**Journal of Engg. Research Vol. 8 No. (3) September 2020 pp. 17-30**

# تحسين أداء سيليكا البولي إيثر سلفون النانونية الهجين لفصل غازات ثاني أكسيد الكربون والميثان بواسطة الأشعة فوق البنفسجية المدمجة والتلدين الحراري

***،***توتوك دي كوسورو ، *أندري سي كومورو، *بوديونو، **قدراتون، *باستيان ويدودو، *بلال برابوو و*داني أوتومو**

*قسم الهندسة الكيميائية، كلية الهندسة، جامعة ديبونجورو، إندونيسيا
**مركز إندونيسيا للنانو، جنوب تانجيرانج، إندونيسيا
***مركز أبحاث الأغشية، جامعة ديبونجورو، إندونيسيا

## الخلاصة

يعتبر أداء غشاء البولي إيثر سلفون البكر منخفض نسبياً بشكل أساسي نحو النفاذية الانتقائية لغازات ثاني أكسيد الكربون والميثان. تم دراسة دمج مختلف الجسيمات النانوية غير العضوية لتعزيز النفاذية الانتقائية للغشاء. ولسوء الحظ، فإن وجود الأنواع غير العضوية في مصفوفة البوليمر غالباً ما تشكل فراغات أقل انتقائية نتيجة لانخفاض التجانس بين الجسيمات النانوية والغشاء. في هذه الدراسة، تم إجراء تعديل على سطح الغشاء باستخدام الأشعة فوق البنفسجية والتلدين الحراري لتحسين النفاذية الانتقائية للغشاء النانوي الهجين من البولي إيثر سلفون لفصل غازات ثاني أكسيد الكربون والميثان. تم تصنيع أغشية نانوية هجينة من بولي إيثر سلفون-ثاني أكسيد السليكون عن طريق فصل الطور المُحدث باستخدام اللامذيبات وتم تعديلها لاحقاً باستخدام الأشعة فوق البنفسجية وطرق التلدين الحراري. أظهرت النتائج التجريبية أن تعرض غشاء البولي إيثر سلفون البكر للأشعة فوق البنفسجية لمدة 10 دقائق يعزز انتقائية الغشاء من 1.25 إلى 3.75 بسبب تكوين الجذور الحرة في العديد من مواقع سطح الغشاء. بينما التعرض للأشعة لوقت أطول يؤدي إلى تقليل انتقائية الغشاء إلى 1.08 بسبب تفكك البوليمر بواسطة الجذور الحرة. أظهر اندماج الأشعة فوق البنفسجية المدمجة وثاني أكسيد السليكون مع الغشاء تأثيراً تآزرياً حيث تحسنت نفاذية غازات ثاني أكسيد الكربون والميثان من 70.69 إلى 9425.84 ومن 40.40 إلى 706.94 على التوالي في حين زادت الانتقائية من 1.75 إلى 13.33. أظهرت الأغشية النانوية الهجينة أفضل أداء انتقائي في النفاذية عندما تعرضت للأشعة فوق البنفسجية لمدة 15 دقيقة وتم تلدينها حرارياً عند 180 درجة مئوية لمدة 20 ثانية لتحقيق انتقائية تعادل 33.33. كشفت هذه الدراسة أن التعرض للأشعة فوق البنفسجية والتلدين الحراري كانا قادرين على زيادة تعلق الجسيمات النانوية لثاني أكسيد السيلكون، والتي أدت في النهاية إلى زيادة أداء الانتقائية لفصل غازات ثاني أكسيد الكربون والميثان.

# Enhancement of nanohybrid PES-nanosilica performance for CO2/CH4 separation through combined UV irradiation and thermal annealing treatments

Tutuk D. Kusworo*,***,****, Andri C. Kumoro*, Budiyono*, Qudratun**, Bastian Widodo*, Bilal T. Prabowo* and Dani P. Utomo*

*Department of Chemical Engineering, Faculty of Engineering, Universitas Diponegoro, Jl. Prof. Soedarto, Tembalang, Semarang, 50275, Indonesia
**Nano Center Indonesia, South Tangerang, Indonesia. Jl. Raya Serpong KO. Batan Lama No. A-12 RT 010/006, Setu, Serpong South Tangerang, 15310, Indonesia
***Membrane Excellent Research, Membrane Research Center (MeR-C), Universitas Diponegoro, Jl. Prof. Soedarto, Tembalang, Semarang, 50275, Indonesia
****Corresponding Author: tdkusworo@che.undip.ac.id

***Submitted:*** 08/11/2017
***Revised:*** 07/02/2020
***Accepted:*** 07/04/2020

## ABSTRACT

Basically, the pristine polyethersulfone membrane has a relatively low performance for selective permeation of $CO_2/CH_4$ gasses. The incorporation of various inorganic nanoparticles has been studied to enhance the permselectivity of the membrane. Unfortunately, the existence of inorganic species in the polymer matrix often forms less selective voids as a result of low affinity between nanoparticles and the membrane. In this study, membrane surface modification comprising of UV irradiation and thermal annealing was performed to improve the permselectivity of nanohybrid polyethersulfone membrane for $CO_2/CH_4$ separation. The polyethersulfone-$SiO_2$ nanohybrid membranes were fabricated via a nonsolvent induced phase separation (NIPS) method and subsequently modified using UV light irradiation and thermal annealing treatments. The experimental results showed that 10 min UV irradiation on pristine polyethersulfone membrane enhances membrane's selectivity from 1.25 to 3.75 due to the formation of free radicals in numerous sites of the membrane surface. However, a longer irradiation time leads to the reduction of membrane's selectivity to 1.08 due to polymer degradation by the free radicals. The combined UV irradiation and $SiO_2$ incorporation to the membrane exhibited a synergistic effect where the permeability of $CO_2$ and $CH_4$ improved from 70.69 to 9425.84 and from 40.40 to 706.94 GPU, respectively, whilst the selectivity increased from 1.75 to 13.33. The nanohybrid membranes showed the best permselectivity performance when they are UV irradiated for 15 min and thermally annealed at 180°C for 20 s to achieve 33.33 of selectivity. This study revealed that UV irradiation and thermal annealing were able to increase the attachment of the $SiO_2$ nanoparticles, which finally increase the permselectivity performance for $CO_2/CH_4$ separation.

**Keywords:** Gas separation**;** Nanohybrid; Polyethersulfone; Silica dioxide nanoparticles; Thermal annealing; UV irradiation.

## INTRODUCTION

Energy supply has been one of the world's most serious problems for decades. This is due to the fact that the sustainability of fossil energy is getting limited. Oil and gas had been reported to supply 51.66% of the world's electrical power demand in 2009. Therefore, efforts on searching for alternative energies as fossil energy substitutes are becoming more challenging for future energy developments.

