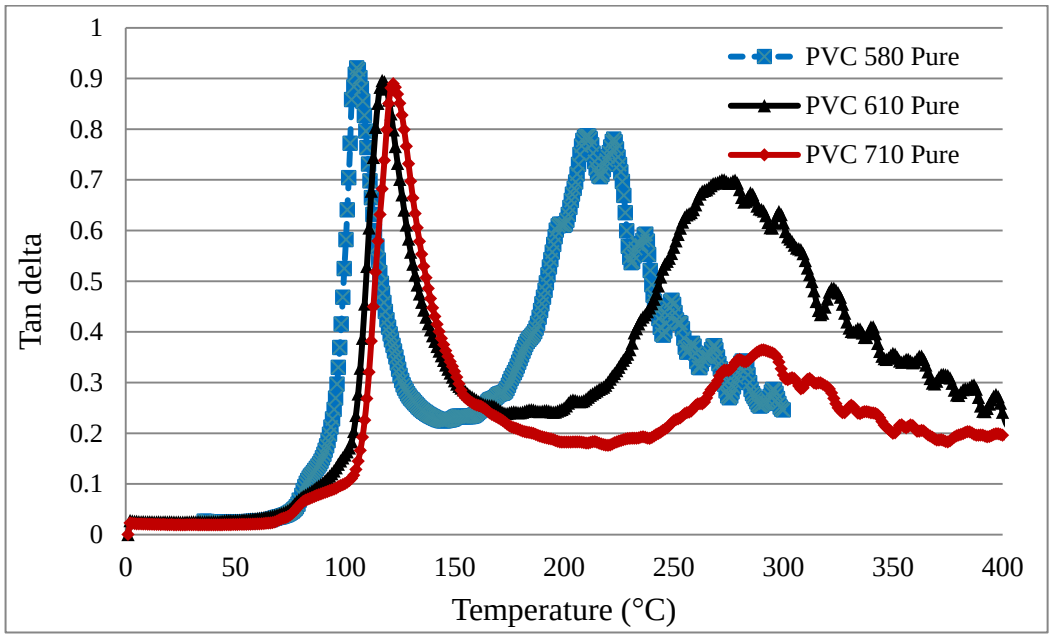
The viscoelastic relaxation properties of the blended membranes were measured in details using dynamic mechanical analysis. This investigation is important in characterizing the material for its glass transition temperature. The different glass transition temperatures of the blended PEG were accessed by DMTA as presented in Figure 11. The changes in storage modulus (*E'*) will change with temperature as the molecular motions within the polymer chains. The second order transitions are observed by the remarkable drop in storage modulus. The glassy state modulus of PVC blended PEG-400 10wt% is much higher than the other samples regardless of temperature because it may well blend with PVC resulting in the increase in T_g higher than non-blended PEG and others.

Due to the influence of PEG resulting in the increase in the viscosity which can obstruct segmental motions within polymer-blended matrix; thus, its effect can lead to present higher T_g; whereas, the higher PEG contents, the T_g is raised. Thus, it can assume that the raising of T_g influences on the immiscibility between PVC and PEG. This effect indicates that the PEG has improved the softness of the membrane property which is involved with the increase in the amorphous state resulting in the increase in gases permeability.

The damping property (Figure 12 (b)) ($tan\ \delta$) is the ratio of the dynamic loss modulus (*E''*) to the dynamic storage modulus (*E'*), clearly shown to T_g of the polymer matrix is found to decrease from 100 °C to 95 °C with adding PEG. It can be replied that PEG is miscibility blends with PVC and blended PEG might be dispersed in PVC matrix.

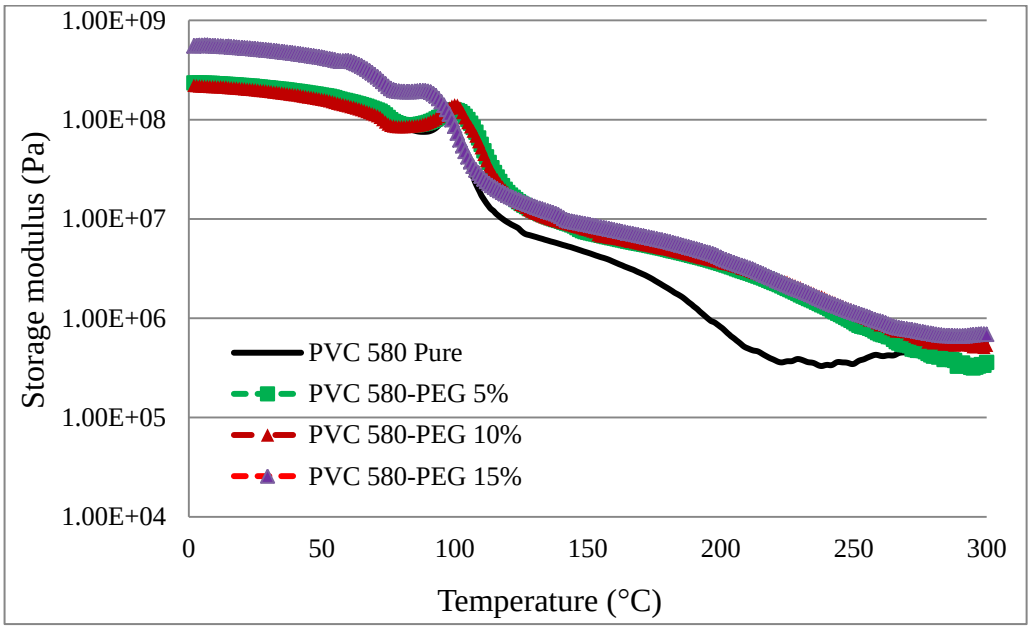


(a)

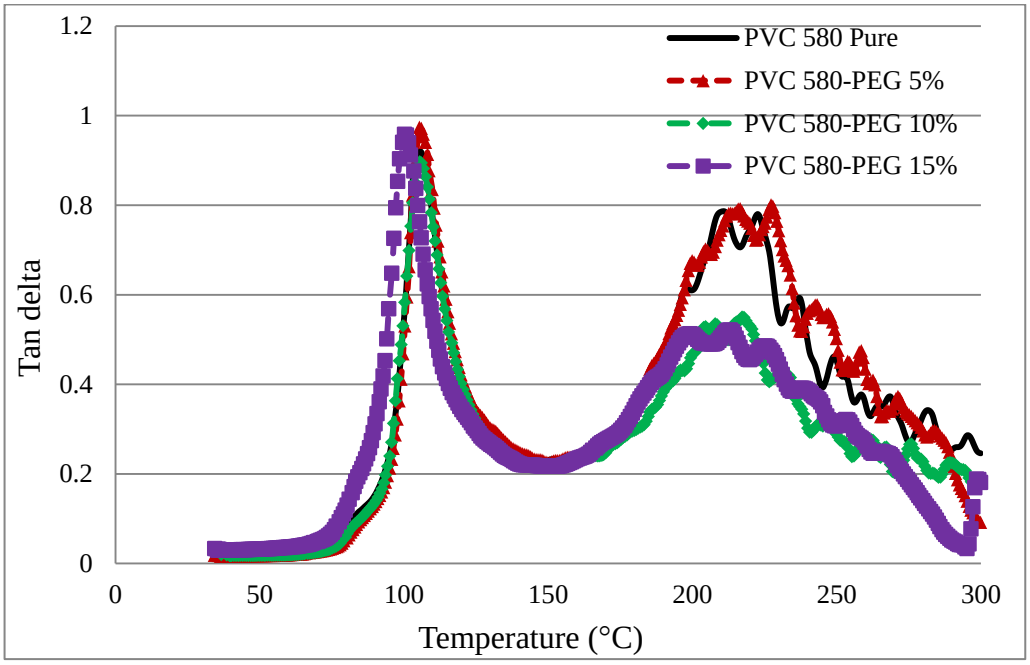


(b)

Figure 11 DMTA thermogram of PVC-580, 610 and 710 (a) storage modulus and (b) *Tan δ*



(a)



(b)

Figure 12 DMTA thermogram of PVC-580 blended PEG-400 (a) storage modulus and (b) *Tan δ*

CONCLUSIONS

Preparation of hollow fiber via dry/wet spinning process is considered viscosity since it is an important factor to adjust other parameters involving all procedures. The proposed operations are the appropriate hollow fibers for required applications prior to determine adjustable conditions. The feasibility preparation of suitable hollow fiber membrane particularly for gas separation is the PVC-580 blended PEG-400 5wt% with the air gap 1 cm, center-tube length of 0.3 cm and wind-up speed 40 rpm particularly when its flow configuration requires countercurrent flow with the feed flows in the fiber bore and permeate is outside the fiber because of its morphology showing the finger-like structures and the dense-inner surface.

The summaries of the ability of a novel spinneret system were concluded as the followings:

(1) The needle length and hollow fiber dimension directly influence on the hollow fiber formation. Shorter center-tube length will provide the defect-free inner surface resulting from the fastness of solvent and non-solvent exchanging within lumen side.

(2) The optimum draw ratio is to produce dense skin surface that results from the polymer chain orientation at the outer surface.

(3) A lower draw ratio provides the larger fiber thickness. The cause of this phenomenon may be explained to reduce the elongation shear rates and shear stresses.

(4) The formation of skin layer membrane can be formed depending on the center-tube length and the coagulation bath; the selective skin layer can be formed on the inside tube, the outside tube or both sides of the hollow fiber membrane.

(5) The ability of center-tube spinneret can be adapted to design as porous or dense surface area that avoids using mix solvent in bore solution.

(6) The increase in center-tube spinneret was discovered that water intrusion is suppressed to a certain extent and the finger-like structure near the lumen side of the hollow fiber becomes sponge-like structure.

(7) With increasing dope concentration, the shear and elongation forces tend to increase. This is explained to the enhanced viscosities of the polymer-blended concentration. There is an amount of chain entanglement that creates more resistance to exchange between non-solvent and solvent during precipitation process; thereby, increasing the elongation rate tend to achieve thick skin surface due to creating macro-void structure in the bulk membrane.

(8) The relaxation of packed molecular orientation of the skin layer of hollow fiber membranes produced via dry/wet spinning method, in a small air gap distance, was also observed.

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CHAPTER 4
GAS PERMEATION OF XSBR COATED PVC BLENDED PEG HOLLOW FIBER MEMBRANE

ABSTRACT

Single gas and CO_2/CH_4 mixed gas permeation from different pressures via the coated XSBR selective layer has been reported as an important material in the mixed gas streams. Interestingly, XSBR layer acted as selective layer and PVC blended PEG-400 acted as supporting layer. PVC-PEG hollow fiber membranes were produced from dry/wet spinning process and prepared from a high polymer content solution that presented a finger-like substructure. These resultant fibers were selected that exhibited in module contactor in order to measure on permeation, retention and gas components by Gas Chromatography (GC). At the single gas measurements, they were shown that the highest CO_2 permeability of 4.24 Barrer, O_2 permeability of 5.38 Barrer and N_2 permeability of 0.33 Barrer resulted in the highest O_2/N_2 selectivity of 16.30, CO_2/N_2 of 12.89, O_2/N_2 of 0.79. In case of mixed gas measurements, GC-chromatogram showed that the highest CH_4 components is 66.38 vol%. Hence, we consider the biogas upgrading might be fabricated by XSBR coating. These results comprised the flexible chain segments of carboxyl groups containing in XSBR structures. To sum up of all experiments in this work, the prepared supporting hollow fiber membrane is produced from high draw ratio spinning due to the suitable morphology and mechanical properties; in addition, coating with XSBR selective layer is discovered for novel rubbery material that is an alternative material of the preparation of membrane for single gas of CO_2, O_2 and mixed gas of CH_4/CO_2 separation.

1. Introduction

1.1 PVC blended PEG supporting hollow fiber membrane

A few works have been produced involving PVC as gas separation membrane materials. Normally, PVC is a low permeability, slightly crystalline region, glassy polymer and a challenge to be the gas separation membrane. As former reports, PVC was used for a crucial role during ultrafiltration (UF) and microfiltration (MF) processes (Khayet *et al*., 2009) due to their structures are limited for reverse osmosis and gas separation. However, the PVC membrane development can be used in several methods to improve its properties to get satisfaction with reverse osmosis (RO) and gas separation (GS) membrane by nonsolvent induced phase separation (NIPS) method. NIPS method was usually asymmetric membrane which was offered dense skin layer and porous support layer (Rajabzadeh *et al*., 2012). As a result, it is believed that the micro-porous substructure of asymmetric membrane grows from nucleation and growth of the polymer lean phase in the polymer/solvent/nonsolvent systems while a dense selective layer responses to selection and adsorption of collective feed gases (Tabatabaei *et al*., 2009). Significantly, membranes for gas separation, both flat sheet and hollow fiber aspects require an ultra-thin necessary defect-free membrane active layer but their properties of homo PVC are still improved.

In case of using PVC in gas separation hollow fiber membrane technology, Blends of PVC and other polymers are easy to fabricate via phase inversion and NIPS. The combination of an additive polymer to establishing brings about improvement of membrane structure (Nunes and Peinmann, 1992). However, viscosity of dope solution limits the polymer concentration during fabrication. Therefore, it needs to develop for mixing solution by the mixtures of polymer solutions that were prepared by spinning method. Additionally, the combination of PEG has been usually used for improving gas separation performance (Lui *et al*., 2013). Among non-solvent additive blending, PEG and PVP, tetra ethylene glycol (TEG) have been usually used for increasing the viscosity, accomplishing hydrophilic

property, improving pore formation suppress macro-void formation in order to enhance membranes with high permeability (Liu *et al*., 2003). In addition, in the case of using PVC blended PEG in gas separation hollow fiber membrane technology; dope viscosity limits the polymer concentration through increasing PEG contents, improving membrane properties, higher dope concentrations might achieve defect free skin layers that unsatisfied with membranes for gas separation. Therefore, they need to deal with suitable polymer and appropriate additive proportions (Jones *et al*., 2011).

