Inorganic filler selection in PDMS membrane for acetone recovery and its application in a condenser–gas membrane system

E.L. Vivas[a], A.B. Beltran[a], H. R. Cascon[a], J. Ahn[a], E. S. Cho[b], W. J. Chung[a]*

[a]*Department of Environmental Engineering and Biotechnology, Myongji University, Yongin City, 449-728, South Korea*
Tel. + 82313368471; Fax +82313372902; email: wjc0828@gmail.com
[b]*Korea Environment Institute, Division of Water & Environment, Jinheungno Eunpyeong-Gu, Seoul, (122-706) South Korea*

ABSTRACT

PDMS mixed matrix membranes (MMMs) with inorganic fillers – TS720 and TS530 silica, NaY type zeolite and multiwalled carbon nanotube (MWCNT) – were prepared by solvent evaporation and then tested for pure gas (N_2, O_2) and acetone/N_2 mixed gas permeability at various pressures at 35°C. The membranes were also tested for thermal stability. Results showed that the presence of the inorganic fillers improved the thermal stability of the PDMS membrane. Based on permeability and selectivity results, PDMS/TS720 MMM exhibited better performance, thus, it was chosen as the coating material in the fabrication of the thin film composite (TFC) membrane to be integrated into the condenser–gas membrane hybrid system. The TFC membrane was prepared by coating a thin layer of PDMS solution containing 20% (w/w) TS720 filler on the flat-sheet ultrafiltration polysulfone support membrane using a roller coating machine. Acetone/N_2 mixed gas permeation experiment was conducted at 35°C and 5 bars to ensure that the TFC membrane was defect-free. Results showed that the TFC membrane has an acetone permeance and selectivity of 964.3 GPU and 8.5, respectively. The condenser–membrane hybrid experiment was performed at various stage cuts (SCs) under controlled operating conditions (pressure, temperature, flow rate and acetone concentration). Results of the hybrid experiment showed an over-all acetone recovery as high as 91.9% at 60% SC.

Keywords: Thin film composite membrane; PDMS; Inorganic filler; Hybrid system; Stage cut

1. Introduction

Acetone is an excellent solvent extensively used in the pharmaceutical, pesticide and coating industries. It is also an important volatile organic compound (VOC) used as a chemical raw material in the production of acetone cyanohydrins, methyl methacrylate (MMA), esters and bisphenol A [1].

In drying, coating and other operations, vapors of acetone are uncontrollably emitted. The volume of acetone involved in such processes is very large and this represents a significant reuse opportunity to reduce economic losses. For the past several years, various VOC recovery procedures were developed in dealing with this problem, such as condensation, carbon adsorption and incineration. However, most of them are still not economically practical [2–4].

Membrane technology has been growing rapidly for the past decades. Membrane-based vapor separation, a major industrial application of the technology, was found to recover solvent vapors and chlorofluorohydrocarbons from a large number of processes that use

*Corresponding author

Table 1
Basic technical information of inorganic fillers used.

Parameter	Inorganic fillers			
	TS530 silica [9]	TS720 silica [10]	NaY Zeolite [11]	MWCNT [12]
Particle size/length (micron)	0.2–0.3	0.2–0.3	< 3.0	0.5–2.0
Physical appearance	Fluffy white powder	Fluffy white powder	White powder	Black powder
B.E.T. surface area (m^2/g)	205–245	105–130	–	–
Density (g/cm^3)	2.2	2.2	1.6–1.7	~ 2.1
X-ray form	Amor-phous	Amor-phous	Crystalline	–
Surface chemistry	Trimethyl silyls	Dimethyl siloxane	–	–

VOCs and produce gaseous emissions [5]. It has been emerging as an alternative for the conventional VOC recovery methods since then.

Theoretical and experimental studies on solvent recovery from air have been done for many organic solvents at different operating conditions using PDMS/polysulfone (PSf) composite hollow fiber membranes. Past studies reported that acetone was successfully recovered using a PDMS hollow fiber module and cooler [6]. Although PDMS is already being used commercially for membrane-based vapor separations due to its high permeability for organic vapors (making it useful for the removal of low concentration organics in air), previous researches verified that there is still a large room for improvement of this coating material in terms of permeation properties [3,6–8].

In this research, various inorganic fillers were blended with PDMS to enhance the permselectivity of the PDMS. The organic–inorganic hybrid dense membranes were partially characterized and tested for acetone permeability and selectivity. The best blend, based on the experiments with the dense membranes, was used as the coating material in the fabrication of the thin film composite (TFC) ultrafiltration polysulfone (UF PSf). Finally, the acetone recovery performance of a hybrid system composed of a TFC-UF-PSf membrane coupled with a condenser was evaluated at different stage cuts (SCs).