Biomethane, which can be obtained from the purification of biogas, is an essential substitute for natural gas (Scholz *et al*., 2015). Unfortunately, the presence of $CO_2$ in biogas causes a serious reduction of its calorific value. In addition, the coexistence of moisture and $CO_2$ in biogas has been reported to reduce the durability of biogas facilities due to improved biogas corrosivity and acidity (Li *et al*., 2004). Absorption of $CO_2$ using amine solution has been one of the most recommended methods to upgrade biogas to biomethane, yet it possesses a complicated process and requires large financial investment (Li *et al*., 2005). The most promising alternative is the separation of $CO_2$ from biogas using membrane separation system.

Zhang *et al*. (2013) observed that one of the common membranes used to upgrade biogas to biomethane is Polyethersulfone (PES). Usually, PES is used as a dense membrane, and therefore a number of research groups suggested modifications to enhance its gas separation performance (Ismail and Kusworo, 2007; Ismail *et al*., 2008; Kapantaidakis *et al*., 2002; and Li *et al*., 2002; Wang *et al*., 2010). PES modification can be done by ultraviolet (UV) irradiation. According to Kwisnek and his co-workers (2011), membrane modifications via UV irradiation offer some advantages; that is, the technology is already well known, has rapid processing, is eco-friendly, and has high energy efficiency. UV irradiation can play two important roles on membrane matrices, i.e., UV-grafting and UV-induced modification using nanoparticle (Mohammad *et al*., 2013). Besides UV irradiation, membrane modification can also be done by adding nanoparticles to the membrane solution to form nanohybrid membranes. According to Ayral *et al*. (2008), the addition of nanosilica will alter the gas transfer mechanism to the molecular diffusion mechanism where the gas molecules enter the solubility site, followed by diffusion through the membrane using concentration gradient as the driving force. These phenomena will lead to enhance the membrane's gas separation performance. Moreover, the incorporation of nanosilica into PES matrix material may increase the membrane's mechanical strength as previously observed by Sharif *et al*. (2012). They found that the presence of nanosilica strengthens the adhesion between the dense top layer and the PES matrix. Surprisingly, nanosilica particles also improve the tensile strength and ultimate elongation of the PES membrane by 2.3 and 5 times, respectively.

Thermal annealing is one of the physical modification techniques that increases the selectivity of the membrane to even higher values. Dong *et al*. (2011) reported that thermal annealing on the polyimide membrane might increase membrane selectivity by 15%. Later, Swaidan *et al*. (2015) also investigated the thermal annealing on the polyimide membrane for propylene/propane gas separation. They revealed that 250°C thermal annealing resulted in a selectivity performance of the polyimide membrane for propylene/propane separation up to 30. Previous studies combined thermal annealing and UV irradiation on both neat PES and PES nanohybrid membranes. This combined treatment has been proven to successfully enhanced the performance of PES membranes for produced water treatment (Kusworo *et al*., 2017a, 2017b). As far as the search of literature has been conducted, no research on the synergistic of thermal annealing and UV irradiation on the PES-nanosilica membrane for gas separation has been reported. Therefore, the objective of the current study is to investigate the influence of UV irradiation and UV irradiation time span on neat PES membrane and nanohybrid membrane PES-nanosilica and the synergistic of UV irradiation and thermal annealing with the variation of thermal annealing duration on nanohybrid membrane gas separation performance. Furthermore, the membrane morphology and gas separation performance of the prepared membranes in the views of their selectivity for $CO_2$ over $CH_4$ were also examined in this study.

## MATERIALS AND METHODS

### Materials

Polyethersulfone (PES) Veradel® PESU 3100P as membrane material was supplied by Solvay Advanced Material (USA). N-Methyl-2-pyrrolidinone (NMP) from Merck was selected as solvent with regard to its low toxicity, while the distilled water was employed as antisolvent in the coagulation process. Ultra-high purity grade of $CO_2$ and 99% of $CH_4$ gas were purchased from PT. Aneka Gas Industri, Indonesia.

**Fabrication of PES membrane and nanohybrid PES-nanosilica membrane**

The pristine PES membrane and nanohybrid PES membranes were prepared following the nonsolvent induced phase separation (NIPS) method. The membrane was prepared by making 25% solid and 75% NMP solution. The solid consists of pure PES or a mixture of PES and 0.5% nanosilica. The solution was stirred for 4 hours and then left for 24 hours to accommodate the trapped air in the bubble completely leaving the solution (Zou *et al*., 2008). The solution was then molded on a flat glass plate using casting knife and immersed in distilled water at ambient temperature (30±2°C) for 24 hours to remove the remaining solvent (Pakizeh *et al*., 2013). The same procedure was carried out for the UV irradiated membrane for 5, 10, and 15 minutes. The irradiation was conducted before immersion of the membrane in distilled water. The membrane was then slowly evaporated at ambient room temperature for 24 hours and further annealed at 180°C for 5, 10, and 20 seconds in an electric oven.

**Membrane Morphology Characterization**

Field emission scanning electron microscopy (FESEM) was employed to observe the membrane's fibers dimension. Prior to image analysis, the membrane samples were cracked in liquid nitrogen. The membranes were strapped on an aluminum disk using a double surface tape, followed by placing and evacuating the sample holder in a sputter-coater with gold.

**Fourier Transform Infrared (FTIR) Analysis**

The purpose of FTIR characterization is to determine the existence of the membrane's functional groups. If infrared radiation frequency is similar to the sample's molecule specific vibration, then the molecule will absorb the radiation (Vinodhini *et al*., 2017). This radiation will pass through the detected sample, and the spectra will show infrared radiation difference as a function of frequency. The position of infrared absorption bands was presented as a wavenumber that is proportional to their frequency. Absorption intensity bands depend on the molecule's dipole moment difference. Upon FTIR examination, all of the functional groups exist in the PES, and the nanosilica contained in the membrane can be discovered.