For some limitation of PVC or other polymer materials to act as gas separation membrane, they demand attention to improve surface with high polar/non-polar selectivity (Bondar *et al*., 1999; Bondar *et al*., 2000). With composite membranes for gas separation, they consist of supporting layer and selecting layer. Considerably, supporting layer materials have been produced from several kinds of materials; for example, Sridhar and co-workers (2007) fully accepted PVDF as porous substrate for composite membrane. Sainan and co-workers (2013) used ceramic supporting layer and PDMS as selective layer for CO_2 separation. Ahmadpour and co-workers (2014) prepared PVC micro-porous substrate by the phase inversion method and used Pebax® MH 1657 as dense skin layer that this composite membrane was studied for CO_2 separation. As previous reviews regarding selective layer, most materials are related to rubbery material due to their applications appropriated with increase in polar gas (CO_2) permeation resulting from high solubility coefficient of rubbery materials (Johnson and Thomas, 1999; Stephen *et al*., 2006). These can be fabricated by coating or dip coating, which an appropriate porous substrate with a dense skin layer that acts as selective layer for applicable selection (Chen *et al*., 2011; Ahmadpour *et al*., 2014).

1.2 XSBR selective layer

Up to date, there are not many rubbery materials that used for membrane for gas separation other than silicone rubber (Tanioka *et al*., 1982). Ettouney and Majeed (1997) studied the importance of the driving pressure for PSF and rubber membranes that ware tested in purity and mixtures of N_2/O_2, CO_2/N_2 and

$CH_4/N_2/CO_2$. They were found that CO_2 were obtained in the permeability functions for all species in PSF. Generally, due to rubbery materials that are flexible, soft, and operate above their glass transition temperatures, they show a high permeability but low in selectivity of gases. Moreover, for many years, silicone rubber polymers, and in particular PDMS have been considerably attained as efficient membrane materials for gas separation because of its high intrinsic permeability of gases (Aoki, 1999). In addition, PDMS was investigated to modify their membrane-forming ability and permselectivity such as PDMS-polycarbonate by Ward and co-workers (1976), PDMS-polyphenyl *t*-ether (Tsurumaki *et al*., 2000) and *t*-amino into PDMS. However, those rubbery materials are limits on any application and costly. Therefore, a large number of researchers have tried to discover other rubbery materials in order to develop membrane technology for advance performances (Widjojo *et al*., 2007).

Carboxylated styrene butadiene, called XSBR, is rubbery materials having gas permeability close to glassy polystyrene (Stephen *et al*., 2006). Generally, XSBR is mainly used for contacting hydrocarbon liquids, oils or greases. Meanwhile, glassy materials normally offer considerably lower constants of diffusion and sorption for small gas molecules than rubbery materials. Normally, XSBR being rubbery at room temperature due to its low glass transition temperature of XSBR, the structures present quite non-polar structure but their structures show a high polar structure influencing on the increase in carboxyl segments. The existence of polar carboxyl groups in XSBR structures and the phase behavior of CO_2 exposed in XSBR. Therefore, it could be a suitable option for CO_2 gas separation membrane. From these reasons, they can be used in selective layer or defect-free skin layer for separation membranes. Especially, the gas separation for CO_2 removal offers a high permeation due to their high affinity between polar segmental chains and acid gases.

From previous reports, many researchers have not used XSBR for membrane materials. Though, some rubbery materials such as PDMS are satisfied with membrane for gas separation as well as XSBR has not been often found in the field of membrane for gas separation. Consequently, this work is a good opportunity to seek out an alternative material for gas separation membrane.

Table 1 Permeability (*P*) and ideal gas selectivity (α) of CO_2, CH_4 and N_2 in various polymers

Reference	**Materials**	***P* (Barrer)**			***α***	
		CO_2	**CH_4**	**N_2**	**CO_2/CH_4**	**CO_2/N_2**
Joly *et al*., (1997)	Polyimide (PI) blended silica nanocomposite	2.8	0.2	0.13	14	22
Chung *et al*., (1999)	PDMS/PVP coated PSF (PDMS:PVP, 3:2 wt%)	16	1.9	3.0	8.2	5.3
Ismail *et al*., (1999)	PSF (dope extrusion rate 1 cm^3/min) tested at 5 bar	65.2	50.2	-	1.39	-
Tiemblo *et al*., (2002)	PVC functionalized with mercapto pyridine	0.54	0.02	-	22.5	-
Cecopieri-Gomez *et al*., (2007)	PPO (Polyphenylene) EC (Ethylene cellulose)	75.8 26.5	11 19	- -	6.89 1.39	- -
Sridhar *et al*., (2007)	PDMS	4553	1339	-	3.4	-
Aroon *et al*., (2010)	PSF/NMP/THF:30/52/18 tested at 8 bar	3.53	0.46	-	7.67	-
Bierbrauer *et al*., (2010)	Fluorothiophenyl-PVC tested at 1 bar	1.54	0.06	0.06	25.6	25.6
Hosseini *et al*., (2010)	Matrimid®5218 blended PBI (air gap 2 cm)	4.90	3.54	-	6.18	-
Jones *et al*., (2010)	PDMS coated PVC (THF/DMAc/ethanol)	6.64	0.74	0.41	9.0	16.2
Reijerkerk *et al*., (2010)	PEBAX®1657/PEG-200 tested at 4 bar	532	49.2	14.7	10.8	36.1
Yong *et al*., (2013)	PIM-1/Matrimid® (15:85) tested at 3.5 bar	413	67.8	81.6	6.1	5.1

1.3 Scope of work

According to all mentions above, we hypothesized that a defect-free hollow fiber with a dense-selective layer tends to enrich CO_2 composition in permeate side and CH_4 composition in retentate side; thereby, in the case of using high draw ratio during spinning process can rapidly form dense skin layer (Peng and Chung, 2008). Besides, the air gap distance is one of the vital parameters that involves with hollow fiber fabrication during dry/wet spinning process. Normally, a dense-selective layer on asymmetric hollow fiber membranes may provide defect pores on skin surface that prepared by too long air gap distance; therefore, the air distance of 1 cm is satisfied with suitable membrane forming due to the properly rapid coalescence of chain entanglement and irregular packing of the kinked molecular chains (Ismail and Yean, 2003) resulting from strong interaction between polymer matrix and solvent. As a consequence, this hollow fiber membrane may provide high gas selectivity.

In this study, the separation and permeation characteristics of different membranes for CO_2, O_2 and N_2 which are the favor gas for membrane investigation were measured. Mixed gas sorption performances of feed gas that contains CO_2:CH_4 ratio 40:60 was studied of separation factor in order to obtain CH_4 enrichment in retentate and CO_2 removal in permeates side. Hollow fiber membrane investigations were prepared from PVC blended PEG-400 hollow fibers that acts as supporting layer with morphologies suitable for gas separation. These prepared hollow fiber membranes were coated by XSBR that acts as skin or selective layer. Then, they were packed into module contactor. Sealing of porous supporting layer was the most important reason for better performance of the prepared hollow fiber membrane. The pressure stream feeds into the outer side of the tubes and the low pressure permeate on the inner side of the fiber bundle (shell-side feed). The membrane performances were characterized by scanning electron microscopy (SEM. All experiments manufactured were also used for the purification of CH_4 in retentate gas and enrichment of CO_2 in the permeate gas. All gas separation experiments were performed at room temperature (about 25 ^oC). Mixed gas compositions within permeate and retentate gas were detected by gas chromatography in order to compute selectivity factor.

2. Materials and Methods

2.1 Contactor module preparation

To application of hollow fiber membrane as prepared in Chapter 3, this work selected fibers from drawing ratio 50 rpm and air gap distance of 1 cm, to establish a module contactor with shell-side feed configuration. The resultant hollow fiber membranes were then immersed in deionized water for 2 days to remove any residuals solvents. Then, dried in vacuum oven at 40 ºC for about 24 hr, the fibers were then used for module aspects. The dried hollow fiber membranes were coated via dipping process with XSBR that was supplied by Synthomer GmbH, after being cured by vacuum oven at 60 ºC for 24 hrs. After drying fibers with a length of 30 cm each assembled into bundle contactor of 10 fibers. One end of the bundle contactor was sealed with epoxy resin which was purchased from Alpha Techno Company, while the shell side of the other end was glued onto a stainless steel holder using similar epoxy as presented membrane contactor in Figure 1.

2.2 Single gas permeation measurements

The single gas or pure gas (99.9%) permeability of the membranes was determined using the permeation test apparatus. The permeability of CO_2, O_2 and N_2 were measured room temperature (about 25 ºC). The module contactor was then connected to the gas permeation apparatus as showed in Figure 2 and tested using single gas comprising of CO_2, O_2 and N_2. Operating pressure was carried out at 1-2.5 bar to measure the feasibility of hollow fiber membrane performance. The gas permeation rates were measured for permeate side by using soap-bubble meter. The gas separation performances of the hollow fiber membrane module contactor were tested by using the membrane apparatus as shown in Figure 2. The permeability factor was calculated by using Eq. (1) (Hasbullah *et al*., 2011; Chmielewski *et al*., 2013; Xin *et al*., 2015).

$$P = \frac{Q_i L}{\Delta P.A} = \frac{Q_i L}{\Delta P.n\pi Dl} \quad (1)$$

Where P is the permeability coefficient of the test gas in Barrer (1 Barrer = 1x10^{-10} cm^3 (STP).cm/cm^{2}s.cmHg; Q_i is the volumetric flow rate of gas (cm^3/s.cm^2)); L is the membrane thickness; ΔP is the pressure difference between the feed side and the permeation side; A is the membrane effective surface area (cm^2); n is the number of fibers; D is the fiber diameter (cm); and l is the effective length of the fiber (cm).

Table 2 Characteristics of the PVC-PEG hollow fiber membrane contactor

Module i.d. (cm)	0.8
Module length (cm)	24
Fiber o.d. (cm)	0.08
Fiber i.d. (cm)	0.06
Effective fiber length (cm)	20
Number of fibers	10
Surface area (cm^2)	50.02

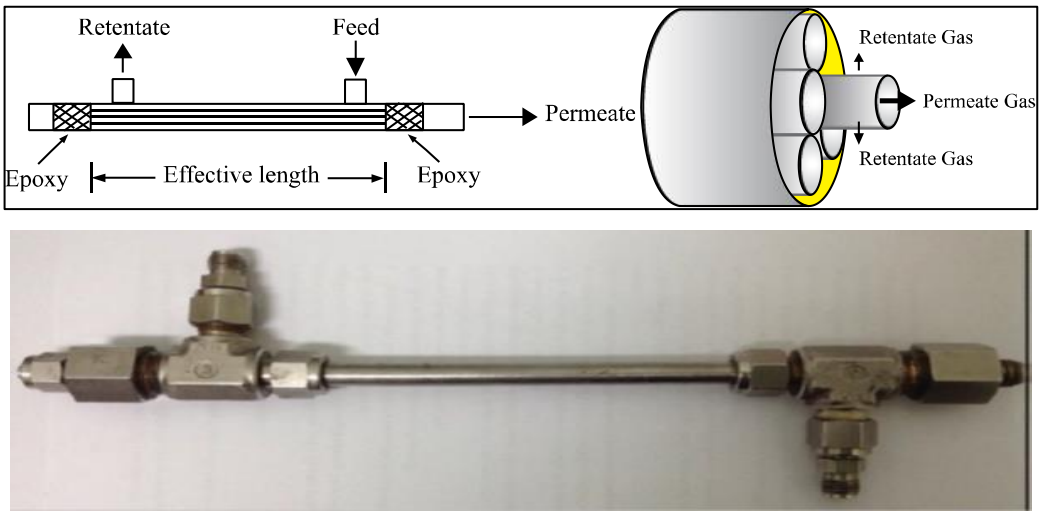

Figure 1 Lab-scale hollow fiber membrane module

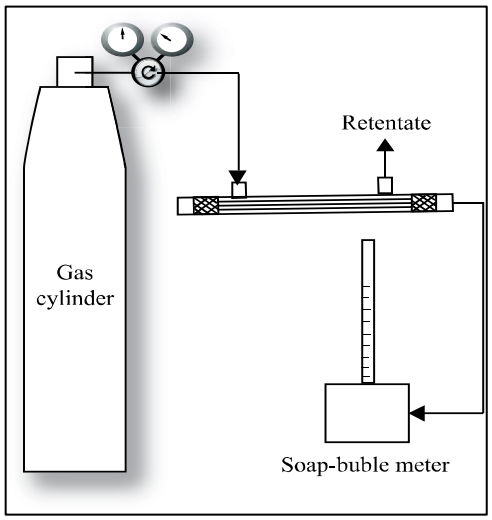

Figure 2 Schematic diagrams of the gas permeation apparatus

While, the selectivity of membranes for single gas is computed by the following equation which is equivalent to the ratio of permeability of each gas (Chmielewski *et al*., 2013; Swaidan *et al*., 2013; Xin *et al*., 2015):

$$\alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \quad (2)$$

2.3 Mixed gas permeation measurements

The mixed gas of CO_2/CH_4 was supplied from Thai Industrial Gas Public Company Limited (TIG). Mixed gas experiment was carried out at 25 ºC using a setup similar to the previous one described in single gas measurement. The feed gas mixture was calibrated CO_2/CH_4 in a proportion of 40:60 vol%. This methodology allows for a direct comparison to the single gas data to elucidate any differences of mixed-gas performances on permeability and selectivity. Under these conditions, the gas collected at the permeate side and the gas in the feed tank were then analyzed by gas chromatograph (HP 6890, Hewlett Packard) equipped with a Thermal Conductivity Detector (GC-TCD) using capillary column (HP-PLOT/Q length 30 m, 0.530 mm I.D, film thickness 40 μm) and helium as carrier gas at 9 psi. Mode:

Splitless injections of 0.20 mL; 250°C injection port temperature; and Initial temp at 60 °C holds 2.5 min.

The selectivity of membrane for mixed-gas CO_2/CH_4 was computed by the ratio of mole fractions of gases on the permeate side (y_i) to the feed side (x_i). Where *y* and *x* are the mole fraction in the permeate and feed respectively (Ozturk and Demirciyeve, 2013; Swidan *et al*., 2013).

$$\alpha_{CO_2/CH_4} = \frac{y_{CO_2}/y_{CH_4}}{x_{CO_2}/x_{CH_4}} \quad (3)$$

2.4 Morphological investigation

Membranes were characterized with scanning electron microscopy (SEM) (Jeol JSM-5800). The samples of membranes were frozen by liquid nitrogen before being tested in order to break them up, and then mounted on sample stubs with double-side tape. The preparing samples were sputtered with thin layer gold. The study of morphology with SEM can be observed cross-section, surface and pore size of membranes.

