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Polyurethane–poly(vinylidene fluoride) (PU–PVDF) thin film composite membranes for gas separation[☆]

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ABSTRACT

Aqueous polyurethane dispersions (PUDs) with poly(dimethylsiloxane) (PDMS), or mixed poly(dimethylsiloxane)/poly(ethylene glycol) (PDMS/PEG) as the soft segment were synthesized, and made into thin films for characterization with differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), size exclusion chromatography (SEC) and transmission electron microscopy (TEM). Seven thin film composite (TFC) membranes prepared on PUDs and PVDF substrates were evaluated by the separation of air as well as hydrocarbon–nitrogen mixtures. A promising membrane was then selected for further investigation of the morphological structure and permselectivities, using pure gases and binary mixtures of ethylene, ethane, propylene and propane with nitrogen at ambient temperature. It was found that PDMS/PEG-based PU membrane was typically solubility-selective for condensable hydrocarbons, and nitrogen permeance was marginally enhanced in hydrocarbon–nitrogen mixtures. It appears that the copolymer membrane with both urethane and PEG segments can effectively tolerate the swelling caused by the condensable gases. As a result, the selectivities of propylene and propane to nitrogen were substantially improved, e.g., in a mixture containing 28% propylene and 72% nitrogen, the selectivity of propylene to nitrogen reached 29.2 with a propylene permeance of 34.4 gas permeation unit (GPU).

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1. Introduction

Rubbery thin film composite membranes have been used in petroleum and chemical industries to preferentially permeate volatile organic compounds (VOC's) for many decades with the benefit of saving energy and valuable hydrocarbons [1–3]. Poly(dimethylsiloxane) (PDMS) is a favorable coating material in polymeric membrane-based gas separation due to its hydrophobicity and thermal stability. Its low glass transition temperature (-129°C) results in extremely high permeation through the membrane for a wide range of gases due to the flexible polymer backbone. However, it is limited in mechanical strength and selectivity particularly for highly condensable hydrocarbons in admixture with permanent gases [4–6]. For example, our previous work [7,8] showed that PDMS coated membrane can be plasticized by propane and propylene, resulting in significant permeance increases for both hydrocarbons and nitrogen in a quaternary mixture of propane, propylene, ethylene and nitrogen, therefore, the selectivities of hydrocarbons to nitrogen were not as high as expected.

Polyurethane copolymers combine rigid hard segment and flexible soft segment, which offer a wide range of variability in structure and properties [9]. Usually the hard segment consists of urethane and urea linkages with rigid and bulky units. The strong molecular interactions of the polar urethane and urea groups and the rigid units make the hard segment act as fillers or physically crosslinked. On the other hand, soft segment is made from singular or mixed long chain diols such as poly(dimethylsiloxane), poly(tertramethylene oxide), poly(ethylene oxide), poly(propylene oxide), poly(monoethylene adipate) and polybutadiene, which contribute to flexibility and elasticity. The hard segment alternates along with soft segment, which produces distinguishing physical and mechanical properties for polyurethane. Many researchers have been investigating segmented polyurethane as a new material to improve the permselectivity for gas separation such as VOCs or CO_2 from N_2 , $\text{H}_2\text{S}/\text{CH}_4$ and O_2/N_2 [10–17]. The structure-gas transport property correlations of those PU film membranes with a variety of singular or mixed soft segments elucidate that the gas permselectivity mainly depends on the contents and types of soft segments as well as their molecular weights. The combination of polysiloxane with polyurethane has attracted special attention due to the advantages of not only better thermal stability and high flexibility at low temperatures but also better mechanical strength and abrasion

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characteristic contributed by polyurethane. Park et al. [16] reported the gas transport properties of mixed polysiloxane/polyether soft segment urethane urea film membranes, and Madhavan and Reddy [17] showed the effect of urethane type and content for hard segment on gas performance in poly(dimethylsiloxane-urethane) film membranes. They found that PDMS-based PU thin film membranes performed higher selectivities with reasonable permeabilities compared to no-filler PDMS for O_2/N_2 and CO_2/N_2 separations. Furthermore, the addition of polyether into PDMS-based PU resulted in further increase in permeabilities and selectivities for nitrogen, oxygen and carbon dioxide due to increased phase separation in the hard and soft segments. The incorporation of PDMS also promoted the difference of solubility parameters between the hard and soft segments. As a result, the dispersed PDMS phases served to produce a more tortuous route for diffusing molecules. Recently Gomes et al. [18] reported the correlation of gas permselectivities with the contents of PDMS/poly(tetramethylene glycol) soft segments for the thin film membranes made from polyurethane dispersions (PUDs). It is interesting to note that $n-C_4H_{10}/CH_4$ selectivity for the gas mixture was higher than the ratio of individual gas permeabilities, indicating a possibility of application of this PUD material for $n-C_4H_{10}/CH_4$ separation.