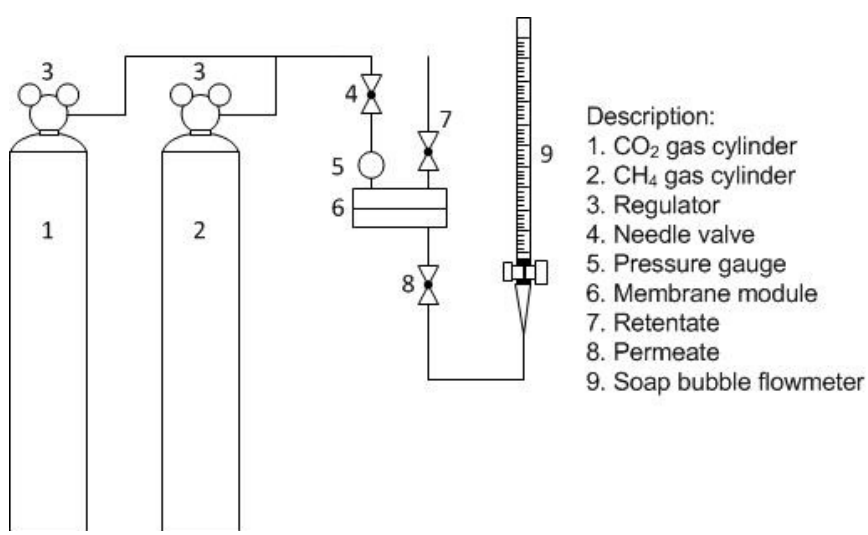


**Figure 1.** Gas separation equipment instrumentation.

**Gas separation test**

The gas permeation properties of the flat nanohybrid membrane and pure polymer film were measured by the variable volume method, using an upstream pressure of 2 bar-g, while the downstream pressure was kept atmospheric. The high-pressure gas adjusted by a line regulator was introduced into the test cell. Permeation experiments were carried out at ambient condition using experimental rig as depicted in **Figure 1.** The permeance (P/L) and selectivity (α) can be expressed as equations (1) and (2), respectively (Ismail *et al*. 2015):

$$\frac{P}{L} = \frac{Q_i}{(\Delta P)(\pi r^2)} \quad (1)$$

where $Q_i$ is the volumetric flow rate of gas '*i*' at standard temperature and pressure, $\Delta P$ is the trans-membrane pressure drop (cmHg), and $r$ = flat sheet membrane radius (cm). The permeance is described in gas permeation units, GPU, (1GPU = $1 \times 10^{-6}$ $cm^3$ (STP) $cm^{-3}$ $s^{-1}$ $cmHg^{-1}$). The ideal separation factor (gas A over gas B) of the membrane was calculated by

$$\alpha = \frac{(P/L)A}{(P/L)B} \quad (2)$$

## RESULTS AND DISCUSSION

**The Effect of UV irradiation on the pristine PES membrane performance for $CO_2/CH_4$ separation**

Pure $CO_2$ and $CH_4$ gasses permeability isotherms for pristine PES membrane and UV irradiated membrane at various exposure time and their selectivity are presented in **Table 1**. As seen in **Table 1**, the pure gas permeability of $CO_2$ and $CH_4$ is 70.69 and 56.56 GPU, respectively, with a selectivity of 1.25 being observed. This low selectivity is more likely due to the close kinetic diameter between $CO_2$ and $CH_4$. The kinetic diameter of $CO_2$ and $CH_4$ is 3.30 and 3.80 Å (Kentish *et al*., 2008), respectively, while the quadrupole moments are $3.14 \times 10^{21}$ and $0 \times 10^{21}$ $C.m^2$ (Bae and Lee, 2005), respectively. Based on their physical properties, the $CO_2/CH_4$ separation over pristine PES membrane is probably via the solution-diffusion mechanism rather than a size-exclusion mechanism. The selectivity of pure PES membrane obtained from this study is in accordance with previous work where the average $CO_2/CH_4$ selectivity using PES membrane was in range between 1.08 and 1.60 at 2 bar transmembrane pressure (Nasir *et al*., 2014), while, by the modification using MDEA, the selectivity was enhanced up to 8.33 (Nasir *et al*., 2014, and Suleman *et al*., 2016).

The UV irradiation was targeted to enhance affinity of the PES membrane's surface to the $CO_2$ molecule, so that its permeability can be increased. UV irradiation on PES membranes increased the $CO_2$ permeability as well as the selectivity at 5- and 10-minute exposure times. $CO_2$ permeability and selectivity increase from 70.69 GPU to 83.17 GPU and from 1.25 to 2.94, respectively, as the PES membrane was UV irradiated for 5 minutes. Konruang *et al*. (2015) also found that UV irradiation on the PES membrane enhances the hydrophilicity of the membrane surface through the formation of free radical sites and hydrophilic functional groups. As proposed earlier, the $CO_2$ permeability through the PES membrane enhanced due to its higher quadrupole moment than that of $CH_4$.

**Table 1.** UV light effect on PES performance in $CO_2$ gas separation from $CH_4$.

| Treatment | Permeability (GPU) | | Selectivity |
|---|---|---|---|
| | $CO_2$ | $CH_4$ | $CO_2/CH_4$ |
| Pure PES | 70.69 | 56.56 | 1.25 |
| PES + 5 min. UV irradiation | 83.17 | 28.28 | 2.94 |
| PES + 10 min. UV irradiation | 353.47 | 94.26 | 3.75 |
| PES + 15 min. UV irradiation | 3534.69 | 3262.79 | 1.08 |

***)** GPU = *Gas Permeation Unit* = 1 x $10^{-6}$ $cm^3$ (STP)/$cm^2$ s cmHg

Both $CO_2$ and $CH_4$ permeability and selectivity are affected by the exposure length of PES membrane to UV irradiation. The selectivity of the nanohybrid PES membrane with 5, 10, and 15 minutes of UV irradiation for $CO_2$/$CH_4$ separation was 2.94, 3.75, and 1.08, respectively. The formation of free radicals and hydrophilic functional groups on the membrane surface as the effect of UV exposure occurred in the first 5 minutes. Therefore, $CO_2$ permeance increases, while $CH_4$ permeance decreases due to differences in quadrupole moment. Long exposure of UV irradiation to PES membrane (15 minutes) resulted in further increase of membrane's permeability for both $CO_2$ and $CH_4$ but with low selectivity. It is presumed that the formed free radicals and carbocation as the effect of high energy beam carried by photon initiate the photodegradation of the PES polymer that led to the formation of an unselective void in the membrane (Yousif and Haddad, 2013). According to Adib *et al*. (2015), high permeability and low selectivity may be caused by the unselective void in the membrane, which drives the molecule transport mechanism to Knudsen diffusion. This unselective void in the membrane can be indicated by the permeation test, where the permeabilities of $CO_2$ and $CH_4$ are close to each other. Actually, the desirable mechanism in this gas separation of $CO_2$ from $CH_4$ is molecular sieving or solution-diffusion with high permeability of $CO_2$ and low permeability of $CH_4$.