3. Results and discussion

Single gas measurements

The results overall permeability and selectivity property were achieved by the coating XSBR skin layer resulting from the flexible chain aggregate coalescences and soluble molecules of rubbery material are dissolved with O_2 and CO_2 rather than N_2. However, this experiment showed that high pressure is the dominant mechanism in gas permeation through XSBR layer. As the gas molecules pass through the molecules of the rubbery materials, they are not rigid or the material has a high free volume, i.e. the materials having a lower T_g have higher gas permeability. Therefore, the existence of carboxyl groups in XSBR structure led to a

higher solubility of O_2 and CO_2 as a present permeability in Figure 3. Additionally, their permeable properties are influenced on different pair-gas selectivity as showed in Figure 4.

Table 3 Gas permeability and selectivity properties of XSBR coated PVC blended PEG-400 hollow fiber membranes and tested at different pressures

Selective layer	Pressure (bar)	[1]Permeability (Barrer)			[2]Ideal selectivity		
		CO_2	O_2	N_2	CO_2/N_2	O_2/N_2	CO_2/O_2
XSBR	1	4.24	5.38	0.33	12.89	16.30	0.79
	1.5	5.35	7.37	1.08	4.95	6.82	0.72
	2	13.88	16.67	4.39	3.16	3.79	0.83
	2.5	20.62	22.34	12.93	1.59	1.73	0.92

[1]Barrer = 10^{-10}cm^3(STP).cm/s.cm^{2}cmHg

[2]Ideal selectivity was computed from Eq.2.

Moreover, the gas permeation for CO_2, O_2 and N_2 were essentially independent of increasing pressure indicating that each single gas was more soluble within XSBR matrix along with pressure increases. Another word, the feed pressure increased the permeation of CO_2 and O_2 became larger than N_2 which could be depended on the fact that the solubility of sorption CO_2 and O_2 in the membrane increased with increasing pressure. In addition, greater kinetic diameter of N_2 (3.64 Å) leads to the small diffusion coefficient whereas it tends less than condensability tends to small solubility coefficient (126.2 K) resulting in less permeable than O_2 (154.6 K) and CO_2 (304.2 K). Looking into the permeability data of the hollow fiber membrane, $P(O_2) > P(CO_2) > P(N_2)$, the kinetic diameter has a dominant effect on the gas permeability. As a result, it can explain that the dense surface and rubbery behavior of XSBR contribute to high gas permeability and polar gas selectivity.

Remarkably, selectivity of all pair gases decrease with feed pressure as it can be seen in Figure 4. The effect of feed pressures was affected on CO_2 and O_2 permeability more significant than that of N_2 permeability. Therefore, pair gases

selectivity depended on permeability of each pressure. The negative effect of the pressure on the membrane selectivity can be attributed to high feed pressure influences over absorption ability of polar selective layer; therefore, increasing feed pressure reduced pair gases selectivity.

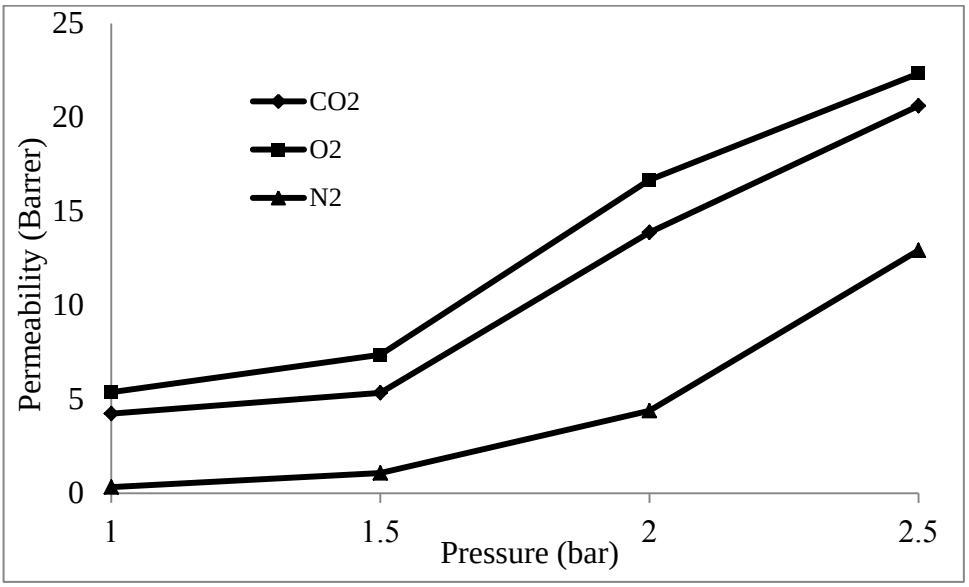

Figure 3 Permeability coefficient through membrane XSBR coated PVC-PEG hollow fiber membranes at 1-2.5 bar feed pressure, flow time 5 minute and 25 ºC.

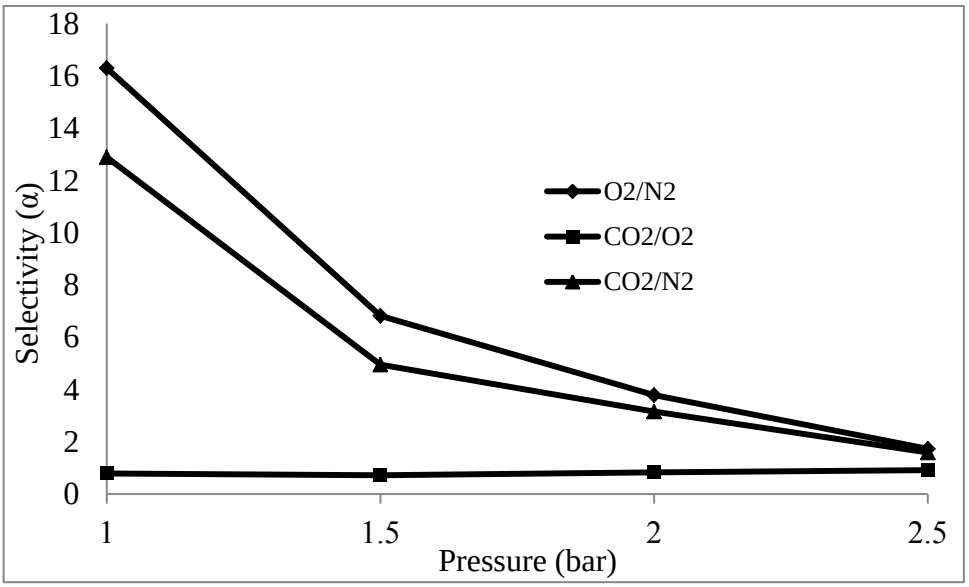

Figure 4 Selectivity coefficient through membrane XSBR coated PVC-PEG hollow fiber membranes at 1-2.5 bar feed pressure, flow time 5 minute and 25 ºC.

Mixed gas measurements

According to the main purpose of this work is to enrich CO_2 composition in the permeate side and to purify CH_4 composition in the retentate side. Therefore, it can be estimated that the components of gas mixture in permeate side should contain CO_2 concentration higher than that of CH_4 due to CO_2 more soluble through XSBR or rubbery materials than CH_4 or light gases (Bondar *et al*., 1999; Bondar *et al*., 2000; Reijerkerk *et al.,* 2010). As expected, the transport behavior of mixed gas across membrane implies that CO_2 transport mechanism in the hollow fiber membrane is quite different to CH_4. This is because the solution-diffusion behavior is the practical transport mechanism across dense layer or non-porous layer (Zulhairun *et al*., 2015).

The concentration of mixed permeate gas was computed from peak area of GC-chromatogram, which was summarized in term of permeate and retentate gas composition (vol%). Table 4 and 5 revealed that the mixed permeating components through the membranes accords closely with the main purpose of CO_2 removal in permeate side and CH_4 enrichment in retentate side. Both membranes can purify CH_4 composition in retentate side from 60 vol% to 66.38 vol% and to 63.47 vol% respectively. On the other hand, CO_2 composition in permeate gas was enriched due to more soluble into XSBR than CH_4. Moreover, unlike single permeate gas, both hollow fiber membranes exhibit larger permeability in single gas than in mixed gas. Hence, we expect that theses membranes can be described as a future developing gas separation by the following reasons:

- An enriched CO_2 acceptance of XSBR coating was caused by the currently induced polar structure of carboxyl segments within XSBR rubber.
- XSBR can be a feasible material for membrane-based biogas upgrading and mixed gas separation. In addition, any pinholes on supporting layer can be caulked by coating method.
- It is the general trend to improve purified biogas and mixed gas by coating with rubbery material.

- The comparison between mixed gas and single gas permeation data leads to the exhibit gas-gas and gas-rubbery polymer interactions, which drastically alter the transport properties of the gases in the hydrophilic membrane.
- It is estimated that the optimize CH_4 enrichment was received for low feed flow and low feed pressure.
- The resultant hollow fiber membrane can increase CH_4 purification in retentate side; whereas, it absorbs CO_2 concentration into the permeate side.

Table 4 The composition of permeate and retentate streams (feed mixture: 60% volume of CH_4 and 40% of CO_2) with membrane XSBR coated PVC-PEG at 1-2.5 bar feed pressure, operating flow time 5 minute and 25 ºC.

Pressure	**Permeate compositions**		**Retentate compositions**	
(bar)	**CO_2 (vol%)**	**CH_4 (vol%)**	**CO_2 (vol%)**	**CH_4 (vol%)**
1	47.54 ± 0.19	52.33 ± 0.19	33.72 ± 0.12	66.38 ± 0.32
1.5	46.11 ± 0.18	53.67 ± 0.14	34.21 ± 0.17	63.47 ± 0.17
2	41.33 ± 0.11	58.04 ± 0.24	36.33 ± 0.02	61.30 ± 0.30
2.5	40.67 ± 0.31	58.13 ± 0.36	37.73 ± 0.10	61.20 ± 0.18

Table 5 Mixed gas (60% volume of CH_4 and 40% volume of CO_2) permeability and selectivity coefficient of membrane XSBR coated PVC-PEG hollow fiber membranes at 1-2.5 bar feed pressure, flow time 5 minute and 25 ºC.

Pressure	**[1]Permeability of permeate**	**[2]Selectivity (CO_2/CH_4)**	
(bar)	**(Barrer)**	**Permeate**	**Retentate**
1	4.38	1.36	0.76
1.5	6.66	1.29	0.80
2	10.34	1.07	0.88
2.5	18.47	1.04	0.92

[1]Permeability was computed from Equation 1

[2]Selectivity was computed from Equation 3

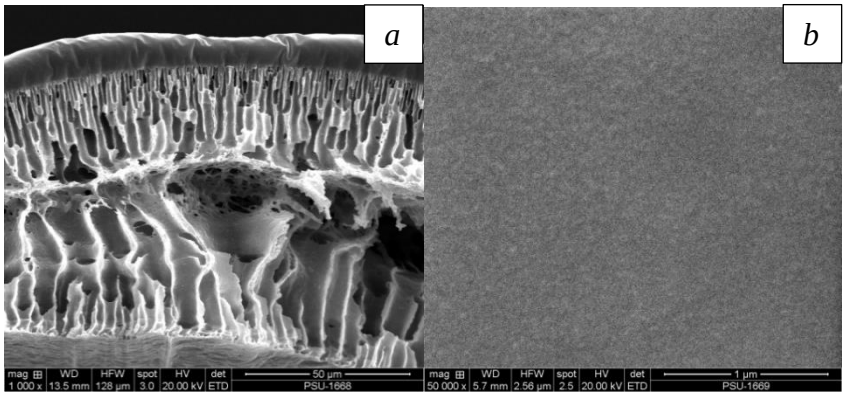

Figure 5 SEM images of XSBR coated PVC-PEG400 hollow fiber membrane (a) cross section (b) skin layer surface

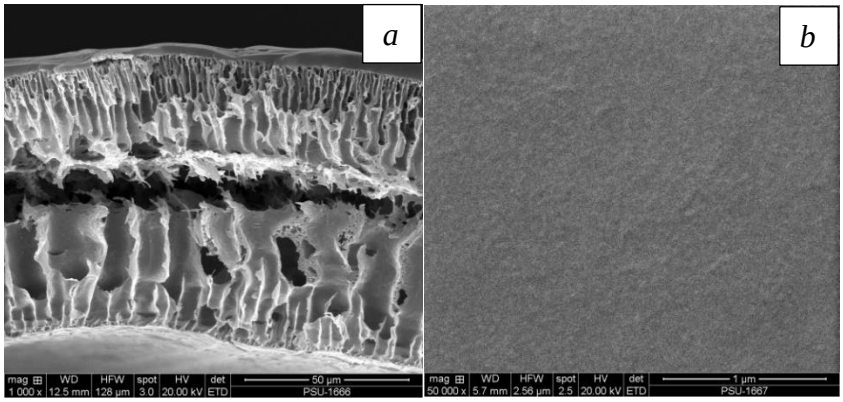

Figure 6 SEM images of XSBR coated PVC-PEG4000 hollow fiber membrane (a) cross section (b) skin layer surface

In case of testing in CO_2/CH_4 (40/60) mixed gases with contactor membrane module, due to normal composition of biogas mainly consists of CO_2 and CH_4 (Ozturk and Demiriyeva, 2013), this mixed gas composition can infer that its ability of mixed gas separation likes biogas separation. From permeability and selectivity data in Table 4, the permeability was measured from soap-bubble meter while GC was used for detecting composition of gas mixture (see Table 4). SEM images of PVC-PEG hollow fiber were coated by XSBR acting as selective layer, shown in Figure 5 and 6, as well as their morphological images presented dense skin layer of XSBR layer and porous support layer of PVC-PEG. Interestingly, the special

property of the resultant hollow fiber membrane in this work is to be a hydrophilic material of supporting layer resulting from PEG addition within PVC based matrix. As the mixed feed gas, when CO_2 gas diffuses through XSBR layer, it could be induced by affinity property and polar functional group of PEG. Consequently, it could refer that the performances of XSBR coated PVC-PEG membrane incorporate with polar structure of both carboxyl group within XSBR and ethylene oxide units within PEG.

