



Laporan Akhir Projek Penyelidikan Jangka Pendek

**A Fundamental Study on The Transfer of
CO₂ Via Mixed Matrix Membrane
Incorporated With Sapo Zeolite**

**By
Dr. Leo Choe Peng
Prof. Abdul Latif Ahmad**

2014

E. ABSTRACT OF RESEARCH

(An abstract of between 100 and 200 words must be prepared in **Bahasa Malaysia and in English**. This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Abstrak Penyelidikan

(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris**.)

Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

The removal of CO₂ from biogas is of great interest as the purified gas, biomethane contains higher calorific value than the biogas. However, the trade-off limitation in between the selectivity and permeability hinders the applicability of polymeric membranes in biogas purification. Blending small pore zeolite into polymeric matrix resulted mixed matrix membranes which can offer dramatic improvement in both selectivity and permeability. In this study, polysulfone mixed matrix membranes incorporated with SAPO zeolite were engineered for CO₂ separation at low pressure. The zeolite was further modified to improve its compatibility in polysulfone and performance in wet biogas. The effects of zeolite loading and modification on the membranes characteristic were studied using SEM, FTIR, EDX and water contact angle. The gas transport properties of the membranes were investigated using gas permeation tests with moisture. The fabricated membrane, PSf/SAPO-34 showed superior performance to other membranes reported in literatures. The advancement in this research was reported in 17 publications in journals and proceedings. The research also contributed significantly in the human capital development (1 Ph.D. student in thesis writing, 1 master student graduated, 1 master student submitted thesis and 4 undergraduate students graduated). Networking with Sime Darby and Petronas Research Sdn. Bhd. were initiated and 1 Science Fund was successfully acquired and completed.

Pemisahan CO₂ daripada biogas sangat menarik kerana gas yang terhasil, biometana mengandungi nilai kalori lebih tinggi daripada biogas. Walau bagaimanapun, had keseimbangan di antara pemilihan dan kebolehtelapan menghalang aplikasi membran polimer dalam penulenan biogas. Menggabungkan zeolite dengan liang kecil ke dalam matriks polimer dapat menghasilkan membran matriks campuran yang boleh menawarkan peningkatan dramatik dalam kedua-dua pemilihan dan kebolehtelapan. Dalam kajian ini, membran matriks campuran polisulfon dan zeolit SAPO zeolite telah direka untuk pemisahan CO₂ pada tekanan rendah. Zeolit juga diubahsuaikan untuk meningkatkan keserasian dalam polisulfon dan prestasi dalam biogas basah. Seterusnya kesan kuantiti zeolit dan pengubahsuaian ke atas ciri-ciri membran dikaji menggunakan SEM, FTIR, EDX dan sudut sentuhan air. Sifat-sifat pengangkutan gas melalui membran juga dikaji menggunakan ujian gas penelapan dengan kelembapan. Membran PSf/SAPO-34 menunjukkan prestasi yang membanggakan berbanding dengan membran lain yang dilaporkan dalam literatur. Kemajuan dalam penyelidikan ini telah dilaporkan dalam 17 penerbitan dalam jurnal dan prosiding. Kajian ini juga memberi sumbangan besar dalam pembangunan modal insan (1 pelajar Ph.D. dalam penulisan tesis, 1 pelajar sarjana tamat pengajian, 1 pelajar sarjana kemukakan tesis, dan 4 pelajar sarjana muda menamatkan pengajian). Jaringan dengan Sime Darby dan Petronas Research Sdn. Bhd. telah dimulakan dan 1 Science Fund telah berjaya diperolehi dan disiapkan.

F. SUMMARY OF RESEARCH FINDINGS*Ringkasan dapatan Projek Penyelidikan*

Mixed matrix membranes were engineered from polysulfone (PSf) and SAPO zeolite in order to achieve CO₂ separation from biogas at low pressure. The selected SAPO-34 and SAPO-44 zeolite possess micro pores which are favourable for the separation of CO₂/CH₄ mixture. A higher CO₂ permeance (314.02 GPU) was achieved by incorporating 10 wt.% of SAPO-34 into asymmetric PSf membrane compared to PSf-44 membrane. Even without strong binding between PSf and SAPO-34, CO₂/N₂ and CO₂/CH₄ selectivities up to 26.1 and 28.2 respectively were observed. The incorporation of hydrophilic SAPO zeolite also improved the applicability of PSf membrane in waste water treatment. PSf-44 membrane showed more promising separation features in ultrafiltration compared to PSf/SAPO-34 membrane due to the pore size difference. In order to improve the compatibility between SAPO-34 membrane, SAPO-34 was further functionalized with amino group and fluorocarbon group. In the amino modification, the effects of solvent in grafting reaction were studied. difference in solvent polarity. Ethanol with polarity index of 5.2 could generate more uniform distribution of grafting site compared to IPA with polarity index of only 3.9. The utilization of a higher polar solvent improved the mobility of silane molecules on the SAPO-34E surface, leading to not only less agglomeration, but also better adhesion. However, moisture in biogas impair the separation of mixed matrix membrane because water molecules show competitive sorption in the Langmuir voids of the polymer, decreasing the solubility of other gas species especially CO₂. The competitive sorption of moisture was amplified drastically in MMMs because most microporous fillers (e.g., silica, alumina, and zeolite) are hydrophilic. Fluorocarbon modification of hydrophilic SAPO-34 zeolite using fluoroalkyl silane was conducted to reduce the competitive adsorption of moisture in MMMs. CO₂ permeance via PSf/SAPO-34 membrane decreased immensely after exposure to humidified CO₂ gas, but membranes exhibited less competitive sorption of moisture after fluoroalkyl modification.

G. COMPREHENSIVE TECHNICAL REPORT*Laporan Teknikal Lengkap*

Applicants are required to prepare a comprehensive technical report explaining the project.
(This report must be attached separately)

Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini.

[Laporan ini mesti dikepilkkan]

Kindly refer to Appendix A for Comprehensive Technical Report.

List the key words that reflect our research:

Senaraikan kata kunci yang mencerminkan penyelidikan anda:

English	Bahasa Malaysia
CO ₂ separation	Pemisahan CO ₂
Mixed matrix membrane	Membran matriks bercampur
SAPO zeolite	Zeolit SAPO

H. a) Results/Benefits of this research
Hasil Penyelidikan

No. Bil:	Category/Number: Kategori/ Bilangan:	Promised	Achieved
1.	Research Publications (Specify target journals) <i>Penerbitan Penyelidikan (Nyatakan sasaran jurnal)</i>		10 (ISI indexed journal) 7 (conference proceeding)
2.	Human Capital Development		
	a. Ph. D Students		1 (Thesis writing)
	b. Masters Students		2 (1 graduated) (1 thesis submitted)
	c. Undergraduates (Final Year Project)		3 (graduated)
	d. Research Officers		
	e. Research Assisstants		
	f. Other: Please specify		
3.	Patents <i>Paten</i>	-	-
4.	Specific / Potential Applications <i>Spesifik/Potensi aplikasin</i>		
• • • • •	5. Networking & Linkages <i>Jaringan & Jalinan</i>		2
• • •	6. Possible External Research Grants to be Acquired <i>Jangkaan Geran Penyelidikan Luar Diperoleh</i>		1
7.	Award <i>Anugerah</i>		3 (Silver Medal PENCIPTA) (PITTCO Travel Award) (Persada Kencana)

- Kindly provide copies/evidence for Category 1 to 6.

Kindly refer to Appendix B (Publications), C (Human Capital Development), D (Networking and Linkages),E (Grant) and F (Award).

b) Equipment used for this research.

Peralatan yang telah digunakan dalam penyelidikan ini.

Items Perkara	Approved Equipment	Approved Requested Equipment	Location
Specialized Equipment Peralatan khusus	Autoclave	Autoclave	Chemical Laboratory
Facility Kemudahan	Mechanical Stirrer Oven	Mechanical Stirrer Oven	Chemical Laboratory Petroleum Laboratory
Infrastructure Infrastruktur			

I. **BUDGET / BAJET**

Total Approved Budget : RM 217,010.00
Total Additional Budget : RM 0
Grand Total of Approved Budget : RM 217,010.00

Yearly Budget Distributed

Year 1 : RM 104,310.00
Year 2 : RM 62,900.00
Year 3 : RM 49,800.00

Additional Budget Approved

Year 1 : RM 104,310.00
Year 2 : RM 62,900.00
Year 3 : RM 49,800.00

Total Expenditure : RM 216,968.98
Balance : RM 41.02

- **Please attach final account statement from Treasury**

Kindly refer to Appendix G





Signature of Researcher
Tandatangan Penyelidik

8 / 1 / 2015

Date
Tarikh

DR. LEO CHOE PENG
Ketua Projek
Garan Universiti Penyelidikan Individu (RTI)
1001 / PJKMIA / 811194

H.	<p>COMMENTS OF PTJ'S RESEARCH COMMITTEE KOMEN JAWATANKUASA PENYELIDIKAN PERINGKAT PTJ</p>
	<p>General Comments: <i>Ulasan Umum:</i></p> <p>Good achievement in publication and training of B.Eng and MSc students</p>
	<p> PROFESSOR DR AHMAD ZUHAIRI ABDULLAH Deputy Dean (Research) School of Chemical Engineering Universiti Sains Malaysia, Engineering Campus Nibong Tebal, Penang, Malaysia.</p> <p>Signature and Stamp of Chairperson of PTJ's Evaluation Committee <i>Tandatangan dan Cop Pengerusi Jawatankuasa Penilaian PTJ</i></p> <p>Date : 12/01/2015..... <i>Tarikh :</i>.....</p> <p>Signature and Stamp of Dean/ Director of PTJ <i>Tandatangan dan Cop Dekan/ Pengarah PTJ</i></p> <p>Date : <i>Tarikh :</i>.....</p> <p> 13/1/15 PROFESOR AZLINA HARUN @ KAMARUDDIN Dekan Pusat Pengajian Kejuruteraan Kimia Kampus Kejuruteraan Universiti Sains Malaysia, Seri Ampangan 14300 Nibong Tebal, Seberang Perai Selatan Pulau Pinang.</p>

APPENDIX A COMPREHENSIVE TECHNICAL REPORT
APPENDIX B RESEARCH PUBLICATIONS
APPENDIX C HUMAN CAPITAL DEVELOPMENT
APPENDIX D NETWORKING AND LINKAGES
APPENDIX E EXTERNAL RESEARCH GRANTS
APPENDIX F AWARDS
APPENDIX G FINAL ACCOUNT STATEMENT

APPENDIX A
COMPREHENSIVE TECHNICAL REPORT

APPENDIX A COMPREHENSIVE TECHNICAL REPORT

The technical report described the important findings on mixed matrix membranes incorporated with SAPO zeolite. The details of methodology, results, discussion and conclusions were documented in publications (Appendix B, Journal Publications 1 to 5, Conference Publication 1 to 3). However, the findings were not limited to these membranes as the research has been extended to other types of gas separation membranes using the equipment and/or chemical acquired using this grant. The extended research findings were reported in the attached publications (Appendix B, Journal Publications 6 to 10, Conference Publication 4 to 7).

PSf/SAPO-44 Membranes

The surface and cross-section SEM images of the MMMs provided evidence for good dispersion of the particles in the polymer for zeolite loading less than 5 wt.%. The PSf-05 MMMs showed the highest performance enhancement on CO₂/N₂ and CO₂/CH₄ separation properties compared to the pure PSf membrane (PSf-00). For higher zeolite loadings (10 wt.% and above), the gas permeation properties of the MMMs were severely disturbed by the massive formation of large interfacial voids across the membrane surface due to the particle agglomeration. Moreover, the poor interaction between PSf and the SAPO-44 particles verified by FTIR analysis strengthen the evidence of interfacial voids formation. In conclusion, an optimum amount of SAPO-44 zeolite loading (5 wt.% or less) in the fabrication of the asymmetric PSf/SAPO-44 MMMs is crucial in order to achieve a good CO₂/CH₄ separation. Without any modification of filler phase, the addition of SAPO-44 inside PSf membrane has significantly enhanced CO₂ removal performance from CH₄. However, modification on SAPO-44 filler and PSf matrix is required in order to embed high loading of SAPO-44 with defect-free MMMs and improve CH₄ refining performance.

Table 1
Pure gas performance of PSf/SAPO-44 membranes with varied loading of zeolite.

Sample	Permeability (GPU) ^a			Ideal selectivity	
	CO ₂	N ₂	CH ₄	$\alpha(\text{CO}_2/\text{N}_2)$	$\alpha(\text{CO}_2/\text{CH}_4)$
PSf-00	22.01 ± 3.42	1.33 ± 0.59	1.26 ± 0.44	16.5	17.3
PSf-05/4	81.93 ± 1.45	3.67 ± 0.92	3.17 ± 1.13	22.3	25.8
PSf-10/4	338.33 ± 2.71	41.26 ± 0.56	31.91 ± 2.26	8.2	10.6
PSf-20/4	351.07 ± 4.92	292.56 ± 5.84	234.05 ± 4.61	1.2	1.5

a 1 GPU = 10⁻¹⁰ cm³ (STP)/cm² cmHg.s.

Durable polysulfone (PSf) membrane is less suitable for wastewater treatment as it is susceptible to severe fouling by the natural organic matter. SAPO-44 zeolite was blended into PSf membranes to mitigate fouling by humic acid. The casting solutions were prepared by blending 5–20 wt.% of SAPO-44 zeolite (average particle size of 138 nm) into a mixture of PSf, 1-methyl-2-pyrrolidinone and 1 wt.% of PVA with a stirring speed of 400 rpm. The weight ratio of polymer to solvent was maintained at 1:4.84. Mixed matrix membranes were then prepared using phase inversion method. SAPO-44 zeolite was weakly adhered to the macroporous layer in asymmetric membranes. Growth of the finger-like macrovoid was promoted by blending SAPO-44 zeolite into PSf/PVA membrane. Larger pore size was also induced in P-1 and P-2 samples, causing lower water contact angle on these mixed matrix membranes. Further adding of zeolite filler resulted in smaller finger-like pores as the exchange between solvent and nonsolvent had been delayed in the viscous solution. Membrane pore size and surface energy were slightly enlarged by blending

15 wt.% or 20 wt.% of zeolite. P-3 membrane with 15 wt.% of SAPO-44 exhibited the highest water flux, with nearly 164 % of increment compared to the control membrane. Fouling mitigation could be achieved without much modification of surface energy depending on the fouling mechanisms. Embedded zeolite may reduce the fouling by humic acid initiated from pore blocking. About 80% permeate flux of P-3 membrane was maintained during the filtration of humic acid solution. However, agglomerated filler in P-4 sample with 20 wt.% of SAPO-44 caused slightly lower water permeability and relative flux of fouling test compared to P-3 membrane.

Table 2
Physical properties and permeability of PSf/SAPO-44 membranes

Sample	Water contact angle (°)	Pore size (nm)	L_p^a (L/m ² h)
PF-0	70.6	35.7	13.56
PF-1	68.5	51.5	14.78
PF-2	64.5	66.8	15.21
PF-3	66.1	39.8	35.81
PF-4	67.0	39.4	33.79

a Applied pressure: 2 bar.

PSf/SAPO-34 Membranes

SAPO-34 zeolite with a framework of 0.38 nm pore size and high CO₂ adsorption affinity was used as inorganic fillers. The asymmetric mixed matrix membrane structure was prepared using the phase inversion method. The effects of zeolite loading (5–30 wt.%) on the membrane characteristics were studied using SEM with EDX, FT-IR, and TGA; while the gas transport properties were investigated using pure gas permeation tests of N₂, CO₂ and CH₄. Well dispersion of SAPO-34 particles in the polymer matrix was observed for zeolite loading less than 10 wt.%. The maximum CO₂ permeance (314.02 GPU) was achieved by incorporating 10 wt.% of SAPO-34 into asymmetric PSf membrane. Even without strong binding between PSf and SAPO-34, CO₂/N₂ and CO₂/CH₄ selectivities up to 26.1 and 28.2 respectively were observed. The surface and cross-section SEM images of the MMMs provided evidence for good dispersion of the particles in the polymer for zeolite loading less than 10 wt.%. The PSf/SAPO-34 membrane with 10 wt.% SAPO-34 loading (PSf-10) showed the highest separation performance enhancement on CO₂/N₂ and CO₂/CH₄ ideal gas pair properties compared to the pure PSf membrane (PSf-00). For the higher zeolite loadings (20 wt.% and above), the gas permeation properties of the MMMs were severely disturbed by the massive formation of large interfacial voids across the membrane surface due to the particle agglomeration. Moreover, TGA and FT-IR results verified the poor interaction between PSf and the SAPO-34 particles which also resulted in great interfacial voids. In order to avoid the formation of interfacial voids, better connection between filler and polymer material is important, which can be done by polymer/filler modification. In conclusion, an optimum amount of SAPO-34 zeolite loading (10 wt.% and below) for fabrication of the asymmetric PSf/SAPO-34 MMMs is essential to achieve a good dispersion of filler inside the polymer phase and excellent CO₂ removal performance that can be applied specifically in natural gas sweetening.

Table 3
Gas permeance and ideal selectivities of PSf/SAPO-34 membranes with varied loading of zeolite

SAPO-34 loading (%, w/w)	Permeance (GPU) ^a			Ideal selectivity	
	CO ₂	N ₂	CH ₄	$\alpha(\text{CO}_2/\text{N}_2)$	$\alpha(\text{CO}_2/\text{CH}_4)$
0	22.01 ± 3.42	1.33 ± 0.59	1.26 ± 0.44	16.5	17.3
5	205.92 ± 7.26	9.63 ± 0.56	9.12 ± 0.65	21.4	22.5
10	314.02 ± 4.65	12.03 ± 1.83	11.16 ± 0.92	26.1	28.2
20	281.18 ± 6.92	26.28 ± 1.49	25.73 ± 2.06	10.7	10.9
30	232.35 ± 3.21	78.10 ± 3.42	77.36 ± 5.28	2.9	3.0

a 1 GPU = 10⁻¹⁰ cm³ (STP)/cm² cmHg s.

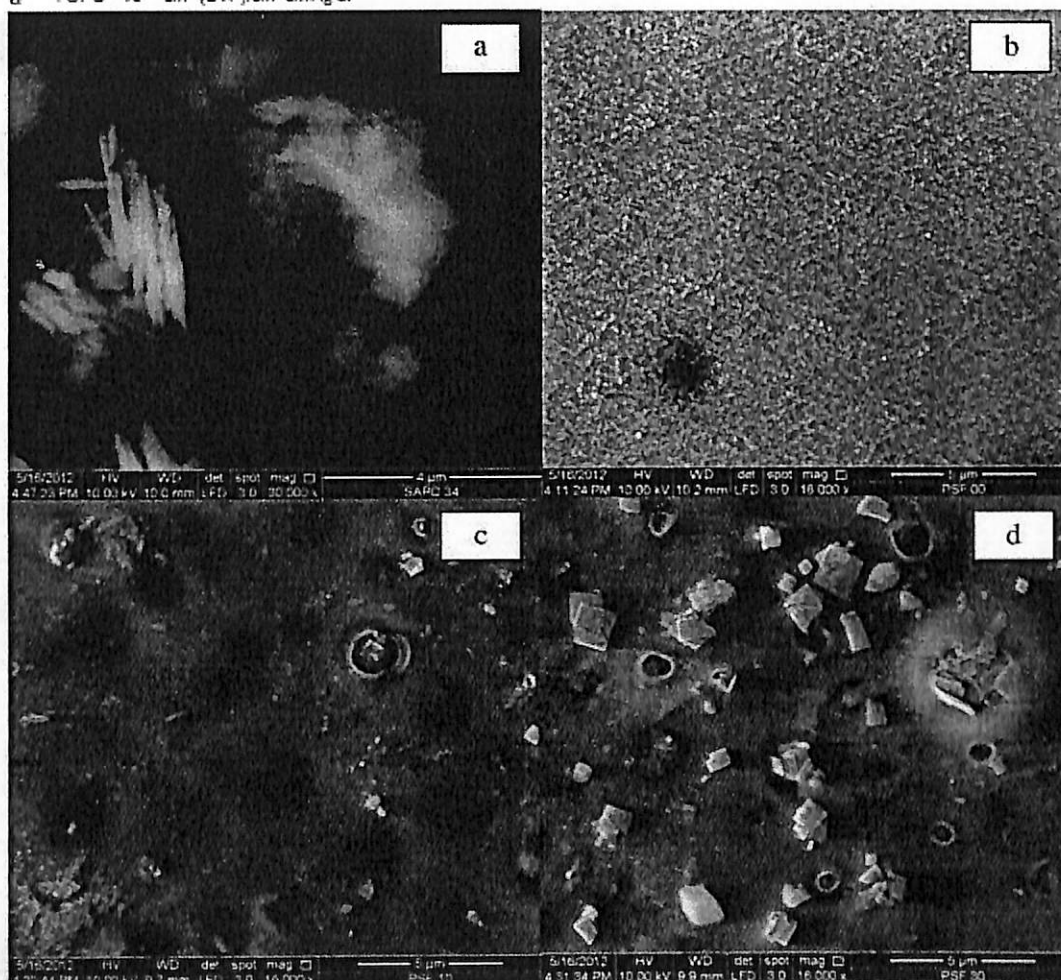


Fig. 1 SEM images of SAPO zeolite and PSf/SAPO-34 membranes.

Although ultrafiltration (UF) membranes are applicable in wastewater and water treatment, most UF membranes are hydrophobic and susceptible to severe fouling by natural organic matter. In this work, polysulfone (PSf) membrane was blended with silicaluminophosphate (SAPO) nanoparticles, SAPO-34, to study the effect of SAPO-34 incorporation in humic acid (HA) fouling mitigation. The casting solution was prepared by blending 5–20 wt% of SAPO-34 nanoparticles into the mixture of PSf, 1-methyl-2-pyrrolidinone and polyvinyl alcohol. All membrane samples were then prepared using the phase inversion method. Blending SAPO-34 zeolite into PSf membranes caused augmentation in surface hydrophilicity and pore size, leading to higher water permeation. In the HA filtration test, mixed matrix membranes (MMMs) with SAPO-34 zeolite showed reduced HA fouling initiated from pore blocking. The MMM with 20 wt% SAPO-34 loading exhibited the highest increment of water permeation (83%) and maintained about 75% of

© Division of Research & Innovation – Universiti Sains Malaysia – 20130312

permeate flux after 2.5 h. However, the SAPO-34 fillers agglomerated in the PSf matrix and induced macrovoid formation on the membrane surface when excessive zeolite was added.

Table 4
Physical properties of PSf/SAPO-34 membranes

Sample	Water contact angle (°)	Pore size (µm)	J_{CO_2} (L/(m ² · h))	HA rejection (%)
Pf-00	77.1 ± 0.02	0.0259 ± 0.005	1.62 ± 0.32	77.08
Pf-05	74.6 ± 0.04	0.0364 ± 0.003	1.90 ± 0.35	86.20
Pf-10	73.0 ± 0.01	0.0377 ± 0.012	2.40 ± 0.64	91.96
Pf-20	68.5 ± 0.02	0.0398 ± 0.007	2.97 ± 0.83	97.95

*Applied pressure: 2 bar.

PSf/SAPO-34 Membranes with Functionalization

SAPO-34 zeolite is the ideal porous filler in Mixed matrix membranes (MMMs) for CO₂ separation because it has strong affinity towards CO₂ and pore size (0.38 nm) which is nearly similar to the molecular sizes of various gasses in natural gas. However, the poor compatibility between zeolite and polymeric matrix causes the formation of non-selective interfacial voids, leading to poor separation of gasses. In this work, 3-aminopropyl trimethoxy silane (APMS) was proposed to modify SAPO-34 zeolite before adding into asymmetric polysulfone (PSf) MMMs prepared via dry-wet phase inversion. The effects of solvent (ethanol or isopropanol) in grafting reaction were studied. The changes in FTIR spectra of both modified SAPO-34 zeolite samples signified that more silane molecules were grafted when ethanol was used. SAPO-34 zeolite dispersed evenly in PSf matrix after modification as shown in EDX analysis. Although showing similar FTIR spectra and morphology, a great improvement in CO₂ selectivity and permeance was only shown by PSf/SAPO-34E MMMs with zeolite modified using APMS in ethanol. The highest CO₂/N₂ selectivity of 28, CO₂/CH₄ selectivity of 31 and a satisfactory CO₂ permeance of 706 GPU were achieved. Besides reduction of filler agglomeration, the improvement could be related to the diminished interfacial voids when SAPO-34 zeolite was modified using APMS in ethanol.

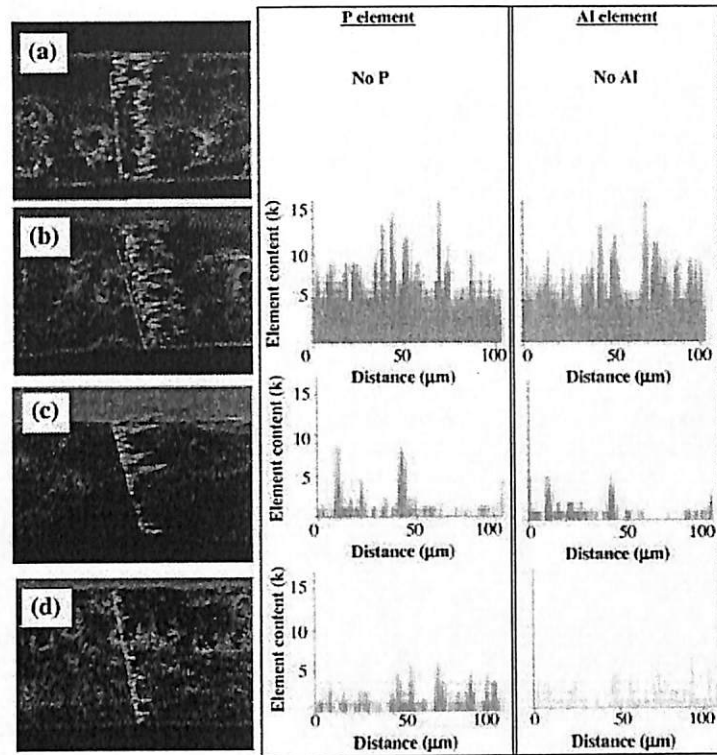


Fig. 2 SEM images and EDX scanning on PSf/SAPO-34 membrane with amino modification.

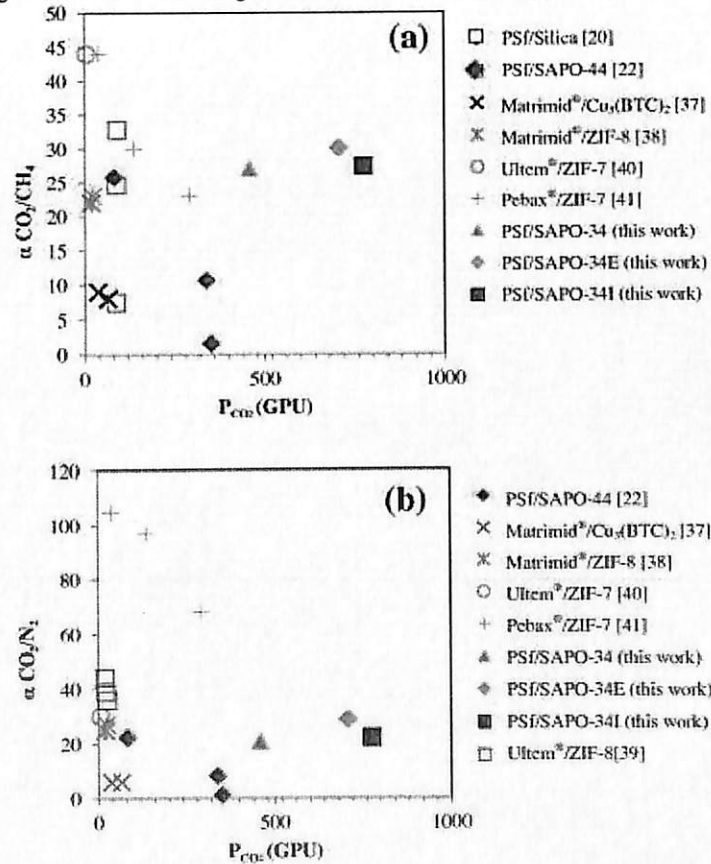


Fig. 3 Separation performance of PSf/SAPO-34 membrane with amino modification.

In order to sustain the performance of mixed matrix membrane (MMM) in the separation of wet gases such as biogas, water-resistant MMMs were fabricated by incorporating fluorocarbon functionalized SAPO-34 zeolite into polysulfone (PSf). 1H,1H,2H,2H-perfluorodecyltriethoxysilane (HFDS) was used to convert the hydrophilic SAPO-34 zeolite into hydrophobic SAPO-34 zeolite to avoid competitive adsorption of moisture. After dispersing the modified filler in polymer solution, asymmetric MMMs were fabricated via dry-wet phase inversion. N₂ adsorption-desorption test and thermal gravimetric analysis indicated that fluorocarbon modification generated minimum impact on the surface area and CO₂ adsorption capability of SAPO-34 zeolite. The water contact angle on SAPO zeolite increased from 33° to 130° after modification, while the membrane hydrophobicity was enhanced about 17.64%. The MMM with 10 wt.% of modified SAPO-34 zeolite (PSf-10/HFDS 1.0) exhibited good adhesion between filler and polymer phases, minimizing defect such as interface voids. PSf-10/HFDS 1.0 MMM also showed great enhancement in ideal gas separation (ideal selectivity CO₂/CH₄ of 38.9 with CO₂ permeance of 278 GPU) compared to the neat PSf membrane and MMMs with unmodified SAPO-34 zeolite. In addition, PSf-10/HFDS 1.0 MMM showed actual gas selectivity at wet condition which is similar to its dry mixed-gas selectivity (2% reduction only). The mixed-gas separation performance for PSf-10/HFDS 1.0 MMM was even sustained in both dry and wet conditions during long-hour test. Compared to the dry mixed-gas results, MMM incorporated with 10 wt.% of unmodified SAPO-34 (PSf-10) suffered more than 90% reduction in separation performance during wet mixed-gas test.

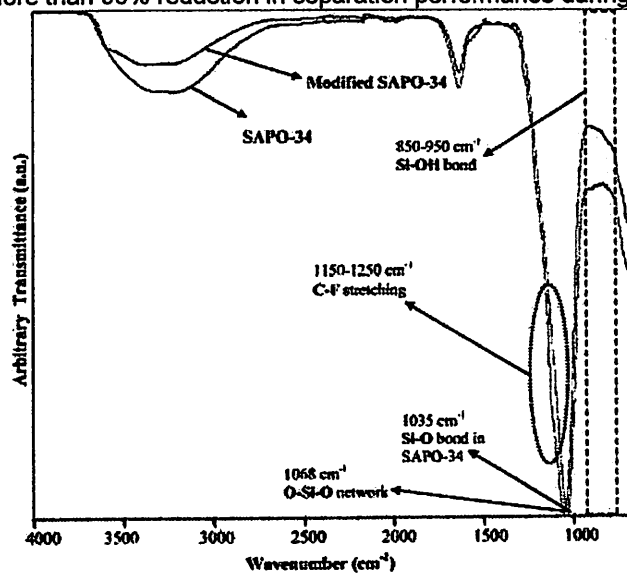


Fig. 4 FT-IR spectra of SAPO-34 and fluorocarbon modified SAPO-34.

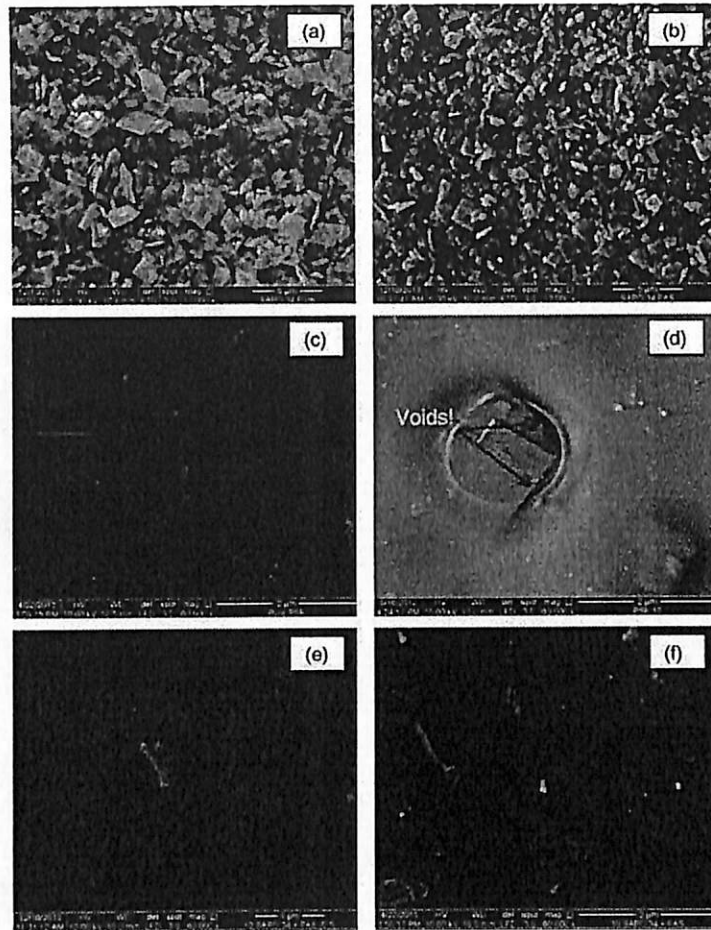


Fig. 5 SEM images of SAPO-34 zeolite and PSf/SAPO-34 membranes with and without fluorocarbon modification.