**The Effect of nanosilica incorporation followed with UV irradiation on the membrane's performance**

The incorporation of nanomaterial in membrane preparation is expected to provide the sieving separation mechanism as well as to improve membrane structural properties. Li . (2007) and Ahn *et al*. (2008) found that mixed matrix membrane or nanohybrid membrane exhibits a better selectivity in gas separation than pure one. However, the nanohybrid membrane reduces the gas permeability because the presence of membrane filler (silica or zeolite) increases the membrane resistance.

This research compares the performance of the nanohybrid membrane and pure membrane for $CO_2/CH_4$ gas separation. **Table 2** presents higher selectivity of nanohybrid membrane with silica than pure membrane. A denser membrane leads to the reduction of $CH_4$ permeability, which promotes higher selectivity. **Table 2** also shows that the reduction of permeability agrees well with the Maxwell model. Maxwell model predicts that membrane with nonporous filler will make the membrane become denser by which it reduces the gas permeability (Ahn *et al*., 2008).

**Table 2**. Permselectivity of pristine PES, nanosilica embedded PES, and UV irradiated nanohybrid membranes.

| Treatment | Permeability (GPU) | | Selectivity |
|---|---|---|---|
| | $CO_2$ | $CH_4$ | $CO_2/CH_4$ |
| Pure PES | 70.69 | 56.56 | 1.25 |
| PES-nanosilica (0.5 wt-%) | 70.69 | 40.40 | 1.75 |
| PES-nanosilica + 5 min. UV irrad. | 282.78 | 235.65 | 1.2 |
| PES-nanosilica + 10 min. UV irrad. | 7069.38 | 706.94 | 10 |
| PES-nanosilica + 15 min. UV irrad. | 9425.84 | 706.94 | 13.33 |

***)** GPU = *Gas Permeation Unit* = 1 x $10^{-6}$ $cm^3$ (STP)/$cm^2$ s cmHg

Although inorganic filler can increase the membrane performance in gas separation, it also tends to reduce the selectivity as the result of unselective voids formed by the detachment of nanoparticle and polymer. UV irradiation for 15 min as posttreatment on the nanohybrid membrane increases the $CO_2$ permeability and $CO_2/CH_4$ selectivity by 13 and 10 times, respectively, more than those of the unmodified nanohybrid membrane. The permeability $CO_2$ increased from 70.69 GPU to 9425.84 GPU and hence it dramatically increased the selectivity from 1.75 to 13.33. These findings could be due to the increases of the attachment of $SiO_2$ nanoparticles into PES polymer caused by UV irradiation on the nanohybrid PES-nanosilica membrane. This result agrees with previous work performed by Zou and co-workers (2008) as they found that UV irradiation repaired the membrane structure mechanically and converted the agglomerate into the mixture.

UV irradiation onto nanohybrid PES-nanosilica membrane will convert the agglomerate of membrane and nanoparticle to form a homogenous mixture. The conversion is initiated by UV irradiation that modifies the membrane's surface structure. The addition of nanosilica without any posttreatment will worsen the performance of the membrane. This is because the particles bond is not strong enough and will create holes or unselective voids in the membrane (Zou *et al*., 2008). There will be also three possibilities on the effect in membrane's permeability by the addition of nanosilica membrane filler. The membrane filler acts as a trigger to molecular sieving mechanism; the membrane filler will disturb membrane's polymer structure and increase permeability; or the membrane filler will block membrane surface and reduce gas permeability (Powell and Qiao, 2006).

**Table 2** shows the effect of UV irradiation time span on membrane performances. As the UV irradiation time span increases, the permeability and selectivity of the membrane in gas separation also increase. The longer UV irradiation on membrane structure induces surface modification that creates a mixture of the nanohybrid membrane. The previous study was conducted by Konruang *et al*. (2015) about the modification of polysulfone membrane using UV irradiation; they explained that the UV irradiation on membrane material increased the hydrophilic property of the polymer. The increase of polymer hydrophilicity may improve the adhesion between polymer and nanoparticles; this would remove the unselective voids and it leads the attachment of the $SiO_2$ nanoparticles selectivity enhancement.

### The Effect of Thermal Annealing on PES Membrane Performance for $CO_2/CH_4$ Separation

Thermal annealing is one of the physical modification techniques to increase membrane resistant to plasticization and increase membrane selectivity to separate $CO_2$ and $CH_4$. Dong *et al.* (2011) showed that thermal annealing can prevent membrane plasticization and increase selectivity. Furthermore, Dong *et al*. (2011) also explained that thermal annealing can form a denser layer in a mixed matrix membrane to increase gas separation performance.

**Table 3** shows that thermal annealing on PES and nanosilica nanohybrid membrane increased the permeability and selectivity of $CO_2/CH_4$. The membrane's selectivity increased from 1.75 to 3 after thermal annealing treatment. The membrane's permeability also increased from 70.69 to 353.47 GPU and from 40.40 to 117.82 GPU for $CO_2$ and $CH_4$, respectively. Ansaloni *et al*. (2015) and Kusworo *et al*. (2013) reviewed that thermal annealing on membrane reduced gas permeability, which leads to plasticization suppression. Plasticization is a condition where the membrane loses its elasticity forming a plastic-like material, which is why the selectivity of the membrane decreases significantly. According to Kusworo *et al*. (2013), thermal annealing reduces membrane segmental mobility in the nanohybrid membrane and makes a denser membrane that affects the decreasing permeability. The denser membrane will stimulate the solution-diffusion mechanism and increase selectivity. This study also confirms the previous study carried out by Zhuang *et al*. (2915). They performed the thermal treatment on the PES membrane at above $T_g$ (glass transition temperature) and found that the thermal treatment caused the polymer to recrystallize, and the membrane gas separation performance enhancement was observed including selectivity, stability, and plasticization resistance.

**Table 3**. Thermal annealing effect on PES performance in $CO_2$ gas separation from $CH_4$.

| Treatment | Permeability (GPU) | | Selectivity |
|---|---|---|---|
| | $CO_2$ | $CH_4$ | $CO_2/CH_4$ |
| PES-nanosilica | 70.69 | 40.40 | 1.75 |
| PES-nanosilica + Thermal annealing | 353.47 | 117.82 | 3 |
| PES-nanosilica + UV irradiation | 9425.84 | 706.94 | 13.33 |
| PES-nanosilica + UV irradiation 10 min -Thermal annealing 180°C for 15 seconds | 8836.73 | 353.47 | 25 |

***)** GPU = *Gas Permeation Unit* = 1 x $10^{-6}$ $cm^3$ (STP)/$cm^2$ s cmHg

**The $CO_2/CH_4$ permselectivity of thermal annealed PES membrane at prolonged annealing time**

As mentioned in the previous discussion, thermal annealing improves the antiplasticization behavior of the PES membrane. The evaluation of the effect of thermal annealing on the membrane performance at various annealing time is presented in **Table 4**. Membrane selectivity increased from 7.5 to 25 for the prolonged thermal annealing from 5 to 10 seconds and stabilized on 33.33 for 20-second thermal treatment. **Table 4** also shows that $CO_2$ and $CH_4$ permeability were increasing with the increase in the thermal annealing time span.