Effect of feed pressure on single and mixed gas permeable property

The potential for behavior difference to occur in mixed gas experiments, much different from that observed in single gas experiments, has been recognized for hollow fiber membranes. For example, at 1 bar of CO_2 feed pressure; permeate single gas showed permeability higher than permeation of mixed gas. Selectivity losses with an applied feed pressure were therefore provided to increasing of all single gas permeation. Meanwhile, the relative decrease in CO_2/CH_4 selectivity with mixed gas is more pronounced with mixed gas feed that is attributed to competition for sorption sites by CH_4 meaning. That means pair gases selectivity of CO_2/gas selectivity almost decreased when feed pressures increased which are typical of dual-mode sorption behavior. Similarly, CO_2/CH_4 selectivity in mixed gas and CO_2/N_2 selectivity in single gas were influenced on feed pressure increased. They may attribute that suppression of plasticization by PEG additives since PEG can absorb CO_2 more than CH_4 and N_2 which are light gases (David *et al.*, 2011; Swaidan *et al.*, 2013). Moreover, this difference in selectivity between mixed gas and single gas measurements was explained to the competitive sorption effect (Matteucci *et al*., 2006). The fact was that possession of CH_4 or N_2 in the mixed gas composition influenced the feed pressure In addition, small amounts of CH_4 from the high feed pressure can permeate through the membrane and lost to the permeate stream. Here, the driving force for CO_2 across the membrane decreased in a mixed gas resulting in gas permeability decreased. In addition to competitive sorption, the highly condensable CO_2 gas may present plasticization effect in polymer matrix, resulting in a reduction of CO_2 permeability and CO_2/gas selectivity (Khan *et al*., 2011; Xin *et al*., 2015).

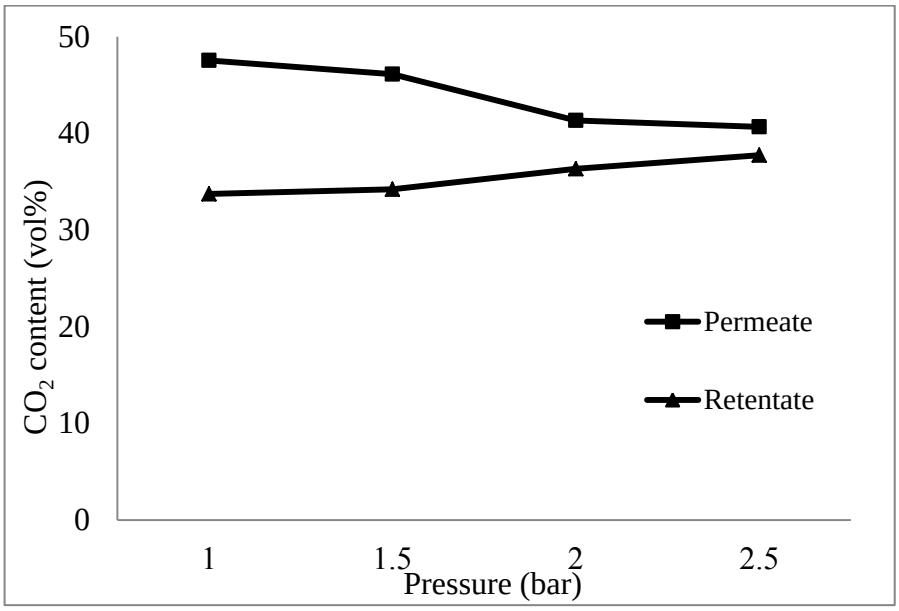

Figure 7 Effect of pressure on CO_2 content in permeate and retentate streams (feed mixture: 60% volume of CH_4 and 40% volume of CO_2) through membrane XSBR coated PVC-PEG hollow fiber membranes at 1-2.5 bar feed pressure, flow time at 5 minute and 25 ºC.

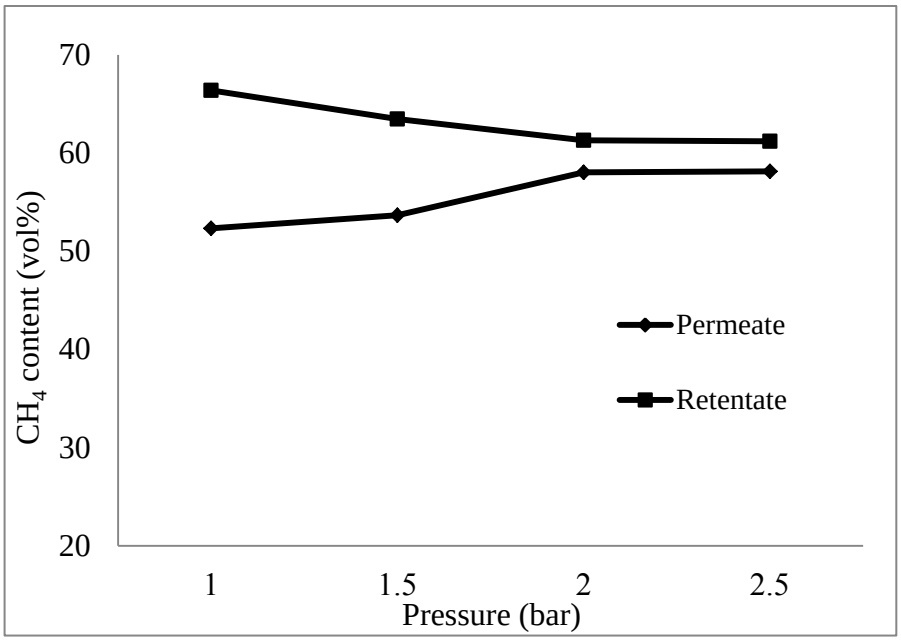

Figure 8 Effect of pressure on CH_4 content in permeate and retentate streams (feed mixture: 60% volume of CH_4 and 40% volume of CO_2) through membrane XSBR coated PVC-PEG hollow fiber membranes at 1-2.5 bar feed pressure, flow time at 5 minute and 25 ºC.

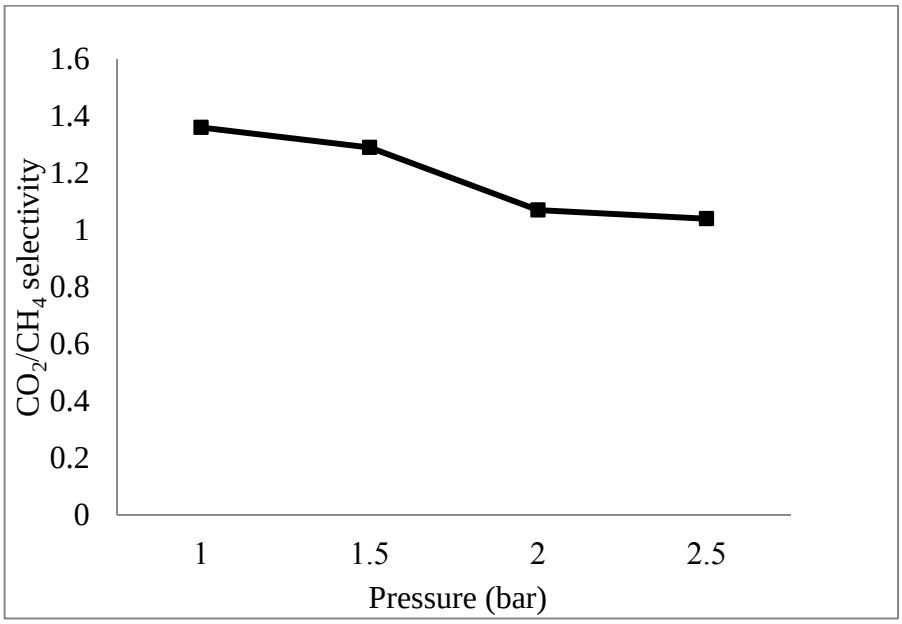

Figure 9 The ratio of mixed CO_2/CH_4 selectivities (feed mixture: 60% volume of CH_4 and 40% volume of CO_2) in permeate side versus feed pressure at 1-2.5 bar, flow time 5 minute and 25 ºC.

In Figure 7, analysis of the retentate gas showed that the CO_2 content in the retentate gas slightly increased at increase in feed pressure whereas the highest CO_2 content in the permeated gas was obtained when feed pressure of 1 bar was used. The combined effect of mixed gas stream may attribute that the plasticization effect of CO_2 at higher feed pressures (Houde *et al*., 1992; Wessling *et al*., 2001; Ismail and Lorna, 2002) led to higher CH_4 permeation as showed in Figure 8. CH_4 can be caused a high concentration which creates a resistance against the CO_2 mass transfer (Ozturk and Demiriciyeva, 2013) on the feed side of the hollow fiber membrane and surface blockage in the polar structure of XSBR as well as competitive sorption effect which results in the less CO_2/CH_4 selectivity as showed in Figure 9.

Effect of feed mixture gas concentration

Permeation of different components in a mixture gas may differ from the single gas permeation due to the competition among permeating gases for the sorption sites of the several membranes and the competition between the mobility of

gases in the bulk membrane (Yeom *et al*., 2000; Pinnau and He, 2004); especially, if CO_2 permeates are the main purpose of mixed gas separation across the membranes (Cakal *et al*., 2012). It is interesting that the competition has much stronger effect on CO_2 than CH_4 solubility hydrophilic membranes (Vopicka *et al*., 2014). Therefore, the influence of mixed feed gas concentration could influence on permeability and selectivity of membrane performances.

As previously reported, Cakal and co-workers (2012) reported that single gas permeability of CO_2 and CH_4 through poly (ether sulfone) membrane is 1.19 and 0.0058 Barrer respectively, its permeability was tested at 35 ºC, 2 bar while CO_2 permeation of this membrane was very limited for CH_4 rich feed CO_2/CH_4 mixture (50/50) due to the previous mentions. Therefore, the CO_2 permeable ability across membrane could be slightly less than CO_2 permeable ability in single gas experiments. Based on the findings of Tin and co-workers (2003) reported that selectivity factors are often shown to be lower than ideal selectivity. It can be attributed that slowly permeating CH_4 may suppress the rapid permeating CO_2. As a consequence, it may lead to a lower separation factor than ideal selectivity. In addition, when CH_4 content was increased in feed stream, it was less effective than that obtained from lower CH_4 content because the existence of CH_4 on membrane surface may enhance probability of collision of CO_2 molecules which obstructed the mass transport of penetrant gas (Merkel *et al*., 2000). Hence, the increase in CH_4 concentration in the feed mixture gas may lose competitive sorption to CO_2 permeating gas (Sadrzadeh *et al*., 2009).

To sum up of this effect, if an existence of high CH_4 content in feed stream can slightly compress the bulk polymer membrane resulting in reducing the amount of free volume available for penetrant gases. Thereby, it could reduce the amount of the CO_2 diffusion coefficient and permeation across membrane resulting in reduction of CO_2/CH_4 selectivity of permeation and changing mass transport separation efficiency.

Conclusions

The XSBR coated PVC hollow fiber membranes can be investigated by shell side feed that is prepared from high stretching during spinning process. The permeability of all single gases increased with the increasing of feed pressure. In contrast, the ideal gas selectivity decreased with increasing of feed pressure and the highest of permeability and selectivity are O_2 and O_2/N_2 respectively. In case of using mixed gas for investigation, the permeability of mixed gas accords closely with single gas. Meanwhile, the selectivity of CO_2/CH_4 tends to possibly remove CO_2 from mixed gas that mostly contains CO_2 and CH_4. At the same time, the CH_4 concentration of retentate side can enrich CH_4 concentration more than feed gas that is a significant feasibility of the resultant membranes. The effect of feed pressure on performance of the membrane with optimum CO_2/CH_4 selectivity conditions was not obtained from high feed pressure due to membrane compaction and gas solubility reduction during separation process. However, single stage membrane processes are not able to upgrade the mixed gas or biogas economically that needs to develop in order to achieve suitable CH_4 concentration for applicable requirements.

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CHAPTER 5
GENERAL CONCLUSIONS

From the research had conducted and guided the preceding preparation of blended PVC flat sheet membrane together with coating XSBR in order to demonstrate the feasibility of gas separation that was the main purpose of this research. The development of membrane preparations in this thesis were divided into two steps that contained flat sheet and hollow fiber membrane configurations. Both configurations were prepared via phase inversion and dry/wet method respectively. Though the PVC blended PEG flat sheet membranes have high porous and high gas permeability, the gas selectivity does not occurred; therefore, XSBR selective layer is coated on PVC-blended that used for supported membrane. Intentionally, the guideline of flat sheet formulation and condition for fabrication can be led to hollow fiber processing that is the step two of this research.

In chapter 2, the different properties of PVC K-Value 580, 610 and 710 have different viscosity that is an important factor to casting and forming membrane. The PVC-580 shown rather low viscosity than 610 and 710; consequently, this is the main factor to select the PVC grades for casting because its morphological images presented finger-like substructures that contained a thin wall pore and a high surface areas resulting in the increase in polar gas adsorption (CO_2 and O_2) and gas permeability corresponding with the XSBR coating on the supported PVC membrane can be prepared from simple casting method. Therefore, the combination of the advantages of polar structure of the XSBR and the finger-like substructures of supporting PVC flat sheet membrane, this coated flat sheet membrane tend to have a high efficiency of O_2 and CO_2 permeability and gas selectivity that might be improved to upgrading biogas application.

In chapter 3, the PVC blended PEG is one of the promising polymer for preparation hollow fiber membrane with respect to its application and design. For a given polymer blend, how to make a high permeability and separation ability membrane by studying the membrane formation protocol, is an important topic because of its viscosity property. Formation of asymmetric hollow fiber membrane

includes many factors; for example, the properties of solvent, the additives, the coagulation, the spinning conditions, the dimension of tube-in-orifice spinneret etc. All of these conditions may affect to the structure of the hollow fiber membranes. In this chapter, it was found that the optimum condition is to consider many variable factors in order to obtain a suitable hollow fiber membrane for gas separation. With observation from all the characterized techniques, the prepared hollow fiber membranes that spun from 50 rpm tends to be the feasible dense skin layer resulting in high gas separation and may induce low gas permeability. Longer center-tube spinneret retarded solvent and non-solvent exchange within inner lumen side resulting from the chain coalescences are extended solidification activity.