APPENDIX B
RESEARCH PUBLICATIONS



The potential of SAPO-44 zeolite filler in fouling mitigation of polysulfone ultrafiltration membrane

C.P. Leo*, N.H. Ahmad Kamil, M.U.M. Junaidi, S.N.M. Kamal, A.L. Ahmad

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

ARTICLE INFO

Article history:

Received 27 July 2012

Received in revised form 1 October 2012

Accepted 11 October 2012

Available online 23 October 2012

Keywords:

Mixed matrix membrane

Zeolite

Fouling

Humic acid

ABSTRACT

Durable polysulfone (PSf) membrane is less suitable for wastewater treatment as it is susceptible to severe fouling by the natural organic matter. In this work, SAPO-44 zeolite was blended into PSf membranes to mitigate fouling by humic acid. The casting solutions were prepared by blending 5–20 wt.% of SAPO-44 zeolite (average particle size of 138 nm) into a mixture of PSf, 1-methyl-2-pyrrolidinone and 1 wt.% of PVA at 75 °C with a stirring speed of 400 rpm. The weight ratio of polymer to solvent was maintained at 1:4.84. Mixed matrix membranes were then prepared using phase inversion method. SAPO-44 zeolite was weakly adhered to the macroporous layer in asymmetric membranes. Growth of the finger-like macrovoid was promoted by blending SAPO-44 zeolite into PSf/PVA membrane. Larger pore size was also induced in P-1 and P-2 samples, causing lower water contact angle on these mixed matrix membranes. Further adding of zeolite filler resulted in smaller finger-like pores as the exchange between solvent and nonsolvent had been delayed in the viscous solution. Membrane pore size and surface energy were slightly enlarged by blending 15 wt.% or 20 wt.% of zeolite. P-3 membrane with 15 wt.% of SAPO-44 exhibited the highest water flux, with nearly 164 % of increment compared to the control membrane. Fouling mitigation could be achieved without much modification of surface energy depending on the fouling mechanisms. Embedded zeolite may reduce the fouling by humic acid initiated from pore blocking. About 80% permeate flux of P-3 membrane was maintained during the filtration of humic acid solution. However, agglomerated filler in P-4 sample with 20 wt.% of SAPO-44 caused slightly lower water permeability and relative flux of fouling test compared to P-3 membrane.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Polysulfone (PSf) is thermally stable, mechanically strong and chemically inert; helping it to exhibit excellent resistance to extreme pH (pH 1–13), high temperature (75 °C) and corrosive oxidants. Due to its great stability under different sterilizing conditions, PSf in the form of thin film has been widely applied for biomedical separation such as hemodialysis [1]. PSf membrane can also be utilized for water treatment as it allows abrasive usage and frequent cleaning [2]. However, PSf membranes are susceptible to fouling by natural organic matter in water due to the undesirable hydrophobicity [3]. Hence, modification of PSf membranes has been extensively researched in order to reduce deposition of the foulants on the hydrophobic surface.

Membrane modification usually involves the improvement of surface energy by introducing hydrophilic groups via adsorption, coating, surface chemical reaction, grafting or blending. Adsorption and coating result in less durable hydrophilic surface while reaction and grafting require hazardous chemical or specific synthesis

condition. Blending remains to be the simplest but yet the most versatile modification method as it can be adopted by common membrane synthesis routes, namely phase inversion. Blending poly(N-vinyl-2-pyrrolidone) (PVP) into PSf membranes have been widely reported to minimize protein fouling. Hydrophilic surface rendered less fouling behavior but PVP leaching was observed during ultrafiltration [4]. Besides blending with hydrophilic polymers, much recent attention has been given to inorganic nanoparticles blending. Blending small amount of ZrO₂, SiO₂, TiO₂ or ZnO nanoparticles with PSf can result great improvement in membrane permeability, selectivity, mechanical strength, thermal resistance and flux decline pattern [5]. These oxide nanoparticles with large surface area not only provide excellent hydrophilicity in the polymer matrix but also additional advantages such as photocatalytic and antibacterial properties. Genné et al. [6] reported that the permeability of PSf/ZrO₂ membranes increased with increasing amount of ZrO₂ but the rejection of Dextran was impaired. However, sulfated Y doped nonstoichiometric ZrO₂ nanoparticles with abundant exposed hydroxide radicals could maintain oil rejection and reduced fouling of modified PSf membranes [6]. The addition of SiO₂ nanoparticles into PSf membranes reduced fouling by oil droplets as well but membrane pores were greatly enlarged [7].

* Corresponding author. Tel.: +60 4 5996425; fax: +60 4 5941013.

E-mail address: chcpleo@eng.usm.my (C.P. Leo).

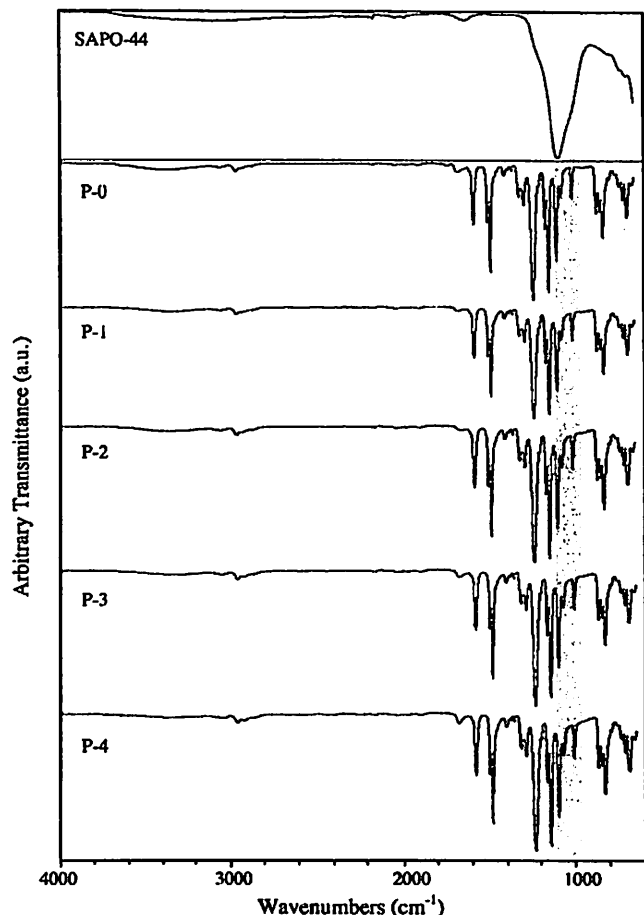


Fig. 5. FTIR patterns of PSf membranes blended with SAPO-44.

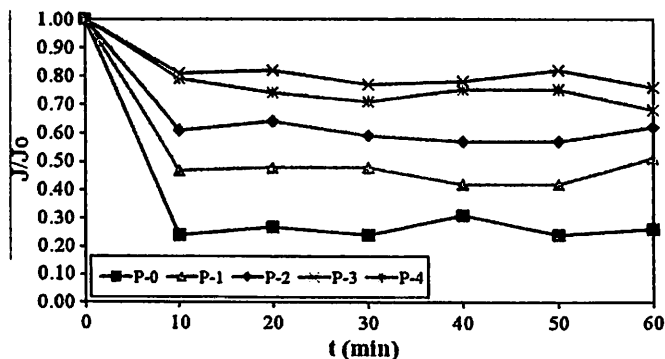


Fig. 6. Relative permeability of PSf membranes blended SAPO-44.

likely due to protonation. Negatively charged defect sites within the tetrahedral framework of SAPO-44 could be counterbalanced by the presences of a proton leading to great affinity of proton instead of foulant [19]. Thus, the flux decline pattern was greatly mitigated by increasing SAPO-44 zeolite content. About 80% permeate flux of P-3 membrane was maintained during the filtration of humic acid solution. The adhered zeolite in the macroporous layer successfully reduces the adsorption of humic acid in the-membrane pores resulting less pore blockage and cake formation [27]. Fouling mitigation can be achieved without much modification of surface energy depending on the fouling mechanisms. Embedded zeolite may reduce fouling initiated from pore blocking. However, P-4 membrane with 20 wt.% of zeolite content exhibited slightly more flux reduction than P-3 membrane which may be related to agglomeration of the zeolite particles.

4. Conclusions

PSf/PVA/SAPO-44 MMMs were successfully prepared by blending zeolite filler during phase inversion. SAPO-44 zeolite was weakly adhered to the macroporous layer in asymmetric membranes. The growth of finger-like macrovoid was promoted by blending SAPO-44 zeolite into PSf/PVA membrane. Larger pore size was also induced in P-1 and P-2 samples, contributing to lower water contact angle on these MMMs. Further adding zeolite filler resulted smaller finger-like pores because the exchange between solvent and nonsolvent had been delayed in the viscous solution. Membrane pore size was slightly enlarged and surface energy was vaguely increased when 15 wt.% or 20 wt.% of zeolite had been blended. P-3 membrane with 15 wt.% of SAPO-44 exhibited the highest water flux with nearly 164% of increment compared to the control membrane. Fouling mitigation could be achieved without much modification of surface energy depending on the fouling mechanisms. Embedded zeolite may reduce the fouling by humic acid which is initiated from pore blocking. About 80% permeate flux of P-3 membrane was maintained during the filtration of humic acid solution. However, agglomerated filler in P-4 sample with 20 wt.% of SAPO-44 caused slightly lower water permeability and relative flux of fouling test compared to P-3 membrane.

Acknowledgements

The authors would like to acknowledge MOSTI for providing Science Fund (06-01-05-SF0579). The authors would also like to thank Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSf/8610013), Research University Individual Grant (1001/PJKMIA/811194) and Short Term Grant (304/PJKMIA/60311016).

References

- [1] J. Vienen, Membranes in hemodialysis, in: Peinemann S.P.N.K.V. (Ed.), Membranes for Life Sciences, Wiley-VCH, New York, 2007, pp. 1–39.
- [2] J.C. Schrotter, B. Bozkaya-Schrotter, Current and Emerging Membrane Processes for Water Treatment, Wiley-VCH, New York, 2010.
- [3] A.W. Zularisam, A.F. Ismail, M.R. Salim, M. Sakinah, O. Hiroaki, Fabrication, fouling and foulant analyses of asymmetric polysulfone (PSf) ultrafiltration membrane fouled with natural organic matter (NOM) source waters, *J. Membr. Sci.* 299 (2007) 97–113.
- [4] D. Rana, T. Matsuura, Surface modification for antifouling membranes, *Chem. Rev.* 110 (2010) 2448–2471.
- [5] L.Y. Ng, A.W. Mohammad, C.P. Leo, N. Hilal, Polymeric membranes incorporated with metal/metal oxide nanoparticles: a comprehensive review, *Desalination* (2010).
- [6] J. Genné, S. Kuypers, R. Leysen, Effect of the addition of ZrO₂ to polysulfone based UF membranes, *J. Membr. Sci.* 113 (1996) 343–350.
- [7] Y. Zhang, P. Cui, T. Du, L. Shan, Y. Wang, Development of a sulfated Y-doped nonstoichiometric zirconia/polysulfone composite membrane for treatment of wastewater containing oil, *Sep. Purif. Technol.* 70 (2009) 153–159.
- [8] L.Y. Ng, C.P. Leo, A.W. Mohammad, Optimizing the incorporation of silica nanoparticles in polysulfone/poly(vinyl alcohol) membranes with response surface methodology, *J. Appl. Polym. Sci.* 121 (2011) 1804–1814.
- [9] Y. Yang, H. Zhang, P. Wang, Q. Zheng, J. Li, The influence of nano-sized TiO₂ fillers on the morphologies and properties of PSf UF membrane, *J. Membr. Sci.* 288 (2007) 231–238.
- [10] T.H. Bae, T.M. Tak, Preparation of TiO₂ self-assembled polymeric nanocomposite membranes and examination of their fouling mitigation effects in a membrane bioreactor system, *J. Membr. Sci.* 266 (2005) 1–5.
- [11] A. Sotito, A. Boromand, S. Balta, J. Kim, B. Van Der Bruggen, Doping of polyethersulfone nanofiltration membranes: antifouling effect observed at ultralow concentrations of TiO₂ nanoparticles, *J. Mater. Chem.* 21 (2011) 10311–10320.
- [12] A. Sotito, A. Boromand, R. Zhang, P. Luis, J.M. Arsuaga, J. Kim, B. Van der Bruggen, Effect of nanoparticle aggregation at low concentrations of TiO₂ on the hydrophilicity, morphology, and fouling resistance of PES-TiO₂ membranes, *J. Colloid Interface Sci.* 363 (2011) 540–550.
- [13] S. Balta, A. Sotito, P. Luis, L. Benea, B. Van der Bruggen, J. Kim, A new outlook on membrane enhancement with nanoparticles: the alternative of ZnO, *J. Membr. Sci.* 389 (2012) 155–161.



Carbon dioxide removal from methane by using polysulfone/SAPO-44 mixed matrix membranes

M.U.M. Junaidi ^a, C.P. Leo ^{a,*}, S.N.M. Kamal ^a, A.L. Ahmad ^a, T.L. Chew ^b

^a School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

^b Department of Petrochemical Engineering, Faculty of Engineering and Green Technology (FEGT), Perak Campus, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia

ARTICLE INFO

Article history:

Received 21 December 2012
Received in revised form 28 January 2013
Accepted 17 February 2013
Available online 15 March 2013

Keywords:

CO₂ separation
Mixed matrix membrane
Natural gas refining
SAPO-44 zeolite

ABSTRACT

Removal of CO₂ in natural gas refining has currently been the only membrane based process practiced on a large scale operation. Despite the predominance of polymeric membranes in the CO₂/CH₄ separation, the tradeoff limitation in between membrane selectivity and permeability hinders a good separation performance of these membranes. Mixed matrix membranes can offer dramatic improvement to overcome this shortcoming. In this study, polysulfone mixed matrix membranes incorporated with small pore zeolite were proposed for CO₂ separation. SAPO-44 zeolite was used as inorganic fillers to enhance gas selectivity. The asymmetric membrane structure was prepared using the phase inversion method in order to improve permeance. The effects of zeolite loading (5–20 wt.%) on the membranes characteristic were studied using SEM and FTIR, while the gas transport properties were investigated using pure gas permeation tests of N₂, CO₂ and CH₄ for each membrane. The most optimum sample is the membrane with 5 wt.% of SAPO-44 loading, which exhibited improved CO₂/N₂ and CO₂/CH₄ selectivities of 22 and 25, respectively, compared to other samples. Devoid of any modification of filler phase, the addition of SAPO-44 inside polysulfone mixed matrix membranes has significantly enhanced CO₂ separation performance.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

In 2010, about 24% of the world's energy demand has been supplied by natural gas [1]. Due to the increment of oil price and civic awareness in green fuel, natural gas is definitely an immensely demanded energy source in the future. The average annual natural gas demand within the Southeast Asia region in 2010 has increased about 102% from the actual annual gas demand in 1993 [2]. Power plant sector consumes most of the current demand, higher than the other major sectors such as transportation and chemical industry. Before the natural gas can be used, sweetening or refining process is required to remove impurities such as carbon dioxide (CO₂), hydrogen sulfide (H₂S), nitrogen (N₂), sulfur containing compound and water with a minimal loss of methane (CH₄) [3]. Conventional gas absorption processes in the natural gas purification, including chemical absorption by alkanolamine solution suffer from many drawbacks such as foaming, flooding, channeling, and high capital costs. Unlike chemical separation, physical separation using membrane systems allows the natural gas refining to be efficiently accomplished as it offers less energy usage, less environmental impact, and ease of operation [4]. Economic analysis by Stern (1994) [5] showed that natural gas reservoirs with more than 20% of CO₂ concentrations are being attractive targets for membrane based separations. In

order for the process to be successful, it requires a membrane with high CO₂/CH₄ selectivity and permeance.

Polymeric membranes such as polyimide (PI), polysulfone (PSf), and cellulose acetate (CA) have been commercially applied in CO₂ separation [6]. However, due to the polymeric membrane tradeoff between its permeability and selectivity as propounded by Robeson [7], these pure membranes are still exhibit less desirable performance. Aroon et al. [8] have studied the CO₂ removal from CH₄ using PSf membranes with different organic additives. PSf membrane with glycerol additive exhibited highest CO₂/CH₄ selectivity (31.6) but, its CO₂ permeance was small (8.23 GPU). Besides organic additives, inorganic fillers especially zeolite has been widely used in the membrane fabrication due to their high selectivity of CO₂ [9,10]. Zeolite membranes are proven to have excellent CO₂ separation performance due to their molecular sieve ability and adsorption affinity [11]. Zeolite membranes with micro-pores structure such as zeolite DDR (0.36×0.44 nm) [12], T-type (0.41 nm) [13], and SAPO (0.38–0.44 nm) [10] had been widely reported in CO₂ separation. Chew et al. [10], in their recent research on the preparation of SAPO-34 membrane have shown tremendous separation performances with CO₂ permeance of 37.6 GPU and CO₂/CH₄ selectivity of 103. Although zeolite membranes superior gas performances surpass Robeson's tradeoff limit [7], these membranes are difficult to be produced at large scale because of the fabrication methods are complicated and time-consuming. Meanwhile, blending zeolites into polymer matrices to form mixed matrix membranes (MMMs) is an alternative

* Corresponding author. Tel.: +60 4 5996425; fax: +60 4 5941013.
E-mail address: chcpleo@eng.usm.my (C.P. Leo).

[11] also used dense membrane structure in the fabrication of polyphosphazene (PPZ) MMMs incorporated with SAPO-34 to improved CO₂/CH₄ separation. Unfortunately, by adding 25 wt.% of SAPO-34, the fabricated MMMs have a smaller CO₂ permeance compared to the control membrane. Meanwhile, their MMMs have slightly enhanced CO₂/CH₄ selectivity by 14%. The incorporation of SAPO-34 inside polymer membrane in both literatures [11,23] has significantly improved CO₂/CH₄ selectivity as the addition of SAPO-44 in PSf membrane in this work. Moreover, by the introduction of asymmetric membrane structure in PSf/SAPO-44 MMMs have greatly improved MMMs permeability and maintained its selectivity.

On the other hand, the decrement in CO₂/N₂ and CO₂/CH₄ selectivities on MMMs was detected as the SAPO-44 loading was increased up to 10 wt.%. Comparing with PSf-00, the CO₂/N₂ selectivity of PSf-10/4 membrane decreased to 8.2 (50.3% reduction), while CO₂/CH₄ selectivity decreased to 10.6 (38.7% reduction). As shown in the SEM images, the large SAPO-44 aggregates disturbed the dense layer surface structure by introducing large interfacial voids [31]. Therefore, the membrane resistance for larger molecule gases such as N₂ and CH₄ was greatly reduced. These gas molecules could easily penetrate into the membrane via Knudsen diffusion mechanism through the generated voids. By addition of more SAPO-44 loading, the CO₂/N₂ and CO₂/CH₄ selectivities performance were severely reduced and the gas permeabilities were drastically increased. The PSf-20/4 samples exhibited the highest CO₂ permeance (351 GPU) with the lowest value of CO₂/N₂ and CO₂/CH₄ selectivities in this study. In order to lessen the gas reduction problem, Karatay et al. [31] have used low molecular weight additive to enhance particle dispersion in their MMMs. Their new developed PES MMMs have improved SAPO-34 dispersion on membrane and enhanced CO₂/CH₄ selectivity (50% increment) by using 10 wt.% SAPO-34 zeolite.

4. Conclusions

The effects of SAPO-44 zeolite loading on the membrane characteristic and gas transport properties for asymmetric PSf/SAPO-44 MMMs had been successfully studied. All of the membrane was prepared using the phase inversion method. The surface and cross-section SEM images of the MMMs provided evidence for good dispersion of the particles in the polymer for zeolite loading less than 5 wt.%. The PSf-05/4 MMMs showed the highest performance enhancement on CO₂/N₂ and CO₂/CH₄ separation properties compared to the pure PSf membrane (PSf-00). For higher zeolite loadings (10 wt.% and above), the gas permeation properties of the MMMs were severely disturbed by the massive formation of large interfacial voids across the membrane surface due to the particle agglomeration. Moreover, the poor interaction between PSf and the SAPO-44 particles verified by FTIR analysis strengthen the evidence of interfacial voids formation. In conclusion, an optimum amount of SAPO-44 zeolite loading (5 wt.% or less) in the fabrication of the asymmetric PSf/SAPO-44 MMMs is crucial in order to achieve a good CO₂/CH₄ separation. Without any modification of filler phase, the addition of SAPO-44 inside PSf membrane has significantly enhanced CO₂ removal performance from CH₄. However, modification on SAPO-44 filler and PSf matrix is required in order to embed high loading of SAPO-44 with defect-free MMMs and improve CH₄ refining performance.

Acknowledgments

The authors would like to acknowledge Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013), Research University Individual Grant (1001/PJKMIA/811194), RU-PRGS (1001/PJKMIA/8035018 and 1001/PJKMIA/8035020) and USM Fellowship. The authors would also like to thank MOSTI for providing Science Fund (06-01-05-SF0579).

References

- [1] T.E. Rufford, et al., The removal of CO₂ and N₂ from natural gas: a review of conventional and emerging process technologies, *Journal of Petroleum Science and Engineering* 94–95 (2012) 123–154.
- [2] D. Intarapavich, et al., Asia-Pacific energy supply and demand to 2010, *Energy* 21 (11) (1996) 1017–1039.
- [3] J. Zaman, Oxidative processes in natural gas conversion, *Fuel Processing Technology* 58 (2–3) (1999) 61–81.
- [4] K.A. Lokhandwala, et al., Membrane separation of nitrogen from natural gas: a case study from membrane synthesis to commercial deployment, *Journal of Membrane Science* 346 (2) (2010) 270–279.
- [5] S. Alexander Stern, Polymers for gas separations: the next decade, *Journal of Membrane Science* 94 (1) (1994) 1–65.
- [6] C.A. Scholes, et al., CO₂ capture from pre-combustion processes—strategies for membrane gas separation, *International Journal of Greenhouse Gas Control* 4 (5) (2010) 739–755.
- [7] L.M. Robeson, The upper bound revisited, *Journal of Membrane Science* 320 (1–2) (2008) 390–400.
- [8] M.A. Aroon, et al., Morphology and permeation properties of polysulfone membranes for gas separation: effects of non-solvent additives and co-solvent, *Separation and Purification Technology* 72 (2) (2010) 194–202.
- [9] G. Li, et al., Thin carbon/SAPO-34 microporous composite membranes for gas separation, *Journal of Membrane Science* 374 (1–2) (2011) 83–92.
- [10] T.L. Chew, A.L. Ahmad, S. Bhatia, Ba-SAPO-34 membrane synthesized from microwave heating and its performance for CO₂/CH₄ gas separation, *Chemical Engineering Journal* 171 (3) (2011) 1053–1059.
- [11] P. Jha, J.D. Way, Carbon dioxide selective mixed-matrix membranes formulation and characterization using rubbery substituted polyphosphazene, *Journal of Membrane Science* 324 (1–2) (2008) 151–161.
- [12] T. Tomita, K. Nakayama, H. Sakai, Gas separation characteristics of DDR type zeolite membrane, *Microporous and Mesoporous Materials* 68 (1–3) (2004) 71–75.
- [13] S.M. Mirfendereski, et al., CO₂ and CH₄ permeation through T-type zeolite membranes: effect of synthesis parameters and feed pressure, *Separation and Purification Technology* 61 (3) (2008) 317–323.
- [14] D. Şen, H. Kalıpcılar, L. Yılmaz, Development of polycarbonate based zeolite 4A filled mixed matrix gas separation membranes, *Journal of Membrane Science* 303 (1–2) (2007) 194–203.
- [15] T.-S. Chung, et al., Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, *Progress in Polymer Science* 32 (4) (2007) 483–507.
- [16] F. Dorosti, et al., Fabrication and characterization of polysulfone/polyimide-zeolite mixed matrix membrane for gas separation, *Chemical Engineering Journal* 171 (3) (2011) 1469–1476.
- [17] T.W. Pechar, et al., Fabrication and characterization of polyimide-zeolite L mixed matrix membranes for gas separations, *Journal of Membrane Science* 277 (1–2) (2006) 195–202.
- [18] S. Rafiq, et al., Separation of CO₂ from CH₄ using polysulfone/polyimide silica nanocomposite membranes, *Separation and Purification Technology* 90 (2012) 162–172.
- [19] J. Zhao, et al., High-performance membranes comprising polyaniline nanoparticles incorporated into polyvinylamine matrix for CO₂/N₂ separation, *Journal of Membrane Science* 403–404 (2012) 203–215.
- [20] S. Li, C.Q. Fan, High-flux SAPO-34 membrane for CO₂/N₂ separation, *Industrial and Engineering Chemistry Research* 49 (9) (2010) 4399–4404.
- [21] P.J.E. Harlick, F.H. Tezel, An experimental adsorbent screening study for CO₂ removal from N₂, *Microporous and Mesoporous Materials* 76 (1–3) (2004) 71–79.
- [22] M.W. Ackley, S.U. Rege, H. Saxena, Application of natural zeolites in the purification and separation of gases, *Microporous and Mesoporous Materials* 61 (1–3) (2003) 25–42.
- [23] Y.C. Hudiono, et al., Novel mixed matrix membranes based on polymerizable room-temperature ionic liquids and SAPO-34 particles to improve CO₂ separation, *Journal of Membrane Science* 370 (1–2) (2011) 141–148.
- [24] S. Ashtekar, et al., Small-pore molecular sieves SAPO-34 and SAPO-44 with chabazite structure: a study of silicon incorporation, *The Journal of Physical Chemistry* 98 (18) (1994) 4878–4883.
- [25] L. Zan, Z.L. Cheng, Synthesis and separating performance of SAPO-44 zeolite membrane, *Chinese Chemical Letters* 16 (3) (2005) 413–415.
- [26] D. Akolekar, et al., Formation of small pore SAPO-44 type molecular sieve, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 146 (1–3) (1999) 375–386.
- [27] D. Rawtani, Y. Agrawal, Multifarious applications of halloysite nanotubes: a review, *Reviews on Advanced Materials Science* 30 (2012) 282–295.
- [28] S. Balta, et al., A new outlook on membrane enhancement with nanoparticles: the alternative of ZnO, *Journal of Membrane Science* 389 (2012) 155–161.
- [29] B. Zornoza, et al., Mesoporous silica sphere-polysulfone mixed matrix membranes for gas separation, *Langmuir* 25 (10) (2009) 5903–5909.
- [30] A.F. Ismail, W. Lorna, Suppression of plasticization in polysulfone membranes for gas separations by heat-treatment technique, *Separation and Purification Technology* 30 (1) (2003) 37–46.
- [31] E. Karatay, H. Kalıpcılar, L. Yılmaz, Preparation and performance assessment of binary and ternary PES-SAPO 34-HMA based gas separation membranes, *Journal of Membrane Science* 364 (1–2) (2010) 75–81.



Carbon dioxide separation using asymmetric polysulfone mixed matrix membranes incorporated with SAPO-34 zeolite



M.U.M. Junaidi^a, C.P. Leo^{a,*}, A.L. Ahmad^a, S.N.M. Kamal^a, T.L. Chew^b

^a School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

^b Department of Petrochemical Engineering, Faculty of Engineering and Green Technology (FEGT), Perak Campus, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia

ARTICLE INFO

Article history:

Received 25 April 2013

Received in revised form 19 August 2013

Accepted 19 August 2013

Available online 21 September 2013

Keywords:

Carbon dioxide separation

Mixed matrix membrane

Polysulfone

Zeolite

ABSTRACT

Tradeoff limitation on selectivity and permeability restricts the use of membranes for CO₂ separation in natural gas industry. Mixed matrix membranes (MMMs) with combined advantages of polymeric matrix and inorganic fillers have been long proposed to overcome this shortcoming, but thick dense symmetric layer structure with a high mass resistance offers improvement in selectivity only. In this study, asymmetric polysulfone MMMs incorporated with small pore zeolite were proposed. SAPO-34 zeolite with a framework of 0.38 nm pore size and high CO₂ adsorption affinity was used as inorganic fillers. The asymmetric mixed matrix membrane structure was prepared using the phase inversion method. The effects of zeolite loading (5–30 wt.%) on the membrane characteristics were studied using SEM with EDX, FT-IR, and TGA; while the gas transport properties were investigated using pure gas permeation tests of N₂, CO₂ and CH₄. Well dispersion of SAPO-34 particles in the polymer matrix was observed for zeolite loading less than 10 wt.%. The maximum CO₂ permeance (314.02 GPU) was achieved by incorporating 10 wt.% of SAPO-34 into asymmetric PSF membrane. Even without strong binding between PSF and SAPO-34, CO₂/N₂ and CO₂/CH₄ selectivities up to 26.1 and 28.2 respectively were observed.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Natural gas reserves are typically contaminated with more than 40% of carbon dioxide (CO₂) and nitrogen (N₂), which greatly reduce the calorific value of the natural gas. For instance, Malaysia's natural gas reserves are contaminated with about 20–30% of CO₂ [1]. The acidic nature of CO₂ also causes serious corrosion in the gas pipeline. Hence, the CO₂ content in the natural gas transportation pipeline is specifically limited to 4 vol.% [2].

Conventionally, natural gas is purified using gas absorption processes which may involve physical absorption using solvents (polycarbonate, tributylphosphate, etc.). However, the by-products from side reactions of solvent with some natural gas components are difficult to be disposed especially at offshore purification plants. Meanwhile, conventional chemical absorption endures from several drawbacks such as flooding, foaming, channeling, and high capital costs [3]. Besides the absorption technology, various potential technologies such as adsorption [4] and membrane separation [5–9] have been studied to separate CO₂ from natural gas. In the adsorption technology, silica-alumina adsorbent combined with pressure swing adsorption (PSA) has been adopted [5]. Whereas in membrane technology, polymeric membranes such as cellulose acetate (CA), polysulfone (PSF) and polyimide (PI) membranes have been

commercially applied [5]. However, these polymeric membranes showed less desirable separation performance due to the tradeoff between permeability and selectivity as propounded by Robeson [6]. Besides polymeric membranes, inorganic membranes, especially zeolite membranes (DDR, Silicalite-1, and SAPO-34) have been also explored in the high pressure gas separation process. The zeolite membranes showed high selectivity towards CO₂ due to difference in diffusivity and competitive adsorption [7]. Although inorganic membranes displayed excellent separation selectivity, large-scale fabrication of these membranes is difficult as it involves expensive raw materials, complex fabrication methods and long preparation time. In order to overcome the limitations imposed by both polymeric membranes and inorganic membranes, the idea to formulate composite membranes has emerged in the past few decades. Mixed matrix membranes (MMMs) are composite polymeric membranes incorporated with inorganic adsorbent or molecular sieve material as fillers [8].

Small pore zeolites especially SAPO-34 appealed as interesting fillers due to its high adsorption affinity to CO₂. SAPO-34 zeolite is a chabazite (CHA) structure zeolite that has a 0.38 nm framework pore size; which is nearly similar to molecule sizes of the various gasses in a natural gas mixture. A recent work by Hudiono et al. [9] described the uses of the SAPO-34 zeolite to enhance separation performance of a neat solid polymerized room-temperature ionic liquid (poly (RTIL)) membrane. The poly (RTIL) material was used in their study because of its "wetting agent" properties, which could improve adhesion between the polymer and the zeolite particles. By adding 20 wt.% of SAPO-34 zeolite into the poly (RTIL) polymer, the CO₂/CH₄ ideal selectivity factor increased to 39,

* Corresponding author. Tel.: +60 4 5996425; fax: +60 4 5941013.
E-mail address: chcpleo@eng.usm.my (C.P. Leo).

MMMs is essential to achieve a good dispersion of filler inside the polymer phase and excellent CO₂ removal performance that can be applied specifically in natural gas sweetening.

Acknowledgments

The authors would like to acknowledge MOSTI for providing Science Fund (06-01-05-SF0579), Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013), RUI Grant (1001/PJKMIA/811194), PRGS Grant, and USM Fellowship. The authors would also like to thank Ms. Low Ee Mee and Mrs. Norfarahiyah for their knowledge sharing and support.