An active coating layer on a highly permeable substrate is a widely accepted concept for TFC membrane preparation. However, it is not always easy to achieve due to the incompatibility of common coating solvent with substrate material. In order to apply polyurethane as a coating material, Duarte et al. [19] used simultaneous casting technique to overcome this challenge for the polyurethane/polyethersulfone composite membrane. Another way is to select a suitable substrate material, which can tolerate the coating solvent. PVDF is one of the good substrate materials with high chemical stability and permeability. Zhen et al. [20] reported divinyl-terminated PDMS–PVDF composite hollow-fiber membrane for the separations of benzene, chloroform, acetone, ethyl acetate and toluene. Our approach is to take the advantage of highly selective polyurethane with its compatible poly(vinylidene

fluoride) to explore PU–PVDF thin film composite membranes. A water-based polyurethane dispersion can also provide a green alternative to the traditional solvent-based TFC membrane formation. The present work reports the synthesis of PUDs containing PDMS or/and PEG, the formation of TFC membrane over PVDF substrate, membrane characterization, the correlation of structure–gas transport property for air, mixed C_2H_4/N_2 and C_3H_6/N_2 , and the permeances and selectivities of a selected composite membrane for pure nitrogen, ethylene, ethane, propylene and propane as well as ethylene–nitrogen and propylene–nitrogen gas mixtures at varying pressure and feed concentration at ambient temperature.

2. Experimental

2.1. Materials

Poly(vinylidene fluoride) (PVDF, Solef 1010, Solvay Solexis), anhydrous 1-methyl-2-pyrrolidinone (NMP, Sigma–Aldrich), lithium nitrate (Fluka), lead acetate (Merck), bimodel polystyrene (PS, M_w : 200,000 and 4000, Sigma–Aldrich), dimethylol propionic acid (DMPA, GEO Specialty Chemicals), isophorone diisocyanate (IPDI, Vestanat IPDI, Degussa), polyethylene glycol (PEG, M_n : 1900, Sigma–Aldrich), hydroxyl alkyl poly(dimethylsiloxane) (PDMS, M_n : 2800, Tegomer H-S₂311, Goldschmidt), glycidoxypropyl trimethoxysilane (Silquest A-187 Silane, Momentive), tetrahydrofuran (THF, reagent grade, EMD Chemicals), triethylamine and ethylenediamine (Sigma–Aldrich), were used as received. Nitrogen, oxygen, air, carbon dioxide, ethylene, ethane, propylene and propane were supplied from BOC Gases, Canada with purities higher than 99.8%.

2.2. PUDs synthesis

Two PUD samples were synthesized using a pre-polymer process [18]. The procedure was summarized in Scheme 1. First diols (PEG and/or Tegomer H-S₂311) and DMPA were polymerized with

Scheme 1. The reaction scheme for the preparation of PUDs.

Table 1
PUD designations and compositions

Sample	Soft segment content (wt.%)		Hard segment content (wt.%)	Solid content (wt.%)
	PEG	PDMS ^a		
PUD-1	0	58.5	41.5	26.3
PUD-2	33.7	33.7	32.6	16.1

^a Tegomer H-S;2311.

excess IPDI into NCO terminated carboxylic pre-polymers. The resultant pre-polymers were neutralized with triethylamine to render it hydrophilic, and followed by dispersion in water by vigorous stirring. The high molecular weight PUDs were obtained by the addition of ethylene diamine as a chain extender into the dispersed pre-polymers in water. Table 1 lists the composition of polymers. Excess amount of IPDI was used in the pre-polymer preparation so that long hard segment could be formed after the chain extension was completed. This approach also allowed the incorporation of hard segment in a controlled fashion.