In chapter 4, in this work we investigated the feasibility of XSBR coated PVC-PEG hollow fiber membrane, more specifically the absorption of CO_2 in mixed gas form CH_4 via contactor module. The dominant experiment of this chapter is using NBR rubber material that acts as selective layer of the supporting PVC blended PEG layer. These resultant hollow fiber membranes were exhibited into contactor module with shell side feed configuration in order to measure the different single gases and mixed gas permeation. The following conclusions can be emphasized:

(1) The curves of pure gas permeability versus feed gas pressures demonstrate that O_2 and CO_2 permeates through the hollow fiber membrane following facilitated transport absorption mechanism across selective and supporting layer; whereas, N_2 gas showed lower permeable through hollow fiber membrane than O_2 and CO_2. These behaviors resulted in inducing of polar structure of XSBR with polar gases (O_2 and CO_2). The descending permeation of the feed pressure on the membrane permeability was more evident for the O_2 and CO_2 than the N_2. However, the increases in feed pressures were influenced to CO_2/N_2, CO_2/O_2 and O_2/N_2 ideal selectivity due to influencing over absorptive performance.

(2) In case of mixed gas permeation and separation performances, the higher the feed pressure caused the more the mixed gas permeability through the hollow fiber membrane manufactured and reduced the CO_2/CH_4 selectivity. This effect caused from the competitive absorption of mixed gas on skin surface resulting in decrease in CO_2 permeation across membrane.

(3) As the first investigation of the single and mixed gas performance of XSBR coated PVC-PEG hollow fiber membrane derived from dense layer of XSBR rubber and good mechanical and chemical of PVC blend PEG, a preliminary conclusion is made that dense matrix and polar structure of XSBR may yield higher permeability and selectivity after trial separations.

As previous experiments above, the apparatus of spinning process and contactor module were established within laboratory procedures that is one of the mainly purposes of this work due to they were created during research period; besides, its performances can be adapted for other applications and researches. After studying of membrane performances both flat sheet and hollow fiber membranes, they were found that the step of hollow fiber membrane preparation showed the feasibility of the spinning process and steps of the surface improvement with XSBR layer. The resultant hollow fiber membrane can present high gas selectivity more than non-improvement skin surface that was not separated gas mixture. Therefore, the efficient performance of O_2 and CO_2 removal from the resultant membranes can slightly lead to separation of CO_2 from biogas or mixed gas containing CO_2 and CH_4.

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APPENDIX A
Data for chapter 2

Swelling measurements

The degree of water swelling (DS) of the resultant membranes at given time is indicated by the following equation:

$$DS = \frac{m_1 - m_0}{m_0} \times 100\%$$

Where m_0 and m_1 are the weights of dry and water swollen membranes respectively. All membranes were carried out at constant temperature of 25 ºC, and the membranes were weighted at room temperature by analyzing balance. All flat sheet membranes were immersed into distilled water at 25 ºC for 24 hr, then dried in vacuum oven at 50 ºC.