2. Experimental

2.1. Materials

The PDMS polymer used in this study was Sylgard 184 silicone elastomer base and curing agent kit manufactured by Dow Corning Corporation. The fillers tested were the following: Cab-O-Sil TS530 and Cab-O-Sil TS720 hydrophobic fumed silica both purchased from Cabot Corporation, USA; NaY type zeolite obtained from JISHIM TECH, South Korea; and

multiwalled carbon nanotubes (MWCNT) purchased from Cheap Tubes Inc., USA. The basic characteristics of these fillers are shown in Table 1. The solvents used were HPLC grade toluene and *n*-hexane. The acetone (99.5% purity) used for the acetone/N_2 gas mixture generation was obtained from Duksan Pure Chemicals Co., Ltd. Nitrogen and oxygen gases (both 99.999% purity) used in the experiments were purchased from Union Gas, South Korea. The flat-sheet UF PSf support membrane was provided by Sepro Membranes, Inc., USA. All reagents were used without further purification.

2.2. Dense membrane preparation

Mixed matrix membranes (MMMs) used in this study were prepared using solvent casting and evaporation. PDMS solutions were prepared by dissolving the silicone elastomer base and curing agent at 10:1 ratio (as prescribed by the manufacturer) in toluene to achieve a 10% (w/w) casting solution. The solution was sonicated for a minimum of 2 h to ensure total mixing and degassing. A pre-weighed amount of filler was then added with the previously prepared PDMS solution to produce a 20% (w/w) filler-loaded PDMS MMM. The MMM solution was then sonicated for at least 2 h to ensure homogeneity. Designated amounts of the MMM solutions were poured in Teflon dishes. Subsequently, the casted solutions were evaporated under vacuum condition initially at room temperature for 24 h, and then cured at 80°C for another 24 h. The formed membranes were stripped off from the Teflon dish and transferred to a plastic Petri dish for storage prior to use.

2.3. Preparation of PDMS-TS720 TFC Membrane

The polymer solution was prepared with the same method used for the dense membrane fabrication but
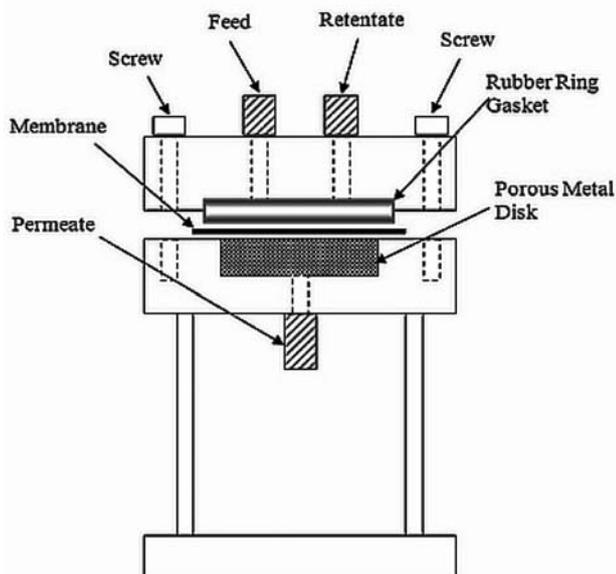
Fig. 1. Schematic diagram of the membrane cell used in the condenser–gas membrane hybrid system.

with *n*-hexane as the solvent since UF PSf was found to have low resistance to chemical attack by toluene during the initial solution-coating experiments. After preparing the polymer solution, clean sheets of UF PSf bare membrane were coated with the PDMS/TS720 polymer solution using an SUS back-up roller coating apparatus. The coated membranes were initially air-dried on the clean bench for 24 h followed by oven drying at 80°C for another 24 h.

2.4. Pure gas and mixed gas permeation experiments

Different PDMS MMMs were tested for pure oxygen and nitrogen permeability using a membrane cell (Fig. 1) at 35°C. Pure gas permeability test was performed at various controlled pressures (3, 4 and 5 bars).

The dense PDMS MMMs were tested for acetone permeability and selectivity using a VOC generator-membrane cell system (Fig. 2, without the condenser). The membrane cell side was operated at various pressures, at 35°C. Acetone concentration in the acetone/N_2 mixed gas feed was maintained in the range of 2–4% (v/v).