2.3. TFC membrane preparation

PDVF substrate was casted on the flat backing material (Spun-bonded polyester, grade 3329, Ahlstrom) using a metal knife with 250 μm gap via a dry-wet phase inversion method. Two substrate solutions were prepared to compare the function of an additive for gas permeation. The names and compositions were as follows: (1) PVDF 1010-22-0: 22% Solef 1010 and 78% NMP; (2) PVDF 1010-22-2.5: 22% Solef 1010, 2.5% lithium nitrate and 75.5% NMP. Both solutions were rolled at 60 °C until the solid completely dissolved prior to casting process.

Four different coating solutions with Silquest A-187 as a post-crosslinker were prepared with following compositions: (1) PUD-1: original PUD-1 solution; (2) PUD-1-5.9: PUD-1 with 5.9 wt.% (relative to polymer) Silquest A-187; (3) PUD-2-2.7: PUD-2 with 2.7 wt.% (relative to polymer) Silquest A-187; (4) PUD-2-3.6: PUD-2 with 3.6 wt.% (relative to polymer) Silquest A-187. Each solution was mixed well by rolling at room temperature for more than 4 h prior to coating process.

Two PVDF substrates were coated by corresponding coating solution individually, and then the formed composite membranes were immediately placed in an oven and heated at 60 °C for 5 h. Then thin film composite (TFC) membranes were used for gaseous permeation experiments directly.

2.4. General characterizations

The samples for the differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FT-IR), size exclusion chromatography (SEC), and transmission electron microscopy (TEM) were prepared by pouring diluted PUD solutions (3 wt.%) into Teflon Petri dishes. The solutions were placed in a fume hood until the water evaporated, and further dried in a vacuum oven at 60 °C for 8 h. The DSC and TGA analysis were performed under a nitrogen atmosphere (50 mL/min) at a heating rate of 10 °C/min with a differential scanning calorimeter (TA Instruments DSC 2920) and a thermogravimetric analyzer (TGA 2950), respectively. The FT-IR spectra were taken with a Bruker Tensor 27 spectrometer in the range of 4000–400 cm^{-1} under a moisture and CO_2 free atmosphere. Polymer molecular weight was determined by size exclusion chromatography (SEC) using a Viscotek SEC system (Viscotek VE1122 HPLC pump coupled with a Viscotek TDA Triple detector and a Viscotek 2501 UV detector at 260 nm), where a set of Viscogel columns (G3000H, G4000H and

G5000H) was used and calibrated with polystyrene standard in tetrahydrofuran (THF). For TEM, samples were immersed in 0.5 M lead acetate solution for 24 h to stain the ionic domains and rinsed with water. A 0.5 mm $\times$ 5 mm strip was then cut from the sample and was embedded in polystyrene (PS) by sandwiching the strip with two pieces of PS plates and heating at 150 °C until the PS completely embedded the sample. Thin slices (80 nm) of the embedded polymer sample were cut using an ultramicrotome (Ultracut-E, Reichert-Jung) and were picked up with 400 mesh carbon coated copper grids. These samples were analyzed using a Philips CM20 STEM equipped with a Gatan UltraScan 1000 CCD camera operating at 120 kV. The TFC membrane samples for scanning electron microscopy (SEM) were prepared by submerging in liquid nitrogen for 2 min and then fracturing. The SEM samples were sputter-coated with gold to enhance conductivity, and were examined using a JEOL 840A scanning electron microscope equipped with Oxford Instruments' image capturing software. All photographs were taken using an accelerating voltage of 20 kV and a working distance of 15 mm.

2.5. Gas permeation measurement

All permeances and selectivities of thin film composite membranes were determined by a standard constant-pressure apparatus as described in our previous work [7] at room temperature for pure gases and binary gas mixtures. Flow-rates were measured by the mass flow controllers/meters (MKS Instruments), which gave nitrogen equivalent standard volumes. The gas mixtures were sampled by an on-line gas chromatograph (Hewlett-Packard 6890) for the composition analysis. The effective membrane area was $2.7 \times 10^{-3} \text{ m}^2$. All the permeances were calculated in GPU (1 GPU = $7.5 \times 10^{-10} \text{ cm}^3 \text{ (STP)/cm}^2 \text{ s Pa} = 10^{-6} \text{ cm}^3 \text{ (STP)/cm}^2 \text{ s cmHg}$). Experimental errors in the determination of permeances and selectivities were usually less than 1%.