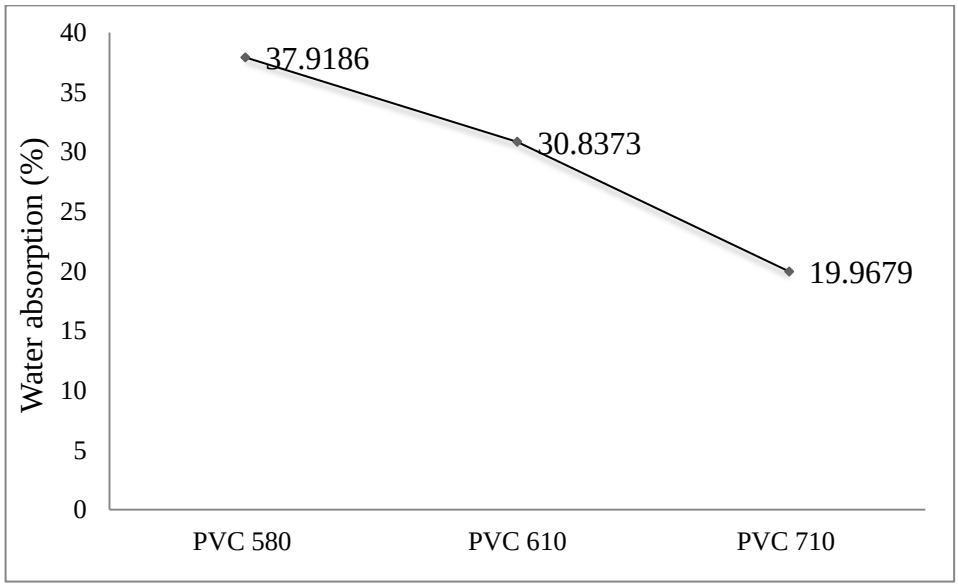

Figure A-1 Water absorption of the different PVC K-values

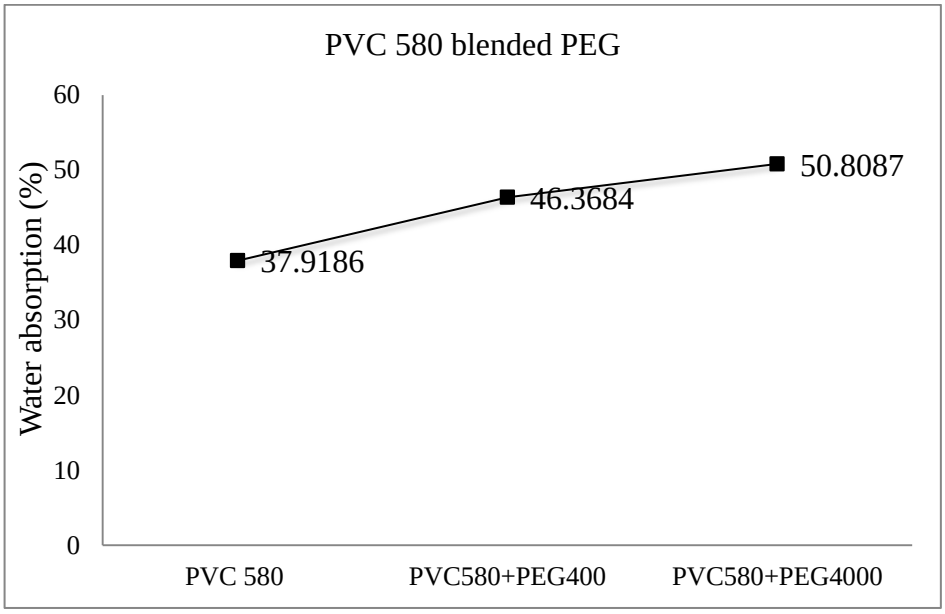

Figure A-2 Water absorption of PVC 580 blended PEG 400-5% and PEG 4000-5%

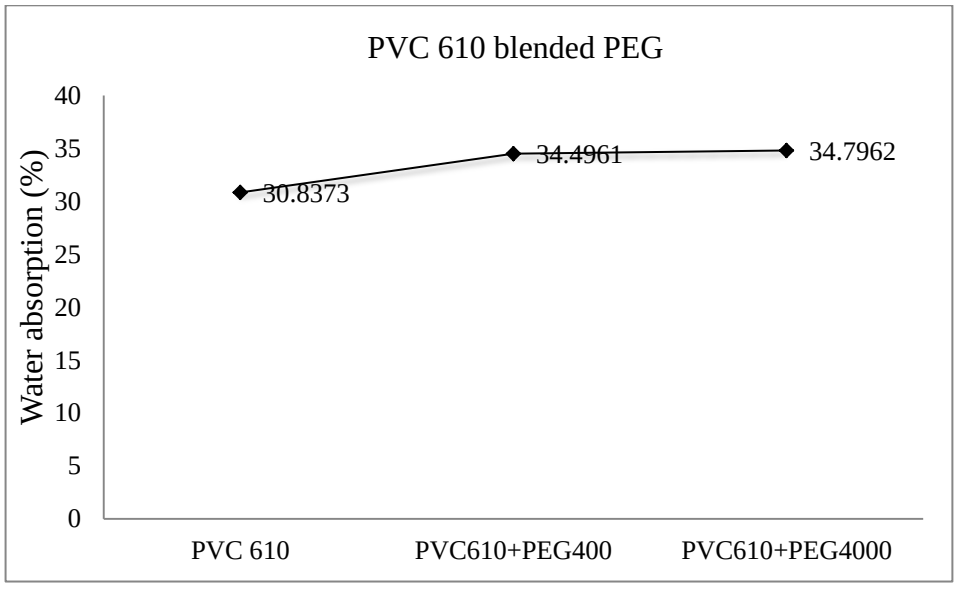

Figure A-3 Water absorption of PVC 610 blended PEG 400-5% and PEG 4000-5%

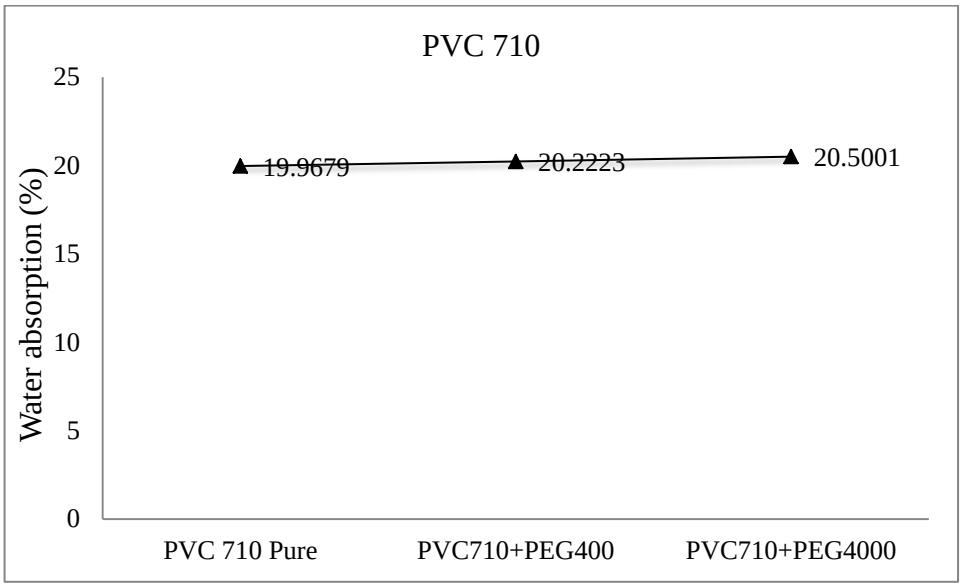

Figure A-4 Water absorption of PVC 710 blended PEG 400-5% and PEG 4000-5%

Water permeability of flat sheet membrane

Figure A-5 Dead-end filtration unit

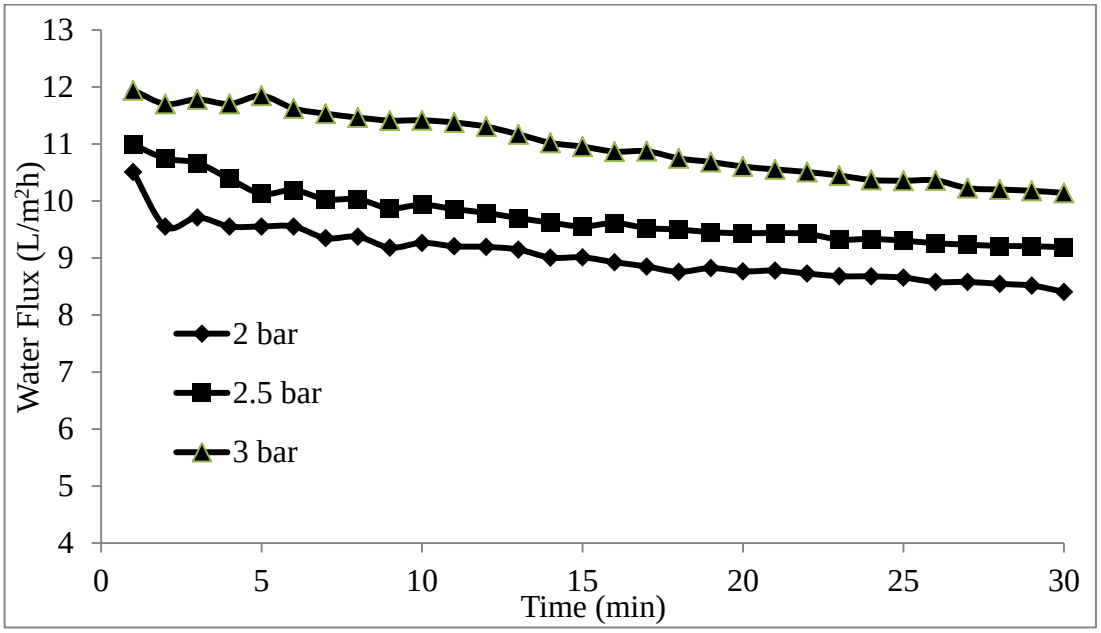

Figure A-6 Water flux of PVC 580 blended PEG 400-5%

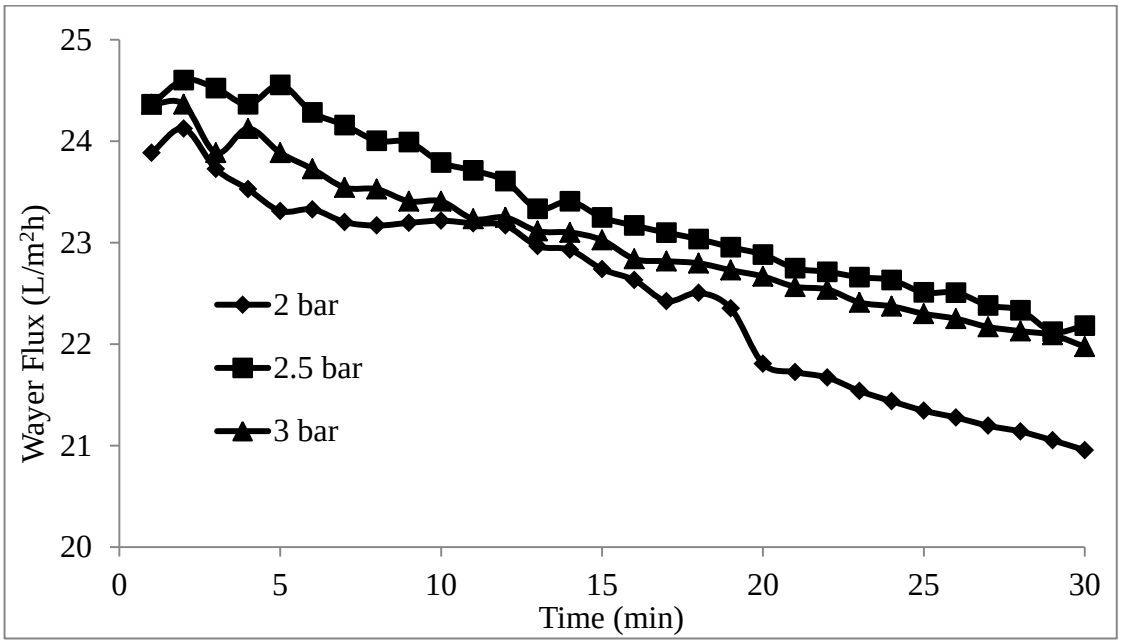

Figure A-7 Water flux of PVC 580 blended PEG 4000-5%

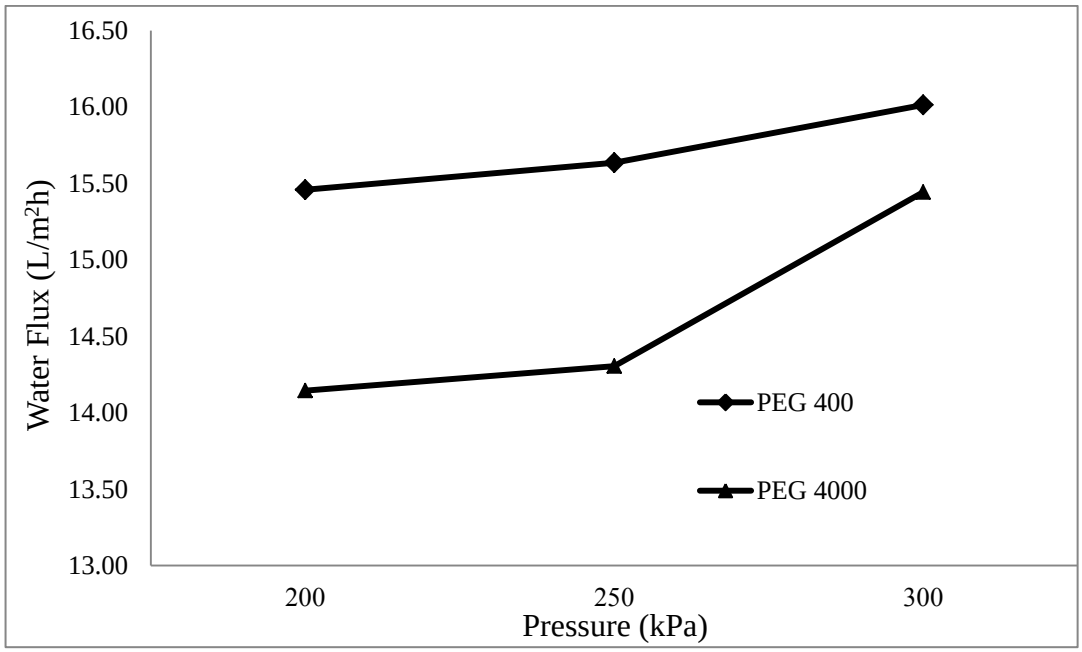

Figure A-8 Hydraulic Permeability of PVC-580 blended with PEG 400 and PEG 4000

APPENDIX B

Data for chapter 3

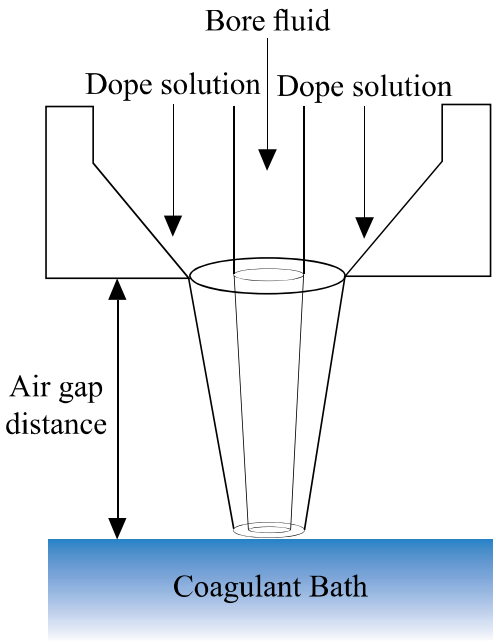

Figure B-1 Schematic diagram of tube-in-orifice spinneret

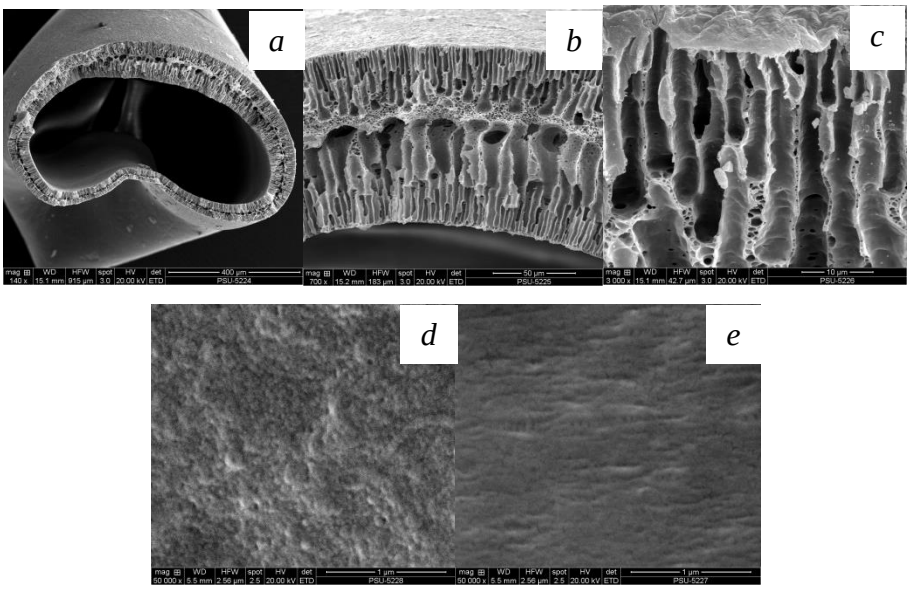

Figure B-2 SEM images of PVC 580 with wind-up speed 40 rpm, air gap distance 1 cm, center-tube length 0.3 cm; (a) cross section (b) and (c) partial enlargement of outer edge of skin layer (d) outer surface (e) inner surface

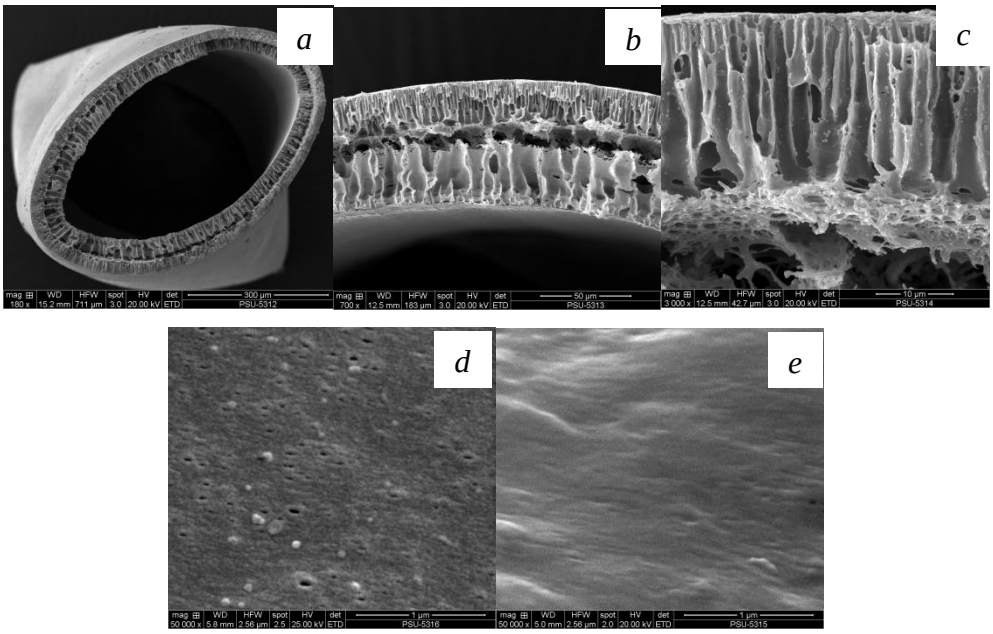

Figure B-3 SEM images of PVC 580 blended PEG 400 5% with wind-up speed 40 rpm, air gap distance 1 cm, center-tube length 0.3 cm; (a) cross section (b) and (c) partial enlargement of outer edge of skin layer (d) outer surface (e) inner surface

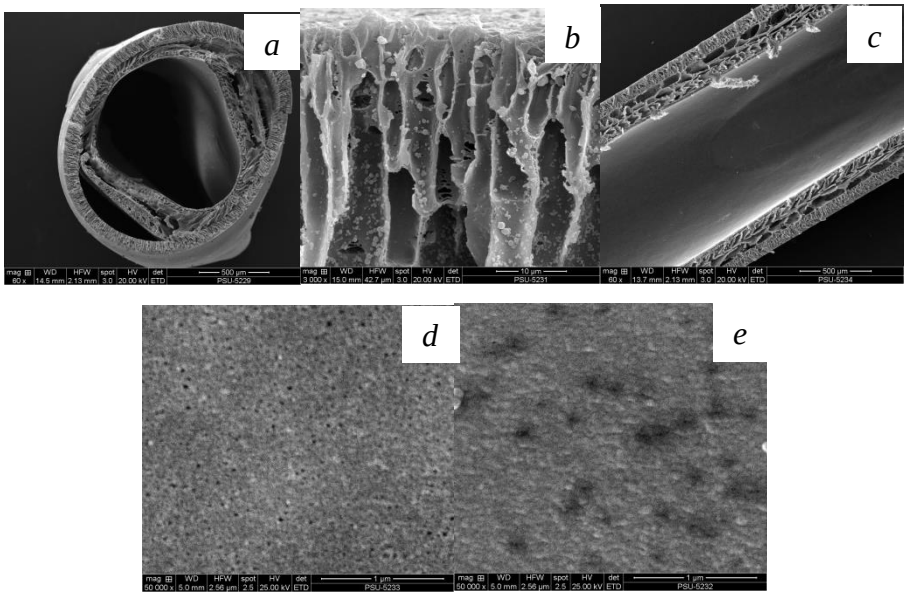

Figure B-4 SEM images of PVC 580 blended PEG 400 5% with wind-up speed 40 rpm, air gap distance 5 cm, center-tube length 0.3 cm; (a) cross section (b) partial enlargement of outer edge of skin layer (c) cut-cleaved section (d) outer surface (e) inner surface

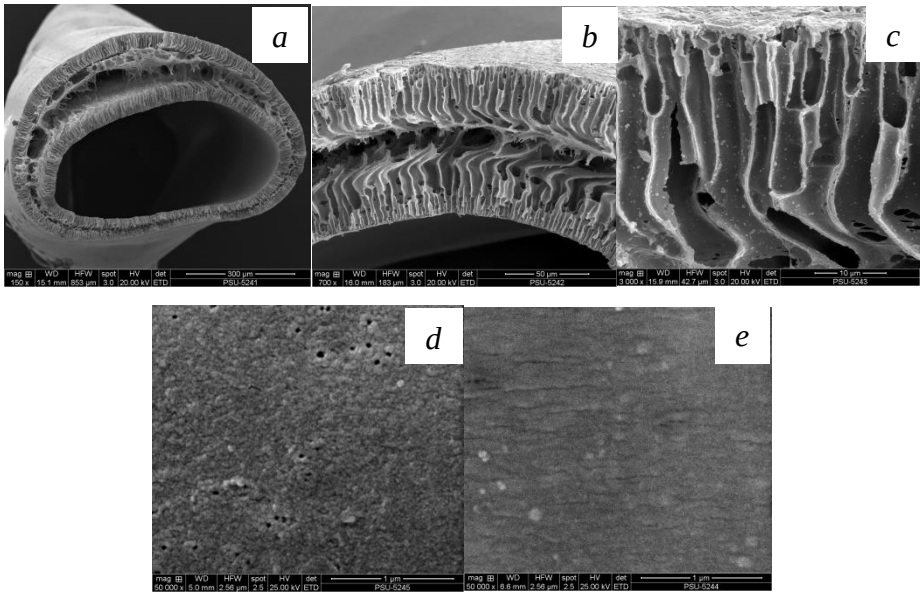

Figure B-5 SEM images of PVC 580 blended PEG 4000 5% with wind-up speed 50 rpm, air gap distance 1 cm, center-tube length 0.3 cm; (a) cross section (b) and (c) partial enlargement of outer edge of skin layer (d) outer surface (e) inner surface

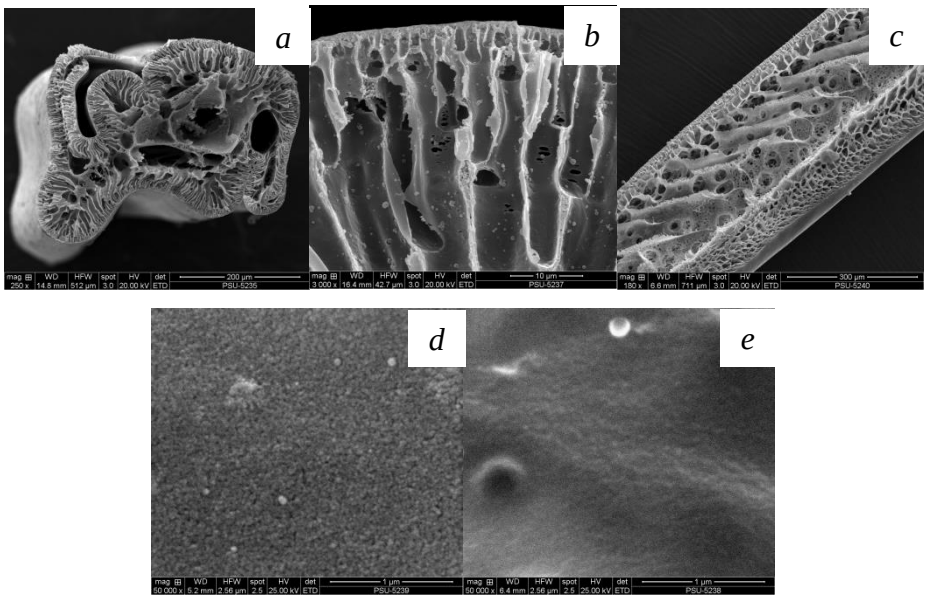

Figure B-6 SEM images of PVC 580 blended PEG 4000 5% with wind-up speed 50 rpm, air gap distance 5 cm, center-tube length 0.3 cm; (a) cross section (b) partial enlargement of outer edge of skin layer (c) cut-cleaved section (d) outer surface (e) inner surface