The PDMS/TS720-coated UF PSf membranes were pretested at 5 bars, 35°C and 1% SC to determine its acetone permeance and selectivity and to assure that the membrane was defect-free before being integrated into the hybrid system.

The condenser–gas membrane hybrid system (Fig. 2) experiment was done under controlled operating conditions of −13°C and 7.5 bars at the condenser side, and 35°C and 5 bars at the membrane side. The system was first allowed to stabilize for at least 60 minutes before sampling. Acetone recovery was determined at 20%, 40% and 60% SCs.

Flow rates of the gas streams were controlled and measured using mass flow controllers (MFCs) and bubble meters.

The pure and mixed gas permeabilities of the dense PDMS MMMs were calculated using Eqs. (1) and (2), respectively. Since the thickness of the TFC membrane was not determined, mixed gas permeance was calculated using Eq. (3). Selectivities were calculated using Eq. (4).

$$P_A = \frac{\ell}{A_M(p_F - p_P)} \frac{273}{T} \frac{1}{76} \frac{dV}{dt}, \tag{1}$$

$$P_{A,M} = \frac{\ell \cdot x_P}{A_M(p_F x_F - p_P x_P)} \frac{273}{T} \frac{1}{76} \frac{dV}{dt}, \tag{2}$$
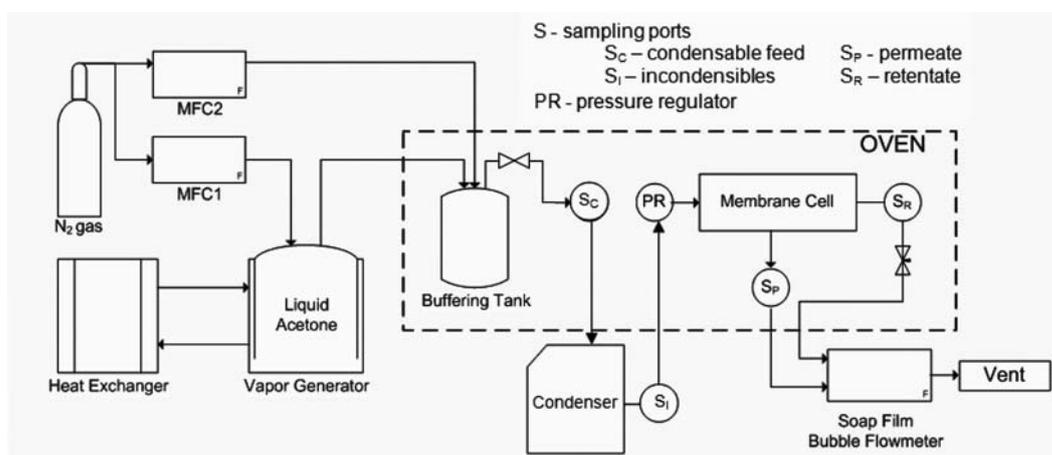
Fig. 2. Schematic diagram of the condenser–membrane hybrid system.
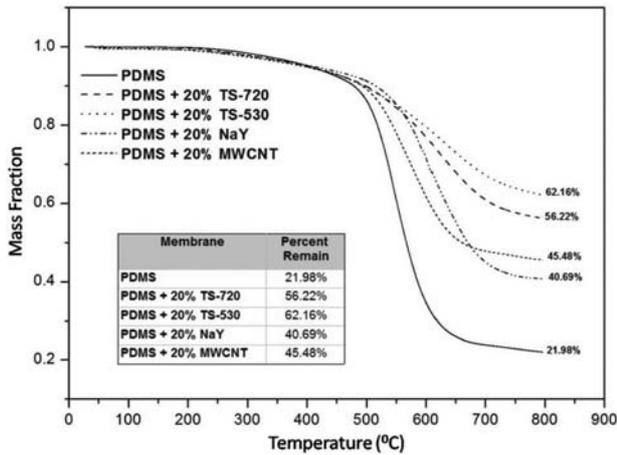
Fig. 3. TGA of the different PDMS MMMs.

$$\rho_{A,M} = \frac{x_P}{A_M(p_F x_F - p_P x_P)} \frac{273}{T} \frac{1}{76} \frac{dV}{dt}, \qquad (3)$$

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{\rho_A}{\rho_B}, \qquad (4)$$

2.5. Analytical methods

Thermal gravimetric analysis (TGA) was done in order to assess the thermal stability of the prepared dense membranes using the TA Instruments Model TGA2950 equipment.

For TFCs, Fourier transform infrared spectroscopy (FTIR) analysis was done to confirm the successful coating of UF PSf with a polymer solution.