However, **Table 4** shows that the longer time of thermal annealing treatment gave higher $CO_2$ permeability. It shows that plasticization was still happening; plasticization would reduce membrane durability. Plasticization is a condition where the membrane loses its plasticity and loses its selectivity performance. Although Dong *et al*. (2011), Ansaloni *et al*. (2015), and Kusworo *et al*. (2013) mentioned that thermal annealing can reduce $CO_2$ permeability because thermal annealing increases membrane density and immobilized membrane matrix movement, the densification of the membrane skin layer also has been revealed by Azhari *et al*. (2016) where the progressive heating on PES membrane suppressed $CO_2$ induced plasticization and the selectivity of $CO_2/CH_4$ separation increased. The high selectivity caused by the enhancement of diffusivity can be a result of the generation of inner-chain charge transfer-complexes and the relatively high selectivity was preserved due to the enhancement of plasticization resistance after being thermally annealed. According to Dong *et al.* (2011), thermal annealing can increase mixed matrix membrane density that finally increases the membrane performance. Density will increase with the increase of thermal annealing time span. Kusworo *et al.* (2017a) reported that the increase of the thermal annealing time span would increase the membrane density, which leads to improve membrane performance for gas separation.

**Table 4**. Permselectivity performance of the thermal annealed nanohybrid PES membrane at various annealing time.

| Treatment | Permeability (GPU) | | Selectivity |
|---|---|---|---|
| | $CO_2$ | $CH_4$ | $CO_2/CH_4$ |
| PES + nanosilica 0.5 wt-% + 15 minutes UV irradiation + thermal annealing T= 180$^{O}$C, 5 seconds | 3534.69 | 471.29 | 7.5 |
| PES + nanosilica 0.5% + 15 minutes UV irradiation + thermal annealing T= 180$^{O}$C, 10 seconds | 8836.73 | 353.47 | 25 |
| PES + nanosilica 0.5% + 15 minutes UV irradiation + thermal annealing T= 180$^{O}$C, 20 seconds | 11782.31 | 353.47 | 33.33 |

***)** GPU = *Gas Permeation Unit* = 1 x $10^{-6}$ $cm^3$ (STP)/$cm^2$ s cmHg

**Fabricated Membrane Characterization**

Membrane characterization was performed by the SEM surface morphology and FTIR tests. SEM surface morphology test is a tool to determine membrane surface condition, while the FTIR test is a tool to determine the functional group in the membrane. Pabby *et al*. (2009) suggested that membrane surface condition determines the gas separation mechanism; therefore membrane characterization must be done as can be seen from **Figure 2** and **Figure 3**.

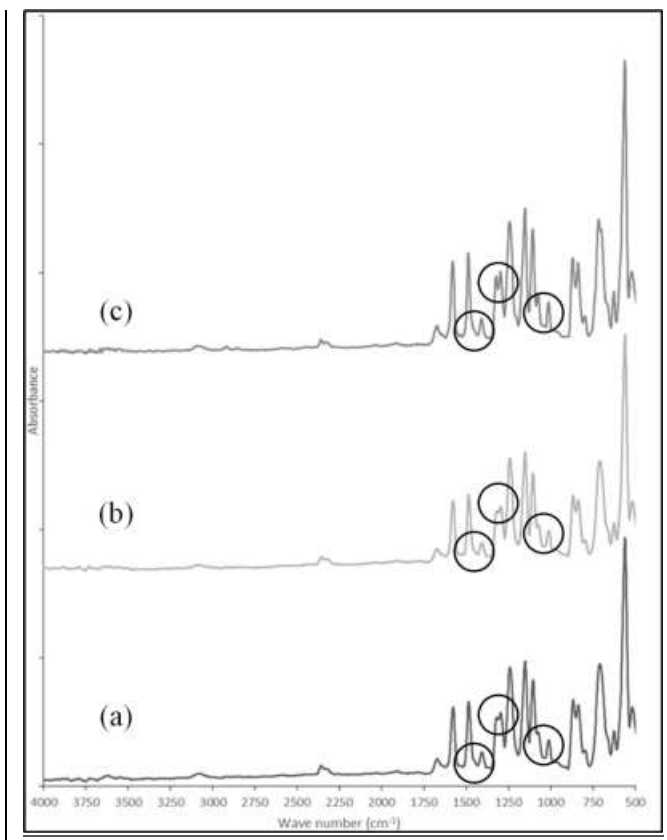


**Figure 2.** FTIR spectra for the (a) PES + nanosilica 0.5%; (b) PES + nanosilica 0.5% with 15 minutes UV irradiation; and (c) PES + nanosilica 0.5% with 15-minute UV irradiation +thermal annealing.

**Fig. 2 (a)-(c)** show PES-nanosilica nanohybrid membrane's FTIR functional group analysis. The FTIR spectra of untreated PES-nanosilica nanohybrid membrane, PES-nanosilica nanohybrid membrane with 15-minute UV irradiation treatment, and PES-nanosilica symmetric nanohybrid membrane with a combined 15-minute UV irradiation and 10-second thermal annealing at 180$^{O}$C treatments were depicted in **Fig. 2 (a), (b),** and **(c),** respectively. PES membrane was characterized with an absorbance peak at wave numbers 1578 and 1486 $cm^{-1}$ in **Figure 2,** which refers to the aromatic group, while nanosilica was characterized with an absorbance peak at wave numbers 1105 and 1075 $cm^{-1}$ in the membrane, which refer to Si-O-C group that was cited from Stuart (2004). Zhang *et al*. (2013) also reported a similar result of nanosilica absorbance peak, which is at wave number 1103 $cm^{-1}$.

**Fig. 2 (a)** and **(b)** show no differences in membrane absorbance peak. From **Fig. 2 (a)** and **(b)** it can be concluded that ultraviolet irradiation treatment did not affect the chemical bonding on membrane between PES and nanosilica. Ultraviolet irradiation only modified membrane-active site or top surface where the separation process occurred (Chung *et al*. 2007). With ultraviolet irradiation treatment, nanosilica on membrane surface will disperse and reduce agglomeration as in **Fig. 3 (b)**.