For a pure gas, permeance J was typically described by a trans-membrane flux V from feed to permeate sides across an effective membrane area A :

$$J = \frac{V}{A(P - p)} \quad (1)$$

where the P and p were the feed and permeate pressures, respectively. Consequently, ideal selectivity S for a pair of gases was:

$$S_{A/B} = \frac{J_A}{J_B} \quad (2)$$

For a mixture, the permeance of component i was expressed as the total trans-membrane flux of a mixture V from feed to permeate sides across an effective membrane area A by Eq. (3):

$$J_t = \frac{Vy_i}{A(Px_i - py_i)} \quad (3)$$

where x_i and y_i were the concentration of component i in the feed and permeate, respectively. The selectivity for component i to component j in a mixture was as follows:

$$S_{i/j} = \frac{J_i}{J_j} \quad (4)$$

3. Results and discussion

3.1. PUD characteristics

Thermal properties, solubility, and molecular weight of PUDs are listed in Table 2. Elastic behavior was ascertained qualitatively by physical observation (Table 2) to check the viability of membrane formation. Only one glass transition temperature ($T_g = -121.5^\circ\text{C}$) was observed for PUD-1, which matched with the T_g of pure PDMS

Table 2
Physical characteristics of polyurethane used in this work

Sample	T_{g1} (°C)	T_{g2} (°C)	DCT ^a (°C)	Solubility in THF	Molecular weight (Da)	Elasticity
PUD-1	−121.5	N/A	247.3	No ^b	25,419	Low
PUD-2	−129.2	−51.0	265.4	Yes	31,568	High
PUD-2-3.6	−124.2	−50.5	266.9	No	N/A	Medium

^a Decomposition temperature at 5% of weight loss.

^b The wet polymer sample was soluble but it became insoluble after being completely dried.

Fig. 1. DSC curves of PUD-1, PUD-2 and PUD-2-3.6.

(−129°C) as the soft segment. Two T_g s were obtained for PUD-2 (T_{g1} = −129.2°C, T_{g2} = −51.0°C) and PUD-2-3.6 (T_{g1} = −124.2°C, T_{g2} = −50.5°C) with the values close to the T_g s of pure PDMS and PEG (−57°C), which confirmed a certain phase segregation of the soft segments [21]. As shown in Fig. 1, a small transition also was observed between −15 and −5°C for each sample. Although the transition origin was not clear, it was not related to the glass transition of the polymer due to the weak and very narrow signal. Moreover, the decomposition temperatures of these samples were similar in the range of 247–270°C as illustrated in Fig. 2. PUD-1 had a different decomposition pattern with PUD-2, exhibiting a much lower weight loss at high temperature which was attributed to the high thermal stability of PDMS. The original PUD-2 and crosslinked PUD-2 (PUD-2-3.6) had almost identical TGA curves with a slightly

Fig. 2. TGA curves of PUD-1, PUD-2 and PUD-2-3.6.

low weight loss of the crosslinked sample at all range of tested temperature, indicating a positive effect of the crosslinking on the thermal stability. The effectiveness of the crosslinking was further confirmed by a solubility test. As can be seen in Table 2, the crosslinked PUD-2 sample (PUD-2-3.6) became insoluble in THF, while the pristine PUD-2 sample was easily dissolved in this solvent. Therefore, it is concluded that post-crosslinking technique using Silquest A-187 can efficiently improve the chemical resistance of the resulting membrane. It is interesting to note that PUD-1 dry sample with the low elasticity only swelled but did not dissolve in THF, demonstrating a higher solvent resistance than PUD-2. This might be attributed to the strong interactions between the polymer chains provided by the highly dense polar groups due to a higher hard segment content as shown in Table 1. However, this result was not caused by the molecular weight since both PUD-1 and PUD-2 had a moderate molecular weight of 25,400, and 31,600 Da, respectively.

The chemical structures of these polymers were also determined with FT-IR spectroscopy as displayed in Fig. 3. All three samples of PUD-1, PUD-2 and PUD-2-3.6 demonstrated characteristic urethane absorption peaks. The peaks at 3333 cm^{−1} (urethane NH stretching), ~1719 cm^{−1} (urethane >C=O), and ~1537 cm^{−1} (C–NH bending) confirmed the polyurethane backbone. PUD-1 with singular PDMS soft segment showed a typical characteristic absorption of PDMS. The strong peak at 2960 cm^{−1} with a shoulder at longer wavelength was attributed to the C–H stretching of Si–CH₃ groups in PDMS. The vibration of Si–O–Si groups at 1094 and 1024 cm^{−1}, the symmetric bending vibration of the methyl group in Si–CH₃ at 1259 cm^{−1} and the rocking vibration of the methyl group in Si–CH₃ at 801 cm^{−1} in the spectrum of PUD-1 proved the presence of siloxane soft segment. An increase in absorption at 2866 cm^{−1} of PUD-2 and PUD-2-3.6 indicated that the C–H stretching of the aliphatic methylene (–CH₂–) groups of PEG segment overlapped that of the

Fig. 3. FT-IR spectra of PUD-1, PUD-2 and PUD-2-3.6.