References

- [1] S.J.M. Rosid, W.A.W. Abu Bakar, R. Ali, Lanthanum oxide based catalysts for methanation reaction in the purification of sour natural gas. Proceedings of Universiti Malaysia Terengganu 10th International Annual Symposium UMTAS 2011: Empowering Science, Technology and Innovation Towards a Better Tomorrow, 2011, pp. 218–225.
- [2] R. Wagner, B. Judd, Gas sweetening fundamentals, Proceedings of the 56th Laurance Reid Gas Conditioning Conference, Norman, OK, 2006.
- [3] M.U.M. Junaidi, C.P. Leo, S.N.M. Kamal, A.L. Ahmad, T.L. Chew, Carbon dioxide removal from methane by using polysulfone/SAPO-44 mixed matrix membranes, *Fuel Processing Technology* 112 (2013) 1–6.
- [4] G. Bellussi, P. Broccia, A. Carati, R. Milini, P. Pollesel, C. Rizzo, M. Tagliabue, Silica-aluminas for carbon dioxide bulk removal from sour natural gas, *Microporous and Mesoporous Materials* 146 (2011) 134–140.
- [5] C.A. Scholes, K.H. Smith, S.E. Kentish, G.W. Stevens, CO₂ capture from pre-combustion processes—strategies for membrane gas separation, *International Journal of Greenhouse Gas Control* 4 (2010) 739–755.
- [6] L.M. Robeson, The upper bound revisited, *Journal of Membrane Science* 320 (2008) 390–400.
- [7] M.A. Carreon, S. Li, J.L. Falconer, R.D. Noble, Alumina-supported SAPO-34 membranes for CO₂/CH₄ separation, *Journal of the American Chemical Society* 130 (16) (2008) 5412–5413.
- [8] O.G. Nik, X.Y. Chen, S. Kaliaguine, Amine-functionalized zeolite FAU/EMT-polyimide mixed matrix membranes for CO₂/CH₄ separation, *Journal of Membrane Science* 379 (1–2) (2011) 468–478.
- [9] Y.C. Hudiono, T.K. Carlisle, A.L. LaFrata, D.L. Gin, R.D. Noble, Novel mixed matrix membranes based on polymerizable room-temperature ionic liquids and SAPO-34 particles to improve CO₂ separation, *Journal of Membrane Science* 370 (1–2) (2011) 141–148.
- [10] P. Jha, J.D. Way, Carbon dioxide selective mixed-matrix membranes formulation and characterization using rubbery substituted polyphosphazene, *Journal of Membrane Science* 324 (2008) 151–161.
- [11] E. Karatay, H. Kalipcilar, L. Yilmaz, Preparation and performance assessment of binary and ternary PES-SAPO 34-HMA based gas separation membranes, *Journal of Membrane Science* 364 (2010) 75–81.
- [12] S.B. Tanteekin-Ersolmaz, Ç. Atalay-Oral, M. Tatlier, A. Erdem-Senatarlar, B. Schoemanb, J. Sterte, Effect of zeolite particle size on the performance of polymer-zeolite mixed matrix membranes, *Journal of Membrane Science* 175 (2000) 285–288.
- [13] M.A. Aroon, A.F. Ismail, M.M. Montazer-Rahmati, T. Matsuura, Morphology and permeation properties of polysulfone membranes for gas separation: effects of non-solvent additives and co-solvent, *Separation and Purification Technology* 72 (2010) 194–202.
- [14] S. Rafiq, Z. Man, A. Maulud, N. Muhammad, S. Maitra, Separation of CO₂ from CH₄ using polysulfone/polyimide silica nanocomposite membranes, *Separation and Purification Technology* 90 (2012) 162–17.
- [15] S. Li, J.L. Falconer, R.D. Noble, SAPO-34 membranes for CO₂/CH₄ separation, *Journal of Membrane Science* 241 (2004) 121–135.
- [16] J. Ahn, W.J. Chung, I. Pinnau, M.D. Guiver, Polysulfone/silica nanoparticle mixed-matrix membrane for gas separation, *Journal of Membrane Science* 314 (2008) 123–133.
- [17] T.W. Pechar, S. Kima, B. Vaughan, E. Marand, M. Tsapatsis, H.K. Jeong, C.J. Cornelius, Fabrication and characterization of polyimide-zeolite L mixed matrix membranes for gas separations, *Journal of Membrane Science* 277 (2006) 195–202.
- [18] T.L. Chew, A.L. Ahmad, S. Bhatia, Rapid synthesis of thin SAPO-34 membranes using microwave heating, *Journal of Porous Materials* 18 (3) (2011) 355–360.
- [19] Y. Li, T.-S. Chung, S. Kulprathipanja, Novel Ag⁺ zeolite/polymer mixed matrix membranes with a high CO₂/CH₄ selectivity, *AIChE Journal* 53 (3) (2007) 610–616.
- [20] A.R. Rojey, A. Deschamps, A. Grehier, E. Robert, Process for separation of the constituents of a mixture in the gas phase using a composite membrane. US patent 4925459, 1990.
- [21] S. Bordiga, L. Regli, C. Lamberti, A. Zecchina, M. Bjørgen, K.P. Lillerud, FTIR adsorption studies of H₂O and CH₃OH in the isostructural H-SSZ-13 and H-SAPO-34: formation of H-bonded adducts and protonated clusters, *Journal of Physical Chemistry B* 109 (16) (2005) 7724–7732.
- [22] X.Y. Chen, H. Vinh-Thang, D. Rodrigue, S. Kaliaguine, Amine-functionalized MIL-53 metal-organic framework in polyimide mixed matrix membranes for CO₂/CH₄ separation, *Industrial and Engineering Chemistry Research* 51 (19) (2012) 6895–6906.
- [23] N. Nyoman Rupiasih, H. Suyanto, M. Sumadiyasa, N. Wendri, Study of effects of low doses UV radiation on microporous polysulfone membranes in sterilization process, *Open Journal of Organic Polymer Materials* 3 (2013) 12–18.
- [24] J.Y. Lee, S.H. Lee, S.W. Kim, Surface tension of silane treated natural zeolite, *Materials Chemistry and Physics* 63 (2000) 251–255.
- [25] F. Dorosti, et al., Fabrication and characterization of polysulfone/polyimide-zeolite mixed matrix membrane for gas separation, *Chemical Engineering Journal* 171 (3) (2011) 1469–1476.
- [26] M.L. Chua, L. Shao, B.T. Low, Y. Xiao, T.-S. Chung, Polyetheramine-polyhedral oligomeric silsesquioxane organic-inorganic hybrid membranes for CO₂/H₂ and CO₂/N₂ separation, *Journal of Membrane Science* 385–386 (2011) 40–48.
- [27] A.F. Ismail, W. Lorna, Suppression of plasticization in polysulfone membranes for gas separation by heat-treatment technique, *Separation and Purification Technology* 30 (2003) 37–46.
- [28] M. Radler, Worldwide look at reserves and production, *Oil and Gas Journal* 49 (2003) 46–47.



Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

The effects of solvents on the modification of SAPO-34 zeolite using 3-aminopropyl trimethoxy silane for the preparation of asymmetric polysulfone mixed matrix membrane in the application of CO₂ separation

M.U.M. Junaidi, C.P. Khoo, C.P. Leo*, A.L. Ahmad

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

ARTICLE INFO

Article history:
Available online xxx

Keywords:
CO₂ separation
Mixed matrix membrane
Silane
Zeolite

ABSTRACT

SAPO-34 zeolite is the ideal porous filler in Mixed matrix membranes (MMMs) for CO₂ separation because it has strong affinity towards CO₂ and pore size (0.38 nm) which is nearly similar to the molecular sizes of various gasses in natural gas. However, the poor compatibility between zeolite and polymeric matrix causes the formation of non-selective interfacial voids, leading to poor separation of gasses. In this work, 3-aminopropyl trimethoxy silane (APMS) was proposed to modify SAPO-34 zeolite before adding into asymmetric polysulfone (PSf) MMMs prepared via dry-wet phase inversion. The effects of solvent (ethanol or isopropanol) in grafting reaction were studied. The changes in FTIR spectra of both modified SAPO-34 zeolite samples signified that more silane molecules were grafted when ethanol was used. SAPO-34 zeolite dispersed evenly in PSf matrix after modification as shown in EDX analysis. Although showing similar FTIR spectra and morphology, a great improvement in CO₂ selectivity and permeance was only shown by PSf/SAPO-34E MMMs with zeolite modified using APMS in ethanol. The highest CO₂/N₂ selectivity of 28, CO₂/CH₄ selectivity of 31 and a satisfactory CO₂ permeance of 706 GPU were achieved. Besides reduction of filler agglomeration, the improvement could be related to the diminished interfacial voids when SAPO-34 zeolite was modified using APMS in ethanol.

© 2013 Elsevier Inc. All rights reserved.

1. Introduction

Zeolites are inorganic aluminosilicate materials which have shown great potential in membrane gas separation due to their well-defined repeating pore structures. The accurate size and shape discrimination resulted from a narrow pore distribution ensures the superior selectivity in gas separation [1]. SAPO-34 zeolite is particularly suitable for gas separation because its chabazite (CHA) structure has a 0.38 nm framework pore size; which is nearly similar to the molecular sizes of various gases, especially in a natural gas application. Thus, SAPO-34 zeolite has been added as the selective fillers in mixed matrix membranes (MMMs) for carbon dioxide (CO₂) separation [2,3]. In general, MMMs composed of polymer as the continuous phase and inorganic filler as the dispersed phase. MMMs exhibit the combined superior properties of both inorganic fillers and polymer to achieve excellent gas separation performance [4]. However, non-selective interfacial voids form in the MMMs due to the poor compatibility between the polymer and inorganic fillers, resulting profound impact on the

separation performance [5]. Silane coupling agents were commonly proposed to improve the compatibility of zeolite in polymeric matrix. Silane coupling agents are silicon-based chemicals which contain two types of reactive groups, namely inorganic and organic groups in the same molecule. The general formula of a silane coupling agent is R-(CH₂)_n-Si-X₃ in which X is a hydrolyzable group, such as methoxy, ethoxy or acetoxy, while R is an organo functional group, such as amino, methacryloxy and epoxy. After grafting on the zeolite, the silane coupling agent acts as an effective interface, which is a complex interaction of chemical and physical factors, such as concentration gradient, expansion coefficient and adhesion. The unique physical and chemical properties of silane coupling agent can even prevent debonding during composite aging [6].

Pechar et al. [7] reported the use of 3-aminopropyltrimethoxysilane (APTMS) to modify ZSM-2 zeolite before blending into polyimide membranes. Although SEM and TEM micrographs showed the absence of voids, the MMMs showed poor performance in terms of CO₂ selectivity and permeability due to the pore blockage on ZSM-2 zeolite [8]. Pechar and co-workers further used silanated zeolite L filler modified with 3-aminopropyltriethoxysilane (APTES) to prepared polyimide MMMs. Both CO₂ selectivity and

* Corresponding author. Tel.: +60 4 5996425; fax: +60 4 5941013.
E-mail address: chepleo@eng.usm.my (C.P. Leo).

4. Conclusions

APMS was selected as the silane coupling agent instead of the other ethoxy group-based silane in this work because the methoxy group is more vulnerable to hydrolysis and it possesses less steric hindrance as compared to ethoxy group. The effects of using two different solvents, namely ethanol and IPA during the silane grafting reaction were studied. XRD patterns of both modified SAPO-34 samples showed the similar trend relative to unmodified SAPO-34 zeolite, but with reduction of intensity in certain range. BET analysis showed that APMS modification of SAPO-34 using ethanol caused a significant decrement in BET surface area of SAPO-34E compared to SAPO-34I with IPA as solvent. The changes in FTIR spectra of both modified SAPO-34 zeolite samples signified the successful reaction of APMS on the surface of SAPO-34 zeolite. More silane molecules were successfully reacted on the SAPO-34 zeolite surface using ethanol as solvent in the grafting reaction. However, all membrane samples possessed similar FTIR spectra and morphology as shown in SEM micrographs. Single gas permeation was carried out to investigate the effects of silane-grafting on the separation performance of these membranes. Both PSf/modified SAPO-34 membranes showed great enhancement in terms of selectivity and permeances relative to the pure PSf membrane in this work. The highest CO₂/N₂ and CO₂/CH₄ selectivities were detected in the PSf/SAPO-34E MMMs with the selectivity value increased to 28 (135% increment) and 31 (124% increment) respectively as compared to the pure PSf membrane. In addition, PSf/SAPO-34E MMMs possessed high CO₂ permeance of 706 GPU. The increment of CO₂ selectivity and permeance could be related to the well dispersion of SAPO-34 zeolite and the reduction of interfacial voids upon the introduction of the coupling agent into the system.

Acknowledgments

The authors would like to acknowledge MOSTI for providing science fund (06-01-05-SF0579), Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013), RUI grant (1001/PJKMIA/811194), PRGS grant (1001/PJKMIA/8035020), and USM Fellowship. The authors would also like to thank Ms. Low Ee Mee and Mrs. Norfarahiyah for their kind support.

References

[1] R.S.C.P. Pandey, *Prog. Polym. Sci.* 26 (2001) 853–893.

- [2] M. Peydayesh, S. Asarehpour, T. Mohammadi, O. Bakhtiari, *Chem. Eng. Res. Des.* (2013), <http://dx.doi.org/10.1013/j.chemd.2013.01.022>.
- [3] U. Cakal, L. Yilmaz, H. Kalipcilar, *J. Membr. Sci.* 17–418 (2012) 45–51.
- [4] D. Sen, H. Kalipcilar, L. Yilmaz, *J. Membr. Sci.* 303 (2007) 194–203.
- [5] X.Y. Chen, O.G. Nik, D. Rodrigue, S. Kaliaguine, *Polymer* 53 (2012) 3269–3280.
- [6] A.F. Ismail, T.D. Kusworo, A. Mustafa, *J. Membr. Sci.* 319 (1–2) (2008) 306–312.
- [7] T.W. Pechar, M. Tsapatsis, E. Marand, R. Davis, *Desalination* 146 (1–3) (2002) 3–9.
- [8] T.W. Pechar, S. Kim, B. Vaughan, E. Marand, M. Tsapatsis, H.K. Jeong, C.J. Cornelius, *J. Membr. Sci.* 277 (1–2) (2006) 195–202.
- [9] A.M.W. Hillock, S.J. Miller, W.J. Koros, *J. Membr. Sci.* 314 (1–2) (2008) 193–199.
- [10] Y. Li, H.M. Guan, T.S. Chung, S. Kulprathipanja, *J. Membr. Sci.* 275 (1–2) (2006) 17–28.
- [11] O.G. Nik, X.Y. Chen, S. Kaliaguine, *J. Membr. Sci.* 379 (1–2) (2011) 468–478.
- [12] M.C. Brochier Salon, M.N. Belgacem, Phosphorus, Sulfur, Silicon Relat. Elem. 186 (2) (2011) 240–254.
- [13] S. Li, J.L. Falconer, R.D. Noble, *J. Membr. Sci.* 241 (1) (2004) 121–135.
- [14] J.Y. Lee, S.H. Lee, S.W. Kim, *Mater. Chem. Phys.* 63 (2000) 251–255.
- [15] N.P. Damayanti, *J. Sol-Gel Sci. Technol.* 56 (1) (2010) 47–52.
- [16] T.L. Chew, A.L. Ahmad, S. Bhatia, *Chem. Eng. J.* 171 (3) (2011) 1053–1059.
- [17] J.Y. Kim, J. Kim, S.T. Yang, W.S. Ahn, *Fuel* 108 (2013) 515–520.
- [18] O.G. Nik, M. Sadrzadeh, S. Kaliaguine, *Chem. Eng. Res. Des.* 90 (9) (2012) 1313–1321.
- [19] G. Clarizia, C. Algieri, A. Regina, E. Drioli, *Micropor. Mesopor. Mater.* 115 (1–2) (2008) 67–74.
- [20] M.F.A. Wahab, A.F. Ismail, S.J. Shilton, *Sep. Purif. Technol.* 86 (2012) 41–48.
- [21] M.U.M. Junaidi, C.P. Leo, S.N.M. Kamal, A.L. Ahmad, T.L. Chew, *Fuel Process. Technol.* 118 (2014) 125–132.
- [22] M.U.M. Junaidi, C.P. Leo, S.N.M. Kamal, A.L. Ahmad, T.L. Chew, *Fuel Process. Technol.* 112 (2013) 1–6.
- [23] S. Balta, A. Sotro, P. Luis, L. Benea, B. Van der Bruggen, J. Kim, *J. Membr. Sci.* 389 (2012) 155–161.
- [24] C.P. Leo, N.H. Ahmad Kamil, M.U.M. Junaidi, S.N.M. Kamal, A.L. Ahmad, *Sep. Purif. Technol.* 103 (2013) 84–91.
- [25] M.A. Aroon, A.F. Ismail, M.M. Montazer-Rahmati, T. Matsuura, *Sep. Purif. Technol.* 72 (2) (2010) 194–202.
- [26] T.H. Young, L.W. Chen, *Desalination* 103 (3) (1995) 233–247.
- [27] J. Han, W. Lee, J.M. Choi, R. Patel, B.R. Min, *J. Membr. Sci.* 351 (1–2) (2010) 141–148.
- [28] A.F. Ismail, P.Y. Lai, *Sep. Purif. Technol.* 33 (2) (2003) 127–143.
- [29] D. Wang, K. Li, W.K. Teo, *J. Membr. Sci.* 115 (1) (1996) 85–108.
- [30] A. Mansourizadeh, A.F. Ismail, *J. Membr. Sci.* 348 (1–2) (2010) 260–267.
- [31] F. Dorosti, M.R. Omidkhah, M.Z. Pedram, F. Moghadam, *Chem. Eng. J.* 171 (3) (2011) 1469–1476.
- [32] P. Jha, J.D. Way, *J. Membr. Sci.* 324 (1–2) (2008) 151–161.
- [33] Y. Zhang, K.J. Balkus Jr., L.H. Musselman, J.P. Ferraris, *J. Membr. Sci.* 325 (1) (2008) 28–39.
- [34] Y.C. Hudiono, T.K. Carlisle, A.L. LaFrate, D.L. Gin, R.D. Noble, *J. Membr. Sci.* 370 (1–2) (2011) 141–148.
- [35] O.G. Nik, B. Nohair, S. Kaliaguine, *Micropor. Mesopor. Mater.* 143 (1) (2011) 221–229.
- [36] J. Hu, H. Cai, H. Ren, Y. Wei, Z. Xu, H. Liu, Y. Hu, *Ind. Eng. Chem. Res.* 49 (24) (2010) 12605–12612.
- [37] S. Basu, A. Cano-Odena, I.F.J. Vankelecom, *Sep. Purif. Technol.* 81 (1) (2011) 31–40.
- [38] Y. Dai, J.R. Johnson, O. Karvan, D.S. Sholl, W.J. Koros, *J. Membr. Sci.* 401–402 (2012) 76–82.
- [39] S. Husain, W.J. Koros, *J. Membr. Sci.* 288 (1–2) (2007) 195–207.
- [40] T. Li, Y. Pan, K.V. Peinemann, Z. Lai, *J. Membr. Sci.* 425–426 (2013) 235–242.

Fouling mitigation in humic acid ultrafiltration using polysulfone/SAPO-34 mixed matrix membrane

M. U. M. Junaidi, C. P. Leo, S. N. M. Kamal and A. L. Ahmad

ABSTRACT

Although ultrafiltration (UF) membranes are applicable in wastewater and water treatment, most UF membranes are hydrophobic and susceptible to severe fouling by natural organic matter. In this work, polysulfone (PSf) membrane was blended with silicaluminophosphate (SAPO) nanoparticles, SAPO-34, to study the effect of SAPO-34 incorporation in humic acid (HA) fouling mitigation. The casting solution was prepared by blending 5–20 wt% of SAPO-34 nanoparticles into the mixture of PSf, 1-methyl-2-pyrrolidinone and polyvinyl alcohol at 75 °C. All membrane samples were then prepared using the phase inversion method. Blending SAPO-34 zeolite into PSf membranes caused augmentation in surface hydrophilicity and pore size, leading to higher water permeation. In the HA filtration test, mixed matrix membranes (MMMs) with SAPO-34 zeolite showed reduced HA fouling initiated from pore blocking. The MMM with 20 wt% SAPO-34 loading exhibited the highest increment of water permeation (83%) and maintained about 75% of permeate flux after 2.5 h. However, the SAPO-34 fillers agglomerated in the PSf matrix and induced macrovoid formation on the membrane surface when excessive zeolite was added.

Key words | humic acid fouling, mixed matrix membrane, SAPO-34 zeolite, ultrafiltration

M. U. M. Junaidi
C. P. Leo (corresponding author)
S. N. M. Kamal
A. L. Ahmad
School of Chemical Engineering,
Engineering Campus,
Universiti Sains Malaysia Seri Ampangan,
14300 Nibong Tebal, Penang,
Malaysia
E-mail: chcpleo@eng.usm.my

INTRODUCTION

With the continuous growth of membrane technology, wastewater treatment and water reclamation using membrane filtration are feasible to fulfill water demand and its safety at reasonable cost. The use of membrane filtration offers several advantages including superior water quality, easy control of operation, low maintenance, and little production of sludge (Yuan & Zydney 2000). Prior to the fine treatment of surface water, groundwater and wastewater, ultrafiltration (UF) is commonly adopted. The pore size of the UF membrane is usually engineered in the range of 0.01–0.001 µm (Chen *et al.* 2009), which is small enough to remove most contaminants such as bacteria, viruses, high molecular-weight substances, colloidal materials, organic and inorganic molecules in water.

Effluent organic matter is the combination of natural organic matter (NOM), soluble microbial products and trace amounts of harmful chemicals, which are usually present in the wastewater (Shon *et al.* 2006). NOM originates from the microbiological degradation of surrounding vegetation and animal decay. NOM such as humic acid (HA), reacts with the widely used oxidants, such as chlorine,

ozone, chlorine dioxide and chloramines, in the conventional water treatment to form a host of disinfection by-products (DBPs) (Krasner *et al.* 2006). DBPs can lead to cancers, miscarriages and nervous system complications. Thus, the NOM treatment process is a vital approach to ensure water safety. UF membrane processes can be used to remove HA effectively from water and wastewater as summarized in many reported works (Jucker & Clark 1994; Yuan & Zydney 2000; Mousa 2007; Lee *et al.* 2008; Peeva *et al.* 2011). Yuan & Zydney (2000) have used polyvinylidene fluoride, polycarbonate and polyethersulfone (PES) UF membranes to remove HA effectively from water, with more than 85% of HA rejection. Several studies (Jucker & Clark 1994; Lee *et al.* 2008; Peeva *et al.* 2011) demonstrated that NOM such as HA, however, has a major influence on the flux decline. Yuan & Zydney (1999) examined the fouling of PES membrane with 0.16 µm pore size. They claimed that the fouling was caused by the convective deposition of HA particles on the membrane surface, causing pore blockage. According to Mousa (2007), fouling due to pore blockage is much more severe than cake layer

as shown in Figure 3(e). Meanwhile, fouled Pf-20 membrane (Figure 3(f)) exhibited less HA deposition, and SAPO-34 aggregates could be still observed. In the HA rejection test, there was an increment rejection trend as the SAPO-34 loading was increased. The highest HA rejection was obtained by Pf-20 sample with 97.9% of HA rejection as tabulated in Table 2. The HA rejection increment for MMMs blended with SAPO-34 in this work were in accordance with work done by Peeva *et al.* (2011).

CONCLUSION

The PSf/PVA/SAPO-34 MMMs were successfully prepared by blending SAPO-34 filler during the phase inversion method. The SAPO-34 particles appeared on the membrane surface, which increased larger surface pore formation. The hydrophilicity of SAPO-34 in MMMs samples resulted in lower contact angle compared to Pf-00 membrane. The water flux was increased as the SAPO-34 loading increased. Pf-20 exhibited highest water permeation flux increment (83%) compared to the Pf-00 membrane. In the HA filtration test, blended SAPO-34 zeolite may reduce the HA fouling initiated by pore blocking. Pf-20 membrane could maintain about 75% of permeate flux during the HA filtration. However, further study is required to investigate the optimum HA fouling mitigation on the PSf MMMs with higher SAPO-34 loading.

ACKNOWLEDGEMENTS

The authors would like to acknowledge Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013), Research University Individual Grant (1001/PJKIMIA/811194), RU-PRGS (1001/PJKIMIA/8035020) and USM Fellowship. The authors would also like to thank MOSTI for providing Science Fund (06-01-05-SF0579).

REFERENCES

- Ahmad, A. L., Majid, M. A. & Ooi, B. S. 2011 Functionalized PSf/SiO₂ nanocomposite membrane for oil-in-water emulsion separation. *Desalination* 268, 266–269.
- Chen, W., Su, Y., Zheng, L., Wang, L. & Jiang, Z. 2009 The improved oil/water separation performance of cellulose acetate-graft-polyacrylonitrile membranes. *Journal of Membrane Science* 337 (1–2), 98–105.
- Chung, T.-S., Jiang, L. Y., Li, Y. & Kulprathipanja, S. 2007 Mixed matrix membranes (MMM) comprising organic polymers with dispersed inorganic fillers for gas separation. *Progress in Polymer Science* 32, 483–507.
- Goh, P. S., Ismail, A. F., Sanip, S. M., Ng, B. C. & Aziz, M. 2011 Recent advances of inorganic fillers in mixed matrix membrane for gas separation. *Separation and Purification Technology* 81, 243–264.
- Han, R., Zhang, S., Liu, C., Wang, Y. & Jian, Y. 2009 Effect of NaA zeolite particle addition on poly(phthalazinone ether sulfone ketone) composite ultrafiltration (UF) membrane performance. *Journal of Membrane Science* 345, 5–12.
- Hoek, E. M. V., Ghosh, A. K., Huang, X., Liong, M. & Zink, J. I. 2011 Physical-chemical properties, separation performance, and fouling resistance of mixed-matrix ultrafiltration membranes. *Desalination* 283, 89–99.
- Jian, P., Yahui, H., Yang, W. & Linlin, L. 2006 Preparation of polysulfone-Fe₃O₄ composite ultrafiltration membrane and its behavior in magnetic field. *Journal of Membrane Science* 284, 9–16.
- Jucker, C. & Clark, M. M. 1994 Adsorption of aquatic humic substances on hydrophobic ultrafiltration membranes. *Journal of Membrane Science* 97, 37–52.
- Krasner, S. W., Weinberg, H. S., Richardson, S. D., Pastor, S. J., Chinn, R., Scimmenti, M. J., Onstad, G. D. & Thruston Jr., A. D. 2006 Occurrence of a new generation of disinfection byproducts. *Environmental Science and Technology* 40 (23), 7175–7185.
- Lee, E. K., Chen, V. & Fane, A. G. 2008 Natural organic matter (NOM) fouling in low pressure membrane filtration – effect of membranes and operation modes. *Desalination* 218, 257–270.
- Lee, J. Y., Lee, S. H. & Kim, S. W. 2000 Surface tension of silane treated natural zeolite. *Material Chemistry and Physics* 63, 251–255.
- Leo, C. P., Cathie Lee, W. P., Ahmad, A. L. & Mohammad, A. W. 2012 Polysulfone membranes blended with ZnO nanoparticles for reducing fouling by oleic acid. *Separation and Purification Technology* 89, 51–56.
- Leo, C. P., Ahmad Kamil, N. H., Junaidi, M. U. M., Kamal, S. N. M. & Ahmad, A. L. 2013 The potential of SAPO-44 zeolite filler in fouling mitigation of polysulfone ultrafiltration membrane. *Separation and Purification Technology* 103, 84–91.
- Li, S., Falconer, J. L. & Noble, R. D. 2004 SAPO-34 membranes for CO₂/CH₄ separation. *Journal of Membrane Science* 241, 121–135.
- Liang, S., Xiao, K., Mo, Y. & Huang, X. 2012 A novel ZnO nanoparticle blended polyvinylidene fluoride membrane for anti-irreversible fouling. *Journal of Membrane Science* 394–395, 184–192.
- Mansourizadeh, A. & Ismail, A. F. 2010 Effect of additives on the structure and performance of polysulfone hollow fiber membranes for CO₂ absorption. *Journal of Membrane Science* 348, 260–267.

Preparation and characterization of polysulfone mixed matrix membrane incorporated with thermodynamically stable nano-Palladium for hydrogen separation

Hani Shazwani Mohd Suhaimi^{1,a}, Leo Cheo Peng^{1,b} and Abdul Latif Ahmad^{1,c}

¹School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

^adiniedanisha@yahoo.com, ^bchcpleo@eng.usm.my, ^cchlatif@eng.usm.my

Keywords: Palladium nanoparticles; Mixed matrix membrane; Gas Separation.

Abstract. Palladium (Pd) nanoparticles offer excellent hydrogen affinity in mixed matrix membrane for gas separation. In order to avoid aggregation, Pd nanoparticles have to be stabilized before blending into polymer matrix. Pd nanoparticles can be thermodynamically stabilized and dispersed using electrostatic and/ or steric forces of a stabilizer which is typically introduced during the formation of Pd nanoparticles in the inversed microemulsion. Polyvinylpyrrolidone, polyethylene glycol (PEG) and sodium hydroxide in ethylene glycol exhibited good effect on particles passivation. However, the effects of these stabilizers on membrane morphology and separation performance were unknown. The aim of this work is to incorporate polymer-stabilized Pd nanoparticles into Polysulfone (PSf) membranes for hydrogen separation. The microstructure of Pd nanoparticles was first analyzed by TEM. Phase inversion method was then adopted for the preparation of asymmetric PSf/nano-Pd MMMs. The separation performance of MMMs was investigated by using nitrogen and hydrogen as test gases and the membrane characteristics were further studied using SEM and FTIR. The highest permeability for H₂ was 255.82 GPU with selectivity of 6.89. The results suggested that PEG provides good contact between nanoparticles and the polymer. TEM and FTIR results revealed that these stabilizers have significant effects on the synthesized Pd nanoparticles size. Also, SEM results showed that the MMMs incorporated with thermodynamically nano-Pd in PEG achieved satisfactory asymmetric structure which explains the good performance in gas separation.

Introduction

Metal nanoparticles have unique physico-chemical properties which differ from bulk material. Chemical preparative methods for synthesizing metal nanoparticles involve the chemical reduction of metallic ions in the presence of a stabilizer which works as a matrix to prevent the nanoparticles from aggregating and allow one to isolate the nanoparticles. Palladium (Pd) nanoparticles have been extensively studied due to their high hydrogen selective permeability.

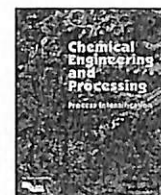
Namini et al. [9] synthesized Pd nanoparticles by exploiting polyethylene glycol (PEG) as both reducing agent and stabilizer via a simple methodology under facile condition. Among the existing chemical reduction methods, polyvinylpyrrolidone (PVP)- in the membrane can enhance demixing of solvent and non-solvent during membrane fabrication, hydrophilicity of the membrane and increase its permeability [1]. In the past, the preparation of metal nanoparticles using ethylene glycol (EG) as both solvent and reducing agent was also extensively reported. The metallic cations are reduced to metallic colloids by receiving electrons from the oxidation of EG to glycol acid, which is present in its deprotonated form as glycolate anions in alkaline solution [2]. However, in those polyol systems, the reducing ability of pure EG is too weak to reduce metallic ions at room temperature; thus it is necessary to speed up the reaction by heating or adding an extra reducing agent such as sodium hydroxide (NaOH). The effects of stabilizers on membrane morphology, as well as the permeability performance in MMMs were studied in this work.

Acknowledgements

The authors would like to acknowledge Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013) and Research University Individual Grant (1001/PJKMIA/811194). The authors would also like to thank MOSTI for providing Science Fund (06-01-05-SF0579) and KPT for providing MyMaster.

References

- [1] M. Amirilargani, E. Saljoughi, T. Mohammadi, and M. R. Moghbeli, Effects of coagulation bath temperature and polyvinylpyrrolidone content on flat sheet asymmetric polyethersulfone membranes, *Polymer Engineering and Science* 50(5) (2010) 885–893.
- [2] D. Berger, G. A. Trăistaru, B. Ş. Vasile, I. Jitaru, and C. Matei, Palladium nanoparticles synthesis with controlled morphology obtained by polyol method, *U.P.B. Sci. Bull Series B* 72(1) (2010) 113-120.
- [3] L. J. Chen, C. C. Wan, and Y. Y. Wang, Chemical preparation of Pd nanoparticles in room temperature ethylene glycol system and its application to electroless copper deposition, *Journal of Colloid and Interface Science*, 297(1) (2006) 143-150.
- [4] A. F. Ismail, and P. Y. Lai, Effects of phase inversion and rheological factors on formation of defect-free and ultrathin-skinned asymmetric polysulfone membranes for gas separation, *Separation and Purification Technology* 33(2) (2003) 127-143.
- [5] Z. Jia, H. Sun, Q. Gu, H. Lang, and H. Abuduwayit, Preparation of palladium nanocrystals by membrane absorption of hydrogen, *Journal of Membrane Science* 380(1–2) (2011) 63-67.
- [6] Klute, Synthesis of palladium nano-particles and their use in Suzuki coupling, <http://www.sciencemadness.org> (2006).
- [7] P. W. Labuschagne, S. G. Kazarian, and R. E. Sadiku, In situ FTIR spectroscopic study of the effect of CO₂ sorption on H-bonding in PEG–PVP mixtures, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 78(5) (2011) 1500-1506.
- [8] A. Mansourizadeh, and A. F. Ismail, Effect of additives on the structure and performance of polysulfone hollow fiber membranes for CO₂ absorption, *Journal of Membrane Science*, 348(1-2) (2010) 260-267.
- [9] P. A. Namini, A. A. Babaluo, and B. Bayati, Palladium nanoparticles synthesis using polymeric matrix: poly(ethyleneglycol) molecular weight and palladium concentration effects, *International Journal of Nanoscience and Nanotechnology* 3(1) (2007) 37-43.
- [10] T. H. Young and L. W. Chen, Pore formation mechanism of membranes from phase inversion process, *Desalination* 103 (1995) 233-247.
- [11] Q. Z. Zheng, P. Wang, and Y. N. Yang, Rheological and thermodynamic variation in polysulfone solution by PEG introduction and its effect on kinetics of membrane formation via phase-inversion process, *Journal of Membrane Science* 279(1-2) (2006) 230-237.



Preparation and characterization of polysulfone mixed matrix membrane incorporated with palladium nanoparticles in the inversed microemulsion for hydrogen separation



H.S.M. Suhaimi, C.P. Leo*, A.L. Ahmad

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

ARTICLE INFO

Article history:

Received 23 September 2013

Received in revised form

30 November 2013

Accepted 13 January 2014

Available online 20 January 2014

Keywords:

Mixed matrix membrane

Palladium nanoparticles

Gas separation

ABSTRACT

Polysulfone (PSf) membrane shows acceptable gas separation performance, but its application is limited by the "trade-off" between selectivity and permeability. In this study, PSf mixed matrix membranes (MMMs) incorporated with palladium (Pd) nanoparticles in the inversed microemulsion were proposed for hydrogen (H_2) separation. Pd nanoparticles can be kinetically stabilized and dispersed using electrostatic and/or steric forces of a stabilizer which is typically introduced during the formation of Pd nanoparticles in the inversed microemulsion. Pd nanoparticles were synthesized by loading ($PdCl_2$) into the polymeric matrix, polyethylene glycol (PEG) which acts as reducing agent and stabilizer. The dry-wet phase inversion method was applied for the preparation of asymmetric PSf MMMs. The effects of Pd (0–4 wt%) on the membrane characteristics and separation performance were studied. Experimental findings verified that the MMMs are able to achieved a high H_2/N_2 selectivity of 21.69 and a satisfactory H_2 permeance of 46.24 GPU due to the changes in membrane structure from fully developed finger-like structure to closed cell structure besides the growth of dense layer. However, the selectivity of H_2/CO_2 decreased due to the addition of PEG.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen (H_2) is the utmost important gas product which is not only useful for chemical production such as hydrocracking, hydrodesulfurization, and Haber process, but also applicable in the energy industry as a clean fuel. H_2 can be directly produced from steam reforming of hydrocarbon, followed by gas purification. Besides pressure swing adsorption and cryogenic separation, membrane separation appears to be an attractive alternative in H_2 purification as it offers: (1) high energy efficiency, (2) cost effectiveness per foot print, (3) simplicity in operation, and (4) environmentally friendly.

Palladium (Pd) dense membranes supported on porous material are generally used for hydrogen separation at high temperature because of their excellent affinity towards hydrogen atoms [1]. The separation of H_2 via Pd membrane involves the reversible adsorption of H_2 molecules at the Pd surface, followed by rapid dissociation and diffusion of atomic H_2 into the metal lattice, where it occupies the octahedral interstitial sites with an increase in the lattice constant [2]. The diffusion of H_2 into the Pd lattice provides larger H_2 storage capacity, and the dissociation of H_2 into the active

atomic H_2 leads to its desirable separation properties [3]. Despite of high selectivity and permeance in H_2 separation, the reliability of Pd membrane remains one of the major problems in H_2 separation. Corrosion causing structural changes usually occur during the use of Pd membrane, causing reduction in its separation performance. For Pd alloy membranes, atomic inter-diffusion of metals between the Pd-based film and the substrate happens at high temperature, resulting performance deterioration. Pd and Pd based membranes also suffered from hydrogen-embrittlement cracking during thermal cycling and readily evidence surface contamination by sulphur-containing species [4]. The use of nano-sized Pd grains was reported as an alternative method to minimize the lattice distortion resulted from the α - β -phase transition. The improvement is due to the increment of the H_2 concentration on the grain surface and subsurface compared with the interior sites of the nano-Pd particles [5].