**Fig. 2 (c)** showed absorbance peak difference at various wavenumber; those are 1075, 1296, 1321, and 1425 $cm^{-1}$. There is absorbance peak increasing from 0.2 to 0.3 at wavenumber 1075 $cm^{-1}$, where Si-O-C and C-O bonds are detected. This phenomenon showed that thermal annealing would increase nanosilica and polymer bond density. Denser polymer bond was caused by condensation reaction between membrane and nanosilica. Absorbance at wavenumbers 1296 and 1321 $cm^{-1}$ also increases from 0.3 to 0.4 after thermal annealing treatment, which shows the increasing density of the C-O ether group and sulfone group, respectively. There is increasing bond density of the C=C double bond in the polymer. With denser membrane after thermal annealing treatment would improve membrane gas separation performance (Süer *et al*. 1994).

**Fig. 3 (a), (b),** and **(c)** show the micrographs of the top layer of the PES-nanosilica nanohybrid membrane without treatment, with 15-minute UV irradiation treatment and combination of UV irradiation treatment with thermal annealing treatments, respectively. **Fig. 3 (a)** reveals a lot of white spots on the PES-nanosilica nanohybrid membrane surface, which are probably the agglomeration of nanosilica on the PES membrane. Nanosilica is a nonporous material that would block inlet gas flow in the membrane. Agglomeration of nanosilica on the PES membrane would decrease $CO_2$ gas permeability and decrease $CO_2/CH_4$ membrane selectivity and hence reduce membrane gas separation performance. **Fig. 3 (b)** discloses fewer white spots on PES-nanosilica nanohybrid membrane's surface. It is observed in **Fig. 3 (b)** that UV irradiation treatment disperses agglomeration of PES and nanosilica uniformly.

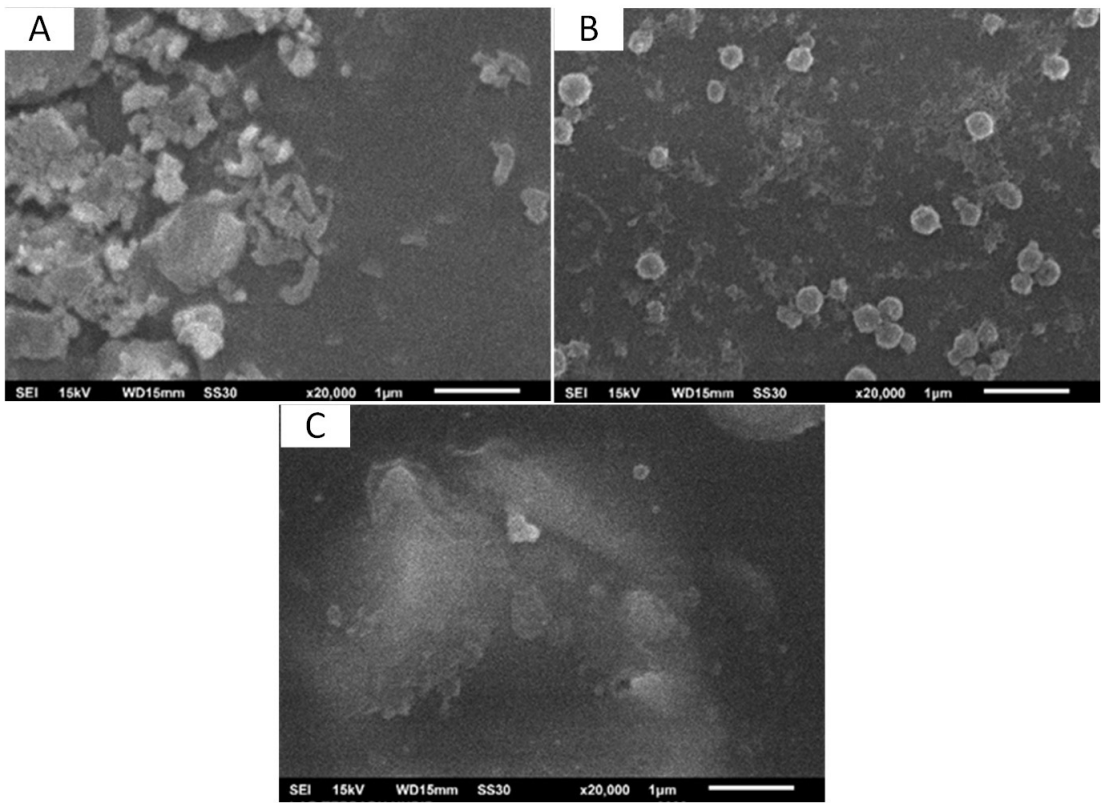


**Figure 3.** SEM images of nanohybrid membrane PES and nanosilica surface (a) without any treatment; (b) with 15-minute UV irradiation treatment; and (c) with 15 UV irradiation and 10-second thermal annealing at 180OC treatment

**Fig. 3 (b)** and **(c)** show the reduction of white spots on the membrane surface before and after thermal annealing treatment, respectively. White spots, which indicate the agglomeration of PES and nanosilica, in **Fig. 3 (c)** are more blur than those in **Fig. 3 (b)**. This fact suggests that thermal annealing would reduce the agglomerate formations on the membrane surface by initiating condensation reaction of PES and nanosilica.

Permselectivity performance in $CO_2/CH_4$ separation based on this study and previous studies is compared with the upper bound curve suggested by Robeson *et al*. (2008), as shown in **Fig. 4**. Robeson's upper bound is a curve that shows the trade-off limit between the selectivity and permeability. The permselectivity performance of the membrane should be high to reach the upper bound limit. Robeson and co-workers evaluated the upper bound relationship between permeability and selectivity. It has been well recognized that only a few polymeric membranes exceed the upper bound curve. In this study, only nanohybrid PES-nanosilica membrane with UV irradiation for 15 minutes followed with thermal annealing at 180°C for 20 second surpassed the Robeson's upper bound. All polymeric membrane materials that surpassed Robeson's upper bound are modified polymeric membranes. This result shows that the proposed treatments in this study successfully overcome the shortcoming of the nanoparticle incorporation into the polymer matrix. The modification also exhibited incredible improvement in $CO_2/CH_4$ permselectivity performance.