Table 3Effect of substrate type and coating gap on permeance and selectivity of a C₃H₆–N₂ mixture

Substrate	Coating gap (μm)	Permeance (GPU)		Selectivity C ₃ H ₆ –N ₂
		N ₂	C ₃ H ₆	
PVDF 1010-22-2.5	25	1.4	27.4	19.7
PVDF 1010-22-0	25	2.4	40.3	17.0
PVDF 1010-22-2.5	12.5	1.5	24.6	16.9
PVDF 1010-22-0	12.5	2.0	37.5	19.0

Feed composition: 75.2% N₂, 24.8% C₃H₆; feed pressure: 770 kPa (a); permeating pressure: 101.3 kPa (a); temperature: 22 °C; stage cut: <1%.**Table 4**

Air separation data for various coating materials on PVDF 1010-22-0

Coating material	Permeance in air (GPU)		Selectivity O ₂ /N ₂
	N ₂	O ₂	
PUD-1	2.4	4.7	2.0
PUD-1-5.9	0.8	1.7	2.0
PUD-2-2.7	1.3	3.0	2.4
PUD-2-3.6	1.2	2.8	2.4

Feed pressure: 770 kPa (a); permeating pressure: 101.3 kPa (a); temperature: 22 °C; stage cut: <1%.

Si–CH₃ groups of PDMS segment. Moreover, the C–O–C stretching peak at 1094 cm^{−1} from the ether group in PEG apparently overlapped with the double peaks at 1094 and 1024 cm^{−1} of Si–O–Si group from PDMS, resulting in a larger peak at 1094 cm^{−1}. This result proved the presence of mixed soft segments in PUD-2 and PUD-2-3.6. However, there was no distinctive evidence of post-crosslinking in FT-IR spectra of PUD-2-3.6 probably due to a low crosslinking density.

3.2. Thin film composite (TFC) membranes

First of all, the function of lithium nitrate as an additive for substrate and the thickness of coating layer controlled by coating gap were examined for gas permeation. Two PVDF substrates prepared from dopes (PVDF 1010-22-0 without additive and PVDF-22-2.5 with 2.5% lithium nitrate) were tested by coating original PDMS-based PU (PUD-1) with 12.5 and 25 μm gaps. Table 3 summarizes the permeances and selectivities of propylene–nitrogen mixture for these four membranes. It is clear that two TFC membranes with PVDF 1010-22-0 substrate (no additive) had higher permeances without losing selectivities. Coating gaps did not impact the selectivities and permeances obviously for these two kinds of substrates. As a result, PVDF 1010-22-0 was selected as the substrate for subsequent work.

Secondly, PDMS-based and PDMS/PEG-based PUs as a coating material on PVDF 1010-22-0 were evaluated using air for gas permeation. A post-crosslinker, Silquest A-187, was added in PUs at various concentrations to form four TFC membranes as shown in Table 4. Apparently TFC membranes with PDMS/PEG-based PU

coating layers (PUD-2-2.7 and PUD-2-3.6) showed higher selectivities for O₂/N₂ separation, the concentration of Silquest A-187 did not influence the selectivities and the permeances significantly in the studied range. However, O₂/N₂ selectivities of PDMS-based PU coated membranes (PUD-1 and PUD-1-5.9) were significantly lower than those of PDMS/PEG-based PU coated membranes (from 2.4 to 2.0). Crosslinked PDMS-based PU membrane (PUD-1-5.9) had substantially lower permeances but showed selectivity equal to PUD-1.