Besides inorganic membranes, polymeric membranes have also been commercialized as they are lower in cost. Polymeric membranes possessed good ability to cope with high pressure-drops and they can be easily scaled up. H_2 separation from highly supercritical gases such as methane, carbon monoxide and nitrogen can be easily achieved by polymeric membranes, because of the extremely high diffusion coefficient of H_2 relative to all other molecules except helium. Even though solubility factor is not favourable for H_2 , the diffusion contribution dominates and gives overall high selectivity.

* Corresponding author. Tel.: +60 4 5996425; fax: +60 4 5941013.
E-mail address: chcpleo@eng.usm.my (C.P. Leo).

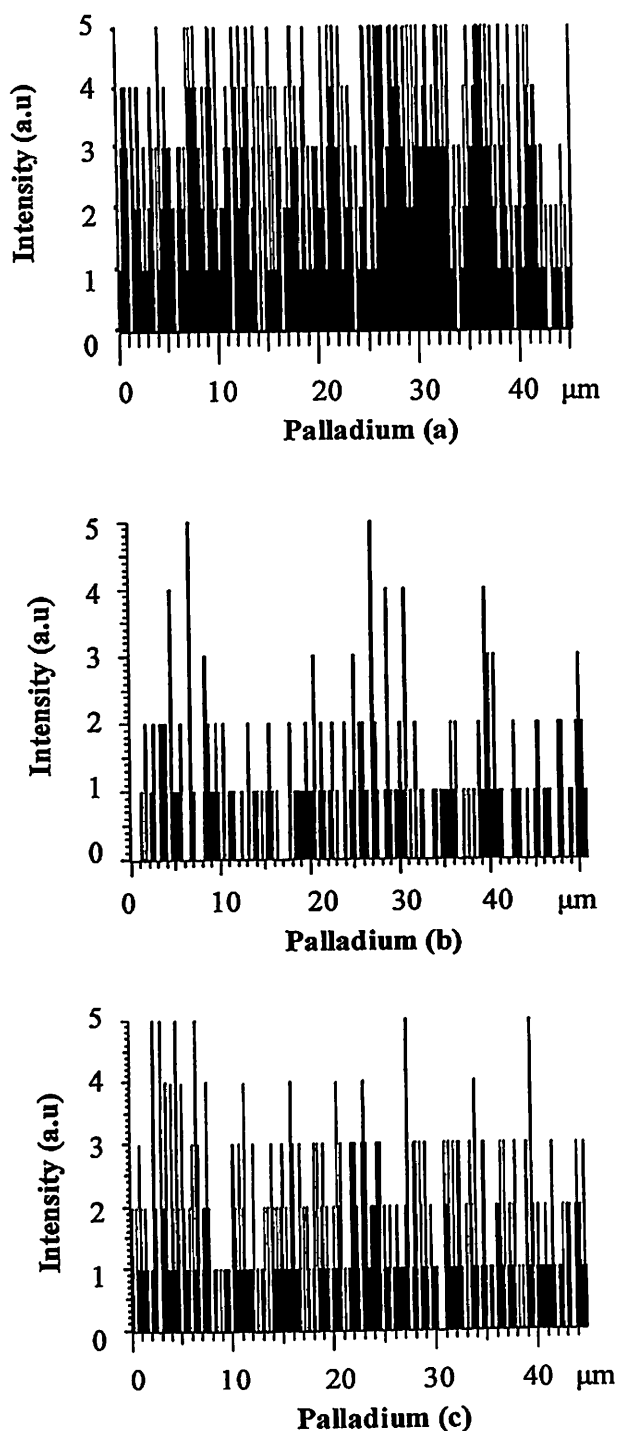


Fig. 8. The EDX result of Pd nanoparticles entrapped PSf membrane (a) Pd.1, (b) Pd.3, and (c) Pd.3.

However, rigidification effects of PEG could dominate in Pd.3 membrane, similar to PSf(PEG).3 membrane.

4. Conclusion

MMMs incorporated with Pd loading have been prepared and their gas separation performance as well as stabilizer effects have been studied extensively. In the synthesis of Pd nanoparticles, the introduction of PEG resulted in an extremely small particles size

with 1.92 nm. The SEM images revealed that the changes in membrane structure contributed towards the membrane performance in gas separation. Under the effects of PEG, the membrane structure changes from fully developed finger-like structure to closed cell structure besides the growth of dense layer. The MMMs exhibited an increment of H₂ permeability compared with pure PSf membrane while the selectivity of H₂/N₂ was significantly increased after embedded with Pd nanoparticles. The highest H₂/N₂ selectivity of 21.69 and a satisfactory H₂ permeance of 46.24 GPU were achieved at 3 wt% Pd nanoparticles loading.

Acknowledgements

The authors would like to acknowledge Ministry of Education Malaysia for providing FRGS (FRGS/2/2013/TK05/USM/02/5) and Ministry of Higher Education Malaysia for providing MyMaster. The authors would also like to thank Universiti Sains Malaysia for facilities, equipments and scholarship provided through Membrane Science and Technology Cluster (1001/PSF/8610013), Research University Individual Grant (1001/PJKMIA/811194) and Fellowship. At last but not least, the authors would like to thank Mr. Yeo Kai Liang for proof-reading this manuscript.

References

- [1] J. Yu, R.Y.F. Liu, B. Poon, S. Nazarenko, T. Koloski, T. Vargo, A. Hiltner, E. Baer, *Journal of Applied Polymer Science* 92 (2004) 749–756.
- [2] F.A. Lewis, *The Palladium/Hydrogen System*, Academic Press Inc., London, 1967.
- [3] M. Moreno, F.J. Ibanez, J.B. Jasinski, F.P. Zamborini, *Journal of the American Chemical Society* (2011) 4389–4397.
- [4] G.Q. Lu, J.C. Diniz da Costa, M. Duke, S. Giessler, R. Socolow, R.H. Williams, T. Kreutz, *Journal of Colloid and Interface Science* 314 (2007) 589–603.
- [5] A. Pundt, R. Kirchheim, *Annual Review of Materials Research* 36 (2006) 555–608.
- [6] R.W. Baker, K. Lokhandwala, *Industrial & Engineering Chemistry Research* 47 (2008) 2109–2121.
- [7] A.F. Ismail, P.Y. Lai, *Separation and Purification Technology* 33 (2003) 127–143.
- [8] J. Ahn, W.-J. Chung, I. Pinnau, M.D. Guiver, *Journal of Membrane Science* 314 (2008) 123–133.
- [9] A.L. Khan, A. Cano-Odena, B. Gutiérrez, C. Minguillón, I.F.J. Vankelecom, *Journal of Membrane Science* 350 (2010) 340–346.
- [10] T.-S. Chung, L.Y. Jiang, Y. Li, S. Kulprathipanja, *Progress in Polymer Science* 32 (2007) 483–507.
- [11] J. Cookson, *Platinum Metals Review* 56 (2012) 83.
- [12] Q.-Z. Zheng, P. Wang, Y.-N. Yang, *Journal of Membrane Science* 279 (2006) 230–237.
- [13] P.A. Namini, A.A. Babalou, B. Bayati, *International Journal of Nanoscience and Nanotechnology* 3 (2007) 37–43.
- [14] Z. Jia, H. Sun, Q. Gu, H. Lang, H. Abuduwaiyt, *Journal of Membrane Science* 380 (2011) 63–67.
- [15] G. Arthanareeswaran, D. Mohan, M. Raajenthiren, *Journal of Membrane Science* 350 (2010) 130–138.
- [16] B. Domènech, M. Muñoz, D.N. Muraviev, J. Macanás, *Catalysis Today* 193 (2012) 158–164.
- [17] T.-H. Young, L.-W. Chen, *Pore formation mechanism of membranes from phase inversion process*, *Desalination* 103 (1995) 233–247.
- [18] S. Wongchitphimon, R. Wang, R. Jiratananon, L. Shi, C.H. Loh, *Journal of Membrane Science* 369 (2011) 329–338.
- [19] J. Ahmad, M.-B. Hägg, *Journal of Membrane Science* 427 (2013) 73–84.
- [20] M.A. Aroon, A.F. Ismail, M.M. Montazer-Rahmati, T. Matsuura, *Separation and Purification Technology* 72 (2010) 194–202.
- [21] S.R. Reijerkerk, M.H. Knoef, K. Nijmeijer, M. Wessling, *Journal of Membrane Science* 352 (2010) 126–135.
- [22] M. Iqbal, Z. Man, H. Mukhtar, B.K. Dutta, *Journal of Membrane Science* 318 (2008) 167–175.
- [23] S. Holloway, *Surface Science* 540 (2003) 1–3.
- [24] S. Clémenson, E. Espuche, L. David, D. Léonard, *Journal of Membrane Science* 361 (2010) 167–175.
- [25] B. Zornoza, S. Irusta, C. Téllez, J. Coronas, *Langmuir* 25 (2009) 5903–5909.
- [26] R. Naim, A.F. Ismail, A. Mansourizadeh, *Journal of Membrane Science* 423–424 (2012) 503–513.
- [27] A.F. Ismail, N.H. Rahim, A. Mustafa, T. Matsuura, B.C. Ng, S. Abdulrah, S.A. Hashemifard, *Separation and Purification Technology* 80 (2011) 20–31.

Preparation and characterization of polysulfone mixed-matrix membrane incorporated with palladium nanoparticles dispersed in polyvinylpyrrolidone for hydrogen separation

H. S. M. Suhaimi · M. N. I. M. Khir · C. P. Leo ·
A. L. Ahmad

Received: 27 November 2013 / Accepted: 27 March 2014 / Published online: 16 April 2014
© Springer Science+Business Media Dordrecht 2014

Abstract Polysulfone (PSf) offers better transport performance for gas permeation, but its application is limited by the “trade-off” between selectivity and permeability as well as the limitation of the “upper bound” that exists in solution-diffusion transportation. The idea of mixed-matrix membranes (MMMs) comprised of a continuous phase of PSf and a dispersed phase of palladium (Pd) nanoparticles has been developed. Membrane characteristics and their gas separation performance were studied. In order to prevent agglomeration, the Pd nanoparticle was stabilized using polyvinylpyrrolidone (PVP). The effects of Pd (0–3 wt%) and a stabilizer on the membrane characteristics were studied using a scanning electron microscope with energy dispersive X-ray, transmission electron micrographs, X-ray diffraction and Fourier transform infrared, while the separation performance was investigated using hydrogen (H₂), nitrogen (N₂), and carbon dioxide (CO₂) as test gases. H₂ separation from highly supercritical gases such as methane, carbon monoxide, and N₂ can be easily achieved by polymeric membranes, because of the extremely high diffusion coefficient of H₂ relative to all other molecules except helium gives overall high selectivities. Experimental findings verified that the MMMs achieved high permeability coupled with a satisfactory selectivity of hydrogen after incorporating Pd nanoparticles dispersed using PVP. High permeability with 3,124 GPU was achieved and the corresponding H₂/N₂ selectivities of the membranes was 20 while H₂/CO₂ was 6.2.

Keywords Mixed-matrix membrane · Palladium nanoparticles · Polysulfone · Gas separation

H. S. M. Suhaimi · M. N. I. M. Khir · C. P. Leo (✉) · A. L. Ahmad
School of Chemical Engineering, Engineering Campus, Universiti
Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau
Pinang, Malaysia
e-mail: chcpleo@eng.usm.my

Introduction

Membrane represents a viable commercial alternative for the separation of gas mixtures due to its high efficiency, easy intensification, simple operation, and low operating cost. It is also worth noting that hydrogen (H₂) recovery is among the first commercial applications of membrane in gas separation because H₂ is highly permeable compared to other gases. H₂ is small in molecular structure and non-condensable, thus glassy polymers have been primarily used to make H₂-selective membrane [16].

Polysulfone (PSf) is one of the most common glassy polymers used for gas separation. This glassy polymer can be formed with a rigid and high-strength structure, which offers better transport performance for gas permeation compared to rubbery material [21]. Similar to other types of polymeric membranes, PSf membranes possess a trade-off between the key parameters for gas separation of permeability and selectivity. In order to improve both permeability and selectivity, as well as to overcome the limitation of the “upper bound” that exists in solution-diffusion transportation via the polymeric membranes, the concept of mixed-matrix membranes (MMMs) comprised of a continuous phase of polymer and a dispersed phase of inorganic filler has been developed.

Studies have shown that hybrid membranes comprised of polymer with embedded inorganic particles showed enhanced membrane stability. The MMMs showed higher gas permeabilities and comparable selectivities to pure polymeric. Ahn et al. [3] have shown a remarkable enhancement in H₂ gas permeability (from 11.8 to 22.7 barrer) by introducing nonporous nanosized silica particles in the PSf membrane. In addition, Galve et al. [11] have studied the combination of ordered mesoporous silica MCM-41 and layered titanasilicate JDF-L1 fillers for 6FDA-based copolyimide MMMs. Regarding H₂/N₂ separation, MMMs containing 4 and 8 % of MCM-41 and JDF-L1, respectively, showed an H₂/N₂ selectivity value of

in the range of 4–8 nm. The increment of dense layer in the membrane structure indicates that Pd contributes to the formation of denser structure as shown in the presented SEM images. In gas performances analysis, the MMMs show an increment of H₂ permeance compared with PSf membrane after incorporation of Pd nanoparticles due to the strong affinity of Pd element on the membrane surface and H₂. The highest H₂/N₂ and H₂/CO₂ selectivities of 20.2 and 6.2 respectively with a greater H₂ permeability of 3124.90 GPU were achieved at 2 wt% of Pd nanoparticles loading. Therefore, the H₂ permeability was achieved in this work compared to that reported in previous work which successfully achieved by reducing N₂ and CO₂ gas crossing through the membrane. Thus, the ideal selectivity of PSf(Pd₂) for H₂/N₂ and H₂/CO₂ significantly greater compared to other researchers as illustrated in Figs. 7 and 8 [2, 8, 9, 13].

Acknowledgements The authors would like to acknowledge Ministry of Education Malaysia for providing FRGS (FRGS/2/2013/TK05/USM/02/5) and MyMaster. The authors would also like to thank Universiti Sains Malaysia for the facilities and equipments provided through the Membrane Science and Technology Cluster (1001/PSF/8610013) and a Research University Individual Grant (1001/PJKMIA/811194) and USM Fellowship.

References

- Ahmad J, Hägg M-B (2013) Preparation and characterization of polyvinyl acetate/zeolite 4A mixed matrix membrane for gas separation. *J Membr Sci* 427:73–84
- Ahmad AL, Jaya MAT, Derek CJC, Ahmad MA (2011) Synthesis and characterization of TiO₂ membrane with palladium impregnation for hydrogen separation. *J Membr Sci* 366:166–175
- Ahn J, Chung W-J, Pinnau I, Guiver MD (2008) Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation. *J Membr Sci* 314:123–133
- Balta S, Sotto A, Luis P, Benea L, Bruggen BVD, Kim J (2012) A new outlook on membrane enhancement with nanoparticles: the alternative of ZnO. *J Membr Sci* 155–161
- Chen C-H, Ma YH (2010) The effect of H₂S on the performance of Pd and Pd/Au composite membrane. *J Membr Sci* 362:535–544
- Chen L-J, Wan C-C, Wang Y-Y (2006) Chemical preparation of Pd nanoparticles in room temperature ethylene glycol system and its application to electroless copper deposition. *J Colloid Interface Sci* 297:143–150
- Chung T-S, Jiang LY, Li Y, Kulprathipanja S (2007) Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. *Prog Polym Sci* 32:483–507
- Clémenson S, Espuche E, David L, Léonard D (2010) Nanocomposite membranes of polyetherimide nanostructured with palladium particles: processing route, morphology and functional properties. *J Membr Sci* 361:167–175
- David OC, Gorri D, Urriaga A, Ortiz I (2011) Mixed gas separation study for the hydrogen recovery from H₂/CO/N₂/CO₂ post combustion mixtures using a Matrimid membrane. *J Membr Sci* 378:359–368
- Doménech B, Muñoz M, Muraviev DN, Macanás J (2012) Catalytic membranes with palladium nanoparticles: from tailored polymer to catalytic applications. *Catal Today* 193:158–164
- Galve A, Sieffert D, Staudt C, Ferrando M, Güell C, Téllez C, Coronas J (2013) Combination of ordered mesoporous silica MCM-41 and layered titanosilicate JDF-L1 fillers for 6FDA-based copolyimide mixed matrix membranes. *J Membr Sci* 431:163–170
- Ismail AF, Lai PY (2003) Effects of phase inversion and rheological factors on formation of defect-free and ultrathin-skinned asymmetric polysulfone membranes for gas separation. *Sep Purif Technol* 33:127–143
- Khan AL, Cano-Odena A, Gutiérrez B, Minguillón C, Vankelecom IFJ (2010) Hydrogen separation and purification using polysulfone acrylate-zeolite mixed matrix membranes. *J Membr Sci* 350:340–346
- Madaeni SS, Moradi P (2011) Preparation and characterization of asymmetric polysulfone membrane for separation of oxygen and nitrogen gases. *J Appl Polym Sci* 121:2157–2167
- Mansoori, S. A. A., Pakizeh, M., Chenar, M. P., (2011) Effect of synthesis parameters on structural characteristics of polysulfone membrane and its gas separation properties. *Journal of membrane science and technology*, 1–2
- Moreno M, Ibanez FJ, Jasinski JB, Zamborini FP (2011) Hydrogen reactivity of palladium nanoparticles coated with mixed monolayers of alkyl thiols and alkyl amines for sensing and catalysis applications. *J Am Chem Soc* 4389–4397
- Shao L, Low BT, Chung T-S, Greenberg AR (2009) Polymeric membranes for the hydrogen economy: contemporary approaches and prospects for the future. *J Membr Sci* 327:18–31
- Suhaimi HSM, Leo CP, Ahmad AL (2014) Preparation and characterization of polysulfone mixed matrix membrane incorporated with palladium nanoparticles in the inverted microemulsion for hydrogen separation. *Chem Eng Process Process Intensif* 77:30–37
- Wang XL, Tu JP, Zhang PL, Zhao XB (2007) Hydrogen storage properties of ball-milled Mg-based composite with PdCl₂ additive. *J Zhejiang Univ (Sci)* 8:1510–1513
- Yu J, Liu RYF, Poon B, Nazarenko S, Koloski T, Vargo T, Hiltner A, Baer E (2004) Polymers with palladium nanoparticles as active membrane materials. *J Appl Polym Sci* 92:749–756
- Zornoza B, Irusta S, Téllez C, Coronas J (2009) Mesoporous silica sphere-polysulfone mixed matrix membranes for gas separation. *Langmuir Artic* 25:5903–5909

Membranes with Great Hydrophobicity: A Review on Preparation and Characterization

N. A. Ahmad,¹ C. P. Leo,¹ A. L. Ahmad,¹ and W. K. W. Ramli²

¹*School of Chemical Engineering, Universiti Sains Malaysia, Nibong Tebal, Pulau Pinang, Malaysia*

²*School of Bioprocess Engineering, Universiti Malaysia Perlis, Arau, Perlis, Malaysia*

Membranes are commonly designed with great hydrophilicity or hydrophobicity to promote or prohibit the transportation of water, respectively. There are vast applications of hydrophobic membranes such as filtration, gas separation, membrane gas absorption, pervaporation, membrane distillation and more that cannot be attained with hydrophilic membranes. However, the development of hydrophobic membranes was relatively slow in the past, as membrane technologists and researchers were more interested in reducing membrane hydrophobicity for permeability enhancement or fouling control in the aqueous separation. Thus, literature related to hydrophobic membranes has not been reviewed elsewhere. This review reported on the characterization and preparation methods for hydrophobic membranes. Hydrophobic ceramic membranes are commonly prepared by chemical modification. Besides using different types of chemicals, the membrane surface is roughened to enhance its hydrophobicity. For polymeric membranes, great hydrophobicity can be engineered using per-fluorinated polymers or phase immersion in a dual coagulation bath. Each technique has its advantages and weaknesses.

Keywords: Membranes, hydrophobic, hydrophilic, applications, preparations

INTRODUCTION

Membranes are either a porous or dense barrier that permit the passage of certain compounds selectively in a fluid (1–3). The permeation of molecules through a membrane barrier is driven by concentration gradient, pressure difference, thermal variation and electrical force across the membrane (4). Surface characteristics are important in membrane separation since the molecules from the feed stream will first come into contact with the membrane surface. The selected molecules are then adsorbed onto the membrane surface and desorbed from the membrane barrier into the permeate side (5). Membrane surfaces should have special features to promote and/or prohibit certain molecules

to pass through the membrane barrier. There are two common surface features of membrane, either hydrophobic or hydrophilic. The hydrophobic property is known as the “water repellent” feature, prohibiting the surface wettability, and the hydrophilicity is the “water loving” property, encouraging water spread (6–9). Water cannot spread on the hydrophobic surface and hence reduces its contact with the surface. Spherical water droplets form on the hydrophobic surface due to low surface energy (9–12). However, a water droplet will spread on a membrane surface and then be adsorbed into a porous membrane if the membrane surface is hydrophilic.

Both hydrophobic and hydrophilic membranes can be applied in pervaporation for the dehydration of solvent and the separation of organic mixture. However, hydrophobic membranes are preferable when removal of only a small amount of solvent is required from a stream comprised mostly of water. Commercial applications of the pervaporation include bio-fuel recovery from fermentation broth and gasoline desulfuration. Polydimethylsiloxane (PDMS) membranes supported by

Received 11 May 2013, Accepted 30 August 2013.

Address correspondence to C. P. Leo, School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, Nibong Tebal, S.P.S., 14300 Pulau Pinang, Malaysia. E-mail: chcleo@usm.my

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lspr.

CONCLUSION

Membrane technology is an alternative method for separation processes since it offers great advantages compared to conventional methods. It shows high efficiency in energy consumption. A large scale of green separation can be conducted without use of any chemical. Hydrophobic polymeric membranes and ceramic membranes have been used in various processes such as osmotic evaporation, membrane distillation, extraction, gas separation and more. Before selecting an appropriate hydrophobic membrane, the membrane hydrophobicity can be evaluated in terms of water contact angle, surface roughness, membrane morphology and surface chemistry. Basic concepts of some hydrophobic characterizations were discussed.

Hydrophobic ceramic membranes are commonly prepared via chemical modification. Organosilane and lipid solution have been used by researchers for chemical modification of ceramic membranes. Organosilane is a popular modification agent due to its flexibility in development of the hydrophobic surface on different materials. Besides the different types of chemicals, the membrane surface is roughened to enhance its hydrophobicity into superhydrophobicity.

Hydrophobic polymeric membranes can be synthesized by directly choosing low surface energy polymer materials, modifying polymer or enhancing membrane hydrophobicity. Low surface energy polymer is directly used in hydrophobic polymeric fabrication since it has low surface wettability. Besides the choice of hydrophobic polymer, preparation method like phase inversion, TIPS and stretching plays an important factor to affect the membrane hydrophobicity. Among these preparation methods, phase inversion is the most well-known method for fabrication of hydrophobic polymeric membrane with various types of morphology. In addition, the membrane hydrophobicity can be enhanced by blending additives in the polymer casting solution, plasma treatment and hydrophobic polymeric coating. Blending the polymer solution is commonly used due to its simplicity. However, each of the membrane preparation techniques has its advantages and weaknesses.

APPENDIX

Abbreviations

AFM	Atomic Force Microscopy
CA _w	Water contact angle
CNTBP	Carbon nanotube bucky-paper
CVD	Chemical vapor deposition
EDX	Energy dispersive X-ray
FAS	Fluoroalkylsilane
LEP	Liquid entry pressure
PEI	Polyetherimide
PES	Polyethersulfone

PP	Polypropylene
PSf	Polysulfone
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
R _q	The root mean square roughness
SEM	Scanning electron microscope
SMM	Surface-modifying macromolecules

Nomenclature

γ _{LS}	Liquid/solid surface tension
γ _L	Liquid surface tension
γ _{LV}	Liquid/vapor surface tension
γ _{SV}	Solid/vapor surface tension
θ	Contact angle
(ΔH)	Enthalpy of melting
°C	Degrees Celsius
% w/w	Mass percentage
%	Percentage
h	hour
wt.%	Weight percentage

ACKNOWLEDGMENTS

The authors thank Mr. Yeo Kai Liang and Ms. Low Ee Mee for proofreading this manuscript.

FUNDING

The authors acknowledge MOSTI for providing Science Fund (06-01-05-SF0579). The authors also thank Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013), Research University Individual Grant (1001/PJKMIA/811194), Short Term Grant (304/PJKMIA/60311016), and Post Graduate Grant (1001/PJKMIA/8035015).

REFERENCES

- André, A., Anne, J., and Christian, G. (2005) Ceramic membrane processing. In *Chemical Processing of Ceramics*, Second Edition; Komarneni, S., and Lee, B., eds.; CRC Press, Boca Raton, FL, 629–666.
- Roque-Malherbe, R.M.A. (2009) *The Physical Chemistry of Materials*; CRC Press, Boca Raton, FL, 467–490.
- David, W., Shilpa, D., William, K., and Theodore, M. (2004) Membrane separation. In *The Engineering Handbook*, 2nd Ed.; Dorf, R.C., ed.; CRC Press, Boca Raton, FL, 63–1 63-15.
- Reif, O. W. (2006). Microfiltration membranes: Characteristics and manufacturing. In *Sterile Filtration*; Jormitz, M., ed.; Springer: Berlin, Heidelberg, 73–103.
- Davis, M.E., and Davis, R.J. (2003) *Fundamentals of Chemical Reaction Engineering*, McGraw-Hill Higher Education: New York.
- Kazunari, A. (2002) Hydrophobic effects. In *Supramolecular Design for Biological Applications*; Yui, N., ed.; CRC Press: Boca Raton, FL, 13–24.

Effects of THF as Cosolvent in the Preparation of Polydimethylsiloxane/Polyethersulfone Membrane for Gas Separation

Siti Nadiah Mustafa Kamal, Choe Peng Leo, Abdul Latif Ahmad, Mohd Usman Mohd Junaidi
School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan,
14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

Polydimethylsiloxane/polyethersulfone (PDMS/PES) asymmetric membranes are widely applied in gas separation. However, the effects of common cosolvent on these membranes remain unknown. In order to study the changes in membrane morphology and gas separation properties, asymmetric PDMS/PES membranes were prepared. The studied parameters were types of cosolvents, tetrahydrofuran (THF) concentration, evaporation time, and PDMS concentration. Membrane morphology was examined using scanning electron microscopy and gas separation was conducted using pure CO₂, N₂, CH₄, and Hat 25°C. The addition of cosolvent into the polymer solution decreased the dope viscosity and delayed liquid-liquid demixing during phase inversion. Macrovoids formation was observed in substructure layer after adding THF and these macrovoids elongated with the reduction in THF content. There were microvoids formed on top of macrovoids and microvoids layer became thicker due to the increasing evaporation time of solvents before coagulation in nonsolvent. The PDMS coating on the PES membrane formed a dense skin layer and exhibited higher selectivity compared to the uncoated membrane. Membrane contained THF cosolvent with 60 s evaporation time and 3 wt% coated PDMS is the optimum membrane among other membranes in this work. The CO₂/N₂ selectivity was enhanced by 73.3% with CO₂ permeance of 44.86 GPU. POLYM. ENG. SCI., 00:000-000, 2013. © 2013 Society of Plastics Engineers

INTRODUCTION

Polymeric membranes have been widely applied in gas separation due to their great flexibility in scale-up, low operating cost, and energy efficiency [1, 2]. In order to achieve excellent gas performance and good mechanical strength for high pressure application, asymmetric polymeric membranes have been widely prepared [3]. Asymmetric membranes are characterized by being composed of an extremely thin and dense film which supported on a

thick porous substructure which may be the same or different material of the membrane. The porous substructure provides the thin membrane with strength and durability which prevents membrane destruction by pressure and temperature [3, 4]. By phase inversion, thin layer of polymer solution is immersed into a coagulation bath for solvent exchange between solvent and nonsolvent (water) to form asymmetric membranes. The phase separation occurs during the solvent exchange process, resulting desired porous structure [5].

During membrane synthesis, the choice of polymer in membrane preparation is very important as it influences the ultimate membrane properties. The most commonly used commercial polymers for gas separation are the phenyl group-based polysulfone (PSf), polyethersulfone (PES), and aromatic polyimide. Glassy polymer, PES has many advantages as a starting material in the preparation of gas separation membrane. PES membranes have been commercialized by Spectrum Laboratories and Sterlitech Corporation. This commercial polymer has a relatively high glass transition temperature ($T_g = 230^\circ\text{C}$) [6, 7] which allows long-term use without any dimensional changes or physical weakening at temperature as high as 200°C. PES is more selective but less permeable compared to other polymers such as PSf. This is because PES has a higher degree of chain rigidity resulted from its regular and polar backbone [6]. Polydimethylsiloxane (PDMS) with low glass transition temperature (T_g) of -123°C is the most common silicon rubber supported on PES membranes because PDMS enhances gas permeation selectively [7]. PDMS has a very flexible polymer siloxane backbone and low intermolecular forces between methyl groups and high bonding energy of siloxane group. The combination of rubbery and glassy polymer, PDMS/PES membrane is effective in gas separation. Rubbery polymer separates gases based on condensability. Generally, the sorption of the gases increases as the condensability of gases increase. Conversely, the relative size (kinetic diameter) of gases is more important than condensability during gas separation via glassy polymer. The gas diffusion increases from smaller to larger molecular size,

Correspondence to: Choe Peng Leo; e-mail: chcpleo@eng.usm.my
DOI 10.1002/pen.23767
Published online in Wiley Online Library (wileyonlinelibrary.com).
© 2013 Society of Plastics Engineers

cosolvent (THF or ethanol) into the polymer dope solution of 20PT-3 and 20PE-3 membranes. Similar trend had been reported in the literature [5], CO₂ and CH₄ permeances decreased after adding THF and ethanol cosolvents into PSf polymer dope solution. The reduction in gas permeance can be related to the formation of sponge structure after adding cosolvent as shown in Fig. 2b and c. Wang et al. [13] reported that PSf membrane with sponge-like structure possess higher resistance in gas separation compared to PSf membrane with finger-like microstructure.

In all cases, H₂ permeation was the highest followed by CO₂, CH₄, and N₂ permeation except the gas permeation in membrane without coating with PDMS solution (20PT). The selectivity and permeance of hydrogen gas is encouraging using cosolvent THF in sample 20PT-3 and 20PT-3-30s as stated in Table 3. The hydrogen permeation in this work enhanced double compare to the literature [30] which has higher on H₂/N₂ selectivity. In addition, the selectivity of CO₂/N₂ was greatly improved in 20PT-3 membrane after coating with 3 wt% of PDMS solution. The selectivity of CO₂/N₂ was two times higher than the selectivity of CO₂/CH₄ for same sample after coating. This is because the sorption of gases increased with the increasing of gas condensability in rubbery polymers [8]. PDMS dense layer most likely was been well engineered on top of the microvoids tailored in 20PT-3 membrane (Fig. 2b). However, the selectivity of the membrane could decrease after coating with high PDMS solution due to depth intrusion of the solution. Thus, the gas permeance and selectivity could be low because the permeative resistance increased [31]. All PDMS/PES membranes showed higher permeance of CH₄ than N₂, showing the domination of PDMS in gas separation. Unlike PES, PDMS is a rubbery polymer which is sorption selective and it permeate CH₄ over N₂ [8].

With THF concentration of 16 wt% in the polymer solution, 20PT-3 membrane showed higher CO₂ permeance than 17PT-3 and 25PT-3. The gas permeance increased at higher polymer concentration or lower THF content in 20PT-3 membrane compared to 17PT-3 membrane because of the entanglement conformation of polymer [30]. The reduction of gas permeance in 25PT-3 membrane can be related to the formation of macrovoid as explained in the morphology study. By the increment of evaporation time before phase inversion, permeances of all gases (CO₂, N₂, and CH₄) were improved. The observation is contrast to the work as reported by Julian and Wenten [23] that the increment in evaporation time resulted thicker skin layer and lower gas permeation. This is because microvoids grew in PES membranes which promote gas permeation in this work. The membranes with higher evaporation time has thicker microvoid layer which encourages gas permeation.

CONCLUSIONS

The morphology and separation properties of PDMS/PES asymmetric membranes have been successfully stud-

ied. THF cosolvent resulted the formation of microvoids and macrovoids in PES membrane. The changes of macrovoid size depended on THF concentration in the polymer solution mainly. In addition, microvoids increased with the increment of evaporation time before phase inversion. Gas separation was dominated of PDMS layer. However, the thickness and separation performance of PDMS layer were affected by the morphology of PES membrane which could be controlled by the cosolvent, THF.

REFERENCES

1. C.-Y. Liang, P. Uchytíl, R. Petrychkovych, Y.-C. Lai, K. Friess, M. Sipek, M.M. Reddy, and S.-Y. Suen, *Sep. Purif. Technol.*, **92**, 57 (2012).
2. J. Han, W. Lee, J.M. Choi, R. Patel, and B. Min, *J. Membr. Sci.*, **351**, (2010).
3. B.S. Minhas and I.-F. Wang, EP 0456 143 A2 (1991).
4. F.X. Muller and J.E. Burkinshaw, EP 0 421 137 A1 (1990).
5. M.A. Aroon, A.F. Ismail, M.M. Montazer-Rahmati, and T. Matsuura, *Sep. Purif. Technol.*, **72**, 2 (2010).
6. R.E. Kesting and A. Fritzsche, *Polymeric Gas Separation Membranes*, Wiley, New York (1993).
7. M. Murder, *Basic Principles of Membrane Technology*, Eschede, Kluwer Academic, The Netherlands (1997).
8. R.W. Baker and K. Lokhandwala, *Ind. Eng. Chem. Res.*, **47**, 7 (2008).
9. M. Sadzadeh, M. Amirilargani, K. Shahidi, and T. Mohammadi, *J. Membr. Sci.*, **342**, 1 (2009).
10. S.S. Madaeni and S. Hoseini, *J. Polym. Res.*, **16**, 5 (2009).
11. S.S. Madaeni, A. Moradi, and V. Kazemi, *Iran. Polym. J.*, **18**, 11 (2009).
12. A. Mansourizadeh and A.F. Ismail, *J. Membr. Sci.*, **348**, 1 (2010).
13. D. Wang, K. Li, and W. Teo, *J. Membr. Sci.*, **115**, 1 (1996).
14. D. Wang, K. Li, and W. Teo, *J. Membr. Sci.*, **176**, 2 (2000).
15. D. Wang, W.K. Teo, and K. Li, *J. Membr. Sci.*, **204**, 1 (2002).
16. J.J. Shieh and T.S. Chung, *J. Membr. Sci.*, **140**, 1 (1998).
17. L. Broens, D.M. Koenhen, and C.A. Smolders, *Desalination*, **22**, 1 (1977).
18. L. Shao, T.S. Chung, G. Wensley, S.H. Goh, and K.P. Pramoda, *J. Membr. Sci.*, **244**, 1 (2004).
19. S.-H. Chen, R.-M. Liou, J.-Y. Lai, and C.-L. Lai, *Eur. Polym. J.*, **43**, 9 (2007).
20. T.-H. Young and L.-W. Chen, *Desalination*, **103**, 3 (1995).
21. M. Hanakawa and S. Minegishi, US 8,205,754 B2 (2012).
22. T.-H. Young, Y.-H. Huang, and L.-Y. Chen, *J. Membr. Sci.*, **164**, 1 (2000).
23. H. Julian and I. Wenten, *IOSR J. Eng.*, **2**, 3 (2012).