The morphology of the TFC membrane subjected for gas transport of vapor–gas mixture separation was investigated using scanning electron microscopy (SEM). The SEM used in the study was the Hitachi Model S-3500N.

The membrane thickness was measured using a precision scale Mitutoyo micrometer.

Acetone concentration of gas samples were determined using gas chromatography (GC) HP 6890 series equipped with flame ionization detector (FID).

3. Results and discussion

3.1. TGA of the PDMS MMMs

Fig. 3 shows the TGA plots of different PDMS MMMs prepared. The TGA plots revealed that the degradation temperatures and the onset of accelerated weight loss of the hybrid PDMS dense membranes were higher as compared to the pure PDMS dense

Table 2
Degradation temperatures of the PDMS MMMs.

Membrane	Degradation temperature (°C)
PDMS	480
PDMS/20% TS720	504
PDMS/20% TS530	493
PDMS/20% NaY	516
PDMS/20% MWCNT	494

membrane. The degradation temperatures are summarized in Table 2.

The thermogram (refer to Fig. 3) showed that all the modified PDMS membranes had higher residual mass than the pure PDMS membrane. This asserted that the rate of degradation of PDMS membrane was decreased; thus, implying that the thermal stability of the PDMS membrane was improved with the addition of the fillers.

The PDMS MMMs tested can be arranged in the following order based on thermal stability: *Pure PDMS < PDMS/NaY < PDMS/MWCNT < PDMS/TS720 < PDMS/TS530.*

3.2. Pure gas permeability experiment

The permeabilities of different PDMS MMMs for N_2 and O_2 are shown in Figs. 4 and 5, respectively. Permeability of both gases was observed to decrease as the pressure was increased from 3 to 4 bars. This behavior was similar to the trends observed by Merkel [13,14].

Nitrogen and oxygen permeability of PDMS MMMs are known to follow Maxwell's theoretical prediction on the behavior of composite materials [15]. The
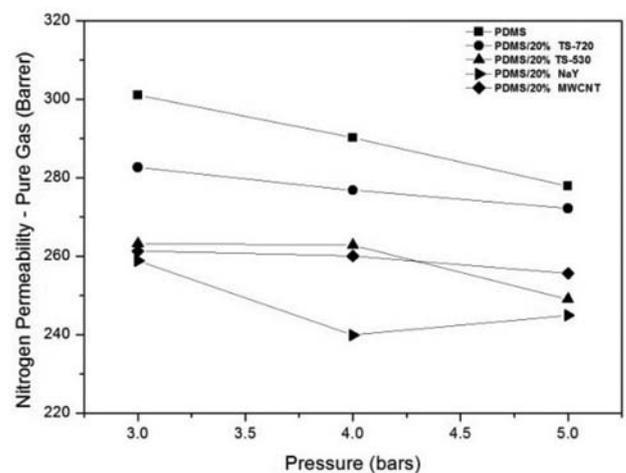
Fig. 4. Permeability of pure nitrogen gas in PDMS MMMs (35°C) as a function of pressure.
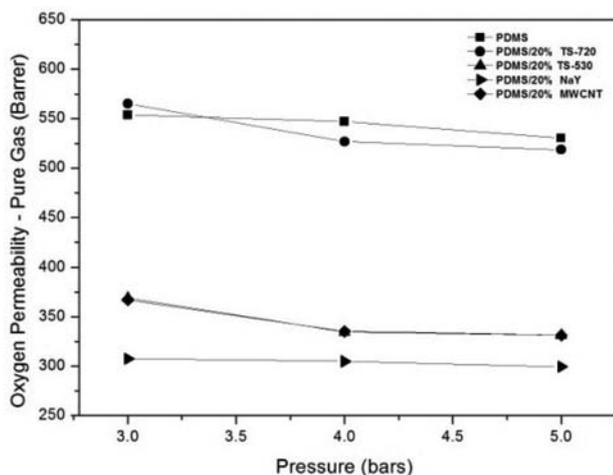
Fig. 5. Permeability of pure oxygen gas in PDMS MMMs (35°C) as a function of pressure.

addition of inorganic filler in PDMS membrane decreases its nitrogen and oxygen permeability and the degree of this decrease can be attributed on the type of filler employed. Results of the pure N_2 gas permeability experiment were in the following order: *PDMS > PDMS/TS720 > PDMS/MWCNT > PDMS/TS530 > PDMS/NaY*. On the other hand, the order of oxygen permeability was as such: *PDMS > PDMS/TS720 > PDMS/MWCNT ≈ PDMS/TS530 > PDMS/NaY*.