In addition, the crosslinked TFC membranes were also investigated by three VOC–N₂ mixtures. We have known from previous work [8] that there is no plasticization taking place in PDMS–polysulfone composite membrane with ethylene–nitrogen mixture. Propylene is a strong sorbate and swells PDMS coating layer, resulting in the enhancement of both propylene and nitrogen permeances simultaneously. Therefore three mixtures of gases with varying propylene concentrations were prepared for studying the membrane performance (36% ethylene–64% nitrogen, 3.7% propylene–96.3% nitrogen and 28% propylene–72% nitrogen). Table 5 lists the permeances and selectivities of PUD-1-5.9, PUD-2-2.7, PUD-2-3.6 and the reported PDMS data [8]. The selectivities of PDMS-based PU membrane (PUD-1-5.9) for these three mixtures varied up to 40% compared to the PDMS coated membrane. Coincidentally, the increased magnitude in selectivity of PUD-1-5.9 from 3.7% to 28.0% in propylene–nitrogen mixture was equal to one of the PDMS coated membrane. However, the permeances of all nitrogen and hydrocarbons were reduced to a large extent for PUD-1-5.9 compared to PDMS coated membrane due to the fact that polyurethane consisted of partially rigid urethane segment. It is also observed for PUD-1-5.9 that nitrogen permeances in VOC–N₂ separations were enhanced considerably compared to O₂/N₂ separation. Therefore, we can conclude that PDMS-based PU material produced trends similar to PDMS coated membrane at various operating conditions for gas separation. For PDMS/PEG-based PU membranes (PUD-2-2.7 and PUD-2-3.6), the selectivities of ethylene to nitrogen in ethylene–nitrogen mixture were slightly higher than those of PDMS and PDMS-based PU membranes (PDMS [8] and PUD-1-5.9). It is interesting to note that the selectivities of propylene to nitrogen in propylene–nitrogen mixture were improved remarkably compared to PUD-1-5.9 and PDMS [8]. The enhanced values based on PDMS [8] were 55% and 139% at 3.7% and 28.0% propylene feed concentrations, respectively. Although their permeances were low for same reason as PDMS-based PU membranes, nitrogen permeances in VOC–N₂ separations were consistent with those of air separation, indicating that nitrogen permeance of PDMS/PEG-based PU membranes was not influenced significantly in the presence of strongly sorbing propylene in the mixture. It appears that the strong chain interactions of hard urethane and the soft PEG segments act as physical crosslinkage to restrict the creation of more swelling for the additional permeation of permanent gases. We did not find any appreciable impact of different post-crosslinker contents on the performance for PUD-2-2.7 and PUD-2-3.6. However, it is essential to maintain a certain amount of Silquest A-187 in PDMS/PEG-based

Table 5Effect of coating material on the permeance and selectivity of VOC–N₂ mixtures

Coating material	Permeance (GPU) and selectivity								
	36% C ₂ H ₄ –64% N ₂			3.7% C ₃ H ₆ –96.3% N ₂			28% C ₃ H ₆ –72% N ₂		
	N ₂	C ₂ H ₄	C ₂ H ₄ –N ₂	N ₂	C ₃ H ₆	C ₃ H ₆ –N ₂	N ₂	C ₃ H ₆	C ₃ H ₆ –N ₂
PUD-1-5.9	4.4	34.1	7.8	5.3	50.3	9.6	4.9	83.6	16.9
PUD-2-2.7	1.1	10.8	9.7	1.3	17.9	14.1	1.3	34.4	29.2
PUD-2-3.6	1.2	13.2	10.9	1.6	19.2	12.3	1.7	39.7	23.0
PDMS Ref. [8]	169.8	1546	9.1	161.5	1468	9.1	199.8	2443	12.2

Feed pressure: 700 ± 10 kPa (a); permeating pressure: 101.3 kPa (a); stage cut: <1%; temperature: 22 °C.

Table 6
Comparison of PU–PVDF membrane with PDMS–PVDF and PU membranes

Sample	Type	Weight ratio PDMS/PEG	Soft segment (T_g (°C))	Nitrogen		Selectivity	
				Permeance (GPU)	Permeability (Barrer (1 Barrer: $7.5 \times 10^{-18} \text{ m}^2 \text{ s}^{-1} \text{ Pa}^{-1}$))	O ₂ /N ₂	CO ₂ /N ₂
PUU (PEG/PDMS) Ref. [16]	Film	1/5.6	−50.8	N/A	2.1	3.5	27.4
PUU (PDMS/PEG) Ref. [16]	Film	4.5/1	−114.5	N/A	54.0	2.3	11.5
PDMS–PUH ₄ ^a Ref. [17]	Film	1/0	−60	N/A	92.5	2.6	15.0
PUUD–F Ref. [18]	Film	1/0	−107	N/A	32	1.9	4.9
PU–PVDF (this work) ^a	Composite membrane	1/1	−124.2 –50.5	1.3	N/A	2.6	22.0
PDMS–PVDF Ref. [20]	Composite membrane	1/0	N/A	14.3	N/A	2.3	N/A

^a Feed pressure: 490 kPa (g).