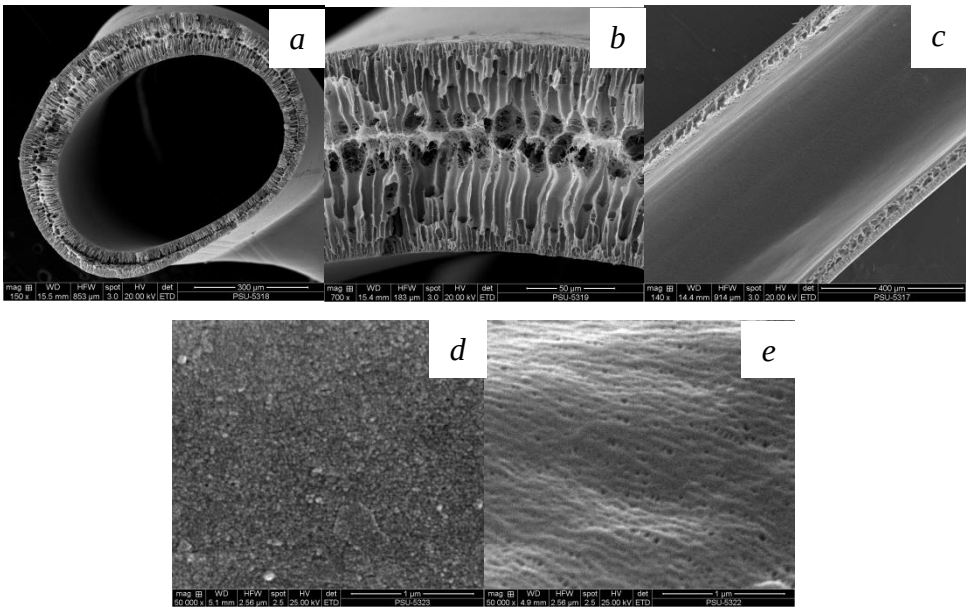

Figure B-7 SEM images of PVC 610 blended PEG 400 5% with wind-up speed 40 rpm, air gap distance 1 cm, center-tube length 0.3 cm; (a) cross section (b) partial enlargement of outer edge of skin layer (c) cut-cleaved section (d) outer surface (e) inner surface

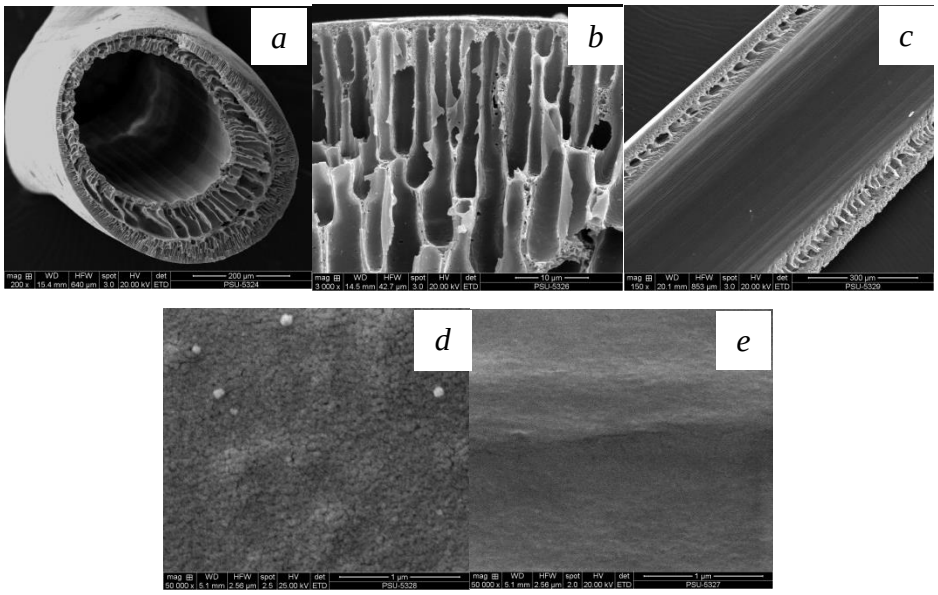

Figure B-8 SEM images of PVC 710 blended PEG 400 5% with wind-up speed 40 rpm, air gap distance 1 cm, center-tube length 0.3 cm; (a) cross section (b) partial enlargement of outer edge of skin layer (c) cut-cleaved section (d) outer surface (e) inner surface

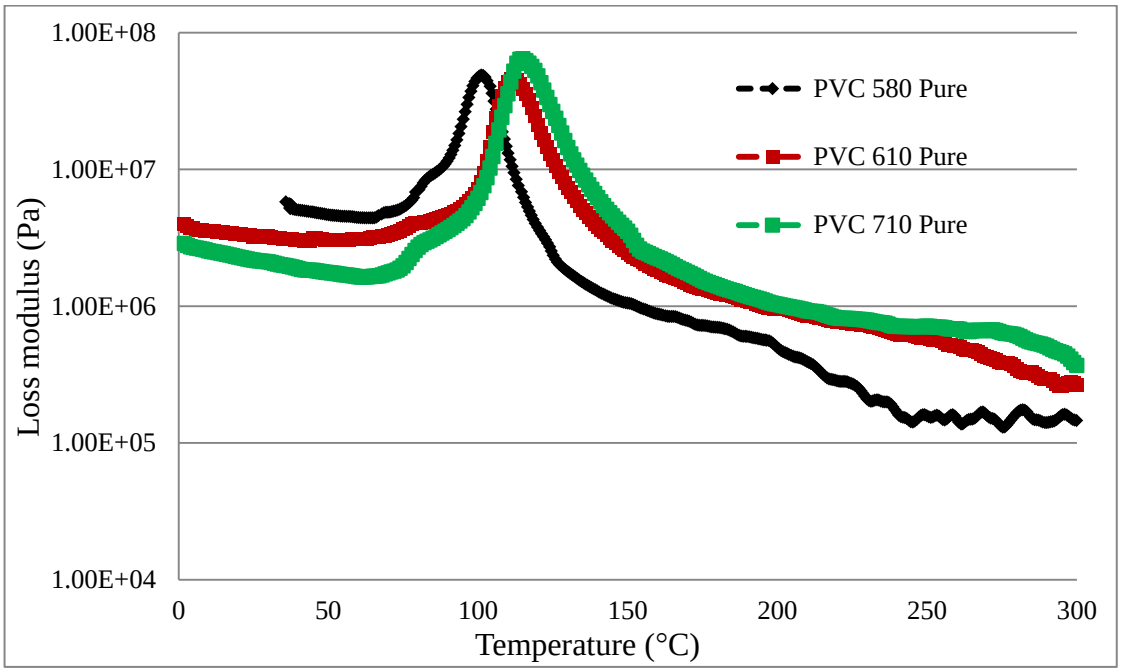

Figure B-9 Loss modulus of the non-blended PVC

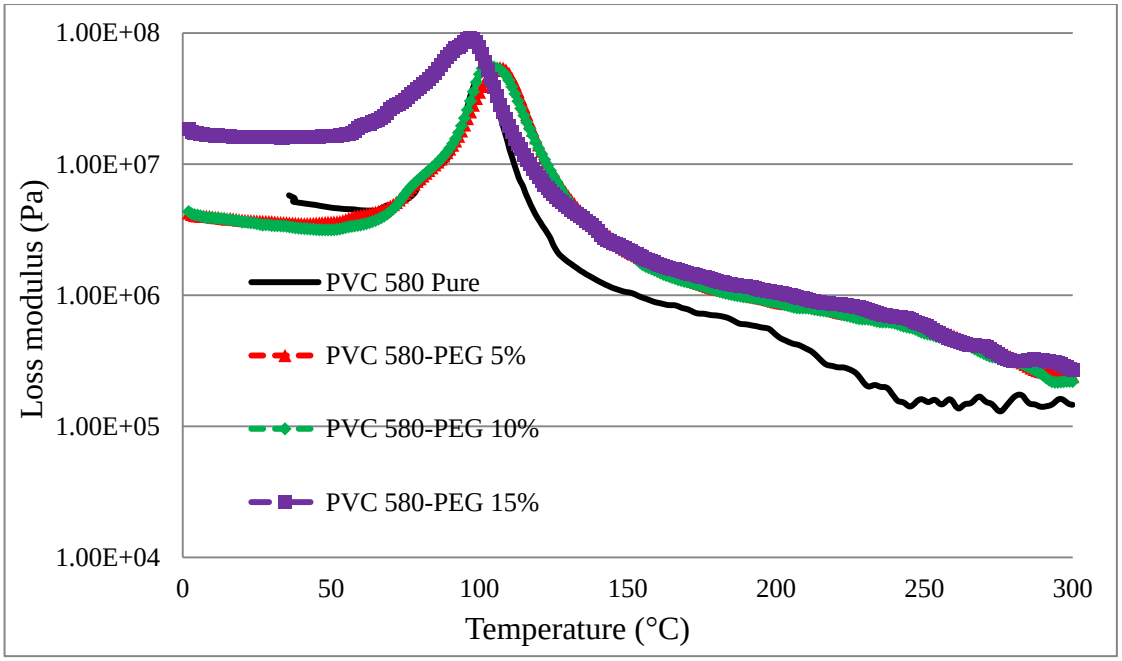

Figure B-10 Loss modulus of the blended PVC

APPENDIX C

Data for chapter 4

Table C-1 Gas Chromatography information of mixed permeate gas from XSBR coated PVC-PEG400 at 1 bar, 25 ºC

Pressure (bar)	Gas	Retention time (min)	Area (25 uV.s)	Amount (vol%)
Calibrated gas	CH_4	1.093	1725.609	60.211
	CO_2	1.280	1583.356	39.567
1	CH_4	1.092	1423.127	52.337
	CO_2	1.278	1896.801	47.542
1.5	CH_4	1.093	1468.089	53.672
	CO_2	1.278	1880.334	46.113
2	CH_4	1.092	1423.127	58.044
	CO_2	1.278	1896.801	41.332
2.5	CH_4	1.093	1468.089	58.132
	CO_2	1.278	1880.334	40.673

Table C-2 Gas Chromatography information of mixed retentate gas from XSBR coated PVC-PEG400at 2 bar, 25 ºC

Pressure (bar)	Gas	Retention time (min)	Area (25 uV.s)	Amount (vol%)
1	CH_4	1.064	2124.61	66.38
	CO_2	1.253	727.15	33.72
1.5	CH_4	1.062	2124.28	63.47
	CO_2	1.250	848.48	34.21
2	CH_4	1.064	2124.61	61.30
	CO_2	1.253	727.15	36.33
2.5	CH_4	1.062	2124.28	61.20
	CO_2	1.250	848.48	37.73

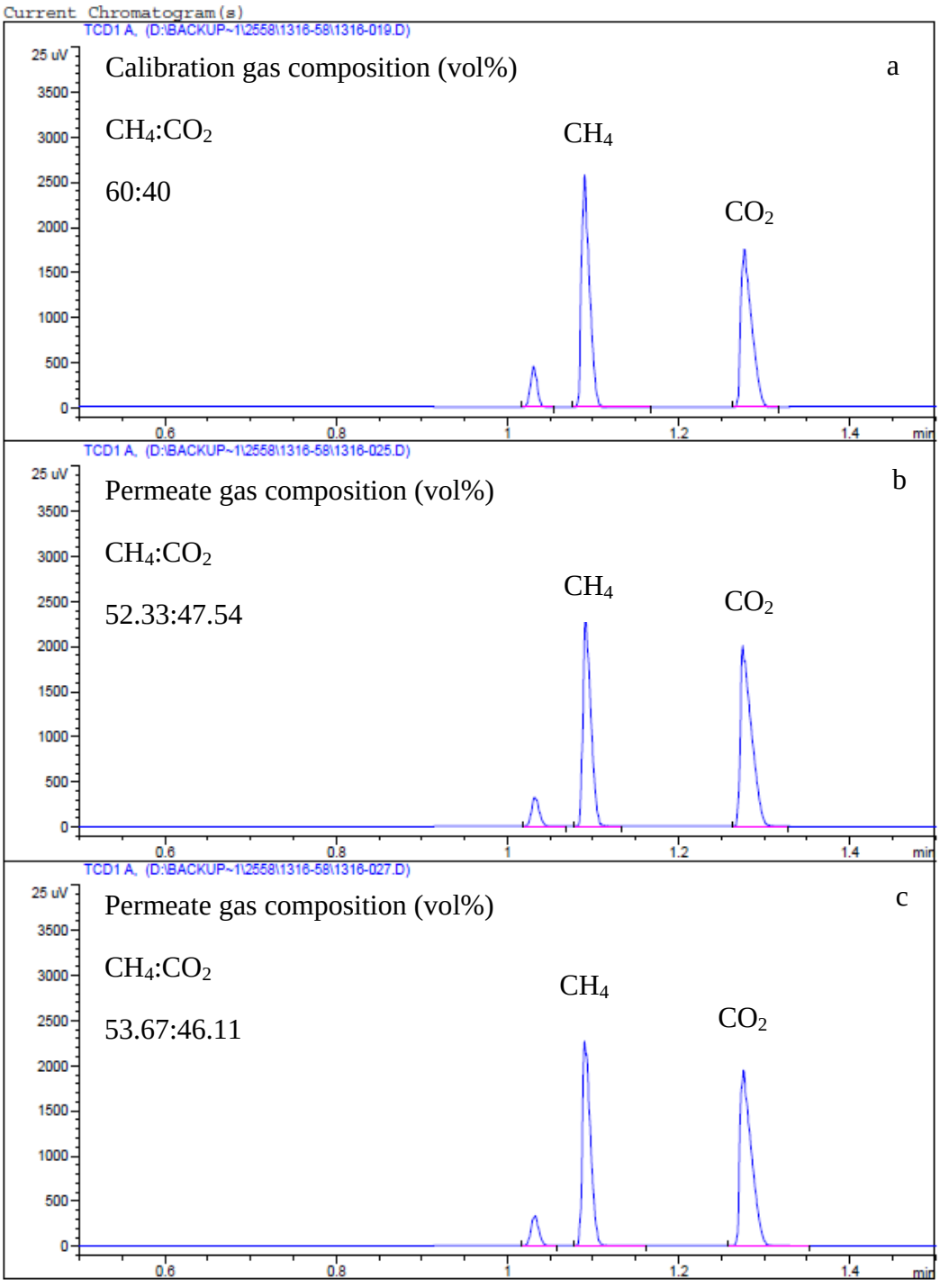

Figure C-1 GC-chromatogram of permeate gas through XSBR coated PVC-PEG hollow fiber membrane tested at 1-2.5 bar 25 ºC (a) calibration gas composition (b) permeate gas at 1 bar and (c) permeate gas at 1.5 bar