Chung [15] reported that addition of inorganic fillers improved the selectivity of the polymer. However, in this experiment, only the PDMS/TS720 MMM improved the O_2/N_2 selectivity for PDMS as shown in Fig. 6. O_2/N_2 selectivity reductions (24–36%) were observed for PDMS membranes filled with TS-530, MWCNT and NaY zeolite.
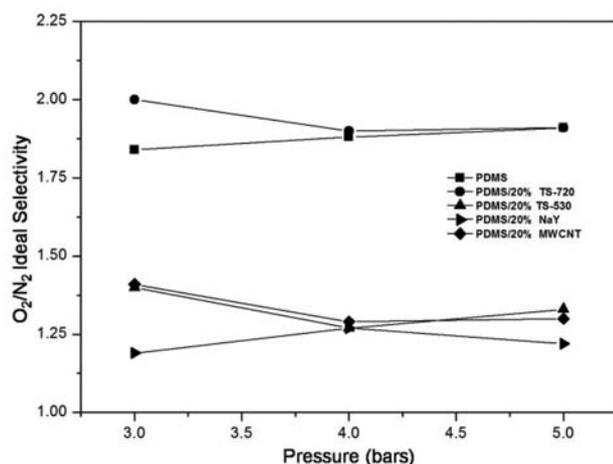
Fig. 6. Ideal O_2/N_2 selectivity of PDMS MMMs (35°C) as a function of pressure.
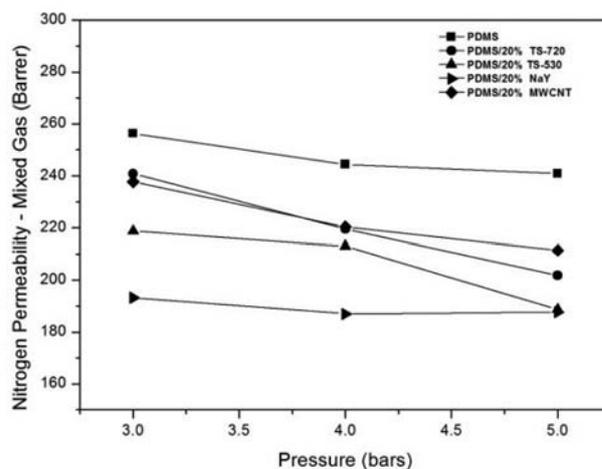
Fig. 7. N_2 permeability (acetone/N_2 mixed gas, 35°C) in PDMS MMMs as a function of pressure.

Only PDMS/TS720 MMM showed improvement in O_2/N_2 selectivity relative to pure PDMS and other PDMS MMMs. The order of acetone permeabilities was as follows: *PDMS/TS720 > PDMS > PDMS/TS530 > PDMS/MWCNT > PDMS/NaY*.

3.3. Acetone/N_2 mixed gas permeability experiment

Nitrogen and acetone permeabilities of different PDMS MMMs, as a function of pressure, during the acetone/N_2 mixed gas permeation experiment are summarized in Figs. 7 and 8, respectively.

For all the PDMS MMMs, nitrogen permeability was observed to decrease as the operating pressure was increased. This behavior was similar to the observations in the pure gas experiment. Choi [16] explained
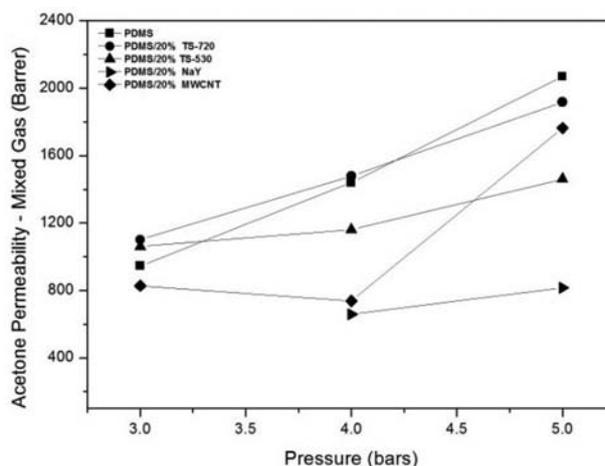
Fig. 8. Acetone permeability (acetone/N_2 mixed gas, 35°C) in different PDMS MMMs as a function of pressure.
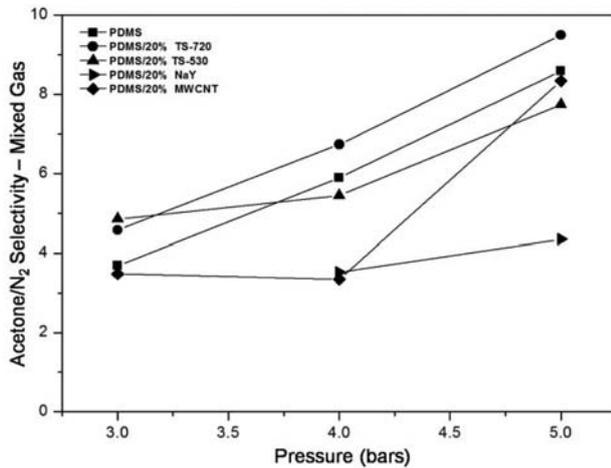
Fig. 9. Acetone selectivity (acetone/N$_2$ mixed gas, 35°C) of PDMS MMMs as a function of pressure.