PU for the chemical resistance and the processability in membrane preparation. PUD-2-3.6 TFC membrane retained excellent performance even after 7-month operation of separating a variety of gases repeatedly. Therefore, it is believed that the life-time of this membrane would be more than 7 months.

It can be concluded from above analysis that the crosslinked PDMS/PEG-based PU was a superior coating material for VOC–N₂ gas separation. The TFC membrane coated PUD-2-3.6 on PVDF 1010-22-0 (PU–PVDF) was selected for comparison with the reported data for pure oxygen, nitrogen and carbon dioxide. It can be seen from Table 6 that PU–PVDF membrane with a weight ratio of PDMS to PEG of 1:1 demonstrated prominent ideal selectivities not only for a pair of oxygen–nitrogen but also for carbon dioxide–nitrogen amongst the PU thin film membranes in which PDMS was singular or major soft segment. As the PDMS content increased in the polyether-based PU membranes, the permeabilities of gases also increased. However, ideal selectivities for above gas pairs were still lower than PEG-based PU with the small amount of PDMS {PUU (PEG/PDMS)} due to PEG's intrinsic properties. Park et al. [16] and Madhavan and Reddy [17] believed that the incorporation of PDMS results in the phase separation in both hard and soft segments due to the difference of solubility parameter and the dispersed PDMS phases, which produces a more tortuous route for diffusing molecules. On the other hand, PU–PVDF composite membrane in this work showed higher oxygen selectivity with lower nitrogen permeance compared with PDMS–PVDF composite membrane [20].

3.3. VOC–N₂ gas separation

Initially, the effect of operating pressure on the permeance and selectivity of pure gases such as nitrogen, ethylene, ethane, propylene and propane were investigated with PU–PVD TFC membrane at 22 °C. Fig. 4 illustrates exponential increase of propylene and propane permeances with the increase of pressure difference, while the permeances of ethylene, ethane and nitrogen remained almost same. The order of permeances was $J_{\text{C}_3\text{H}_6} > J_{\text{C}_3\text{H}_8} > J_{\text{C}_2\text{H}_6} \approx J_{\text{C}_2\text{H}_4} > J_{\text{N}_2}$. As a result, the ideal selectivities of propylene and propane to nitrogen increased remarkably up to 140 as shown in Fig. 5. Again, the ideal selectivities of ethylene and ethane to nitrogen were independent of pressure difference. Furthermore, the variation of gas permeation between pure and mixed gases was explored through the mixtures of ethylene–nitrogen and propylene–nitrogen at 22 °C. Fig. 6 demonstrates the effect of ethylene feed concentration on permeance and selectivity for ethylene–nitrogen mixtures. As the ethylene concentration in the feed was increased from 1.7% to 37.7%, ethylene permeances increased considerably and nitrogen permeances remained same, resulting in 45.3% increase in the selectivity of ethylene to nitrogen. Fig. 7 shows the permeation performance of propylene–nitrogen mixtures with the increase of propylene feed concentration. It appears that propylene perme-

Fig. 4. Effect of pressure difference on the pure gas permeances of PU–PVDF thin film composite membrane at 22 °C. Permeate pressure: 101.3 kPa (a).

ances increased significantly as a result of increased propylene concentrations in the feed. However, nitrogen permeances were enhanced slightly and comparable to the values of pure nitrogen and nitrogen in ethylene–nitrogen mixture. It could be due to the fact that the presence of propylene in the mixture did not cause an additional increase of nitrogen permeance in the membrane. This led to 105% increase in the selectivity of propylene to nitrogen as the propylene concentration was increased from 1.5% to 29.1% in the feed. Furthermore, Fig. 8 compares the ideal selectivities of pure gases with the selectivities in gas mixtures at different pressures or partial pressures. It was observed that ethylene selectivities determined by partial pressure difference

Fig. 5. Effect of pressure difference on the ideal selectivity of PU–PVDF thin film composite membrane for pure gases at 22 °C. Permeate pressure: 101.3 kPa (a).