1 **The effects of solvents on the modification of SAPO-34 zeolite using 3-**
2 **aminopropyl trimethoxy silane for the preparation of asymmetric**
3 **polysulfone mixed matrix membrane in the application of CO₂**
4 **separation.**

5

6 **M.U. M. Junaidi, C. P. Khoo, C.P. Leo*, A.L. Ahmad**

7

8 *School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri*
9 *Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia*

10

11 **ABSTRACT**

12 SAPO-34 zeolite is and ideal porous filler in mixed matrix membranes (MMMs) for CO₂
13 separation because it has strong affinity towards CO₂ and pore size (0.38 nm) which is
14 nearly similar to the molecular sizes of various gases in natural gas. However, the poor
15 compatibility between zeolite and polymeric matrix causes the formation of non-selective
16 interfacial voids, leading to poor separation of gases. In this work, 3-aminopropyl
17 trimethoxy silane (APMS) was proposed to modify SAPO-34 zeolite before adding into
18 asymmetric polysulfone (PSf) MMMs prepared via dry-wet phase inversion. The effects
19 of solvent (ethanol or isopropanol) in grafting reaction were studied. The changes in
20 FTIR spectra of both modified SAPO-34 zeolite samples signified that more silane
21 molecules were grafted when ethanol was used. SAPO-34 zeolite dispersed evenly in PSf
22 matrix after modification as shown in EDX analysis. Although showing similar FTIR
23 spectra and morphology, a great improvement in CO₂ selectivity and permeance was only
24 shown by PSf/SAPO-34E MMMs with zeolite modified using APMS in ethanol. The
25 highest CO₂/N₂ selectivity of 28.66, CO₂/CH₄ selectivity of 30.07 and a satisfactory CO₂
26 permeance of 706.43 GPU were achieved. Besides reduction of filler agglomeration, the

The authors would like to acknowledge MOSTI for providing Science Fund (06-01-05-SF0579), Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013), RUI Grant (1001/PJKMIA/811194), PRGS Grant, and USM Fellowship. The authors would also like to thank Ms. Low Ee Mee for her knowledge sharing and support.

References

- [1] 1. R.S.C. P. Pandey, *Prog. Polym. Sci.* 26 (2001) 853-893.
- [2] M. Peydayesh, S. Asarehpour, T. Mohammadi, O. Bakhtiari, *Chem. Eng. Res. Des.* (2013) <http://doi.org/10.1013/j.cherd.2013.01.022>.
- [3] U. Cakal, L. Yilmaz, H. Kalipcilar, *J. Membr. Sci.* 17-418 (2012) 45-51.
- [4] D. Şen, H. Kalıpcılar, L. Yilmaz, *J. Membr. Sci.* 303 (2007) 194-203.
- [5] X.Y. Chen, O.G. Nik, D. Rodrigue, S. Kaliaguine, *Polymer*, 53 (2012) 3269-3280.
- [6] A.F. Ismail, T.D. Kusworo, A. Mustafa, *J. Membr. Sci.* 319 (1-2) (2008) 306-312.
- [7] T.W. Pechar, M. Tsapatsis, E. Marand, *R. Desalination*, 146 (1-3) (2002) 3-9.
- [8] T.W. Pechar, S. Kim, B. Vaughan, E. Marand, M. Tsapatsis, H.K. Jeong, C.J. Cornelius, *J. Membr. Sci.* 277 (1-2) (2006) 195-202.
- [9] A.M.W. Hillock, S.J. Miller, W.J. Koros, *J. Membr. Sci.* 314 (1-2) (2008) 193-199.

Organo Silane Interfacial Enhanced SAPO-34 Zeolite in Polysulfone Mixed Matrix Membrane: Effect of Membrane Hydrophobicity towards Gas Separation Performance

M.U.M. Junaidi, C.P. Leo*, S.N.M. Kamal, A.L. Ahmad

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

ABSTRACT

One of the major challenges in the development of mixed matrix membranes (MMMs) is the poor adhesion between selective selective filler and polymer matrix. The presence of defects can severely weaken the separation performance of the membrane. Thus, silane coupling modification is generally used to eliminate such defects. In this work, flouroalkyl silane (FAS) with chemical name of triethoxy-1H,1H,2H,2H-perflourodecyl silane ($C_{16}H_{19}O_3F_{17}Si$) is used to alter SAPO-34 zeolite. The effect of hydrophobicity towards membrane characteristic and gas transport properties was studied. All of the membranes were fabricated using the phase inversion method. The contact angle analysis explained surface modification with FAS has enhanced the hydrophobicity nature of SAPO-34. The PSf-10/FAS MMMs exhibited good adhesion between filler and polymer phases, minimizing defects proposed by voids formation. However, particles agglomeration was still occurring when 20 wt % of FAS modified zeolites were incorporated in PSf matrix. The TGA analysis has proven that FAS modification had not distracted CO_2 adsorption affinity of SAPO-34. PSf-10/FAS MMMs showed the highest performance enhancement on CO_2/N_2 and CO_2/CH_4 separation properties compared to the PSf-10 MMMs and neat PSf membrane. In hydrophobicity study towards pure gas permeation test, PSf-10 MMMs exhibited mass reduction in gas separation performance due to the SAPO-34 pores were blocked by the

*Corresponding author. Tel.: +60 4 5996425; fax: +60 4 5941013
Email address: chcpleo@eng.usm.my (C.P. Leo)

276 permeation test, PSf-10 MMMs exhibited mass reduction in gas separation performance
277 due to the SAPO-34 pores were blocked by the adsorbed water. By the silane
278 modification proposed by FAS on the SAPO-34 zeolite, the hydrophobicity enhancement
279 on MMMs was able to lessen the water adsorption of SAPO-34 zeolites and maintain
280 MMMs separation performance.

281

282 Acknowledgements

283

284 The authors would like to acknowledge Universiti Sains Malaysia for the financial
285 support provided through Membrane Science and Technology Cluster
286 (1001/PSF/8610013), Research University Individual Grant (1001/PJKMIA/811194),
287 USM Fellowship and RU-PGRS. The authors would also like to thank MOSTI for
288 providing Science Fund (06-01-05-SF0579).

289

290 References

291

- 292 [1] Ward, J.K. and W.J. Koros, *Crosslinkable mixed matrix membranes with surface*
293 *modified molecular sieve for natural gas: I. Preparation and experimental result.*
294 *Journal of Membrane Science*, 2011. 377(0): p. 75-81.
- 295 [2] T.W. Pechar, S. Kima, B. Vaughan, E. Marand, M. Tsapatsis, H.K. Jeong, C.J.
296 Cornelius, *Fabrication and characterization of polyimide-zeolite L mixed matrix*
297 *membranes for gas separations.* *Journal of Membrane Science*, 2006. 277: p 195-
298 202.

Preparation and characterization of polysulfone mixed matrix membrane incorporated with SAPO-34 zeolite for gas separation

M. U. M. Junaidi, C. P. Leo*, A. L. Ahmad, T. L. Chew, S. N. M. Kamal.

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300, Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia.

* e-mail: chcpleo@eng.usm.my

Abstract – Asymmetric pure PSf and 10 wt% SAPO-34/PSf MMMs were fabricated in order to investigate the effects of evaporation time on the membrane morphology and gas performance properties. The evaporation times were varied from 0s to 180s. All membranes were prepared using dry-wet phase inversion method. The cross-section SEM images provide indication that different evaporation period could affect the membrane dense skin layer thickness for asymmetric structure. Membrane fabrication with longer evaporation time tends to have thicker skin layer with high mass resistance and a shorter evaporation period will produce a thinner top layer structure with more lower transport resistance. This behaviour was proved in this work CO₂/N₂ ideal separation properties, which membrane samples with 180s evaporation time have lower gas permeances rates. The highest CO₂/N₂ selectivity (26.1) was obtained by 10 wt% SAPO-34 MMMs with 90s evaporation period with CO₂ permeance of 3140 barrer, which is caused by good formation of thin dense skin and the addition of CO₂ selective SAPO-34 particles.

Keywords: Mixed matrix membrane; SAPO-34 zeolite; Gas Separation.

1. Introduction

Nowadays, carbon dioxide (CO₂) is greatly released worldwide due to the fast modern civilization and industrialization. CO₂ has been identified as the major contributor of the green house effects that causes global warming. Ever since the analysis for CO₂ concentration have been started in 1958, CO₂ concentration at the atmospheric level has increased up to 22 % in 2009 [1] and has been responsible for 60% of the increment in world temperature [2]. Combustion in fossil fuel power plants generates about 30% of CO₂ and the rest of emission is produced from transportation, oil and gas industry sectors [3].

Serious concern on CO₂ concentration has further ignited the development of CO₂ capture and storage technology to recover the undesired CO₂ and store it for further processes and applications. The most feasible methods in CO₂ capture are absorption, adsorption, cryogenic separation and membrane technology [4]. CO₂ removal using membrane separation is currently of great interest

due to its' low energy consumption, small footprint, simple operation and ease in scale up. In the seek of solution to surpass the limitations of preoccupied conventional polymeric membranes, the idea to formulate composite membranes has appeared in the past few decades. The remote and well-commercialize polymers materials is merged with CO₂ selective particles to form mixed matrix membranes (MMMs). MMMs usually contain inorganic adsorbent and molecular sieves material as fillers [5]. These composite membranes have shown great potential as alternative to industrial polymeric membrane because of their higher separation performance and compatibility with the commercial polymeric membrane modules.

Recent works on MMMs [6-7] have focused more on dense polymeric matrix with little improvement in gas permeance. Asymmetric MMMs membrane with dense skin supported on porous polymeric matrix is proposed in this work to achieve not only improved selectivity of CO₂ but also greater permeance. Asymmetric MMMs can be easily prepared using phase inversion method. The phase inversion involves the immersion of

Evaporation time (s)	Permeability (barrer)		Selectivity $\alpha(\text{CO}_2/\text{N}_2)$
	CO ₂	N ₂	
0	3874.69	3994.76	0.97
90	3140.02	120.35	26.1
180	360.60	94.12	3.45

Table 2. Permeabilities and ideal selectivities of polysulfone blend with 10 wt% SAPO-34 MMMs at different evaporation time at ambient temperature and 50 psig.

Fig. 4 represents the performance of membrane samples with 90s and 180s evaporation time membranes on revised Robeson plot for CO₂/N₂ gas pair. Clearly, membrane samples performance with no evaporation step are located further away from trade-off line due to the severe loss CO₂/N₂ selectivity, which of The CO₂/N₂ performance plot of 10 wt% SAPO-34 MMMs with 90s evaporation period has surpass the trade-off line, which prove that this MMMs has encounter the polymeric limitation imposed by Robeson [18]. Nonetheless, pure PSf membrane with same evaporation period is still under the polymeric limitation. By increasing the evaporation time to 180s, the CO₂/N₂ performance was decrease as the performance plots for both membranes were pulled far away from trade-off line.

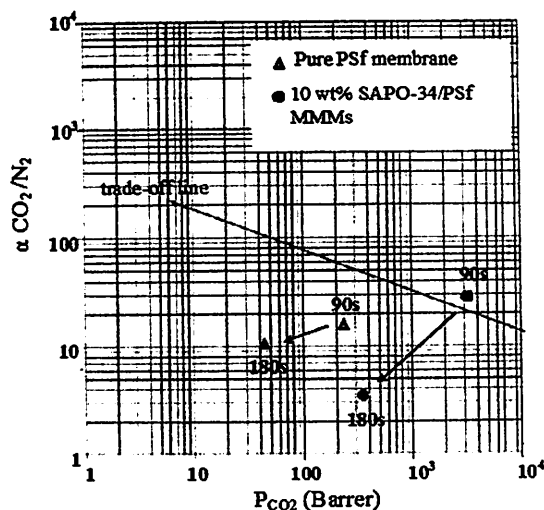


Fig. 4. Comparison of membranes prepared with 90s and 180s evaporation time on Robeson plot [18] for CO₂/N₂ gas pair.

4. Conclusions

Asymmetric pure PSf and 10 wt% SAPO-34/PSf MMMs were fabricated in order to investigate the effects of evaporation time on the membrane morphology and gas performance properties. All membranes were prepared using dry-wet phase inversion method. The cross-section SEM images provide indication that different evaporation period could affect the membrane

dense skin layer thickness for asymmetric structure. Membrane fabrication with longer evaporation time tends to have thicker skin layer with high mass resistance and a shorter evaporation period will produce a thinner top layer structure with more lower transport resistance. This behaviour was proved in their CO₂/N₂ ideal separation properties, which membrane samples with 180s evaporation time have lower gases permeances. The highest CO₂/N₂ selectivity was obtained by 10 wt% SAPO-34 MMMs with 90s evaporation period, which is cause by good formation of thin dense skin and the addition of CO₂ selective SAPO-34 particles.

5. Acknowledgement

The authors would like to acknowledge MOSTI for providing Science Fund (06-01-05-SF0579). The authors also would like to thank Universiti Sains Malaysia to provide financial support in this work through Membrane Science and Technology Cluster (1001/PSF/100013) and RUI Grant (1001/PJKIMIA/811194).

References

- [1] D. J. Hofmann, J. H. Butler, P. P. Tans, A new look at atmospheric carbon dioxide, *Atmosphere Environment* 43 (2009) 2084–2086.
- [2] R. Monastersky, A burden beyond bearing, *Nature* 458 (2009) 1091–1094.
- [3] D. Aaron, C. Tsouris, Separation of CO₂ from flue gas: a review, *Separation Science Technology* 40 (2005) 321–348.
- [4] J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R. D. Srivastava, Advances in CO₂ capture technology – The US Department of Energy's Carbon Sequestration Program, *International Journal Greenhouse Gas Conference 2* (2008) 9–20.
- [5] O. G. Nik, X. Y. Chen, S. Kaliaguine, Amine-functionalized zeolite FAU/EMT-polyimide mixed matrix membranes for CO₂/CH₄ separation, *Journal of Membrane Science* 379(1-2) (2011) 468 – 478.
- [6] P. Jha, J. D. Way, Carbon dioxide selective mixed-matrix membranes formulation and characterization using rubbery substituted polyphosphazene, *Journal of Membrane Science* 324 (2008) 151 – 161.
- [7] E. Karatay, H. Kalipcilar, L. Yilmaz, Preparation and performance assessment of binary and ternary PES-SAPO 34-HMA based gas separation membranes, *Journal of Membrane Science* 364 (2010) 75 – 81.
- [8] M. A. Aroon, A. F. Ismail, M. M. Montazer-Rahmati, T. Matsuura, Morphology and permeation properties of polysulfone membranes for gas separation: Effects of non-solvent additives and co-solvent, *Separation and Purification Technology* 72 (2010) 194 – 202.
- [9] T. L. Chew, A. L. Ahmad, S. Bhatia, Rapid synthesis of thin SAPO-34 membranes using microwave heating, *Journal of Porous Material* 18 (3) (2011) 355 – 360.
- [10] Y. C. Hudiono, T. K. Carlisle, A. L. LaFrate, D. L. Gin, R. D. Noble, Novel mixed matrix membranes based on polymerizable room-temperature ionic liquids and SAPO-34 particles to improve CO₂ separation, *Journal of Membrane Science* 370 (2011) (1-2) 141–148.

Preparation and characterization of polysulfone mixed matrix membrane incorporated with thermodynamically stable nano-Palladium for hydrogen separation

Hani Shazwani Mohd Suhaimi^{1, a}, Leo Cheo Peng^{1, b} and Abdul Latif Ahmad^{1, c}

¹School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

^adiniedanisha@yahoo.com, ^bchcpleo@eng.usm.my, ^cchlatif@eng.usm.my

Keywords: Palladium nanoparticles; Mixed matrix membrane; Gas Separation.

Abstract. Palladium (Pd) nanoparticles offer excellent hydrogen affinity in mixed matrix membrane for gas separation. In order to avoid aggregation, Pd nanoparticles have to be stabilized before blending into polymer matrix. Pd nanoparticles can be thermodynamically stabilized and dispersed using electrostatic and/ or steric forces of a stabilizer which is typically introduced during the formation of Pd nanoparticles in the inversed microemulsion. Polyvinylpyrrolidone, polyethylene glycol (PEG) and sodium hydroxide in ethylene glycol exhibited good effect on particles passivation. However, the effects of these stabilizers on membrane morphology and separation performance were unknown. The aim of this work is to incorporate polymer-stabilized Pd nanoparticles into Polysulfone (PSf) membranes for hydrogen separation. The microstructure of Pd nanoparticles was first analyzed by TEM. Phase inversion method was then adopted for the preparation of asymmetric PSf/nano-Pd MMMs. The separation performance of MMMs was investigated by using nitrogen and hydrogen as test gases and the membrane characteristics were further studied using SEM and FTIR. The highest permeability for H₂ was 255.82 GPU with selectivity of 6.89. The results suggested that PEG provides good contact between nanoparticles and the polymer. TEM and FTIR results revealed that these stabilizers have significant effects on the synthesized Pd nanoparticles size. Also, SEM results showed that the MMMs incorporated with thermodynamically nano-Pd in PEG achieved satisfactory asymmetric structure which explains the good performance in gas separation.

1. Introduction

Metal nanoparticles have unique physico-chemical properties which differ from bulk material. Chemical preparative methods for synthesizing metal nanoparticles involve the chemical reduction of metallic ions in the presence of a stabilizer such as a polymer, ligand, surfactant, or solvent which works as a matrix to prevent the nanoparticles from aggregating and allow one to isolate the nanoparticles. Palladium (Pd) nanoparticles have been extensively studied due to their high hydrogen selective permeability. Higher efficiency and cost effectiveness of the H₂ production can be achieved by adding Pd nanoparticles into membrane [1].

Namini et al. [17] synthesized Pd nanoparticles by exploiting polyethylene glycol (PEG) as both reducing agent and stabilizer via a simple methodology under facile condition. The interaction between PEG additive and polymeric membrane casting dope depends on not only the polymer and solvent, but also PEG molecular weight and concentration. The interaction may couple with the condition of phase inversion to affect the thermodynamics and kinetics of membrane formation process, resulting in different structures and performances of final membranes [19]. Among the existing chemical reduction methods, polyvinylpyrrolidone (PVP)- protected Pd particle size could be well controlled by varying the synthesis conditions, such as reducing agent, reducing temperature, molecular weight of protective polymer, pH and reaction time. Without a protective agent, the Pd particles will aggregate and

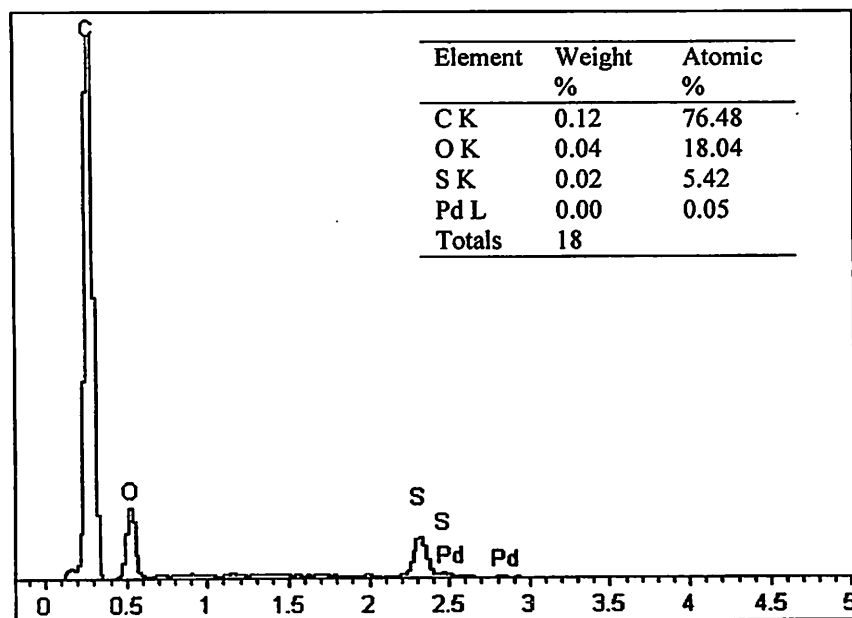


Fig. 4 The EDX result of PSf/Pd_PEG

4. Conclusion

The changes on membrane morphology and separation performance of PSf/Pd membranes have been studied under the effects of stabilizer. Extremely small Pd nanoparticles have been successfully synthesized using PEG as reducing agent. However, there was an existence of impurities, mainly PdCl₂ covered the metal cluster, which has not fully reacted. The addition of Pd_PEG enhanced asymmetric membrane morphology resulted from the improved demixing during phase inversion. The selectivity of H₂/N₂ for PSf/Pd_PEG membrane has been increased as much as 82.8% compared to the neat PSf membrane. However, the existence of PVP and EG could have contributed into membrane morphology negatively during phase inversion.

5. Acknowledgements

The authors would like to acknowledge Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013) and Research University Individual Grant (1001/PJKMIA/811194). The authors would also like to thank MOSTI for providing Science Fund (06-01-05-SF0579) and KPT for providing MyMaster.

6. References

- [1] Ahmad, A. L., M. A. T. Jaya, et al. (2011). "Synthesis and characterization of TiO₂ membrane with palladium impregnation for hydrogen separation." *Journal of Membrane Science* 366(1–2): 166-175.
- [2] Ahmad, J. and M.-B. Hägg (2013). "Preparation and characterization of polyvinyl acetate/zeolite 4A mixed matrix membrane for gas separation." *Journal of Membrane Science* 427(0): 73-84.
- [3] Amirilargani, M.; Saljoughi, E.; Mohammadi, T.; Moghbeli, M.R. (2010). "Effects of coagulation bath temperature and polyvinylpyrrolidone content on flat sheet asymmetric polyethersulfone membranes." *Polymer Engineering and Science*
- [4] Berger, G. A. Trăistaru, B. Ș. Vasile, I. Jitaru, C. Matei. (2010). "Palladium nanoparticles synthesis with controlled morphology obtained by polyol method." *U.P.B. Sci. Bull., Series B, Vol. 72, Iss. 1.*

Synthesis and Characterization of Superhydrophobic Alumina Membrane with Different Silanes Chain

N. A. Ahmad, T. Rachandran, *C. P. Leo and A. L. Ahmad

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia.

*Corresponding author: hcpleo@eng.usm.my, Tel: +60 4 5996425, Fax: +60 4 5941013

Abstract

Silane grafting allows the conversion of hydrophilic ceramic membranes into superhydrophobic thin layer, unfortunately with a great increment of mass transfer resistance. In this study, superhydrophobic alumina membranes were synthesized by direct grafting of varied types of silane in ethanol or hexane with different grafting durations (5, 10, 20 and 30 min). In order to reduce transport resistance generated from silane grafting, different types of silanes chain (long, short and ring chain) were used. In general, the grafting duration and the silane chain affected the membrane hydrophobicity significantly. Long grafting time and long silane chain with long non-polar tail resulted superhydrophobic membranes with an average water contact angle of $152.26^\circ \pm 3.92$. Meanwhile, the alumina membrane grafted with short silane chain only showed a water contact angle of $128.06^\circ \pm 3.92$. In contrast, grafting the alumina membrane with the aromatic ring silane caused the same hydrophilic feature and water adsorption. The grafted membranes showed great resistance in nitrogen (N_2) permeation commonly due to the penetration of silane into porous structure. Nitrogen permeation flux reduced from 3.966 L/min to 3.782 L/min, 1.018 L/min and 0.6672 L/min after grafted with short, amino and long silane chain respectively for 20 min. In conclusion, the selection of the silane chains are significantly important to control the membrane hydrophobicity and mass transfer resistances.

Keywords: Alumina membrane, Silane, Grafting, Resistance

1.0 INTRODUCTION

Hydrophobic membrane is either a porous or dense barrier that selectively permits the passage of nonpolar compounds in a feed stream. Hydrophobicity of a membrane is an important factor to promote separation of the nonpolar compound. A hydrophobic surface shows "water repellent" feature which is antagonistic to a hydrophilic surface, leading to lesser bonds formed between the hydrophobic surfaces with polar molecules such as water.

Hydrophobic membranes with large liquid entry pressure, fast permeation of nonpolar molecules, excellent rejection of polar compound, great mechanical strength and outstanding chemical stability are recently required in the advanced membrane separation process. Membranes with superhydrophobic features (water contact angle $>150^\circ$) are most desirable in membrane distillation, osmotic evaporation, membrane gas absorption and filtration.

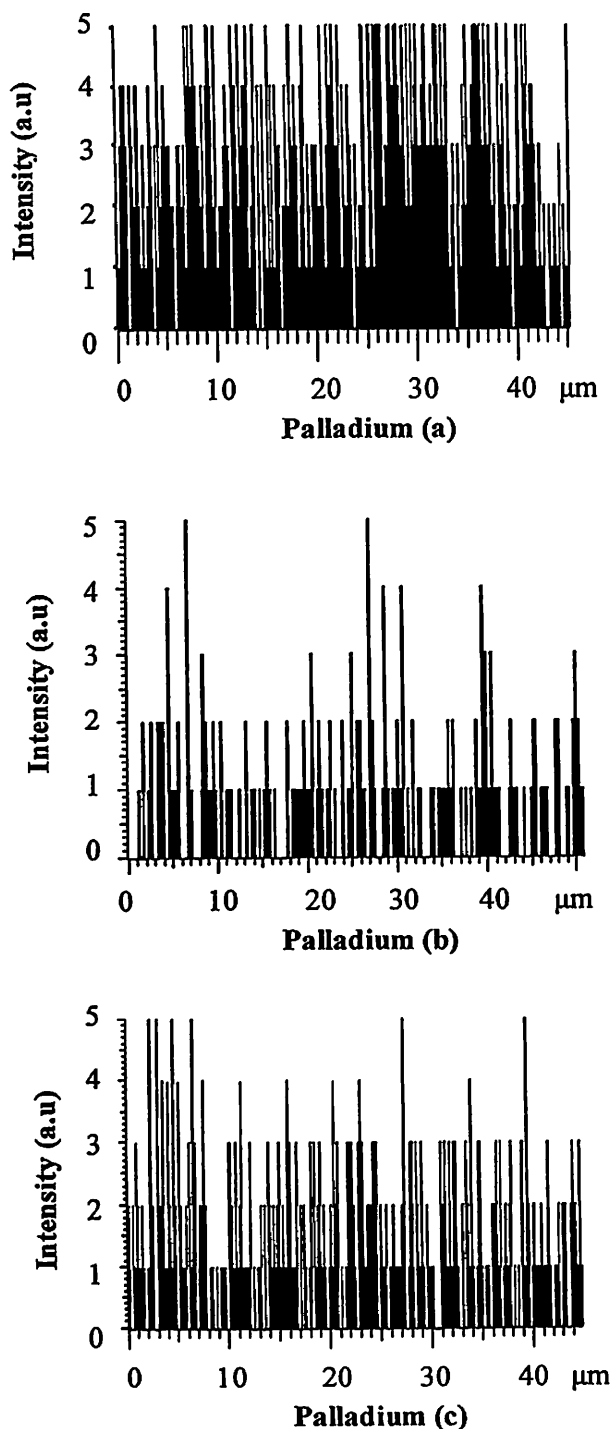


Fig. 8. The EDX result of Pd nanoparticles entrapped PSf membrane (a) Pd.1, (b) Pd.3, and (c) Pd.3.

However, rigidification effects of PEG could dominate in Pd.3 membrane, similar to PSf(PEG)₃ membrane.

4. Conclusion

MMMs incorporated with Pd loading have been prepared and their gas separation performance as well as stabilizer effects have been studied extensively. In the synthesis of Pd nanoparticles, the introduction of PEG resulted in an extremely small particles size

with 1.92 nm. The SEM images revealed that the changes in membrane structure contributed towards the membrane performance in gas separation. Under the effects of PEG, the membrane structure changes from fully developed finger-like structure to closed cell structure besides the growth of dense layer. The MMMs exhibited an increment of H₂ permeability compared with pure PSf membrane while the selectivity of H₂/N₂ was significantly increased after embedded with Pd nanoparticles. The highest H₂/N₂ selectivity of 21.69 and a satisfactory H₂ permeance of 46.24 GPU were achieved at 3 wt% Pd nanoparticles loading.

Acknowledgements

The authors would like to acknowledge Ministry of Education Malaysia for providing FRGS (FRGS/2/2013/TK05/USM/02/5) and Ministry of Higher Education Malaysia for providing MyMaster. The authors would also like to thank Universiti Sains Malaysia for facilities, equipments and scholarship provided through Membrane Science and Technology Cluster (1001/PSF/8610013), Research University Individual Grant (1001/PJKMIA/811194) and Fellowship. At last but not least, the authors would like to thank Mr. Yeoo Kai Liang for proof-reading this manuscript.

References

- [1] J. Yu, R.Y.F. Liu, B. Poon, S. Nazarenko, T. Koloski, T. Vargo, A. Hiltner, E. Baer, *Journal of Applied Polymer Science* 92 (2004) 749–756.
- [2] F.A. Lewis, *The Palladium/Hydrogen System*, Academic Press Inc., London, 1967.
- [3] M. Moreno, F.J. Ibanez, J.B. Jasinski, F.P. Zamborini, *Journal of the American Chemical Society* (2011) 4389–4397.
- [4] G.Q. Lu, J.C. Diniz da Costa, M. Duke, S. Giessler, R. Socolow, R.H. Williams, T. Kreutz, *Journal of Colloid and Interface Science* 314 (2007) 589–603.
- [5] A. Pundt, R. Kirchheim, *Annual Review of Materials Research* 36 (2006) 555–608.
- [6] R.W. Baker, K. Lokhandwala, *Industrial & Engineering Chemistry Research* 47 (2008) 2109–2121.
- [7] A.F. Ismail, P.Y. Lai, *Separation and Purification Technology* 33 (2003) 127–143.
- [8] J. Ahn, W.-J. Chung, I. Pinnau, M.D. Guiver, *Journal of Membrane Science* 314 (2008) 123–133.
- [9] A.L. Khan, A. Cano-Odena, B. Gutiérrez, C. Minguillón, I.F.J. Vankelecom, *Journal of Membrane Science* 350 (2010) 340–346.
- [10] T.-S. Chung, L.Y. Jiang, Y. Li, S. Kulprathipanja, *Progress in Polymer Science* 32 (2007) 483–507.
- [11] J. Cookson, *Platinum Metals Review* 56 (2012) 83.
- [12] Q.-Z. Zheng, P. Wang, Y.-N. Yang, *Journal of Membrane Science* 279 (2006) 230–237.
- [13] P.A. Namini, A.A. Babalou, B. Bayati, *International Journal of Nanoscience and Nanotechnology* 3 (2007) 37–43.
- [14] Z. Jia, H. Sun, Q. Gu, H. Lang, H. Abuduwaiyt, *Journal of Membrane Science* 380 (2011) 63–67.
- [15] G. Arthanareeswaran, D. Mohan, M. Raajenthiren, *Journal of Membrane Science* 350 (2010) 130–138.
- [16] B. Domènech, M. Muñoz, D.N. Muraviev, J. Macanás, *Catalysis Today* 193 (2012) 158–164.
- [17] T.-H. Young, L.-W. Chen, *Pore formation mechanism of membranes from phase inversion process*, *Desalination* 103 (1995) 233–247.
- [18] S. Wongchitphimon, R. Wang, R. Jiraratananon, L. Shi, C.H. Loh, *Journal of Membrane Science* 369 (2011) 329–338.
- [19] J. Ahmad, M.-B. Hägg, *Journal of Membrane Science* 427 (2013) 73–84.
- [20] M.A. Aroon, A.F. Ismail, M.M. Montazer-Rahmati, T. Matsuura, *Separation and Purification Technology* 72 (2010) 194–202.
- [21] S.R. Reijerkerk, M.H. Knoef, K. Nijmeijer, M. Wessling, *Journal of Membrane Science* 352 (2010) 126–135.
- [22] M. Iqbal, Z. Man, H. Mukhtar, B.K. Dutta, *Journal of Membrane Science* 318 (2008) 167–175.
- [23] S. Holloway, *Surface Science* 540 (2003) 1–3.
- [24] S. Clémenson, E. Espuche, L. David, D. Léonard, *Journal of Membrane Science* 361 (2010) 167–175.
- [25] B. Zornoza, S. Irusta, C. Téllez, J. Coronas, *Langmuir* 25 (2009) 5903–5909.
- [26] R. Naim, A.F. Ismail, A. Mansourizadeh, *Journal of Membrane Science* 423–424 (2012) 503–513.
- [27] A.F. Ismail, N.H. Rahim, A. Mustafa, T. Matsuura, B.C. Ng, S. Abdulrah, S.A. Hashemifard, *Separation and Purification Technology* 80 (2011) 20–31.

Template Removal from SAPO-44 Zeolite Membrane: Effects of Temperature

S.N.M. Kamal^a, C.P. Leo^{a*}, A.L. Ahmad^a, M.U.M. Junaidi^a and T.L. Chew^b.

^aSchool of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

^bDepartment of Petrochemical Engineering, Faculty of Engineering and Green Technology (FEGT), Perak Campus, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia
chcpleo@eng.usm.my

ABSTRACT

In the form of thin film, SAPO-44 zeolite with attractive microporous structure offers molecular sieving of gas mixture. Crystalline sample of small-pore SAPO-44 has been prepared by using cyclohexylamine as a template. The organic template has to be removed from SAPO-44 zeolite membranes carefully after hydrothermal synthesis to avoid defects. In this work, the influences of calcination temperature during template removal on membrane characteristics and separation performance were reported. The microstructure of SAPO-44 membrane was characterized by using XRD, FTIR and SEM. Single gas permeation experiments were also conducted with CO₂ and N₂ gases. The crystallinity of SAPO-44 zeolite membrane was clearly shown in the XRD pattern at 2θ of 10.0°, 16.0° and 21.0°. Template removal could be achieved at temperature as low as 375°C as indicated in FT-IR spectrum. The bands of cyclohexylamine at 2950 and 2860cm⁻¹ became weaker at higher temperature and totally disappeared at 600°C. However, the crystallinity of SAPO-44 zeolite was lost due to the disorganisation of zeolite. A CO₂/N₂ selectivity of 1.07 was achieved when the calcinations process was conducted at 375°C.