Fig. 10. FTIR spectra of bare and composite UF PSf membranes.

that the decrease in permeability resulted from the compaction of the membrane caused by increasing pressure. It was also noted that nitrogen permeability in acetone/N$_2$ mixed gas decreased from 9–20% as compared to the pure gas.

The order of nitrogen permeabilities observed is as follows: *PDMS > PDMS/MWCNT > PDMS/TS720 > PDMS/TS530 > PDMS/NaY*.

Acetone permeability increased as the operating pressure was increased. This behavior is typical for a highly condensable vapor like acetone that can be easily sorbed by an organic membrane, causing the membrane to swell thus, increasing the transport rate of the organic vapor. As the membrane was being plasticized, the presence of acetone in the membrane increased the resistance for the permanent gas (nitrogen) to pass. This phenomenon reduced the permeability of the nitrogen gas through the membranes [16].

Acetone selectivities of the different PDMS MMMs were obtained and plotted against pressure as shown in Fig. 9. Acetone/N$_2$ selectivity increased for all the PDMS MMMs as pressure was increased. The order of acetone selectivities was: *PDMS/TS720 > PDMS > PDMS/TS530 > PDMS/MWCNT > PDMS/NaY*.

Based on permeability and selectivity results, PDMS/TS720 blend was chosen to be employed in the fabrication of the solution-coated UF PSf composite gas membrane. The resulting PDMS/TS720-coated UF PSf would be integrated into the condenser–gas membrane hybrid system for acetone recovery.

3.4. Coating confirmatory tests of PDMS/TS720/UF PSf

A sample composite membrane was examined under the FTIR spectroscopy to check if the UF PSf was

successfully coated with the PDMS/TS720 polymer solution. A comparative FTIR analysis was done and results are shown in Fig. 10.

The distinct peaks of the uppermost spectrum at the wave number region 969–1,281 cm^{-1}, signify the surface identity of the bare UF PSf. The disappearance of these peaks and being replaced with new distinct peaks, as illustrated in the PDMS/TS720-coated UF PSf spectrum, indicated that the UF PSf surface was coated with a selective layer of the polymer solution.

To further confirm that the UF PSf was coated successfully, comparative cross-section SEM analysis of the bare and coated UF PSf was performed as shown in Fig. 11. The cross-section images revealed the presence of the selective layer on the UF PSf support which has an average thickness of 0.56 μm.

3.5. Pretesting of the TFC membrane

Acetone/N$_2$ permeation experiment was performed to determine the acetone permeance and selectivity of the PDMS/TS720-coated UF PSf and to assure that it is defect-free before being integrated to the condenser–membrane hybrid system. The data obtained with the TFC membrane were compared to that of the PDMS/TS720 dense membrane and are summarized in Table 3.