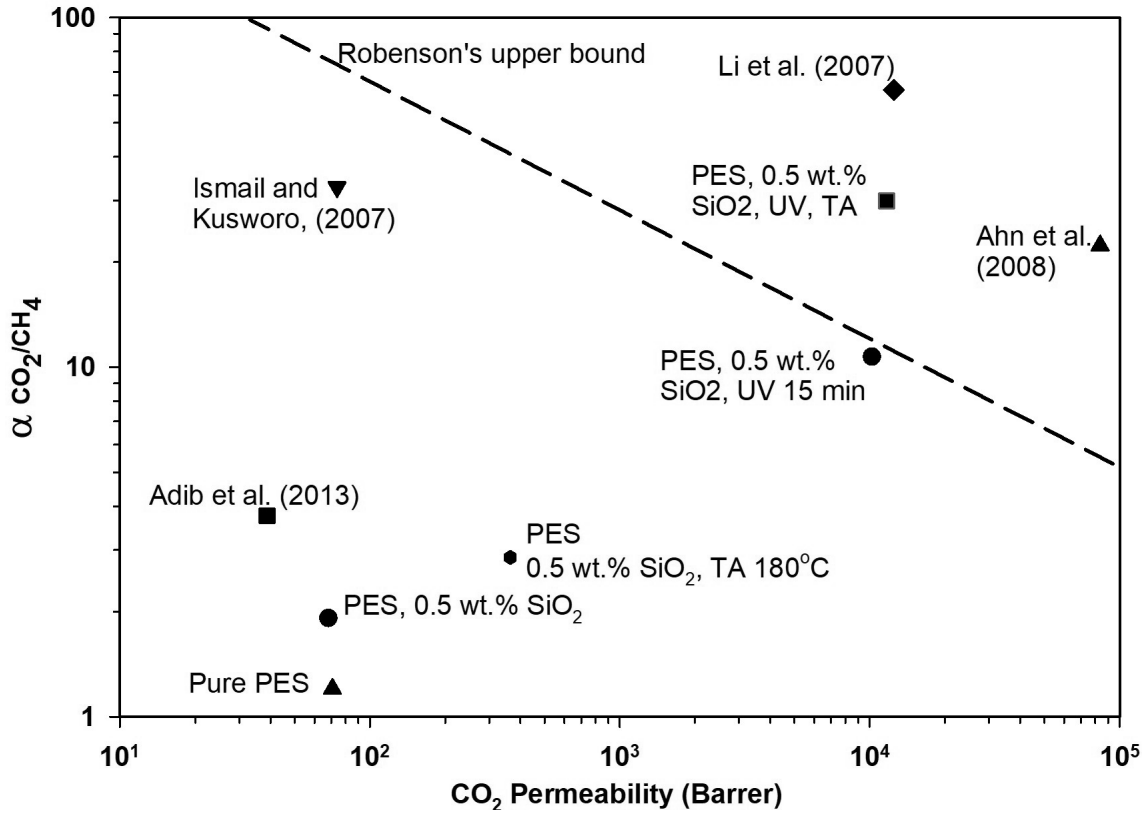


**Figure 4.** Comparison of $CO_2$ permeability and $CO_2/CH_4$ selectivity of PES-nanosilica nanohybrid membrane current research with other researches

## CONCLUSIONS

The modification of PES membrane through UV irradiation increases the permeability of $CO_2$ and selectivity due to the formation of free radicals and hydrophilic functional group on the membrane surface sites, in which both properties are strongly depending on irradiation time span. The addition of nanosilica filler in PES nanohybrid membrane promotes higher selectivity than that of pure PES membrane. The combination of UV irradiation and nanosilica also increases nanohybrid PES-nanosilica membrane gas separation performance in terms of high $CO_2$ permeability and selectivity. Thermal annealing treatment at 180°C for 20 seconds on UV irradiated PES-nanosilica nanohybrid membrane shows remarkable enhancement in permselectivity performance that surpasses Robeson's upper bound.

## ACKNOWLEDGMENT

The author would like to thank the management board and staff of Waste Treatment Laboratory of the Department of Chemical Engineering, Diponegoro University, and International Publication Research (RPI) Grant under Diponegoro University Non-Tax National Revenue 2017 for the supports and facilities during the research.

## REFERENCES

**Adib, H., Hassanajili, S., Mowla, D. & Emaeilzadeh, F.J., (2015).** Fabrication of integrally skinned asymmetric membranes based on nanocomposite polyethersulfone by supercritical CO2 for gas separation. Supercrit. Fluids. 97, 6-15.

**Ahn, J., Chung, W.J., Pinnau, I. & Guiver, M. D. (2008).** Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation. Journal of Membrane science, **314**(1), 123-133.

**Ansaloni, L., Minelli, M., Baschetti, M.G. & Sarti, G.C. (2015).** Effects of thermal treatment and physical aging on the gas transport properties in matrimid®. Oil & Gas Science and Technology–Revue d'IFP Energies nouvelles, **70**(2), 367-379.

**Ayral, A., Julbe, A., Rouessac, V., Roualdes, S. & Durand, J. (2008).** Microporous silica membrane: basic principles and recent advances. Membrane science and technology, 13, 33-79.

**Azhari, M.A., Nooririnah, O. & Ismail, A.F., (2016).** Effect of progressive heating on CO2/CH4 separation using assymetric hollow fiber polysulfone membrane. Journal of Engineering and Applied Science. 11, 1958-1961.

**Bae, Y.S. & Lee, C.H. (2005).** Sorption kinetics of eight gases on a carbon molecular sieve at elevated pressure. Carbon, **43**(1), 95-107.

**Chung, T.S., Jiang, L.Y., Li, Y. & Kulprathipanja, S., (2007).** Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. Progress Polymer Science, 32, 483-507.

**Dong, G., Li, H. & Chen, V., (2011).** Plasticization mechanisms and effects of thermal annealing of Matrimid hollow fiber membranes for $CO_2$ removal. Journal Membrane Science. 369, 206-220.

**Ismail, N.H., Salleh, W.N.W., Sazali, N. & Ismail, A.F. (2015).** The effect of polymer composition on CO2/CH4 separation of supported carbon membrane. Chemical Engineering, 45.

**Ismail, A.F., Kusworo, T.D. & Mustafa, A., (2008).** Enhanced gas permeation performance of polyethersulfone mixed matrix hollow fiber membranes using novel Dynasylan Ameo silane agent. Journal Membrane Science. 319, 306-312.

**Ismail, A.F. & Kusworo, T.D., (2007).** Fabrication and characterization of polyimide/polyethersulfone-fumed silica mixed matrix membrane for gas separation. Jurnal Reaktor. 11, 30-37.

**Kapantaidakis, G., Koops, G. & Wessling, M., (2002).** Preparation and characterization of gas separation hollow fiber membranes based on polyethersulfone-polyimide miscible blends. Desalination. 145, 353-357.

**Kentish, S.E., Scholes, C.A. & Stevens, G.W. (2008).** Carbon dioxide separation through polymeric membrane systems for flue gas applications. Recent Patents on Chemical Engineering, **1**(1), 52-66.