Keywords: SAPO-44 zeolite, Calcination temperature, Gas separation

INTRODUCTION

Zeolite is an attractive membrane material because its microporous structure offers excellent selectivity in gas separation. In addition, zeolite membrane shows high resistant to most corrosive chemicals and solvents [1]. Based on pore structure, zeolite can be classified into three major classes which are small (i.e. 0.30 – 0.4 nm with 6-, 8-, and 9- membered ring), medium (i.e. 0.5 – 0.60 nm with 10- membered ring) and large (i.e. 0.70 – 0.80 nm with 12- membered ring) [2, 3]. In order to form the desired porous structure and to avoid defects in the thin film, the organic template has to be removed from the zeolite membrane carefully after hydrothermal synthesis.

Until now, calcination and extraction are two general methods for removing the organic component. The organic template was commonly removed at calcination temperature in range of 250°C to 800°C, but preferably within 350 - 650°C in an oxidizing atmosphere to totally burn off the organic template [4]. During calcination, template removal process frequently results in crack crystals which may introduce large pores, affecting the actual molecular sieve effect of the membrane. About 0.5 – 0.9% contraction of the framework occurred at 340-400°C during template degradation and desorption [5]. The thermal contraction may result in mechanical stress in zeolite layer and caused crack formation in

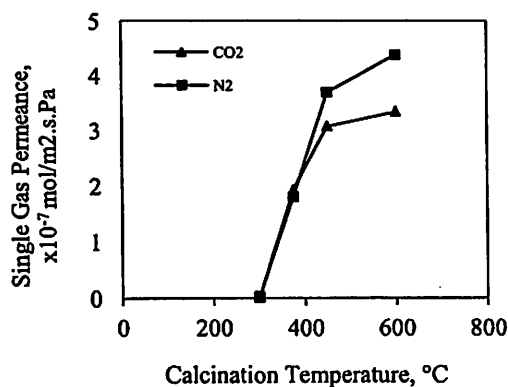


Figure 5: Effect of Calcinations Temperature on Single Permeance CO₂ and N₂ at 200kpa Pressure Difference across SAPO-44

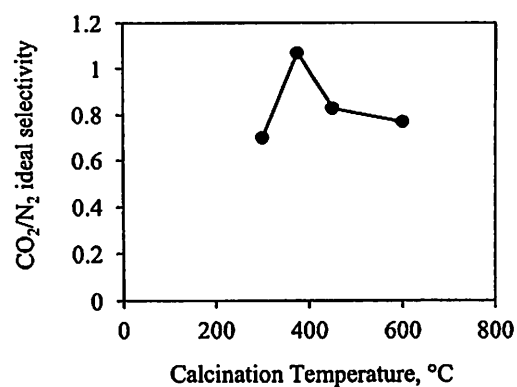


Figure 6: Selectivity of CO₂/N₂ at Different Calcinations Temperature

Higher selectivity of CO₂/N₂ (1.07) was achieved when the calcination process was applied at ~350 to 375°C, whereby the template had been removed from the SAPO-44 zeolite without cracks and microvoids. The selectivity improvement was not observed at higher calcination temperatures due to the defect formation at 450 °C and 600 °C as discussed earlier. Thus, the membrane ought to be calcined below 450°C to avoid crack formation during the heating process. However, the selectivity of the membrane is low and need more investigation. There are few factors that might effect the membrane performance such as the distribution of the zeolite crystals on the support disc, chemical composition of the SAPO-44 zeolite and interaction between zeolite membrane and alumina support that need to be considered in the future research.

CONCLUSIONS

Inorganic template (cyclohexylamine) has been successfully removed from zeolite SAPO-44 during the calculation process. The highest CO₂/N₂ selectivity (1.07) was achieved by membrane sample with calcination temperature of 375°C, without having cracks and microvoids on the membrane. By increasing the calcination temperature higher than 450°C, the membrane defects were occurred and the crystallinity of zeolite was lost. For the future work, the new method to remove the organic template such as microwave digestion (MWD) is recommended in order to improve the membrane performance. The important requirements in the zeolite membrane calcination process such as complete removal of template, minimum operating time and ideal structural and surface properties of inorganic framework can be fulfilled by using MWD method.

ACKNOWLEDGEMENTS

The authors would like to acknowledge MOSTI for providing Science Fund (06-01-05-SF0579). The authors also would like to thank Universiti Sains Malaysia to provide financial support in this work through Membrane Science and Technology Cluster (1001/PSF/100013) and RUI Grant (1001/PJKMIA/81194).



Preparation and characterization of polysulfone mixed-matrix membrane incorporated with palladium nanoparticles dispersed in polyvinylpyrrolidone for hydrogen separation

H. S. M. Suhaimi · M. N. I. M. Khir · C. P. Leo ·
A. L. Ahmad

Received: 27 November 2013 / Accepted: 27 March 2014 / Published online: 16 April 2014
© Springer Science+Business Media Dordrecht 2014

Abstract Polysulfone (PSf) offers better transport performance for gas permeation, but its application is limited by the “trade-off” between selectivity and permeability as well as the limitation of the “upper bound” that exists in solution-diffusion transportation. The idea of mixed-matrix membranes (MMMs) comprised of a continuous phase of PSf and a dispersed phase of palladium (Pd) nanoparticles has been developed. Membrane characteristics and their gas separation performance were studied. In order to prevent agglomeration, the Pd nanoparticle was stabilized using polyvinylpyrrolidone (PVP). The effects of Pd (0–3 wt%) and a stabilizer on the membrane characteristics were studied using a scanning electron microscope with energy dispersive X-ray, transmission electron micrographs, X-ray diffraction and Fourier transform infrared, while the separation performance was investigated using hydrogen (H₂), nitrogen (N₂), and carbon dioxide (CO₂) as test gases. H₂ separation from highly supercritical gases such as methane, carbon monoxide, and N₂ can be easily achieved by polymeric membranes, because of the extremely high diffusion coefficient of H₂ relative to all other molecules except helium gives overall high selectivities. Experimental findings verified that the MMMs achieved high permeability coupled with a satisfactory selectivity of hydrogen after incorporating Pd nanoparticles dispersed using PVP. High permeability with 3,124 GPU was achieved and the corresponding H₂/N₂ selectivities of the membranes was 20 while H₂/CO₂ was 6.2.

Keywords Mixed-matrix membrane · Palladium nanoparticles · Polysulfone · Gas separation

H. S. M. Suhaimi · M. N. I. M. Khir · C. P. Leo (✉) · A. L. Ahmad
School of Chemical Engineering, Engineering Campus, Universiti
Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau
Pinang, Malaysia
e-mail: chcpleo@eng.usm.my

Introduction

Membrane represents a viable commercial alternative for the separation of gas mixtures due to its high efficiency, easy intensification, simple operation, and low operating cost. It is also worth noting that hydrogen (H₂) recovery is among the first commercial applications of membrane in gas separation because H₂ is highly permeable compared to other gases. H₂ is small in molecular structure and non-condensable, thus glassy polymers have been primarily used to make H₂-selective membrane [16].

Polysulfone (PSf) is one of the most common glassy polymers used for gas separation. This glassy polymer can formed with a rigid and high-strength structure, which offers better transport performance for gas permeation compared to rubbery material [21]. Similar to other types of polymeric membranes, PSf membranes possess a trade-off between the key parameters for gas separation of permeability and selectivity. In order to improve both permeability and selectivity, as well as to overcome the limitation of the “upper bound” that exists in solution-diffusion transportation via the polymeric membranes, the concept of mixed-matrix membranes (MMMs) comprised of a continuous phase of polymer and a dispersed phase of inorganic filler has been developed.

Studies have shown that hybrid membranes comprised of polymer with embedded inorganic particles showed enhanced membrane stability. The MMMs showed higher gas permeabilities and comparable selectivities to pure polymeric. Ahn et al. [3] have shown a remarkable enhancement in H₂ gas permeability (from 11.8 to 22.7 barrer) by introducing nonporous nanosized silica particles in the PSf membrane. In addition, Galve et al. [11] have studied the combination of ordered mesoporous silica MCM-41 and layered titanasilicate JDF-L1 fillers for 6FDA-based copolyimide MMMs. Regarding H₂/N₂ separation, MMMs containing 4 and 8 % of MCM-41 and JDF-L1, respectively, showed an H₂/N₂ selectivity value of

in the range of 4–8 nm. The increment of dense layer in the membrane structure indicates that Pd contributes to the formation of denser structure as shown in the presented SEM images. In gas performances analysis, the MMMs show an increment of H₂ permeance compared with PSf membrane after incorporation of Pd nanoparticles due to the strong affinity of Pd element on the membrane surface and H₂. The highest H₂/N₂ and H₂/CO₂ selectivities of 20.2 and 6.2 respectively with a greater H₂ permeability of 3124.90 GPU were achieved at 2 wt% of Pd nanoparticles loading. Therefore, the H₂ permeability was achieved in this work compared to that reported in previous work which successfully achieved by reducing N₂ and CO₂ gas crossing through the membrane. Thus, the ideal selectivity of PSf(Pd₂) for H₂/N₂ and H₂/CO₂ significantly greater compared to other researchers as illustrated in Figs. 7 and 8 [2, 8, 9, 13].

Acknowledgements The authors would like to acknowledge Ministry of Education Malaysia for providing FRGS (FRGS/2/2013/TK05/USM/02/5) and MyMaster. The authors would also like to thank Universiti Sains Malaysia for the facilities and equipments provided through the Membrane Science and Technology Cluster (1001/PSF/8610013) and a Research University Individual Grant (1001/PJKMIA/811194) and USM Fellowship.

References

- Ahmad J, Hägg M-B (2013) Preparation and characterization of polyvinyl acetate/zeolite 4A mixed matrix membrane for gas separation. *J Membr Sci* 427:73–84
- Ahmad AL, Jaya MAT, Derek CJC, Ahmad MA (2011) Synthesis and characterization of TiO₂ membrane with palladium impregnation for hydrogen separation. *J Membr Sci* 366:166–175
- Ahn J, Chung W-J, Pinnau I, Guiver MD (2008) Polysulfone/silica nanoparticle mixed-matrix membranes for gas separation. *J Membr Sci* 314:123–133
- Balta S, Sotto A, Luis P, Benea L, Bruggen BVD, Kim J (2012) A new outlook on membrane enhancement with nanoparticles: the alternative of ZnO. *J Membr Sci* 155–161
- Chen C-H, Ma YH (2010) The effect of H₂S on the performance of Pd and Pd/Au composite membrane. *J Membr Sci* 362:535–544
- Chen L-J, Wan C-C, Wang Y-Y (2006) Chemical preparation of Pd nanoparticles in room temperature ethylene glycol system and its application to electroless copper deposition. *J Colloid Interface Sci* 297:143–150
- Chung T-S, Jiang LY, Li Y, Kulprathipanja S (2007) Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. *Prog Polym Sci* 32:483–507
- Clémenson S, Espuche E, David L, Léonard D (2010) Nanocomposite membranes of polyetherimide nanostructured with palladium particles: processing route, morphology and functional properties. *J Membr Sci* 361:167–175
- David OC, Gorri D, Urriaga A, Ortiz I (2011) Mixed gas separation study for the hydrogen recovery from H₂/CO/N₂/CO₂ post combustion mixtures using a Matrimid membrane. *J Membr Sci* 378:359–368
- Doménech B, Muñoz M, Muraviev DN, Macanás J (2012) Catalytic membranes with palladium nanoparticles: from tailored polymer to catalytic applications. *Catal Today* 193:158–164
- Galve A, Sieffert D, Staudt C, Ferrando M, Güell C, Téllez C, Coronas J (2013) Combination of ordered mesoporous silica MCM-41 and layered titanosilicate JDF-L1 fillers for 6FDA-based copolyimide mixed matrix membranes. *J Membr Sci* 431:163–170
- Ismail AF, Lai PY (2003) Effects of phase inversion and rheological factors on formation of defect-free and ultrathin-skinned asymmetric polysulfone membranes for gas separation. *Sep Purif Technol* 33:127–143
- Khan AL, Cano-Odena A, Gutiérrez B, Minguillón C, Vankelecom IFJ (2010) Hydrogen separation and purification using polysulfone acrylate-zeolite mixed matrix membranes. *J Membr Sci* 350:340–346
- Madaeni SS, Moradi P (2011) Preparation and characterization of asymmetric polysulfone membrane for separation of oxygen and nitrogen gases. *J Appl Polym Sci* 121:2157–2167
- Mansoori, S. A. A., Pakizeh, M., Chenar, M. P., (2011) Effect of synthesis parameters on structural characteristics of polysulfone membrane and its gas separation properties. *Journal of membrane science and technology*, 1–2
- Moreno M, Ibanez FJ, Jasinski JB, Zamborini FP (2011) Hydrogen reactivity of palladium nanoparticles coated with mixed monolayers of alkyl thiols and alkyl amines for sensing and catalysis applications. *J Am Chem Soc* 4389–4397
- Shao L, Low BT, Chung T-S, Greenberg AR (2009) Polymeric membranes for the hydrogen economy: contemporary approaches and prospects for the future. *J Membr Sci* 327:18–31
- Suhaimi HSM, Leo CP, Ahmad AL (2014) Preparation and characterization of polysulfone mixed matrix membrane incorporated with palladium nanoparticles in the inverted microemulsion for hydrogen separation. *Chem Eng Process Process Intensif* 77:30–37
- Wang XL, Tu JP, Zhang PL, Zhao XB (2007) Hydrogen storage properties of ball-milled Mg-based composite with PdCl₂ additive. *J Zhejiang Univ (Sci)* 8:1510–1513
- Yu J, Liu RYF, Poon B, Nazarenko S, Koloski T, Vargo T, Hiltner A, Baer E (2004) Polymers with palladium nanoparticles as active membrane materials. *J Appl Polym Sci* 92:749–756
- Zomoza B, Irusta S, Téllez C, Coronas J (2009) Mesoporous silica sphere-polysulfone mixed matrix membranes for gas separation. *Langmuir Artic* 25:5903–5909

Membranes with Great Hydrophobicity: A Review on Preparation and Characterization

N. A. Ahmad,¹ C. P. Leo,¹ A. L. Ahmad,¹ and W. K. W. Ramli²

¹*School of Chemical Engineering, Universiti Sains Malaysia, Nibong Tebal, Pulau Pinang, Malaysia*

²*School of Bioprocess Engineering, Universiti Malaysia Perlis, Arau, Perlis, Malaysia*

Membranes are commonly designed with great hydrophilicity or hydrophobicity to promote or prohibit the transportation of water, respectively. There are vast applications of hydrophobic membranes such as filtration, gas separation, membrane gas absorption, pervaporation, membrane distillation and more that cannot be attained with hydrophilic membranes. However, the development of hydrophobic membranes was relatively slow in the past, as membrane technologists and researchers were more interested in reducing membrane hydrophobicity for permeability enhancement or fouling control in the aqueous separation. Thus, literature related to hydrophobic membranes has not been reviewed elsewhere. This review reported on the characterization and preparation methods for hydrophobic membranes. Hydrophobic ceramic membranes are commonly prepared by chemical modification. Besides using different types of chemicals, the membrane surface is roughened to enhance its hydrophobicity. For polymeric membranes, great hydrophobicity can be engineered using per-fluorinated polymers or phase immersion in a dual coagulation bath. Each technique has its advantages and weaknesses.

Keywords: Membranes, hydrophobic, hydrophilic, applications, preparations

INTRODUCTION

Membranes are either a porous or dense barrier that permit the passage of certain compounds selectively in a fluid (1–3). The permeation of molecules through a membrane barrier is driven by concentration gradient, pressure difference, thermal variation and electrical force across the membrane (4). Surface characteristics are important in membrane separation since the molecules from the feed stream will first come into contact with the membrane surface. The selected molecules are then adsorbed onto the membrane surface and desorbed from the membrane barrier into the permeate side (5). Membrane surfaces should have special features to promote and/or prohibit certain molecules

to pass through the membrane barrier. There are two common surface features of membrane, either hydrophobic or hydrophilic. The hydrophobic property is known as the “water repellent” feature, prohibiting the surface wettability, and the hydrophilicity is the “water loving” property, encouraging water spread (6–9). Water cannot spread on the hydrophobic surface and hence reduces its contact with the surface. Spherical water droplets form on the hydrophobic surface due to low surface energy (9–12). However, a water droplet will spread on a membrane surface and then be adsorbed into a porous membrane if the membrane surface is hydrophilic.

Both hydrophobic and hydrophilic membranes can be applied in pervaporation for the dehydration of solvent and the separation of organic mixture. However, hydrophobic membranes are preferable when removal of only a small amount of solvent is required from a stream comprised mostly of water. Commercial applications of the pervaporation include bio-fuel recovery from fermentation broth and gasoline desulfuration. Polydimethylsiloxane (PDMS) membranes supported by

Received 11 May 2013, Accepted 30 August 2013.

Address correspondence to C. P. Leo, School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, Nibong Tebal, S.P.S., 14300 Pulau Pinang, Malaysia. E-mail: chcleo@usm.my

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/lspr.

CONCLUSION

Membrane technology is an alternative method for separation processes since it offers great advantages compared to conventional methods. It shows high efficiency in energy consumption. A large scale of green separation can be conducted without use of any chemical. Hydrophobic polymeric membranes and ceramic membranes have been used in various processes such as osmotic evaporation, membrane distillation, extraction, gas separation and more. Before selecting an appropriate hydrophobic membrane, the membrane hydrophobicity can be evaluated in terms of water contact angle, surface roughness, membrane morphology and surface chemistry. Basic concepts of some hydrophobic characterizations were discussed.

Hydrophobic ceramic membranes are commonly prepared via chemical modification. Organosilane and lipid solution have been used by researchers for chemical modification of ceramic membranes. Organosilane is a popular modification agent due to its flexibility in development of the hydrophobic surface on different materials. Besides the different types of chemicals, the membrane surface is roughened to enhance its hydrophobicity into superhydrophobicity.

Hydrophobic polymeric membranes can be synthesized by directly choosing low surface energy polymer materials, modifying polymer or enhancing membrane hydrophobicity. Low surface energy polymer is directly used in hydrophobic polymeric fabrication since it has low surface wettability. Besides the choice of hydrophobic polymer, preparation method like phase inversion, TIPS and stretching plays an important factor to affect the membrane hydrophobicity. Among these preparation methods, phase inversion is the most well-known method for fabrication of hydrophobic polymeric membrane with various types of morphology. In addition, the membrane hydrophobicity can be enhanced by blending additives in the polymer casting solution, plasma treatment and hydrophobic polymeric coating. Blending the polymer solution is commonly used due to its simplicity. However, each of the membrane preparation techniques has its advantages and weaknesses.

APPENDIX

Abbreviations

AFM	Atomic Force Microscopy
CA _w	Water contact angle
CNTBP	Carbon nanotube bucky-paper
CVD	Chemical vapor deposition
EDX	Energy dispersive X-ray
FAS	Fluoroalkylsilane
LEP	Liquid entry pressure
PEI	Polyetherimide
PES	Polyethersulfone

PP	Polypropylene
PSf	Polysulfone
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
R _q	The root mean square roughness
SEM	Scanning electron microscope
SMM	Surface-modifying macromolecules

Nomenclature

γ_{LS}	Liquid/solid surface tension
γ_L	Liquid surface tension
γ_{LV}	Liquid/vapor surface tension
γ_{SV}	Solid/vapor surface tension
θ	Contact angle
(ΔH)	Enthalpy of melting
°C	Degrees Celsius
% w/w	Mass percentage
%	Percentage
h	hour
wt.%	Weight percentage

ACKNOWLEDGMENTS

The authors thank Mr. Yeo Kai Liang and Ms. Low Ee Mee for proofreading this manuscript.

FUNDING

The authors acknowledge MOSTI for providing Science Fund (06-01-05-SF0579). The authors also thank Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013), Research University Individual Grant (1001/PJKMIA/811194), Short Term Grant (304/PJKMIA/60311016), and Post Graduate Grant (1001/PJKMIA/8035015).

REFERENCES

1. André, A., Anne, J., and Christian, G. (2005) Ceramic membrane processing. In *Chemical Processing of Ceramics*, Second Edition; Komarneni, S., and Lee, B., eds.; CRC Press, Boca Raton, FL, 629–666.
2. Roque-Malherbe, R.M.A. (2009) *The Physical Chemistry of Materials*; CRC Press, Boca Raton, FL, 467–490.
3. David, W., Shilpa, D., William, K., and Theodore, M. (2004) Membrane separation. In *The Engineering Handbook*, 2nd Ed.; Dorf, R.C., ed.; CRC Press, Boca Raton, FL, 63–163-15.
4. Reif, O. W. (2006). Microfiltration membranes: Characteristics and manufacturing. In *Sterile Filtration*; Jormitz, M., ed.; Springer: Berlin, Heidelberg, 73–103.
5. Davis, M.E., and Davis, R.J. (2003) *Fundamentals of Chemical Reaction Engineering*, McGraw-Hill Higher Education: New York.
6. Kazunari, A. (2002) Hydrophobic effects. In *Supramolecular Design for Biological Applications*; Yui, N., ed.; CRC Press: Boca Raton, FL, 13–24.

Effects of THF as Cosolvent in the Preparation of Polydimethylsiloxane/Polyethersulfone Membrane for Gas Separation

Siti Nadiah Mustafa Kamal, Choe Peng Leo, Abdul Latif Ahmad, Mohd Usman Mohd Junaidi
School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan,
14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

Polydimethylsiloxane/polyethersulfone (PDMS/PES) asymmetric membranes are widely applied in gas separation. However, the effects of common cosolvent on these membranes remain unknown. In order to study the changes in membrane morphology and gas separation properties, asymmetric PDMS/PES membranes were prepared. The studied parameters were types of cosolvents, tetrahydrofuran (THF) concentration, evaporation time, and PDMS concentration. Membrane morphology was examined using scanning electron microscopy and gas separation was conducted using pure CO₂, N₂, CH₄, and Hat 25°C. The addition of cosolvent into the polymer solution decreased the dope viscosity and delayed liquid–liquid demixing during phase inversion. Macrovoids formation was observed in substructure layer after adding THF and these macrovoids elongated with the reduction in THF content. There were microvoids formed on top of macrovoids and microvoids layer became thicker due to the increasing evaporation time of solvents before coagulation in nonsolvent. The PDMS coating on the PES membrane formed a dense skin layer and exhibited higher selectivity compared to the uncoated membrane. Membrane contained THF cosolvent with 60 s evaporation time and 3 wt% coated PDMS is the optimum membrane among other membranes in this work. The CO₂/N₂ selectivity was enhanced by 73.3% with CO₂ permeance of 44.86 GPU. POLYM. ENG. SCI., 00:000–000, 2013. © 2013 Society of Plastics Engineers

INTRODUCTION

Polymeric membranes have been widely applied in gas separation due to their great flexibility in scale-up, low operating cost, and energy efficiency [1, 2]. In order to achieve excellent gas performance and good mechanical strength for high pressure application, asymmetric polymeric membranes have been widely prepared [3]. Asymmetric membranes are characterized by being composed of an extremely thin and dense film which supported on a

thick porous substructure which may be the same or different material of the membrane. The porous substructure provides the thin membrane with strength and durability which prevents membrane destruction by pressure and temperature [3, 4]. By phase inversion, thin layer of polymer solution is immersed into a coagulation bath for solvent exchange between solvent and nonsolvent (water) to form asymmetric membranes. The phase separation occurs during the solvent exchange process, resulting desired porous structure [5].

During membrane synthesis, the choice of polymer in membrane preparation is very important as it influences the ultimate membrane properties. The most commonly used commercial polymers for gas separation are the phenyl group-based polysulfone (PSf), polyethersulfone (PES), and aromatic polyimide. Glassy polymer, PES has many advantages as a starting material in the preparation of gas separation membrane. PES membranes have been commercialized by Spectrum Laboratories and Sterlitech Corporation. This commercial polymer has a relatively high glass transition temperature ($T_g = 230^\circ\text{C}$) [6, 7] which allows long-term use without any dimensional changes or physical weakening at temperature as high as 200°C. PES is more selective but less permeable compared to other polymers such as PSf. This is because PES has a higher degree of chain rigidity resulted from its regular and polar backbone [6]. Polydimethylsiloxane (PDMS) with low glass transition temperature (T_g) of -123°C is the most common silicon rubber supported on PES membranes because PDMS enhances gas permeation selectively [7]. PDMS has a very flexible polymer siloxane backbone and low intermolecular forces between methyl groups and high bonding energy of siloxane group. The combination of rubbery and glassy polymer, PDMS/PES membrane is effective in gas separation. Rubbery polymer separates gases based on condensability. Generally, the sorption of the gases increases as the condensability of gases increase. Conversely, the relative size (kinetic diameter) of gases is more important than condensability during gas separation via glassy polymer. The gas diffusion increases from smaller to larger molecular size,

Correspondence to: Choe Peng Leo; e-mail: chcpleo@eng.usm.my
DOI 10.1002/pen.23767
Published online in Wiley Online Library (wileyonlinelibrary.com).
© 2013 Society of Plastics Engineers

cosolvent (THF or ethanol) into the polymer dope solution of 20PT-3 and 20PE-3 membranes. Similar trend had been reported in the literature [5], CO₂ and CH₄ permeances decreased after adding THF and ethanol cosolvents into PSf polymer dope solution. The reduction in gas permeance can be related to the formation of sponge structure after adding cosolvent as shown in Fig. 2b and c. Wang et al. [13] reported that PSf membrane with sponge-like structure possess higher resistance in gas separation compared to PSf membrane with finger-like microstructure.

In all cases, H₂ permeation was the highest followed by CO₂, CH₄, and N₂ permeation except the gas permeation in membrane without coating with PDMS solution (20PT). The selectivity and permeance of hydrogen gas is encouraging using cosolvent THF in sample 20PT-3 and 20PT-3-30s as stated in Table 3. The hydrogen permeation in this work enhanced double compare to the literature [30] which has higher on H₂/N₂ selectivity. In addition, the selectivity of CO₂/N₂ was greatly improved in 20PT-3 membrane after coating with 3 wt% of PDMS solution. The selectivity of CO₂/N₂ was two times higher than the selectivity of CO₂/CH₄ for same sample after coating. This is because the sorption of gases increased with the increasing of gas condensability in rubbery polymers [8]. PDMS dense layer most likely was been well engineered on top of the microvoids tailored in 20PT-3 membrane (Fig. 2b). However, the selectivity of the membrane could decrease after coating with high PDMS solution due to depth intrusion of the solution. Thus, the gas permeance and selectivity could be low because the permeative resistance increased [31]. All PDMS/PES membranes showed higher permeance of CH₄ than N₂, showing the domination of PDMS in gas separation. Unlike PES, PDMS is a rubbery polymer which is sorption selective and it permeate CH₄ over N₂ [8].

With THF concentration of 16 wt% in the polymer solution, 20PT-3 membrane showed higher CO₂ permeance than 17PT-3 and 25PT-3. The gas permeance increased at higher polymer concentration or lower THF content in 20PT-3 membrane compared to 17PT-3 membrane because of the entanglement conformation of polymer [30]. The reduction of gas permeance in 25PT-3 membrane can be related to the formation of macrovoid as explained in the morphology study. By the increment of evaporation time before phase inversion, permeances of all gases (CO₂, N₂, and CH₄) were improved. The observation is contrast to the work as reported by Julian and Wenten [23] that the increment in evaporation time resulted thicker skin layer and lower gas permeation. This is because microvoids grew in PES membranes which promote gas permeation in this work. The membranes with higher evaporation time has thicker microvoid layer which encourages gas permeation.

CONCLUSIONS

The morphology and separation properties of PDMS/PES asymmetric membranes have been successfully stud-

ied. THF cosolvent resulted the formation of microvoids and macrovoids in PES membrane. The changes of macrovoid size depended on THF concentration in the polymer solution mainly. In addition, microvoids increased with the increment of evaporation time before phase inversion. Gas separation was dominated of PDMS layer. However, the thickness and separation performance of PDMS layer were affected by the morphology of PES membrane which could be controlled by the cosolvent, THF.

REFERENCES

1. C.-Y. Liang, P. Uchytíl, R. Petrychovych, Y.-C. Lai, K. Friess, M. Sipek, M.M. Reddy, and S.-Y. Suen, *Sep. Purif. Technol.*, **92**, 57 (2012).
2. J. Han, W. Lee, J.M. Choi, R. Patel, and B. Min, *J. Membr. Sci.*, **351**, (2010).
3. B.S. Minhas and I.-F. Wang, EP 0456 143 A2 (1991).
4. F.X. Muller and J.E. Burkinshaw, EP 0 421 137 A1 (1990).
5. M.A. Aroon, A.F. Ismail, M.M. Montazer-Rahmati, and T. Matsuura, *Sep. Purif. Technol.*, **72**, 2 (2010).
6. R.E. Kesting and A. Fritzsche, *Polymeric Gas Separation Membranes*, Wiley, New York (1993).
7. M. Murder, *Basic Principles of Membrane Technology*, Eschede, Kluwer Academic, The Netherlands (1997).
8. R.W. Baker and K. Lokhandwala, *Ind. Eng. Chem. Res.*, **47**, 7 (2008).
9. M. Sadrzadeh, M. Amirilargani, K. Shahidi, and T. Mohammadi, *J. Membr. Sci.*, **342**, 1 (2009).
10. S.S. Madaeni and S. Hoseini, *J. Polym. Res.*, **16**, 5 (2009).
11. S.S. Madaeni, A. Moradi, and V. Kazemi, *Iran. Polym. J.*, **18**, 11 (2009).
12. A. Mansourizadeh and A.F. Ismail, *J. Membr. Sci.*, **348**, 1 (2010).
13. D. Wang, K. Li, and W. Teo, *J. Membr. Sci.*, **115**, 1 (1996).
14. D. Wang, K. Li, and W. Teo, *J. Membr. Sci.*, **176**, 2 (2000).
15. D. Wang, W.K. Teo, and K. Li, *J. Membr. Sci.*, **204**, 1 (2002).
16. J.J. Shieh and T.S. Chung, *J. Membr. Sci.*, **140**, 1 (1998).
17. L. Broens, D.M. Koenhen, and C.A. Smolders, *Desalination*, **22**, 1 (1977).
18. L. Shao, T.S. Chung, G. Wensley, S.H. Goh, and K.P. Pramoda, *J. Membr. Sci.*, **244**, 1 (2004).
19. S.-H. Chen, R.-M. Liou, J.-Y. Lai, and C.-L. Lai., *Eur. Polym. J.*, **43**, 9 (2007).
20. T.-H. Young and L.-W. Chen, *Desalination*, **103**, 3 (1995).
21. M. Hanakawa and S. Minegishi, US 8,205,754 B2 (2012).
22. T.-H. Young, Y.-H. Huang, and L.-Y. Chen, *J. Membr. Sci.*, **164**, 1 (2000).
23. H. Julian and I. Wenten. *IOSR J. Eng.*, **2**, 3 (2012).

1 **The effects of solvents on the modification of SAPO-34 zeolite using 3-**
2 **aminopropyl trimethoxy silane for the preparation of asymmetric**
3 **polysulfone mixed matrix membrane in the application of CO₂**
4 **separation.**

5

6 **M.U. M. Junaidi, C. P. Khoo, C.P. Leo*, A.L. Ahmad**

7

8 *School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri*
9 *Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia*

10

11 **ABSTRACT**

12 SAPO-34 zeolite is and ideal porous filler in mixed matrix membranes (MMMs) for CO₂
13 separation because it has strong affinity towards CO₂ and pore size (0.38 nm) which is
14 nearly similar to the molecular sizes of various gases in natural gas. However, the poor
15 compatibility between zeolite and polymeric matrix causes the formation of non-selective
16 interfacial voids, leading to poor separation of gases. In this work, 3-aminopropyl
17 trimethoxy silane (APMS) was proposed to modify SAPO-34 zeolite before adding into
18 asymmetric polysulfone (PSf) MMMs prepared via dry-wet phase inversion. The effects
19 of solvent (ethanol or isopropanol) in grafting reaction were studied. The changes in
20 FTIR spectra of both modified SAPO-34 zeolite samples signified that more silane
21 molecules were grafted when ethanol was used. SAPO-34 zeolite dispersed evenly in PSf
22 matrix after modification as shown in EDX analysis. Although showing similar FTIR
23 spectra and morphology, a great improvement in CO₂ selectivity and permeance was only
24 shown by PSf/SAPO-34E MMMs with zeolite modified using APMS in ethanol. The
25 highest CO₂/N₂ selectivity of 28.66, CO₂/CH₄ selectivity of 30.07 and a satisfactory CO₂
26 permeance of 706.43 GPU were achieved. Besides reduction of filler agglomeration, the

The authors would like to acknowledge MOSTI for providing Science Fund (06-01-05-SF0579), Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013), RUI Grant (1001/PJKMIA/811194), PRGS Grant, and USM Fellowship. The authors would also like to thank Ms. Low Ee Mee for her knowledge sharing and support.

References

- [1] I. R.S.C. P. Pandey, *Prog. Polym. Sci.* 26 (2001) 853-893.
- [2] M. Peydayesh, S. Asarehpour, T. Mohammadi, O. Bakhtiari, *Chem. Eng. Res. Des.* (2013) <http://doi.org/10.1013/j.cherd.2013.01.022>.
- [3] U. Cakal, L. Yilmaz, H. Kalipcilar, *J. Membr. Sci.* 17-418 (2012) 45-51.
- [4] D. Şen, H. Kalıpçılar, L. Yilmaz, *J. Membr. Sci.* 303 (2007) 194-203.
- [5] X.Y. Chen, O.G. Nik, D. Rodrigue, S. Kaliaguine, *Polymer*, 53 (2012) 3269-3280.
- [6] A.F. Ismail, T.D. Kusworo, A. Mustafa, *J. Membr. Sci.* 319 (1-2) (2008) 306-312.
- [7] T.W. Pechar, M. Tsapatsis, E. Marand, *R. Desalination*, 146 (1-3) (2002) 3-9.
- [8] T.W. Pechar, S. Kim, B. Vaughan, E. Marand, M. Tsapatsis, H.K. Jeong, C.J. Cornelius, *J. Membr. Sci.* 277 (1-2) (2006) 195-202.
- [9] A.M.W. Hillock, S.J. Miller, W.J. Koros, *J. Membr. Sci.* 314 (1-2) (2008) 193-199.