Results showed that though the TFC membrane has slightly lower acetone selectivity, it is more applicable in the operation of the condenser–gas membrane hybrid system since it has remarkably higher acetone permeance.
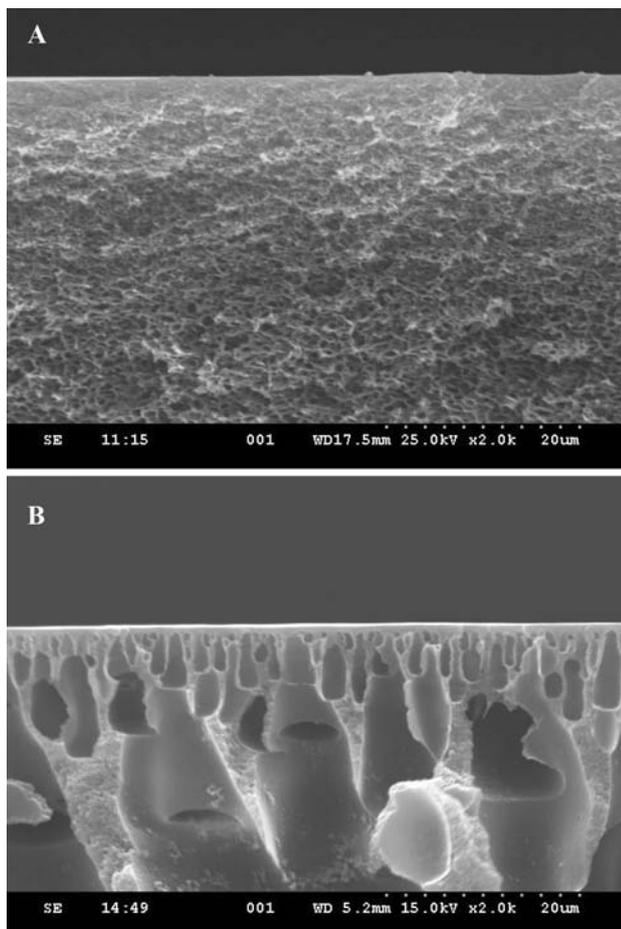
Fig. 11. Cross-section SEM images of the (a) pristine UF PSf and (b) solution-coated UF PSf.

3.6. Performance evaluation of the hybrid system

The performance of the condenser–gas membrane hybrid was evaluated in terms of over-all acetone recovery at 20%, 40% and 60% SCs as shown in Fig. 12.

Over-all acetone recovery increased as the SC was increased, as high as 91.9% at 60% SC. However, a high

Table 3
Comparative results of the permeation testing of the PDMS/TS720 dense and composite membranes

Membrane	Permeance (GPU)		Acetone selectivity
	Acetone	Nitrogen	
Dense MMM (152.78 μm thick)	12.5	1.3	9.5
TFC membrane	964.3	114.1	8.5
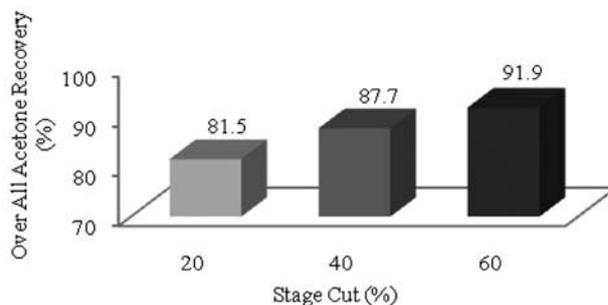
Fig. 12. Over-all acetone recovery across the condenser-gas membrane hybrid system at increasing SC.

recovery at high SC does not guarantee feasibility of the hybrid system for industrial application. Generally, the volume of a treatable gas feed using a gas separation membrane highly depends on the feed flow rate, which is negatively affected as SC is increased. At high SCs, treatment/separation rate is very slow; volume capacity in a given period of time is low, thus, requiring higher energy and operation costs. In short, running the hybrid system at high SCs is economically impractical.

To make the condenser–gas membrane hybrid system developed in this research more economically feasible, further optimization of the operating conditions should be explored and the TFC membrane should be improved. One area that needs attention is the observed aggregation of TS720 nanoparticles within the selective layer of the PDMS/TS720-coated UF PSf. A new mixing and coating mechanism to homogenously disperse the nanoparticles might further improve the acetone permeance and selectivity of the TFC membrane. Achieving this will contribute much in acquiring high acetone recoveries at low SCs.

4. Conclusions

Different PDMS MMMs were prepared and tested for thermal stability, pure gas (N_2 and O_2) and acetone/N_2 mixed gas permeabilities. Results of the TGA analysis showed that the thermal stability of the PDMS membrane was improved with the addition of the inorganic fillers (TS720, TS530, MWCNT and NaY type zeolite). Based on pure and mixed gas permeability and selectivity results, PDMS/TS720 blend was chosen in the fabrication of the TFC UF PSf to be integrated into the condenser–gas membrane hybrid system. Compared with the dense PDMS/TS720 membrane, the PDMS/TS720-coated UF PSf was indeed more applicable in the operation of the hybrid system because of its remarkably higher acetone permeance. The performance of the hybrid system was evaluated

and as high as 91.9% over-all acetone recovery at 60% SC was achieved. However, high acetone recovery at high SCs is still energy-intensive for industrial application of the hybrid system. Further research is still necessary to attain a satisfactory performance at lower SC (i.e. TFC material improvement).