**Konruang, S., Sirijarukul, S., Wanichapichart, P., Yu, L. & Chittrakarn, T., (2015).** Ultraviolet-ray treatment of polysulfone membranes on the O2/N2 and CO2/CH4 separation performance. Journal Applied Polymer. Science. **132**(25): 1-8.

**Kusworo, T.D., Utomo, D.P. & Aryanti, N., (2017a).** Synergistic Effect of UV Irradiation and Thermal Annealing to Develop High Performance Polyethersulfone-nano Silica Membrane for Produced Water Treatment. Journal of Environment and Chemical Engineering. **5**(4): 3290-3301.

**Kusworo, T.D., Aryanti, N., Anggita, R.A., Setyorini, T.A.D. & Utomo, D.P. (2017b).** Surface Modification and Performance Enhancement of Polyethersulfone(PES) Membrane Using Combination of Ultra Violet Irradiation and Thermal Annealing for Produced Water Treatment. Journal of Environmental Science and Technology, 10: 35-43.

**Kusworo, T.D., Ismail, A.F., Mustafa, A. & Budiyono. (2013).** Studies of thermal annealing on suppression of plasticization of the asymmetric hollow fiber mixed matrix membranes. World Applied Science Journal. 28: 09-19.

**Kwisnek, L., Heinz, S., Wiggins, J.S. & Nazarenko, S., (2011).** Multifunctional thiols as additives in UV-cured PEG-diacrylate membranes for $CO_2$ separation. Journal Membrane Science. 369: 429-436.

**Li, Y., Chung, T.S. & Kulprathipanja, S., (2007).** Novel $Ag^+$-zeolite/polymer mixed matrix membranes with a high $CO_2/CH_4$ selectivity, America institute of chemical engineers journal. 53: 610-616.

**Li, S., Alvarado, G., Noble, R.D. & Falconer, J.L., (2005).** Effects of impurities on CO 2/CH 4 separations through SAPO-34 membranes. Journal Membrane. Science. 251: 59-66.

**Li, S., Falconer, J.L. & Noble, R.D., (2004).** SAPO-34 membranes for $CO_2/CH_4$ separation. Journal Membrane Science. 241: 121-135.

**Li, D.F., Chung, T.S., Wang, R. & Liu, Y., (2002).** Fabrication of fluoropolyimide / polyethersulfone (PES) dual-layer asymmetric hollow fiber membranes for gas separation. Journal Membrane Science. 198: 211-223.

**Mohammad, A.W., Ahmad, A. & Ng, L.Y., (2013).** Alteration of polyethersulphone membranes through UV-induced modification using various materials: A brief review, Arabian Journal of Chemistry. 10, Supplement 2, S1821-S1834.

**Nasir, R., Mukhtar, H. & Man, Z. (2014).** Fabrication, Characterization and Performance Study of N-methyl-diethanolamine. Journal of Applied Sciences, **14**(11): 1186-1191.

**Pabby, A.K., Risvi, S.S.H. & Sastre, A.M., (2009).** Handbook of membrane separations: Chemical, pharmaceutical, food, and biotechnological applications, Taylor and Francis Group, New York.

**Pakizeh, M., Mansoori, S.A.A., Chenar, M.P. Namvar-Mahboub & M., Braz., (2013).** Modification of PSf membrane nanostructure using different fabrication parameters and investigation of the CO2 separation properties of PDMS-coated PSf composite membranes. Journal of Chemical Engineering. 30: 345-354.

**Powell, C.E. & Qiao, G.G. (2006).** Polymeric $CO_2/N_2$ gas separation membranes for the capture of carbon dioxide from power plant flue gases. Journal Membrane Science. 279: 1-49.

**Robeson, L.M. (2008).** The upper bound revisited. Journal of membrane science, 320(1-2): 390-400.

**Scholz, M., Alders, M., Lohaus, T. & Wessling, M., (2015).** Structural optimization of membrane-based biogas upgrading processes. Journal Membrane Science. 474:1-10.

**Sharif, A., Koolivand, H., Khanbabaie, G., Hemmati, M., Aalaie, J., Kashani, M.R. & Gheshlaghi, A., (2012).** Improvement of $CO_2/CH_4$ separation characteristics of polyethersulfone by modifying with polydimethylsiloxane and nano-silica, Journal of Polymer Research, **19**(7): 9916.

**Suleman, M.S., Lau, K.K. & Yeong, Y.F., (2016).** Plasticization and Swelling in Polymeric Membranes in CO2 Removal from Natural Gas. Chemical Engineering Technology. 39: 1-14.

**Süer, M.G., Baç, N. & Yilmaz, L., (1994).** Gas permeation characteristics of polymer-zeolite mixed matrix membranes. Journal Membrane Science. 91: 77-86.

**Stuart, B. (2004).** Infrared Spectroscopy: Fundamentals and Applications, John Wiley & Sons. Ltd, Chicester.

**Swaidan, R.J., Ma, X., Litwiller, E. & Pinnau, I., (2015).** Enhanced propylene/propane separation by thermal annealing of an intrinsically microporous hydroxyl-functionalized polyimide membrane. Journal Membrane Science. 495: 235-241.

**Vinodhini, P.A., Sangeetha, K., Gomathi, T., Sudha, P.N., Venkatesan, J. & Sukumaran, A., (2017).** FTIR, XRD and DSC studies of nanochitosan, cellulose acetate and polyethylene glycol blend ultrafiltration membranes. International Journal of Biological and Macromolecul. In Press (2017).

**Wang, D., Li, K. & Teo, W., (2000).** Highly permeable polyethersulfone hollow fiber gas separation membranes prepared using water as non-solvent additive. Journal Membrane Science. 176: 147-158.

**Yousif, E. & Haddad, R., (2013).** Photodegradation and photostabilization of polymers, especially polystyrene. SpringerPlus, 2: p.398.

**Zhang, Y., Sunarso, J., Liu, S. & Wang, R., (2013).** Current status and development of membranes for CO2/CH4 separation: a review. International Journal of Greenhouse Gas Control. 12: 84-107.

**Zhuang, G.L., Wey, M.Y. & Tseng, H.H., (2015).** The density and crystallinity properties of PPO-silica mixed-matrix membranes produced via the in situ sol-gel method for H2/CO2 separation. II: effect of thermal annealing treatment, Chem. Eng. Res. Desalination. 104: 319-332.

**Zou, H., Wu, S. & Shen, J., (2008).** Polymer/Silica Nanocomposites: Preparation, Characterization, Properties, and Applications, Chem. Rev. (Washington, DC, U.S.), **108**(9): 3893-3957.