Organo Silane Interfacial Enhanced SAPO-34 Zeolite in Polysulfone Mixed Matrix Membrane: Effect of Membrane Hydrophobicity towards Gas Separation Performance

M.U.M. Junaidi, C.P. Leo*, S.N.M. Kamal, A.L. Ahmad

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

ABSTRACT

One of the major challenges in the development of mixed matrix membranes (MMMs) is the poor adhesion between selective selective filler and polymer matrix. The presence of defects can severely weaken the separation performance of the membrane. Thus, silane coupling modification is generally used to eliminate such defects. In this work, fluoroalkyl silane (FAS) with chemical name of triethoxy-1H,1H,2H,2H-perfluorodecyl silane ($C_{16}H_{19}O_3F_{17}Si$) is used to alter SAPO-34 zeolite. The effect of hydrophobicity towards membrane characteristic and gas transport properties was studied. All of the membranes were fabricated using the phase inversion method. The contact angle analysis explained surface modification with FAS has enhanced the hydrophobicity nature of SAPO-34. The PSf-10/FAS MMMs exhibited good adhesion between filler and polymer phases, minimizing defects proposed by voids formation. However, particles agglomeration was still occurring when 20 wt % of FAS modified zeolites were incorporated in PSf matrix. The TGA analysis has proven that FAS modification had not distracted CO_2 adsorption affinity of SAPO-34. PSf-10/FAS MMMs showed the highest performance enhancement on CO_2/N_2 and CO_2/CH_4 separation properties compared to the PSf-10 MMMs and neat PSf membrane. In hydrophobicity study towards pure gas permeation test, PSf-10 MMMs exhibited mass reduction in gas separation performance due to the SAPO-34 pores were blocked by the

*Corresponding author. Tel.: +60 4 5996425; fax: +60 4 5941013
Email address: chcpleo@eng.usm.my (C.P. Leo)

276 permeation test, PSf-10 MMMs exhibited mass reduction in gas separation performance
277 due to the SAPO-34 pores were blocked by the adsorbed water. By the silane
278 modification proposed by FAS on the SAPO-34 zeolite, the hydrophobicity enhancement
279 on MMMs was able to lessen the water adsorption of SAPO-34 zeolites and maintain
280 MMMs separation performance.

281

282 Acknowledgements

283

284 The authors would like to acknowledge Universiti Sains Malaysia for the financial
285 support provided through Membrane Science and Technology Cluster
286 (1001/PSF/8610013), Research University Individual Grant (1001/PJKMIA/811194),
287 USM Fellowship and RU-PGRS. The authors would also like to thank MOSTI for
288 providing Science Fund (06-01-05-SF0579).

289

290 References

291

- 292 [1] Ward, J.K. and W.J. Koros, *Crosslinkable mixed matrix membranes with surface*
293 *modified molecular sieve for natural gas: I. Preparation and experimental result.*
294 *Journal of Membrane Science*, 2011. 377(0): p. 75-81.
- 295 [2] T.W. Pechar, S. Kima, B. Vaughan, E. Marand, M. Tsapatsis, H.K. Jeong, C.J.
296 Cornelius, *Fabrication and characterization of polyimide-zeolite L mixed matrix*
297 *membranes for gas separations.* *Journal of Membrane Science*, 2006. 277: p 195-
298 202.

Preparation and characterization of polysulfone mixed matrix membrane incorporated with SAPO-34 zeolite for gas separation

M. U. M. Junaidi, C. P. Leo*, A. L. Ahmad, T. L. Chew, S. N. M. Kamal.

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300, Nibong Tebal, Seberang Perai Selatan, Pulau Pinang, Malaysia.

* e-mail: hcpleo@eng.usm.my

Abstract – Asymmetric pure PSf and 10 wt% SAPO-34/PSf MMMs were fabricated in order to investigate the effects of evaporation time on the membrane morphology and gas performance properties. The evaporation times were varied from 0s to 180s. All membranes were prepared using dry-wet phase inversion method. The cross-section SEM images provide indication that different evaporation period could affect the membrane dense skin layer thickness for asymmetric structure. Membrane fabrication with longer evaporation time tends to have thicker skin layer with high mass resistance and a shorter evaporation period will produce a thinner top layer structure with more lower transport resistance. This behaviour was proved in this work CO₂/N₂ ideal separation properties, which membrane samples with 180s evaporation time have lower gas permeances rates. The highest CO₂/N₂ selectivity (26.1) was obtained by 10 wt% SAPO-34 MMMs with 90s evaporation period with CO₂ permeance of 3140 barrer, which is cause by good formation of thin dense skin and the addition of CO₂ selective SAPO-34 particles.

Keywords: Mixed matrix membrane; SAPO-34 zeolite; Gas Separation.

1. Introduction

Nowadays, carbon dioxide (CO₂) is greatly released worldwide due to the fast modern civilization and industrialization. CO₂ has been identified as the major contributor of the green house effects that causes global warming. Ever since the analysis for CO₂ concentration have been started in 1958, CO₂ concentration at the atmospheric level has increased up to 22 % in 2009 [1] and has been responsible for 60% of the increment in world temperature [2]. Combustion in fossil fuel power plants generates about 30% of CO₂ and the rest of emission is produced from transportation, oil and gas industry sectors [3].

Serious concern on CO₂ concentration has further ignited the development of CO₂ capture and storage technology to recover the undesired CO₂ and store it for further processes and applications. The most feasible methods in CO₂ capture are absorption, adsorption, cryogenic separation and membrane technology [4]. CO₂ removal using membrane separation is currently of great interest

due to its' low energy consumption, small footprint, simple operation and ease in scale up. In the seek of solution to surpass the limitations of preoccupied conventional polymeric membranes, the idea to formulate composite membranes has appeared in the past few decades. The remote and well-commercialize polymers materials is merged with CO₂ selective particles to form mixed matrix membranes (MMMs). MMMs usually contain inorganic adsorbent and molecular sieves material as fillers [5]. These composite membranes have shown great potential as alternative to industrial polymeric membrane because of their higher separation performance and compatibility with the commercial polymeric membrane modules.

Recent works on MMMs [6-7] have focused more on dense polymeric matrix with little improvement in gas permeance. Asymmetric MMMs membrane with dense skin supported on porous polymeric matrix is proposed in this work to achieve not only improved selectivity of CO₂ but also greater permeance. Asymmetric MMMs can be easily prepared using phase inversion method. The phase inversion involves the immersion of

Evaporation time (s)	Permeability (barrer)		Selectivity $\alpha(\text{CO}_2/\text{N}_2)$
	CO ₂	N ₂	
0	3874.69	3994.76	0.97
90	3140.02	120.35	26.1
180	360.60	94.12	3.45

Table 2. Permeabilities and ideal selectivities of polysulfone blend with 10 wt% SAPO-34 MMMs at different evaporation time at ambient temperature and 50 psig.

Fig. 4 represents the performance of membrane samples with 90s and 180s evaporation time membranes on revised Robeson plot for CO₂/N₂ gas pair. Clearly, membrane samples performance with no evaporation step are located further away from trade-off line due to the severe loss CO₂/N₂ selectivity, which of The CO₂/N₂ performance plot of 10 wt% SAPO-34 MMMs with 90s evaporation period has surpass the trade-off line, which prove that this MMMs has encounter the polymeric limitation imposed by Robeson [18]. Nonetheless, pure PSf membrane with same evaporation period is still under the polymeric limitation. By increasing the evaporation time to 180s, the CO₂/N₂ performance was decrease as the performance plots for both membranes were pulled far away from trade-off line.

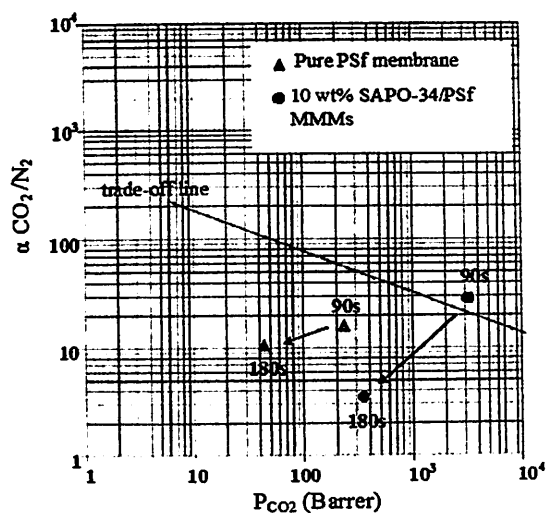


Fig. 4. Comparison of membranes prepared with 90s and 180s evaporation time on Robeson plot [18] for CO₂/N₂ gas pair.

4. Conclusions

Asymmetric pure PSf and 10 wt% SAPO-34/PSf MMMs were fabricated in order to investigate the effects of evaporation time on the membrane morphology and gas performance properties. All membranes were prepared using dry-wet phase inversion method. The cross-section SEM images provide indication that different evaporation period could affect the membrane

dense skin layer thickness for asymmetric structure. Membrane fabrication with longer evaporation time tends to have thicker skin layer with high mass resistance and a shorter evaporation period will produce a thinner top layer structure with more lower transport resistance. This behaviour was proved in their CO₂/N₂ ideal separation properties, which membrane samples with 180s evaporation time have lower gases permeances. The highest CO₂/N₂ selectivity was obtained by 10 wt% SAPO-34 MMMs with 90s evaporation period, which is cause by good formation of thin dense skin and the addition of CO₂ selective SAPO-34 particles.

5. Acknowledgement

The authors would like to acknowledge MOSTI for providing Science Fund (06-01-05-SF0579). The authors also would like to thank Universiti Sains Malaysia to provide financial support in this work through Membrane Science and Technology Cluster (1001/PSF/100013) and RUI Grant (1001/PJKIMIA/811194).

References

- [1] D. J. Hofmann, J. H. Butler, P. P. Tans, A new look at atmospheric carbon dioxide, *Atmosphere Environment* 43 (2009) 2084–2086.
- [2] R. Monastersky, A burden beyond bearing, *Nature* 458 (2009) 1091–1094.
- [3] D. Aaron, C. Tsouris, Separation of CO₂ from flue gas: a review, *Separation Science Technology* 40 (2005) 321–348.
- [4] J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R. D. Srivastava, Advances in CO₂ capture technology – The US Department of Energy's Carbon Sequestration Program, *International Journal Greenhouse Gas Conference 2* (2008) 9–20.
- [5] O. G. Nik, X. Y. Chen, S. Kaliaguine, Amine-functionalized zeolite FAU/EMT-polyimide mixed matrix membranes for CO₂/CH₄ separation, *Journal of Membrane Science* 379(1-2) (2011) 468–478.
- [6] P. Jha, J. D. Way, Carbon dioxide selective mixed-matrix membranes formulation and characterization using rubbery substituted polyphosphazene, *Journal of Membrane Science* 324 (2008) 151–161.
- [7] E. Karatay, H. Kalipcilar, L. Yilmaz, Preparation and performance assessment of binary and ternary PES-SAPO 34-HMA based gas separation membranes, *Journal of Membrane Science* 364 (2010) 75–81.
- [8] M. A. Aroon, A. F. Ismail, M. M. Montazer-Rahmati, T. Matsuura, Morphology and permeation properties of polysulfone membranes for gas separation: Effects of non-solvent additives and co-solvent, *Separation and Purification Technology* 72 (2010) 194–202.
- [9] T. L. Chew, A. L. Ahmad, S. Bhatia, Rapid synthesis of thin SAPO-34 membranes using microwave heating, *Journal of Porous Material* 18 (3) (2011) 355–360.
- [10] Y. C. Hudiono, T. K. Carlisle, A. L. LaFrate, D. L. Gin, R. D. Noble, Novel mixed matrix membranes based on polymerizable room-temperature ionic liquids and SAPO-34 particles to improve CO₂ separation, *Journal of Membrane Science* 370 (2011) (1-2) 141–148.

Preparation and characterization of polysulfone mixed matrix membrane incorporated with thermodynamically stable nano-Palladium for hydrogen separation

Hani Shazwani Mohd Suhaimi^{1, a}, Leo Cheo Peng^{1, b} and Abdul Latif Ahmad^{1, c}

¹School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

^adiniedanisha@yahoo.com, ^bchcpleo@eng.usm.my, ^cchlatif@eng.usm.my

Keywords: Palladium nanoparticles; Mixed matrix membrane; Gas Separation.

Abstract. Palladium (Pd) nanoparticles offer excellent hydrogen affinity in mixed matrix membrane for gas separation. In order to avoid aggregation, Pd nanoparticles have to be stabilized before blending into polymer matrix. Pd nanoparticles can be thermodynamically stabilized and dispersed using electrostatic and/ or steric forces of a stabilizer which is typically introduced during the formation of Pd nanoparticles in the inversed microemulsion. Polyvinylpyrrolidone, polyethylene glycol (PEG) and sodium hydroxide in ethylene glycol exhibited good effect on particles passivation. However, the effects of these stabilizers on membrane morphology and separation performance were unknown. The aim of this work is to incorporate polymer-stabilized Pd nanoparticles into Polysulfone (PSf) membranes for hydrogen separation. The microstructure of Pd nanoparticles was first analyzed by TEM. Phase inversion method was then adopted for the preparation of asymmetric PSf/nano-Pd MMMs. The separation performance of MMMs was investigated by using nitrogen and hydrogen as test gases and the membrane characteristics were further studied using SEM and FTIR. The highest permeability for H₂ was 255.82 GPU with selectivity of 6.89. The results suggested that PEG provides good contact between nanoparticles and the polymer. TEM and FTIR results revealed that these stabilizers have significant effects on the synthesized Pd nanoparticles size. Also, SEM results showed that the MMMs incorporated with thermodynamically nano-Pd in PEG achieved satisfactory asymmetric structure which explains the good performance in gas separation.

1. Introduction

Metal nanoparticles have unique physico-chemical properties which differ from bulk material. Chemical preparative methods for synthesizing metal nanoparticles involve the chemical reduction of metallic ions in the presence of a stabilizer such as a polymer, ligand, surfactant, or solvent which works as a matrix to prevent the nanoparticles from aggregating and allow one to isolate the nanoparticles. Palladium (Pd) nanoparticles have been extensively studied due to their high hydrogen selective permeability. Higher efficiency and cost effectiveness of the H₂ production can be achieved by adding Pd nanoparticles into membrane [1].

Namini et al. [17] synthesized Pd nanoparticles by exploiting polyethylene glycol (PEG) as both reducing agent and stabilizer via a simple methodology under facile condition. The interaction between PEG additive and polymeric membrane casting dope depends on not only the polymer and solvent, but also PEG molecular weight and concentration. The interaction may couple with the condition of phase inversion to affect the thermodynamics and kinetics of membrane formation process, resulting in different structures and performances of final membranes [19]. Among the existing chemical reduction methods, polyvinylpyrrolidone (PVP)- protected Pd particle size could be well controlled by varying the synthesis conditions, such as reducing agent, reducing temperature, molecular weight of protective polymer, pH and reaction time. Without a protective agent, the Pd particles will aggregate and

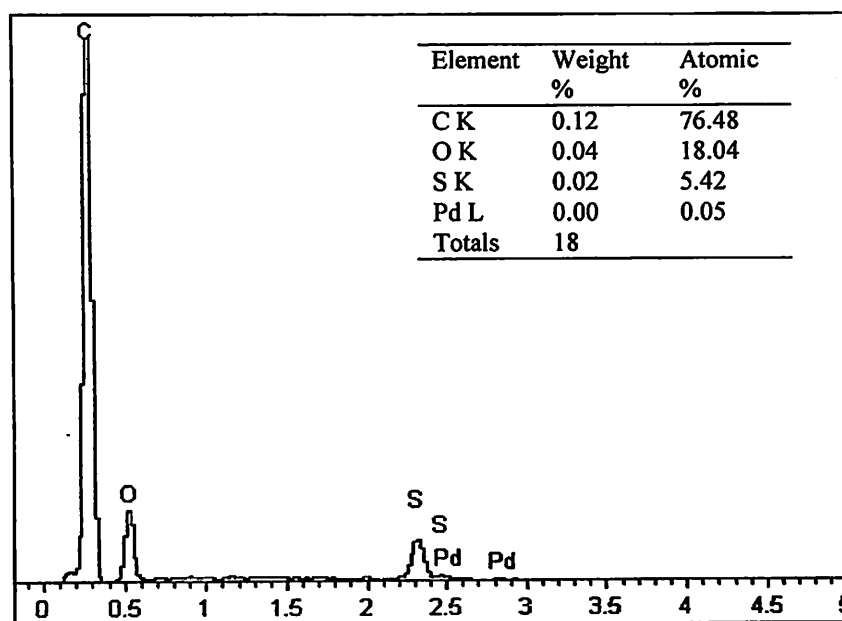


Fig. 4 The EDX result of PSf/Pd_PEG

4. Conclusion

The changes on membrane morphology and separation performance of PSf/Pd membranes have been studied under the effects of stabilizer. Extremely small Pd nanoparticles have been successfully synthesized using PEG as reducing agent. However, there was an existence of impurities, mainly PdCl₂ covered the metal cluster, which has not fully reacted. The addition of Pd_PEG enhanced asymmetric membrane morphology resulted from the improved demixing during phase inversion. The selectivity of H₂/N₂ for PSf/Pd_PEG membrane has been increased as much as 82.8% compared to the neat PSf membrane. However, the existence of PVP and EG could have contributed into membrane morphology negatively during phase inversion.

5. Acknowledgements

The authors would like to acknowledge Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013) and Research University Individual Grant (1001/PJKMIA/811194). The authors would also like to thank MOSTI for providing Science Fund (06-01-05-SF0579) and KPT for providing MyMaster.

6. References

- [1] Ahmad, A. L., M. A. T. Jaya, et al. (2011). "Synthesis and characterization of TiO₂ membrane with palladium impregnation for hydrogen separation." *Journal of Membrane Science* 366(1–2): 166-175.
- [2] Ahmad, J. and M.-B. Hägg (2013). "Preparation and characterization of polyvinyl acetate/zeolite 4A mixed matrix membrane for gas separation." *Journal of Membrane Science* 427(0): 73-84.
- [3] Amirilargani, M.; Saljoughi, E.; Mohammadi, T.; Moghbeli, M.R. (2010). "Effects of coagulation bath temperature and polyvinylpyrrolidone content on flat sheet asymmetric polyethersulfone membranes." *Polymer Engineering and Science*
- [4] Berger, G. A. Trăistaru, B. Ș. Vasile, I. Jitaru, C. Matei. (2010). "Palladium nanoparticles synthesis with controlled morphology obtained by polyol method." *U.P.B. Sci. Bull., Series B, Vol. 72, Iss. 1.*

Template Removal from SAPO-44 Zeolite Membrane: Effects of Temperature

S.N.M. Kamal^a, C.P. Leo^{a*}, A.L. Ahmad^a, M.U.M. Junaidi^a and T.L. Chew^b.

^aSchool of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, Seri Ampangan, 14300 Nibong Tebal, S.P.S., Pulau Pinang, Malaysia

^bDepartment of Petrochemical Engineering, Faculty of Engineering and Green Technology (FEGT), Perak Campus, Universiti Tunku Abdul Rahman, Jalan Universiti, Bandar Barat, 31900 Kampar, Perak, Malaysia
chcpleo@eng.usm.my

ABSTRACT

In the form of thin film, SAPO-44 zeolite with attractive microporous structure offers molecular sieving of gas mixture. Crystalline sample of small-pore SAPO-44 has been prepared by using cyclohexylamine as a template. The organic template has to be removed from SAPO-44 zeolite membranes carefully after hydrothermal synthesis to avoid defects. In this work, the influences of calcination temperature during template removal on membrane characteristics and separation performance were reported. The microstructure of SAPO-44 membrane was characterized by using XRD, FTIR and SEM. Single gas permeation experiments were also conducted with CO₂ and N₂ gases. The crystallinity of SAPO-44 zeolite membrane was clearly shown in the XRD pattern at 2θ of 10.0°, 16.0° and 21.0°. Template removal could be achieved at temperature as low as 375°C as indicated in FT-IR spectrum. The bands of cyclohexylamine at 2950 and 2860cm⁻¹ became weaker at higher temperature and totally disappeared at 600°C. However, the crystallinity of SAPO-44 zeolite was lost due to the disorganisation of zeolite. A CO₂/N₂ selectivity of 1.07 was achieved when the calcinations process was conducted at 375°C.

Keywords: SAPO-44 zeolite, Calcination temperature, Gas separation

INTRODUCTION

Zeolite is an attractive membrane material because its microporous structure offers excellent selectivity in gas separation. In addition, zeolite membrane shows high resistant to most corrosive chemicals and solvents [1]. Based on pore structure, zeolite can be classified into three major classes which are small (i.e. 0.30 – 0.4 nm with 6-, 8-, and 9- membered ring), medium (i.e. 0.5 – 0.60 nm with 10- membered ring) and large (i.e. 0.70 – 0.80 nm with 12- membered ring) [2, 3]. In order to form the desired porous structure and to avoid defects in the thin film, the organic template has to be removed from the zeolite membrane carefully after hydrothermal synthesis.

Until now, calcination and extraction are two general methods for removing the organic component. The organic template was commonly removed at calcination temperature in range of 250°C to 800°C, but preferably within 350 - 650°C in an oxidizing atmosphere to totally burn off the organic template [4]. During calcination, template removal process frequently results in crack crystals which may introduce large pores, affecting the actual molecular sieve effect of the membrane. About 0.5 – 0.9% contraction of the framework occurred at 340-400°C during template degradation and desorption [5]. The thermal contraction may result in mechanical stress in zeolite layer and caused crack formation in

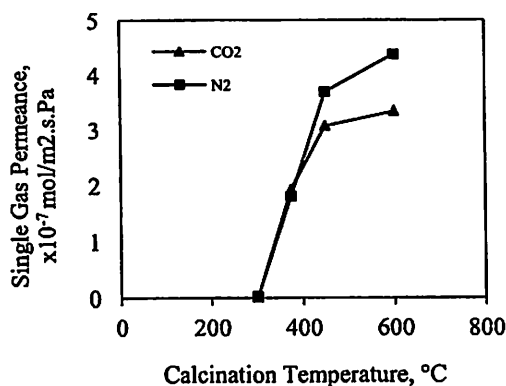


Figure 5: Effect of Calcinations Temperature on Single Permeance CO₂ and N₂ at 200kpa Pressure Difference across SAPO-44

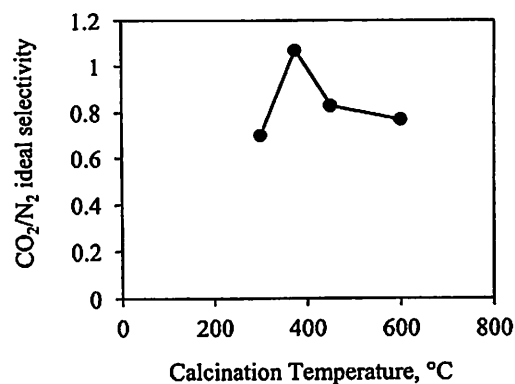


Figure 6: Selectivity of CO₂/N₂ at Different Calcinations Temperature

Higher selectivity of CO₂/N₂ (1.07) was achieved when the calcination process was applied at ~350 to 375°C, whereby the template had been removed from the SAPO-44 zeolite without cracks and microvoids. The selectivity improvement was not observed at higher calcination temperatures due to the defect formation at 450 °C and 600 °C as discussed earlier. Thus, the membrane ought to be calcined below 450°C to avoid crack formation during the heating process. However, the selectivity of the membrane is low and need more investigation. There are few factors that might effect the membrane performance such as the distribution of the zeolite crystals on the support disc, chemical composition of the SAPO-44 zeolite and interaction between zeolite membrane and alumina support that need to be considered in the future research.

CONCLUSIONS

Inorganic template (cyclohexylamine) has been successfully removed from zeolite SAPO-44 during the calculation process. The highest CO₂/N₂ selectivity (1.07) was achieved by membrane sample with calcination temperature of 375°C, without having cracks and microvoids on the membrane. By increasing the calcination temperature higher than 450°C, the membrane defects were occurred and the crystallinity of zeolite was lost. For the future work, the new method to remove the organic template such as microwave digestion (MWD) is recommended in order to improve the membrane performance. The important requirements in the zeolite membrane calcination process such as complete removal of template, minimum operating time and ideal structural and surface properties of inorganic framework can be fulfilled by using MWD method.

ACKNOWLEDGEMENTS

The authors would like to acknowledge MOSTI for providing Science Fund (06-01-05-SF0579). The authors also would like to thank Universiti Sains Malaysia to provide financial support in this work through Membrane Science and Technology Cluster (1001/PSF/100013) and RUI Grant (1001/PJKMIA/81194).

Synthesis and Characterization of Superhydrophobic Alumina Membrane with Different Silanes Chain

N. A. Ahmad, T. Rachandran, *C. P. Leo and A. L. Ahmad

School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia.

*Corresponding author: chcpleo@eng.usm.my, Tel: +60 4 5996425, Fax: +60 4 5941013

Abstract

Silane grafting allows the conversion of hydrophilic ceramic membranes into superhydrophobic thin layer, unfortunately with a great increment of mass transfer resistance. In this study, superhydrophobic alumina membranes were synthesized by direct grafting of varied types of silane in ethanol or hexane with different grafting durations (5, 10, 20 and 30 min). In order to reduce transport resistance generated from silane grafting, different types of silanes chain (long, short and ring chain) were used. In general, the grafting duration and the silane chain affected the membrane hydrophobicity significantly. Long grafting time and long silane chain with long non-polar tail resulted superhydrophobic membranes with an average water contact angle of $152.26^\circ \pm 3.92$. Meanwhile, the alumina membrane grafted with short silane chain only showed a water contact angle of $128.06^\circ \pm 3.92$. In contrast, grafting the alumina membrane with the aromatic ring silane caused the same hydrophilic feature and water adsorption. The grafted membranes showed great resistance in nitrogen (N_2) permeation commonly due to the penetration of silane into porous structure. Nitrogen permeation flux reduced from 3.966 L/min to 3.782 L/min, 1.018 L/min and 0.6672 L/min after grafted with short, amino and long silane chain respectively for 20 min. In conclusion, the selection of the silane chains are significantly important to control the membrane hydrophobicity and mass transfer resistances.

Keywords: Alumina membrane, *Silane, Grafting, Resistance*

1.0 INTRODUCTION

Hydrophobic membrane is either a porous or dense barrier that selectively permits the passage of nonpolar compounds in a feed stream. Hydrophobicity of a membrane is an important factor to promote separation of the nonpolar compound. A hydrophobic surface shows "water repellent" feature which is antagonistic to a hydrophilic surface, leading to lesser bonds formed between the hydrophobic surfaces with polar molecules such as water.

Hydrophobic membranes with large liquid entry pressure, fast permeation of nonpolar molecules, excellent rejection of polar compound, great mechanical strength and outstanding chemical stability are recently required in the advanced membrane separation process. Membranes with superhydrophobic features (water contact angle $>150^\circ$) are most desirable in membrane distillation, osmotic evaporation, membrane gas absorption and filtration.

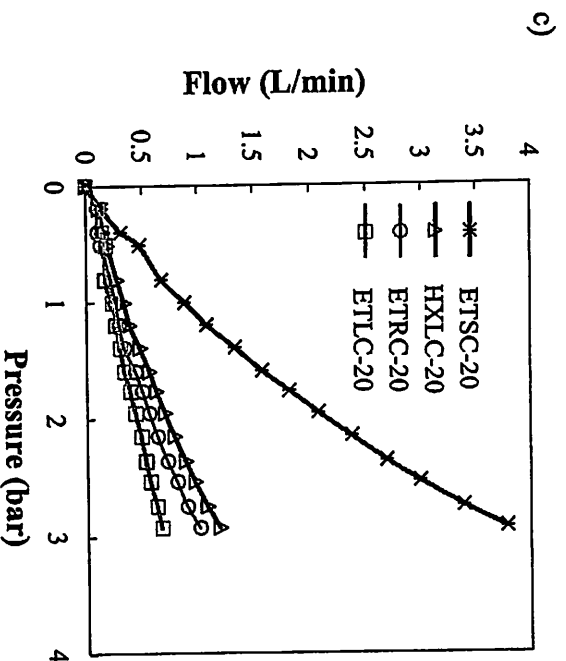


Figure 5: Mass transfer resistance in grafted alumina membranes; a) effect of LC-ethanol grafting solution, b) effect of LC-hexane grafting solution and c) membrane grafting in 20 min with different silane chains.

4. Conclusion

Membrane grafting with silane is well known as a grafting agent to produce hydrophobic membrane. However, not all silane types capable to modify the hydrophilic nature of ceramic membrane into hydrophobic membrane. Silane structure with long $-CF_2-$ chain and low surface tension group could form a superhydrophobic alumina membrane. Membrane grafting with LC-ethanol produced the superhydrophobic alumina membranes ETLIC-20 (152.26 ± 3.92) and HXLC-20 (148.24 ± 1.53). However, LC silane with long $-CF_2-$ chain showed higher membrane resistance due to membrane blockage in the membrane barrier and reduce the membrane pore size. The presence of amino group in the silane structure (SC) contents protonated amino groups which can chemical bonding with OH on the membrane surface and water. Thus, the presence of amino groups remain the hydrophilic nature of the ceramic membrane. In conclusion, the selection of the silane chains are significantly important to control the membrane hydrophobicity and mass transfer resistances.

Acknowledgements

The authors would like to acknowledge MOSTI for providing Science Fund (06-01-05-SF0579). The authors would also like to thank Universiti Sains Malaysia for the financial support provided through Membrane Science and Technology Cluster (1001/PSF/8610013), Research University Individual Grant (1001/PJKMIA/811194) and Post Graduate Grant (1001/PJKMIA/8035015). At last but not least, the authors would like to thank Mr. Wan Muhammad Haniffah Wan Husin for proof-reading this manuscript.

CURRENT APPLICATIONS, PREPARATION METHODS AND POTENTIALS OF HYDROPHOBIC POLYMERIC MEMBRANES

N.A. Ahmad, C.P. Leo*, A.L. Ahmad

School of Chemical Engineering, Engineering Campus, University Sains Malaysia
14300 Penang, Malaysia.

*Corresponding author. Tel.: +60 4 5996425; fax: +60 4 5941013
Email address: cfcpleo@eng.usm.my (C.P. Leo)

Acknowledgements
MOSTI for Science Fund (06-01-05-SF0579), Universiti Sains Malaysia for Membrane Science and Technology Cluster (1001/PSF/8610013), Research University Individual Grant (1001/PJKMIA/811194) Short Term Grant (304/PJKMIA/60311016).

BACKGROUND

Membrane is a barrier that selectively permits the passage of certain compounds in a fluid. The hydrophobic property is also known as "water repellent" feature, prohibiting the surface wettability which reduces water contact with the surface. Thus, hydrophobic membranes are able to retain the passage of water through the barrier. In addition, great hydrophobicity on membrane surface positively increases the non-polar molecules flux. It is due to the high affinity of the non-polar molecules towards the hydrophobic surface with low surface energy resulted from the absence of hydroxyl (OH) group. There are vast applications of hydrophobic membrane such as filtration, gas separation, membrane gas absorption, pervaporation, membrane distillation and more which cannot be attained by hydrophilic membranes. The great hydrophobicity, nearly superhydrophobicity can be now developed and enhanced on polymeric membranes via different techniques.

Preparation Hydrophobic Polymeric Membranes from Hydrophobic Polymer

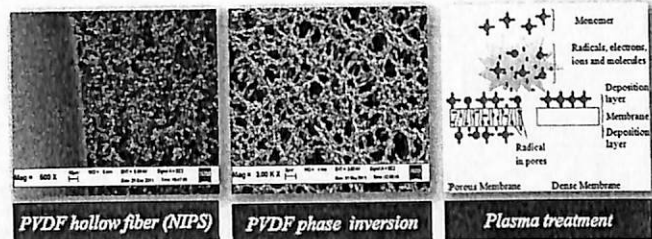
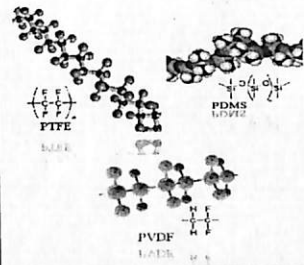
Stretching	Phase inversion	Thermally induced phase separation (TIPS)	Non-solvent induced phase separation (NIPS)
<ul style="list-style-type: none"> The partially crystalline polymeric material is stretched into a rolled sheet uniaxially or biaxially. Mean pore size and porosity increase with an increase in longitudinal stretching ratio, transverse stretching ratio and heat setting temperature. Heat process: to stabilize the porous structure, membrane dimensions and mechanical properties of the final membrane. The higher the heat setting temperature, the lower the enthalpy and consequently the lower the crystallinity (reduce stiffness (elastic modulus) and strength of the polymer) 	<ul style="list-style-type: none"> The polymer solution is transformed into a solid state in a controlled manner. Control initial state of phase transition can form porous or nonporous membranes. Precipitation by solvent evaporation: form a dense homogeneous membrane Precipitation by vapour phase: form a porous membrane without top layer Precipitation by controlled evaporation: form a skinned membrane Thermal precipitation: form a skinned membrane/ microfiltration membrane Additional of pore forming/nonsolvent additives in casting solution can modify membrane morphology and its properties. 	<ul style="list-style-type: none"> Thermoplastic polymer is heated into a melt then mixed with liquid crystal to form homogenous mixture. The liquid crystal phase is separated into droplet as the system is cooled to room temperature to form polymer-dispersed liquid crystal (PDLC) film. Cooling rate affects membrane properties. Slower cooling rate produces larger spherulites. Quenching results in significantly smaller spherulites than controlled cooling. Increase in the total volume of the spherulites results in shrinkage of the polymer, which becomes brittle and easily cracks. Pre-treatment processing such as stretching might be applied to improve the desired separation characteristics of the membrane. Can be used to generate dense and porous films. 	<ul style="list-style-type: none"> The polymer solution is composed of at least one polymer and at least one good solvent and may contain additives. Polymer solution is casted then immersed in a coagulation bath containing a nonsolvent for the polymer. Demixing and polymer precipitation rates produce membranes with different structures Higher the mutual affinity (or miscibility) between the solvent and nonsolvent : fast demixing and form more porous membrane Low mutual affinity: form an asymmetric membrane with a dense nonporous top layer Single and double coagulating bath affect membrane hydrophobicity

Coagulant	Contact angle value (°) [1]	
	Double-coagulation bath ^a	Single-coagulation bath ^b
Water	-	84 ± 1
Methanol	139 ± 1	144 ± 1
Ethanol	138 ± 1	146 ± 2
n-Propanol	136 ± 2	145 ± 2
n-Butanol	137 ± 1	146 ± 3

^a The PVDF casting film was passed through alcohol for 2 s and then immersed into water bath.
^b The PVDF casting film was immersed into water or alcohol bath only.