Acknowledgment

Symbols

P_A	Permeability of gas A (cm^3 (STP) cm/cm^2 cm Hg s)
P_B	Permeability of gas B (cm^3 (STP) cm/cm^2 cm Hg s)
$P_{A,M}$	Permeability of gas A using mixed gas as feed (cm^3 (STP) cm/cm^2 cm Hg s)
$\rho_{A,M}$	Permeance of gas A using mixed gas as feed (cm^3 (STP)/cm^2 cm Hg s)
ρ_A	Permeance of gas A (cm^3 (STP)/cm^2 cm Hg s)
ρ_B	Permeance of gas B (cm^3 (STP)/cm^2 cm Hg s)
p_F	Feed pressure (bars)
p_P	Permeate pressure (bars)
ℓ	Membrane thickness (cm)
A_M	Membrane Area (cm^2)
T	Operating temperature (K)
dV/dt	Flow rate at steady state condition (cm^3 (STP)/s)
x_F	Feed concentration of A (volume fraction)
x_P	Permeate concentration of A (volume fraction)
$\alpha_{A/B}$	Membrane selectivity

References

[1] C. Hongquan, C. Forthcoming major reversal in acetone supply and demand. [Online] China Chemical Reporter. 2008. Available: http://www.thefreelibrary.com/Forthcoming+major+reversal+in+acetone+supply+and+demand.-a0173464864.
[2] R.W. Baker, N. Yoshioka, J.M. Mohr, and A.J. Khan, Separation of organic vapors from air. J. Membr. Sci., 31 (1987) 257–271.
[3] H. Paul, C. Philipsen, F,J. Gerner, and H. Strathmann, H. Removal of organic vapors from air by selective membrane permeation. J. Membr. Sci., 36 (1988) 363–372.
[4] A.C. Larsson and R. Wimmerstedt, Solvents fluxes measured on a membrane model. J. Membr. Sci., 84 (1993) 139–150.
[5] R.W. Baker, J. Kaschemekat, and J.G. Wijmans, Membrane systems for profitable VOC recovery. CHEMTECH,26 (1996) 37.
[6] K. Kimmerle, C.M. Bell, W. Gudernatsch, and W.E.H. Chmiel, Solvent recovery from air. J. Membr. Sci., 36 (1988) 477.
[7] R.W. Baker and J.G. Wijmans, *Membrane separation of organic vapors from gas streams*, in Paul, D.R. and Yampol'skii Y.P. (Eds.). Polymeric Gas Separation Membranes. CRC Press, Boca Raton, FL, 1994, p. 353.
[8] A. Singh, B.D. Freeman, and I. Pinnau, I. Pure and mixed gas acetone/nitrogen permeation properties of polydimethylsiloxane [PDMS]. J. Poly. Sci.: Part B: Poly. Phys., 36 (1998) 289–301.
[9] CAB-O-SIL® TS-720 Treated Fumed Silica. Product Data Sheet. [Online] 2009. Available: http://www.cabot-corp.com.
[10] CAB-O-SIL® TS-530 Treated Fumed Silica. Product Data Sheet. [Online] 2009. Available: http://www.cabot-corp.com.
[11] NaY Zeolite. JISHIM TECH Manual. [Online] 2009. Available: http://www.jishim.com/e_product01_1.html.
[12] Multi-walled carbon nanotubes. (short MWNTs >95wt% / 20-30nm OD) Product Data Sheet. [Online] 2009. Available: http://www.cheaptbesinc.com.
[13] T.C. Merkel, V.I. Bondar, K. Nagai, B.D. Freeman, and I. Pinnau, Gas sorption, diffusion, and permeation in poly(dimethylsiloxane). J. Poly. Sci.: Part B: Poly. Phys., 38 (2000) 415–434.
[14] H. X. Rao, F.N. Liu, and Z.Y. Zhang, Preparation and oxygen/nitrogen permeability of PDMS crosslinked membrane and PDMS/tetraethoxysilicone hybrid membrane. J. Membr. Sci., 303 (2007) 132–139.
[15] T. Chung, L.Y. Jiang, Y. Li, and S. Kulprathipanja, Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. Prog. Polym. Sci., 32 (2007) 483–507.
[16] S.H. Choi, J.H. Kim, and S.B. Lee, Sorption and permeation behaviors of a series of olefins and nitrogen through PDMS membranes. J. Membr. Sci., 299 (2007) 54–62.