Fig. 6. Effect of ethylene feed concentration on permeance and selectivity of PU-PVDF thin film composite membrane for ethylene–nitrogen mixture at 22 °C. Feed pressure: 677 ± 2 kPa (a). Permeate pressure: 101.3 kPa (a). Stage cuts: <1%.

Fig. 7. Effect of propylene feed concentration on permeance and selectivity of PU-PVDF thin film composite membrane for propylene–nitrogen mixture at 22 °C. Feed pressure: 688 ± 2 kPa (a). Permeate pressure: 101.3 kPa (a). Stage cuts: <1%.

and ideal selectivities had similar trend with increasing pressure difference, which could be attributed to the minimum plasticizing effect of ethylene on the polymer. For strongly sorbing propylene, the ideal selectivities were still higher than the selec-

Fig. 8. Effect of pressure difference on the pure and mixed gas selectivities.

Fig. 9. TEM image of a thin slice (80 nm thick) of PUD-2-3.6. Scale bar: 200 nm.

tivities in the mixtures in the entire pressure difference range as reported in our previous work on PDMS coated membrane [7].

Our PU-PVDF membrane data show a typically solubility-selective behavior for highly condensable hydrocarbons, where their permeances were determined by the solubilities. Moreover, the permeances of permanent gases in the presence of highly condensable hydrocarbons in the mixtures were marginally enhanced due to the dual features of the soft and hard segments of polyurethane. It appears that urethane segment aggregated to form hard domains, which dispersed in PDMS and PEG soft matrix, functioning as a swelling suppressor. The strong chain interactions made the hard segment and the PEG segment act as physically crosslinked to restrict the creation of extra swelling in the polymer for additional permeation of permanent gases. This effect was still enhanced for polyurethane dispersion compared to pristine polyurethane since the ionic units (carboxylic groups) on the main chain of the polymer promoted the phase separation. It is clear from the TEM image of the lead stained sample in Fig. 9 that uniformly distributed dark spots with an average size of approximately 15 nm could be attributed to the carboxylic group containing hard domains whereas the grey matrix represents the soft domains. Though the TEM did not give any information on the phase separation between the PDMS and PEG soft segments, the well distinguished two glass transition temperatures of the polymer as discussed in Section 3.1 indicated the presence of the individual PDMS and PEG domains. Consequently the active layer of the membrane could be considered as a multiphase morphological structure which might produce torturous paths with less resistance for diffusing penetrants. Similar morphological structures of polyurethanes have also been reported in literature [16,17]. Furthermore, the physical crosslinking in the polyurethane restricted the swelling ratio of the soft segment, and resulted in a low additional permeation of permanent gases upon swelling, leading to an enhanced selectivity. This could be an ideal membrane material to recover highly condensable hydrocarbons from permanent gases for polymeric membrane-based gas separation. On the other hand, the SEM image of the fracture surface of PU-PVDF TFC membrane (Fig. 10) exhibits that PUD coating layer adhered on highly porous PVDF substrate firmly, indicating the PVDF porous membrane

Fig. 10. SEM image of the fracture surface of PU–PVDF thin film composite membrane. Coating material: PUD-2-3.6. Substrate: PVDF 1010-22-0.

could be an ideal supporting material for PUD active layers for gas separation.

4. Conclusions

It was shown that aqueous PDMS/PEG-based polyurethane can be successfully adhered on compatible PVDF substrate to form a suitable PU–PVDF thin film composite membrane for gas separation. The observed incompatibility of flexible PDMS/PEG soft segments and rigid hard segment in the active layer confirmed the torturous paths with less resistance for diffusing penetrants. Moreover, urethane hard segment dispersed well in PDMS and PEG segments, acting as a swelling suppressor. It appears that strong chain interactions made the hard and the PEG segments act as physically crosslinked to restrict the creation of more swelling for the additional permeation of permanent gases. As a result, PU–PVDF membrane showed a typical solubility-selective behavior for highly condensable hydrocarbons with the nature of PDMS and PEG for gas permeation while the permeance of permanent gas was marginally increased in the presence of highly condensable hydrocarbon in the mixture. The above mechanisms were believed to be responsible for the improved selectivities of propylene and propane to nitrogen for pure and mixed gases. Further study will focus on enhancing permeance without loss of selectivity.

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