Table 1
Hydrophobic Polymer material with its free surface energy (SFE) at 20 °C [7,8]

Polymer	Surface energy, γ_s (10^3 N/m)
Polytetrafluoroethylene (PTFE)	19.1
Polydimethylsiloxane (PDMS)	19.8
Polytrifluoroethylene (PTFE)	23.9
Polypropylene (PP)	30.0
Polyvinylidene fluoride (PVDF)	30.3



Hydrophobicity enhancement of polymeric membranes

Blending with additives	Plasma treatment	Hydrophobic polymeric coating	APPLICATIONS & POTENTIAL APPLICATIONS
<ul style="list-style-type: none"> Blend polymer casting solution with hydrophobic additives or hydrophobic polymer through phase inversion Example: Phenyl isocyanate, surface-modifying macromolecules (SMM) and nanocomposite nanofiber Produces membranes with a single and thin hydrophobic layer with ultrafiltration (UF) or microfiltration (MF) range. IMPROVEMENTS Additional 50wt% PTFE particle in PVDF : improved the thermal efficiency up to 80%, formation of fully sponge-like structure, salt rejection around 99.8% at 80°C in direct contact membrane distillation [2]. Additional phenyl isocyanate in the ethyl cellulose membrane: reduced the permeation rate of water and enabled in production of anhydrous hydrazine. Additional 8 wt% clay nanocomposite nanofiber into PVDF casting solution: improved static water contact 20% to 154.2±3.0, the LEP point increased to 200±6 kPa, improved the membrane thermal stability [3]. 	<ul style="list-style-type: none"> A glow of discharge is used to break monomer gas and form free electrons, ions, excited molecules and radicals. Adsorption and polymerization of ionized monomer to form clear, dense and thin coating layer on membrane surface under vacuum condition. Examples of monomer: tetrafluoromethane (CF₄), sulphur hexafluoride (SF₆), hexamethyldisiloxane (HMDSO) and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Affecting factors: type of monomer, intensity (glow power discharge), gas flow rate, and pressure and treatment duration. IMPROVEMENTS CF₄ plasma modification of the hydrophilic PES membrane into hydrophobic membrane increased contact angle by 53% and the LEP from 0.1 to 3.7 bars due to the F/C ratio increase on the modified membrane surface [4]. 	<ul style="list-style-type: none"> The hydrophobic polymer dissolves in solvent to coat on hydrophilic membrane. Affecting factors: coating duration, heating time, selection of materials and preparation of coating solution which affect the membrane pore blockage. IMPROVEMENTS Coated silicon rubber on hydrophilic poly (phthalazine ether sulfone ketone) (PPEK) membrane can improve contact angle up to 83% become 128°, higher permeate flux of silicone rubber solution, the LEP increased from 0.02 to 0.18 Mpa and rejection of modified membrane up to 99% consistently in Vacuum Membrane Distillation (VMD) [5]. Coated PTFE on carbon nanotube (CNT) bucky-paper (CNTBP) raised contact angle up to 20% became 155°, LEP point from 112.1 to 145.9 psi, also enhance the membrane mechanical stability [9]. 	<ul style="list-style-type: none"> Osmotic Evaporation (OE) Concentrating of aqueous solution containing heat sensitive compounds Membrane distillation (MD) Production of high-purity water, concentration of ionic, colloidal or other non-volatile aqueous solution and removal of trace volatile organic compounds Gas separation as contactor in chemical absorption to remove CO₂, H₂S, SO₂ from flue and natural gases Filtration widely used in solvent recovery, biodiesel, oil separation.

CONCLUSION AND RECOMMENDATION

Hydrophobic polymeric membranes can be synthesized directly choosing the low surface energy polymer materials, modifying hydrophilic polymer or enhancing membrane hydrophobicity. Some techniques are simple and efficient but each of them has its limitation.

REFERENCES

- [1] Pithon, J.A., et al., Preparation and characterization of highly hydrophobic poly(vinylidene fluoride)-Gly nanocomposite nanofiber membranes (PVDF-gly NNFs) for distillation using direct contact membrane distillation. *Journal of Membrane Science*, 2012, 217-20(2): p. 80-90.
- [2] Wei, X., et al., CF₄ plasma surface modification of asymmetric hydrophilic polytetrafluoroethylene membranes for direct contact membrane distillation. *Journal of Membrane Science*, 2012, 449-450(2): p. 164-174.
- [3] Jin, Z., et al., Hydrophobic modification of poly(phthalazine ether sulfone ketone) hollow fiber membrane for vacuum membrane distillation. *Journal of Membrane Science*, 2009, 316(1-2): p. 20-27.
- [4] Dumée, L., et al., The impact of hydrophobic coating on the performance of carbon nanotube bucky-paper membranes in membrane distillation. *Desalination*, 2011, 281(2): p. 64-67.
- [5] Brooks, B.W., Properties of polymers: By D. W. Van Krevelen, Elsevier, Amsterdam, 1972, xi + 427 pp., price \$27.25. *The Chemical Engineering Journal*, 1972, 30(1): p. 316.
- [6] Dumée, L., et al., Solid surface energy data (SFE) for common polymers. 2012.
- [7] Dumée, L., et al., The impact of hydrophobic coating on the performance of carbon nanotube bucky-paper membranes in membrane distillation. *Desalination*, 2011, 281(2): p. 64-67.

APPENDIX C
HUMAN CAPITAL DEVELOPMENT

SMUSTAF HCMS 2.0 Human Capital Management System

Main SKT LPP CV CV(Promotion) User Comments

Job Description Task List / Project Report / Review Print SKT

DR. LEO CHOE PENG | PENSYARAH UNIVERSITI DS51

Year Selection

Year: 2014

C. SUPERVISION (YEAR 2014)

C.01 Post-Graduate Supervision

- MMed/MSurg/MPath/MComm

- Ph.D(Thesis - Research)

- Master(Dissertation - Course Work

- Ph.D(Dissertation - Mix Mode)

- Master(Dissertation - Mix Mode)

- Master(Thesis - Research)

-HCMS -

New Record

No.	Category	Thesis / Research Title	Student Name	Attachment
1.	Master(Dissertation - Mixed Mode)	Antioxidant Content of Propolis and the Effect of Microwave Assisted Extraction	Norhaziya binti Hamzah	

- Data From SMU-Pelajar -

No	Category	Thesis Title	Student	Supervisor Type	Tahun Berijazah
Berijazah					
1.	PhD	Superhydrophobic Polymeric Hollow Fiber Membrane Contractors For CO2 Absorption-	HARITH NOORI MOHAMMED (P-JD0094)	PENYELIA BERSAMA	2014
2.	Master(Research)	Synthesis and Characterization of Superhydrophobic Alumina Membrane Via Chemical and Morphological Modification-	NOR AINI BINTI AHMAD (P-JM0264)	PENYELIA UTAMA	2014
Aktif					
1.	Master(Research)	Preparation and characterization of ceramic membranes for microfiltration applications-	FAZREEN AMIRA BINTI ISMAIL (P-JM0269)	PENYELIA BERSAMA	
2.	PhD	Mixed Matrix Membranes Incorporated with Thermodynamically Stable Palladium Nanoparticles for Hydrogen Separation-	HANI SHAZWANI BINTI MOHD SUHAIMI (P-JD0014/14(R))	PENYELIA UTAMA	
3.	PhD	Process Optimization Studies of High Pressure CO2 Separation from Natural Gas using Membranes-	JIMOH KAYODE ADEWOLE (P-JD0004/12(R))	PENYELIA BERSAMA	
4.	PhD	Encapsulations of Palladium Nanoparticles in Polymeric Thin Film for Coupling Reaction-	KHAIRULNISA NADIAH BINTI HUSSAIN (P-JD0021/14(R))	PENYELIA UTAMA	
5.	PhD	Polysulfone Mixed Matrix Membranes for Carbon Dioxide Separation-	MOHD USMAN BIN MOHD JUNAIDI (P-JD0002/13(R))	PENYELIA UTAMA	
6.	PhD	Superhydrophobic Membrane With Functional Filler for Membrane Gas Absorption Gas Purification-	NOR AINI BINTI AHMAD (P-JD0015/14(R))	PENYELIA UTAMA	
7.	Master(Research)	Characterization and Ultrasonic Assisted Hydrolytic Extraction of Malaysian Propolis-	YEO KAI LIANG (P-JM0013/13(R))	PENYELIA UTAMA	

©2011. Hak Cipta Terpelihara. Universiti Sains Malaysia, Pulau Pinang

- A. Teaching
- B. Working Paper / Presentation
- C. Supervision
 - >> Post-Graduate Supervision
 - >> Under-Graduate Supervision
 - >> Professional Service
- D. Research
- E. Publication
- F. Consultancy
- G. Academic Advisor / Mentor
- H. Service To The University / Community
- I. Editor / Examiner
- J. Academic Recognition and Leadership
- K. Professional Clinical Services

**SYNTHESIS AND CHARACTERIZATION OF SUPERHYDROPHOBIC
ALUMINA MEMBRANE WITH MINIMUM MEMBRANE RESISTANCE
VIA STEAM TREATMENT**



NOR AINI AHMAD

UNIVERSITI SAINS MALAYSIA

2013

SINTESIS DAN PERINCIAN MEMBRAN ALUMINA SUPERHIDROPOBIK DENGAN RINTANGAN MEMBRAN YANG MINIMUM MENGGUNAKAN KAEDAH STIM

ABSTRAK

Hidropobik dikenali sebagai sifat "hindar air", mengurangkan kebolehasahan permukaan. Oleh itu, membran berliang hidropobik mempunyai keupayaan untuk menghalang laluan air semasa proses pemisahan seperti penapisan minyak, penyulingan membran dan penyerapan gas membran. Walaupun membran seramik mempunyai kekuatan mekanikal yang tinggi, rintangan kimia yang cemerlang dan kestabilan haba yang hebat, ciri-ciri semula jadi hidrofilik membran seramik menghadkan penggunaannya untuk proses yang dinyatakan. Sehubungan itu, pengubahsuaian ke arah membran seramik yang mempunyai sifat superhidropobik dengan sudut sentuhan air melebihi 150° sangat menarik. Pengubahsuaian membran menggunakan kaedah cantuman silan telah dilaporkan secara meluas kerana pengendalian yang mudah, tetapi pertumbuhan struktur hidropobik memperkenalkan rintangan tambahan dalam pemindahan jisim. Matlamat utama dalam kajian ini, adalah untuk mensintesis membran superhidropobik dengan rintangan membran yang minimum. Dalam kajian ini juga, kesan kepekatan (heptadecafluoro-1,1,2,2-tetra hydrodecyl) triethoxysilane (HFDS) pada rintangan pemindahan jisim membran alumina superhidropobik turut dikaji. Selain cantuman langsung, cantuman HFDS turut dilakukan pada filem alumina nipis yang disediakan melalui kaedah sol-gel dengan pengkalsinan atau kaedah stim untuk mengurangkan liang tersumbat. Pada permulaannya, sokongan alumina dicantum secara langsung dengan perbezaan nisbah isipadu (heptadecafluoro-1,1,2,2-tetra hydrodecyl) triethoxysilane (HFDS) terhadap etanol (0,1-2,5 ml HFDS:50 ml etanol). Cantuman langsung HFDS pada

membran memberikan sudut sentuhan air statik dalam lingkungan 85.84 ° (0.1ml HFDS) hingga 138.91 ° (1.0 ml HFDS). Isipadu HFDS melebihi 1.0 ml, tidak memberikan perubahan yang ketara pada sudut sentuhan air statik disebabkan oleh ketepuan ikatan antara kumpulan OH pada permukaan membran alumina dan kumpulan terhidrolisis HFDS. Peningkatan kepekatan HFDS, menyebabkan liang membran tersumbat ekoran daripada penembusan rantaian HFDS. Jumlah rintangan membran meningkat daripada $4.05 \times 10^{10} \text{ m}^{-1}$ hingga $1.52 \times 10^{12} \text{ m}^{-1}$ selepas bercantum dengan 2.5 ml HFDS. Bagi menghasilkan membran superhidropobik kaedah sol-gel telah digunakan untuk menghasilkan permukaan kasar sebelum cantuman silan. Selanjutnya, pengkalsinan lapisan alumina sol-gel pada suhu 450 °C dan cantuman silan dengan 1 ml HFDS meningkatkan sudut sentuhan air sehingga 156.1 °. Sudut sentuhan air sedikit tinggi dicatatkan iaitu 158.4 ° pada membran sol-gel selepas kaedah stim dan cantuman HFDS dengan nisbah 1 ml HFDS kepada 50 ml etanol. Kaedah sol-gel bukan sahaja meningkatkan kekasaran permukaan malah rintangan di dalam membran dapat dikurangkan berbanding cantuman langsung membran dengan kepekatan HFDS yang sama. Kaedah stim menggalakkan pembentukan kesan meteor pada bumi yang membentuk kawah, menjana permukaan dengan mikro-kekasaran dan nano- kekasaran untuk mencapai sifat superhidropobik. Kesan kaedah stim, membran sol-gel mempunyai rintangan membran yang lebih rendah dan mengurangkan liang berbanding dengan membran sol-gel dikalsin pada suhu 450 °C. Tambahan itu, parameter yang berbeza dikaji dengan menggunakan kaedah stim seperti masa salutan celup sol-gel, tempoh stim dan rendaman pada suhu air yang berbeza. Lapisan sol-gel yang terhasil kurang dari 7 saat salutan celup, dirawat dengan stim selama 1 min dan direndam di dalam air pada suhu 100 °C selama 10 minit disyorkan menghasilkan membran alumina superhidropobik dengan rintangan

membran yang minimum. Membran alumina superhidropobik telah berjaya digunakan dalam pembersihan minyak tanah untuk penyingkiran air dalam emulsi air-minyak. Kira-kira 99 % daripada air yang dikeluarkan dari emulsi air-minyak dan penelapan fluks lebih daripada 100 ml/min diperhatikan sepanjang penapisan.

contact angle was observed due the saturation of bonding between the OH groups of the alumina and the hydrolysable groups of the HFDS. The increment of HFDS concentration, however, caused membrane pore blockage due to the penetration of HFDS chain. Total membrane resistance increased from $4.05 \times 10^{10} \text{ m}^{-1}$ to $1.52 \times 10^{12} \text{ m}^{-1}$ after grafting with 2.5 ml of HFDS. In order to produce superhydrophobic membrane, sol-gel method was used to create rough surface before silane grafting. Further calcination of the sol-gel alumina layer at $450 \text{ }^\circ\text{C}$ and silane grafting with 1 ml of HFDS improved the water contact angle up to 156.1 ° . A slightly higher water contact angle of 158.4 ° was recorded for the sol-gel membrane after steam treatment and HFDS grafting with 1 ml of HFDS in 50 ml of ethanol. Sol-gel method not only enhanced surface roughness but also reduced membrane resistance in membrane compared to direct grafted membrane with the same grafting concentration. Steam treatment encouraged the formation of a surface with crater like due to meteor striking earth effect, generating surface with micro-roughness and nano-roughness to achieve superhydrophobicity. After steam treatment, sol-gel membrane has lower membrane resistance and pore reduction compared to the sol-gel membrane calcined at $450 \text{ }^\circ\text{C}$. Thus, different parameters in steam treatment such as sol-gel dip coating time, steam duration and water temperature have been further studied. Sol-gel coating prepared under 7 s of dip coating, steam treated for 1 min and immersed in $100 \text{ }^\circ\text{C}$ of water for 10 minutes are recommended to synthesis the superhydrophobic alumina membrane with minimum membrane resistance. The superhydrophobic alumina membrane was successfully applied in kerosene purification, for the removal of water in water-oil emulsion. About 99 % of the water was removed from the water-oil emulsion and a permeate flux more than 100 ml/min was observed throughout the filtration.

Leo Choe Peng

From: Siti Nadiah <sitinadiah.mustafa@yahoo.com>
Sent: Monday, 14 July, 2014 5:35 PM
To: Leo Choe Peng
Subject: Fw: Verification of Plagarism Screening

FYI

On Monday, July 14, 2014 4:57 PM, Ahmad Zuhairi Abdullah <chzuhairi@usm.my> wrote:

Ok, acceptable level.

Warmest regards,

~~~~~  
DR AHMAD ZUHAI RI ABDULLAH  
Associate Professor,  
Deputy Dean (Research),  
School of Chemical Engineering,  
Universiti Sains Malaysia, Engineering Campus,  
14300 Nibong Tebal, Penang, Malaysia.  
Tel: +604-599 6411 Fax: +604-594 1013  
Email: [chzuhairi@usm.my](mailto:chzuhairi@usm.my) or [azuhairi@yahoo.com](mailto:azuhairi@yahoo.com)  
Department's Website: <http://chemical.eng.usm.my/>  
Personal Website: <http://azuhairi.webs.com/>  
~~~~~

From: Samsuri Musa
Sent: Monday, July 14, 2014 4:43 PM
To: Siti Nadiah
Cc: Ahmad Zuhairi Abdullah; Hasmah Muhammad Yadzi
Subject: RE: Verification of Plagarism Screening

Dear Siti Nadiah,

Please find your report as attached.

SAMSURI MUSA

From: Siti Nadiah [<mailto:sitinadiah.mustafa@yahoo.com>]
Sent: Monday, 14 July, 2014 2:45 PM
To: Samsuri Musa
Subject: Re: Verification of Plagarism Screening

Dear Sir,
Here I attached a thesis draft copy.
Name : SITI NADIAH BINTI MUSTAFA KAMAL (P-JM0275)
Thesis title : SYNTHESIS OF INORGANIC AND POLYMERIC MEMBRANES WITH SAPO-44 ZEOLITE FOR GAS SEPARATION

Thank You.

Regards,

Siti Nadiah

On Friday, July 11, 2014 12:43 PM, Siti Nadiah <sitinadiah.mustafa@yahoo.com> wrote:

Okay, noted.thank you.

Regards,
Siti Nadiah

On 11 Jul 2014, at 12:41 pm, Samsuri Musa <sammusa@usm.my> wrote:

Dear Siti Nadiah,

- i. Please submit your draft copy in one Words files.
- ii. Please state your full name and thesis title
- iii. Submit to my email and you will get the result by next working days.

Regards ,

SAMSURI MUSA

From: Siti Nadiah [<mailto:sitinadiah.mustafa@yahoo.com>]

Sent: Friday, 11 July, 2014 12:31 PM

To: Samsuri Musa

Subject: Verification of Plagarism Screening

Assalamualaikum.

Encik Shamsuri, sy Siti Nadiah Bt Mustafa Kamal (MSc student).

Saya nak tanya Encik boleh buat check untuk 'plagarism' thesis sebelum submit 10 copies ke IPS?

Apa yang perlu saya sediakan (spt borang & format thesis (PDF/word))?

T/Kasih

Siti Nadiah
013-9279220

Dr Leo

MIXED MATRIX MEMBRANE FOR ULTRAFILTRATION

BY

NUR HAZWANI AHMAD KAMIL

**Thesis submitted in partial fulfilment of the requirements for the degree of Bachelor of
Chemical Engineering**

May 2012

**UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
Diterima pada**
28 MAY 2012
Pusat Pengajian Kejuruteraan Kimia



UNIVERSITI SAINS MALAYSIA

FINAL YEAR PROJECT

ACADEMIC SESSION 2012/2013

RESEARCH PROPOSAL

**SILANE MODIFICATION OF SAPO ZEOLITE FOR PREPARING MIXED
MATRIX MEMBRANE IN THE APPLICATION OF CO₂ SEPARATION**

NAME : KHOO CHIN PENG

MATRIC NUM: 104712

SUPERVISOR: DR.LEO CHOE PENG

**SYNTHESIS AND CHARACTERIZATION OF POLYSULFONE/METAL-
ORGANIC FRAMEWORKS (MOFs) MEMBRANE FOR CARBON DIOXIDE
(CO₂) GAS SEPARATION**

NURSYUHADA BINTI ABU SALIM

REPORT 3

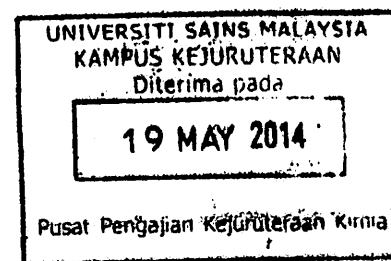
EKC499 FINAL YEAR PROJECT

School of Chemical Engineering

Universiti Sains Malaysia, Malaysia

Supervisor: Dr. Leo Choe Peng

May, 2014



APPENDIX D
NETWORKING AND LINKAGES

Date : 27 February 2014

Mohd Usman Bin Mohd Junaidi
School of Chemical Engineering,
Universiti Sains Malaysia,
14300 Nibong Tebal, Penang,
Malaysia
Tel: +6017-5413255
e-mail: usmanjunaidi@yahoo.com

Ahmad Jaril Asis
Vice President I (R&D – Processing & Engineering)
Sime Darby Research Sdn. Bhd.
Lot 2664, Jalan Pulau Carey,
42960 Pulau Carey,
Selangor Darul Ehsan.

Through,

Assoc Prof Mohd Azmier Ahmad,
Deputy Dean (Student Affairs & Networking),
School of Chemical Engineering,
Universiti Sains Malaysia.

Dear Sir / Madam,

**CONFIRMATION ON ACCEPTANCE OF INDUSTRIAL TRAINING PLACEMENT FOR
UNIVERSITI SAINS MALAYSIA CHEMICAL ENGINEERING UNDERGRADUATE STUDENT**

Your recent notification dated 24 January 2014 on the acceptance of my application for an industrial training in your company is referred. Thank you very much for giving me the opportunity to receive some industrial experience in your esteemed company.

I, **Mohd Usman Bin Mohd Junaidi (880505-105413)**, hereby accept the offer for a training period from **1 April 2014 to 30 June 2014.**

This acceptance is made with the knowledge that I shall be bound by all prevailing rules, regulations and policies of the company. Thank you.

Yours sincerely,



(MOHD USMAN BIN MOHD JUNAIDI)

Collaborative work with Petronas

----- Forwarded Message -----

From: "ABDUL LATIF AHMAD" <chlatif@eng.usm.my>

To: "Farahdila Bt Kadir Khan (CO2M/PRSB)"

<farahdila@petronas.com.my>

Cc: chcpleo@eng.usm.my, "Shamsina Bt Sabdin (CO2M/PRSB)"

<shamsin@petronas.com.my>, "W Nurul FFazida Bt W Mustapa

(CO2M/PRSB)" <nurulffazida@petronas.com.my>, "M Hanif B M

Halim (CO2M/PRSB)" <hanifhalim@petronas.com.my>, "Athirah Bt M

Tamidi (CO2M/PRSB)" <athirah tamidi@petronas.com.my>, "Soh Wei

Kian (CO2M/PRSB)" <weikian.soh@petronas.com.my>

Sent: Tuesday, January 28, 2014 12:01:40 PM

Subject: Re: Visit to USM on 28th November

Assalamualaikum Mrs Farahdila,

First of all thank you very much for sending the email regarding the collaborations.

I have to apologize for late replying since I was not in the campus in the past one week. I saw the email but was not able to discuss with Dr. Leo Choe Peng. We look forward for the validation activity. For that purpose we propose in the middle of February since most chinese lecturers and students will be taking one week off next for chinese new year celebration. At the same time, it will give us ample time for the preparation.

We are looking forward to hear from you.

rgds
Latif

----- Original Message -----

From: "Farahdila Bt Kadir Khan (CO2M/PRSB)"
<farahdila@petronas.com.my>

To: chcpleo@eng.usm.my, chlatif@eng.usm.my

Cc: "Shamsina Bt Sabdin (CO2M/PRSB)"

<shamsin@petronas.com.my>, "W Nurul FFazida Bt W Mustapa
(CO2M/PRSB)" <nurulffazida@petronas.com.my>, "M Hanif B M
Halim (CO2M/PRSB)" <hanifhalim@petronas.com.my>, "Athirah Bt M
Tamidi (CO2M/PRSB)" <athirah_tamidi@petronas.com.my>, "Soh Wei
Kian (CO2M/PRSB)" <weikian.soh@petronas.com.my>

Sent: Monday, January 20, 2014 2:43:26 PM

Subject: RE: Visit to USM on 28th November

Dear Prof Latif & Mrs Leo,

Follow up from PETRONAS Research team visit to USM in Nov 2013, we are really interested to explore further in detail specifically on the following products:

1) Mixed Matrix Membrane: the USM membrane team has found the "secret formula" that allows the particles to be homogenously distributed in the polymer dope and prevents agglomeration during spinning. This has allowed the team to achieve permeances of 200 to 300 GPU and selectivity of ~30 in their flat sheet single gas separation testing.

2) Membrane Contactor: the USM membrane team was successful in modifying the surface of a PVDF membrane which allows it to be compatible with amine. The surface modification technique has allowed USM to come up with a Superhydrophobic membrane (contact angle more than 150 degrees). This technique can be used to modify any hydrophilic membrane to hydrophobic.

[[cid:image001.png@01CF15E9.ECC43A80](#)]

3) Ceramic : The MST cluster's work in ceramic membrane is concentrating on the thin layer (i.e separating layer) and not on the support. For lab testing purposes, the ceramic membrane was formed into discs. The support can be bought offshelf and the thin layer can be coated onto any support shape. USM's specialty is on the thin layer

[[cid:image002.png@01CF15E9.ECC43A80](#)]

As for the next step, we would like to propose for both parties to sign NDA and then proceed with 'Validation Activity' before start discussion on the possible next step arrangement in order to further improve the product for scale

up testing. For the validation activity, is it possible for USM membrane team to prepare the above 3 membrane products (MMM, MC & ceramic) and PRSB membrane team will come to USM and witness the membrane performance testing in order to ensure it is suit with our intended application and align with our understanding?

After satisfied with the validation activity results, PRSB & USM can start discuss on the possible next step arrangement in order to further develop the products toward scale up improvement studies/testing activities. PRSB membrane team will then table it to our management for approval.

Appreciate for your reply soonest and thank you in advance for the cooperation. Hope for a great success ahead.

p/s: Pls fwd any other papers published related to the topics highlighted above (if any)

Thank you.

Regards,
Farahdila binti Kadir Khan,
CO2M R&D Staff Researcher,
PETRONAS Research Sdn Bhd (PRSB).

APPENDIX E
EXTERNAL RESEARCH GRANTS



USM UNIVERSITI
SAINS
MALAYSIA

Rujukan : H0293
Tarikh : 3 Julai 2012

Dr. Leo Choe Peng
Pusat Pengajian Kejuruteraan Kimia
Universiti Sains Malaysia
Kampus Kejuruteraan
14300 Nibong Tebal
PULAU PINANG

Pejabat Pengurusan dan
Kreativiti Penyelidikan
*Research Creativity and
Management Office*

Universiti Sains Malaysia
Aras 5, Bangunan Canselor
11800, USM Pulau Pinang, Malaysia
T (6)04-653 3108/3178/3988/5019
F (6)04-656 6466/8470
(6)04-653 2350
L www.research.usm.my
www.usm.my

Puan,

KEPUTUSAN PERMOHONAN SCIENCE FUND 2012

Sukacita dimaklumkan bahawa pihak kami telah mendapat pengesahan bahawa projek puan seperti berikut telah diluluskan:

Client	Project No.	Project Lead	Project Title	Total Grant (RM)
S & T Services	06-01-05-SF0579	Dr. Leo Choe Peng	"Superhydrophobic Ceramic Membrane For Carbon Dioxide Removal"	143,000.00

- Tempoh Projek : 24 bulan (Jun 2012 – Mei 2014)
- Ahli Kumpulan : I) Profesor Abdul Latif Ahmad (USM)
II) Profesor Ir. Dr. Abdul Wahab Mohammad (UKM)
- No. Akaun : 305/PJKIMIA/6013605
- Agihan mengikut tahun seperti yang diluluskan oleh MOSTI adalah seperti berikut:

PERKARA	Tahun 1 (2012)
Vot 11000 (Wages and Allowances for Temporary & Contract Personnel)	30,000.00
Vot 21000 (Travel and Transportation)	3,500.00
Vot 24000 (Rental)	1,000.00
Vot 27000 (Research Materials and Supplies)	20,000.00
Vot 28000 (Minor Modifications and Repairs)	1,000.00
Vot 29000 (Special Services)	13,000.00
Vot 35000 (R&D Equipment and Accessories)	0.00
JUMLAH BESAR	68,500.00

APPENDIX F
AWARDS

Pecipta'13

INTERNATIONAL CONFERENCE AND EXPOSITION ON
INVENTION OF INSTITUTIONS OF HIGHER LEARNING

SILVER

This is to certify that

SUPERAL MEMBRANE

Winner at **PECIPTA International Conference
and Exposition on Invention of Institutions of
Higher Learning**

held at

**Kuala Lumpur Convention Centre
7 - 9 November 2013**

Pecipta'13

Co-Organised By



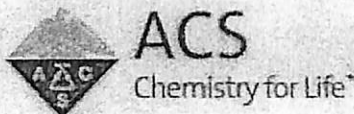
Co-Hosted By



Co-Sponsored By



YB. DATO' SERI IDRIS BIN JUSOH
Menteri Pendidikan II



2014 ACS-Pittcon International Delegation

November 27, 2013

Dr. Leo Choe Peng
Universiti Sains Malaysia
School of Chemical Engineering, Engineering Campus
14300 Nibong Tebal, Seberang Perai Selatan
Pulau Pinang, Malaysia

Dear Dr. Peng:

I am pleased to invite you to participate in the 2014 Pittsburg Conference on Analytical Chemistry & Applied Spectroscopy (Pittcon). The conference will take place at the McCormick Place in Chicago, Illinois on March 2-6, 2014. To learn more about the conference, visit www.pittcon.org.

To assist you in attending this event you will be provided with:

- Round trip economy class air travel up to \$1,500
- Five-night shared hotel accommodations during the conference
- Complimentary conference registration
- A US\$400.00 allowance for meals, local expenses, and airport transfers
- Travel medical insurance coverage

If you decide to accept our invitation, please respond no later than **Wednesday, December 18, 2013** by returning the enclosed response form via e-mail to l_brown2@acs.org or fax +1.202.872.6317.

In addition to your acceptance, we will need:

- A copy of the first two pages of your passport (including birth date, full name, passport number, etc.)
- A copy of your unexpired non-immigrant US visa to travel to the US

Note: if you do not yet have a non-immigrant US visa or if it has expired, you must apply for it immediately, and keep the Office of International Activities (OIA) informed of the process. Bring a copy of this letter with you. The name this letter is addressed to must match the name on your passport; if it does not match, please contact us immediately to have a new letter issued to you. They must have a copy of your visa no later than **January 31, 2014** in order to book your travel. Information on how to apply for a visa is available from your local US Embassy or Consulate and on the [ACS website](http://www.acs.org).

Please note that we cannot provide funding for or reimburse your visa fees.

Once the OIA receives all of the above-mentioned required documents, OIA staff will coordinate directly with the travel agency to book your flights. You will not have to disburse any funds to purchase your air ticket, as it will be charged directly to ACS.

I look forward to receiving your response and am delighted that we can extend to you the opportunity to participate in Pittcon 2014.

Sincerely,

H.N. Cheng, Ph.D.
Chair, ACS Committee on International Activities

Brad Miller, Ph.D.
Director, ACS Office of International Activities



THIS IS TO CERTIFY THAT
Nor Aini Ahmad
from the School of Chemical Engineering

HAS BEEN RECOGNIZED WINNER OF
PERSADA KENCANA AWARD

FOR EXCELLENT ACHIEVEMENT IN CATEGORY OF
BEST RESEARCH

A handwritten signature in black ink, which appears to be 'Omar Osman', is positioned above a horizontal line.

PROFESOR DATO' OMAR OSMAN
VICE-CHANCELLOR
UNIVERSITI SAINS MALAYSIA

APPENDIX G
FINAL ACCOUNT STATEMENT

JABATAN BENDAHARI
PENYATA PERBELANJAAN SEHINGGA 24 DISEMBER 2014

Projek :

No. Akaun : 1001.PJKIMIA.811194.

Vot	Nama Vot	Peruntukan Projek	Perbelanjaan Terkumpul Sehingga Thn Lalu	Baki Peruntukan Tahun Lalu	Peruntukan Thn Semasa	Jumlah Peruntukan Thn Semasa	Tanggung Semasa	Bayaran Thn Semasa	Jum Belanja Thn Semasa	Baki Projek
111	GAJI	70,155.28	0.00	52,155.28	18,000.00	70,155.28	0.00	17,941.89	17,941.89	52,213.39
115	LAIN-LAIN EMOLUMEN	-1,500.00	0.00	-1,500.00	0.00	-1,500.00	0.00	0.00	0.00	-1,500.00
221	PERJALANAN DAN SARA HIDUP	3,766.84	0.00	-3,233.16	7,000.00	3,766.84	0.00	603.33	603.33	3,163.51
223	PERHUBUNGAN DAN UTILITI	700.00	0.00	400.00	300.00	700.00	0.00	50.00	50.00	650.00
224	SEWAAN	-143.73	0.00	-643.73	500.00	-143.73	0.00	0.00	0.00	-143.73
226	BEKALAN BAHAN MENTAH	7,000.00	0.00	6,000.00	1,000.00	7,000.00	0.00	0.00	0.00	7,000.00
227	BEKALAN DAN BAHAN LAIN	-16,401.65	0.00	-32,401.65	16,000.00	-16,401.65	6,245.40	29,015.80	35,261.20	-51,662.85
228	PENYELENGGARAN & PEMBAIKAN KECIL	0.00	0.00	0.00	0.00	0.00	2,300.00	0.00	2,300.00	-2,300.00
229	PERKHIDMATAN IKTISAS & HOSPITALITI	5,663.50	0.00	-1,336.50	7,000.00	5,663.50	12,560.00	9,323.80	21,883.80	-16,220.30
335	HARTA MODAL	8,841.00	0.00	8,841.00	0.00	8,841.00	0.00	0.00	0.00	8,841.00
Jumlah		78,081.24	0.00	28,281.24	49,800.00	78,081.24	21,105.40	56,934.82	78,040.22	41.02