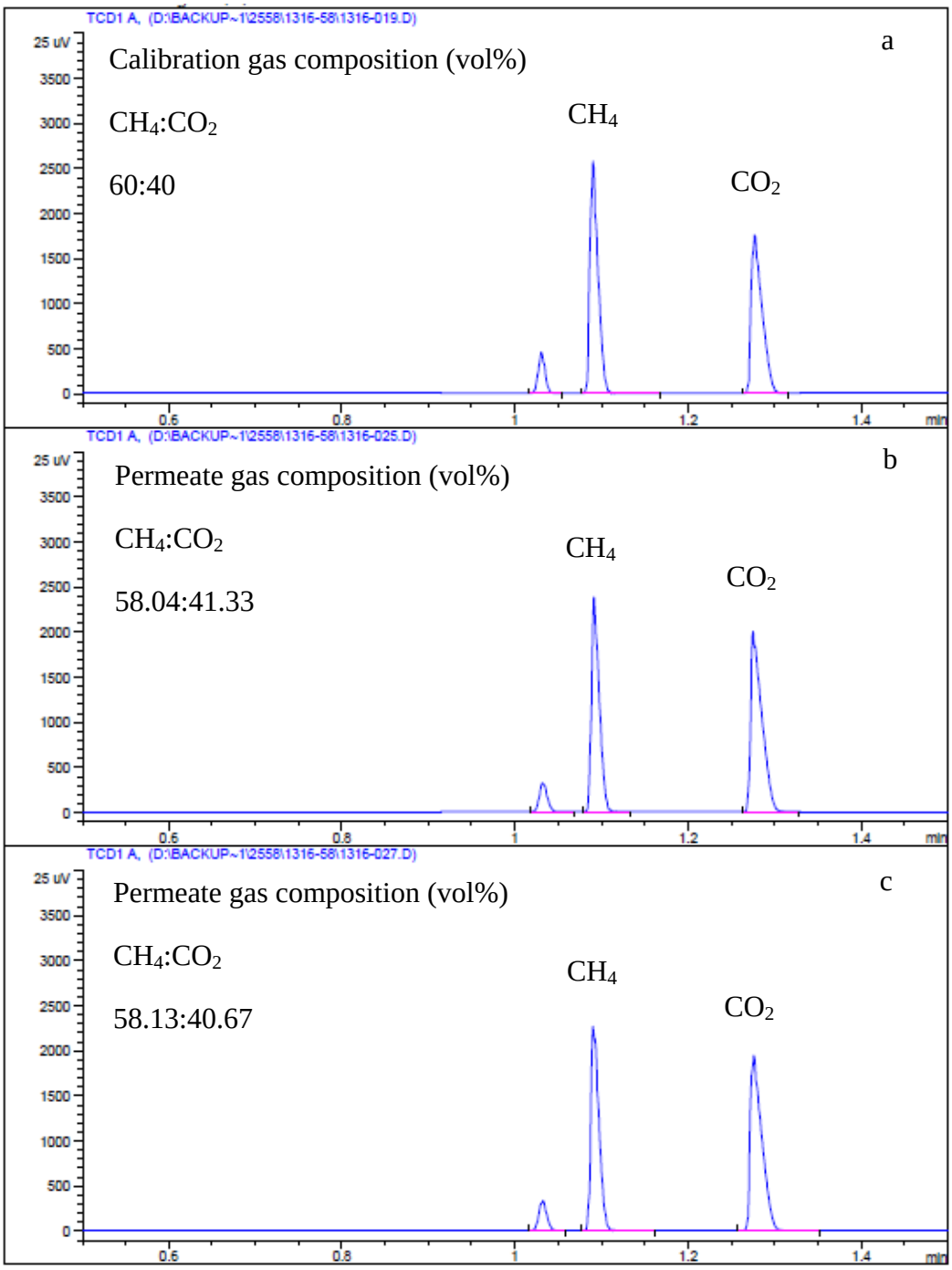

Figure C-2 GC-chromatogram of permeate gas through XSBR coated PVC-PEG hollow fiber membrane tested at 1-2.5 bar 25 ºC (a) calibration gas composition (b) permeate gas at 2 bar and (c) permeate gas at 2.5 bar

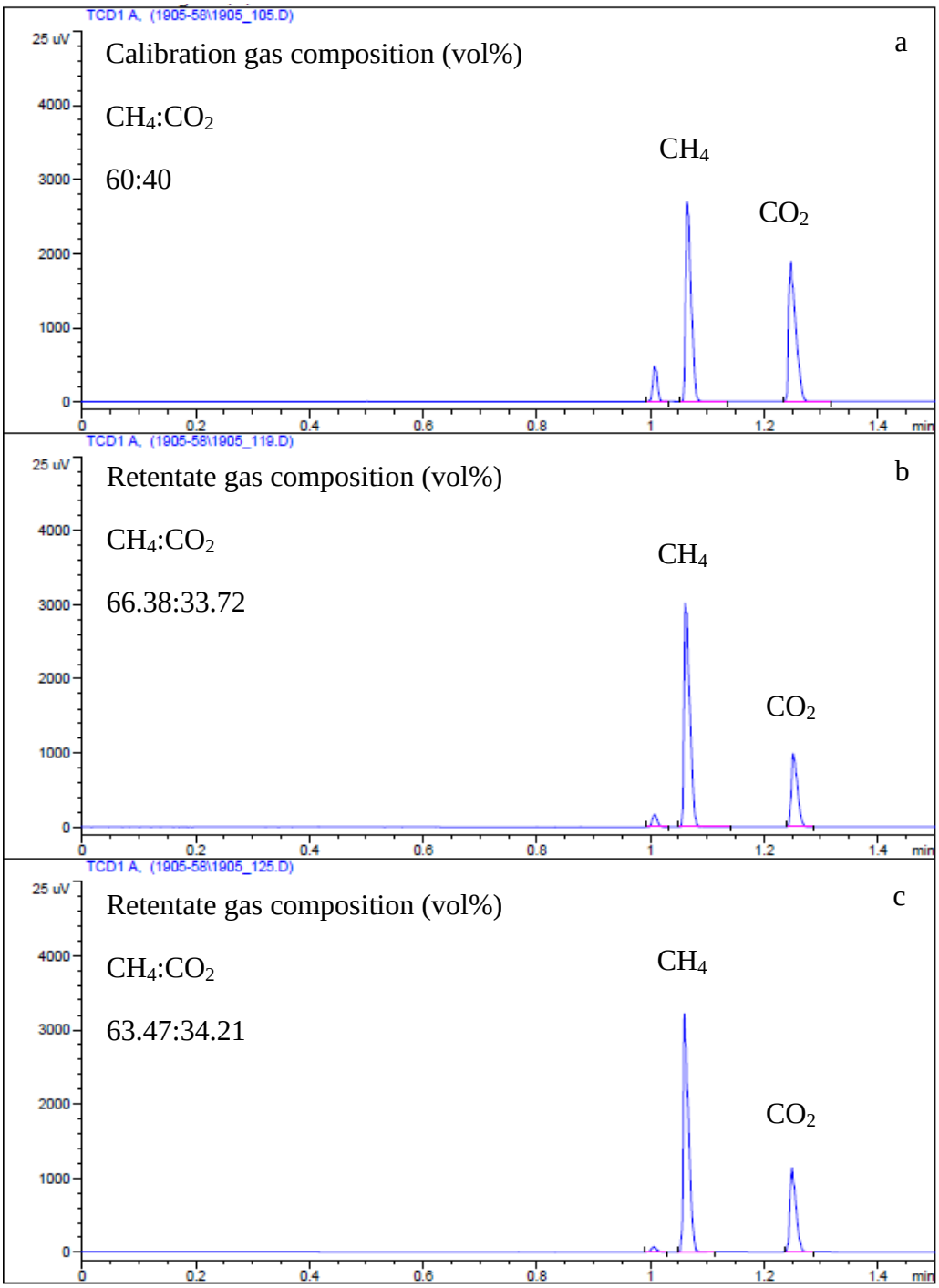

Figure C-3 GC-chromatogram of retentate gas through XSBR coated PVC-PEG hollow fiber membrane tested at 1-2.5 bar 25 ºC (a) calibration gas composition (b) permeate gas at 1 bar and (c) permeate gas at 1.5 bar

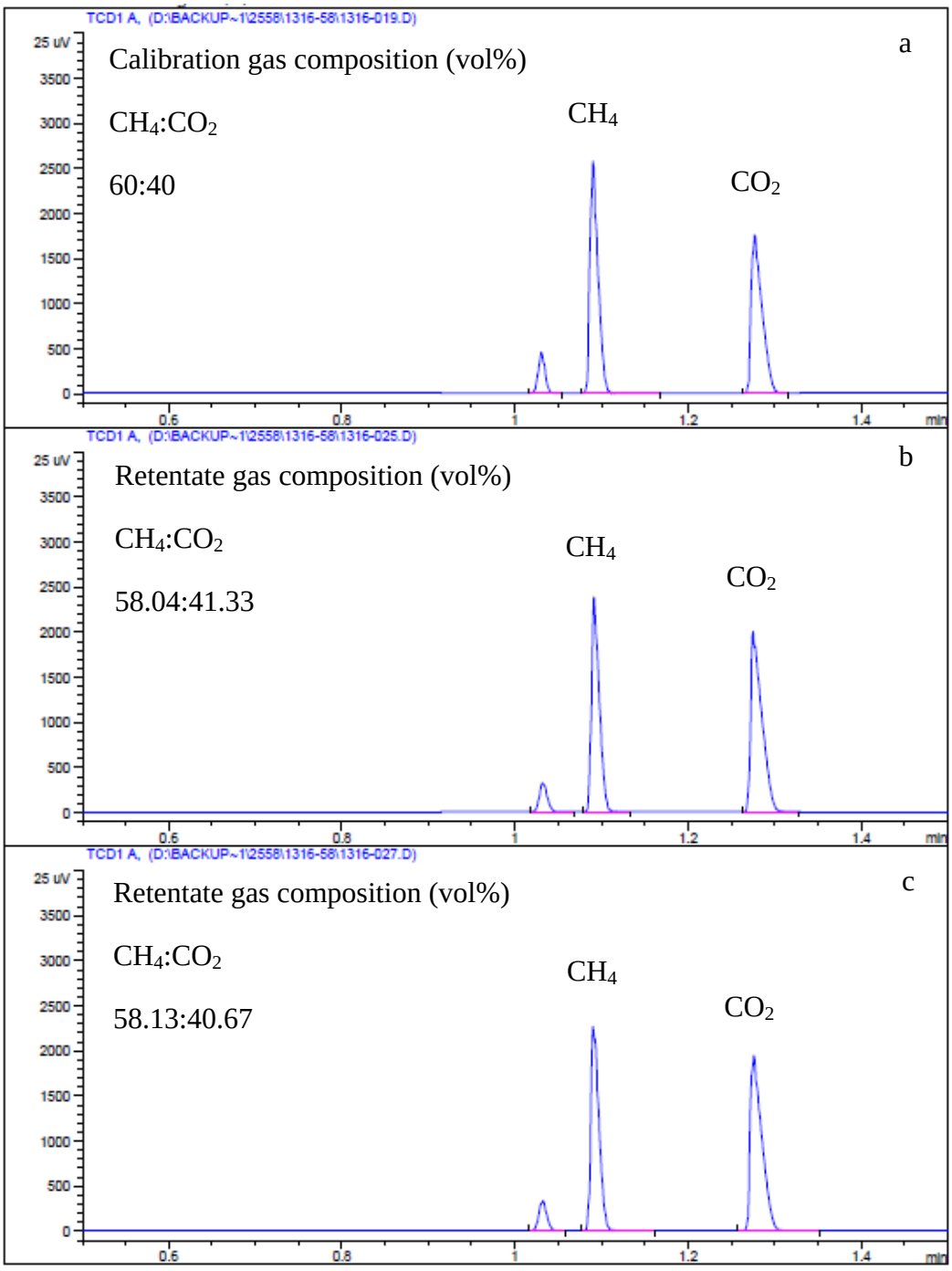

Figure C-4 GC-chromatogram of retentate gas through XSBR coated PVC-PEG hollow fiber membrane tested at 1-2.5 bar 25 ºC (a) calibration gas composition (b) permeate gas at 2 bar and (c) permeate gas at 2.5 bar

VITAE

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Educational Attainment

Degree	Name of Institution	Year of Graduation
B.Sc.	Prince of Songkla University (Hatyai)	2000
M. Sci.	Prince of Songkla University (Hatyai)	2007

List of Publications

Lamlong, C., Taweepreda, W., Nu-Mard, R., Songsiriritthigul, P., 2015. Investigation of Sulfur Crosslinking Interfacial of Natural Rubber Blending with Carboxylated Styrene Butadiene Rubber Using X-Ray Absorption Spectroscopy, Advanced Materials Research. 1087, 131-136. (SCOPUS).

List of Proceedings

Lumlong, C.; Taweepreda, W. 2014. Gas Permeability of Rubber Coated PVC-PEG Membrane, International Engineering for Sustainability Conference (iNESCO), 18th - 20th April, Penang, Malaysia.

Lamlong, C., Taweepreda, W., 2015. Fabrication and Characterization of PVC-PEG Hollow Fiber Membrane, The 5th International Conference on Thai Institute of Chemical Engineering and Applied Chemistry Conference (ITIChE2015), 8th - 10th November, Pattaya, THAILAND.