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Synthesis and characterization of bis (4-maleimidophenyl) fluorene and its semi interpenetrating network membranes with polyether imide (Ultem® 1000)[☆]

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ABSTRACT

A semi-interpenetrating network (semi-IPN) of bis (4-maleimidophenyl) fluorene (cardo-BMI) and polyether imide (PEI, Ultem® 1000) was prepared. The structure of bis (4-maleimidophenyl) fluorene and the corresponding semi-IPNs was determined by nuclear magnetic resonance and Fourier transform infrared spectroscopy, respectively. The thermal properties of the cardo-BMI and semi-IPNs were evaluated by thermogravimetry and differential scanning calorimetry. The semi-IPNs exhibited thermal stability up to 480 °C. The morphology of the semi-IPNs was evaluated by scanning electron microscopy. Asymmetric membranes were prepared from the semi-IPN material by the wet phase inversion method. The pure gas permeation properties of the PEI and semi-IPN membranes were evaluated for oxygen (O₂), nitrogen (N₂), carbon dioxide (CO₂) and methane (CH₄) by the constant pressure and variable volume method at an absolute feed pressure of 0.69 MPa at 22 °C. The CO₂/N₂ selectivity of 39.2 ± 3.0 with a CO₂ permeance of 18.3 ± 4.0 GPU of semi-IPN membrane was higher than the PEI membranes (selectivity 21.6 ± 4.1 and CO₂ permeance 0.5 ± 0.1 GPU). The highest CO₂/CH₄ selectivity of the semi-IPN membrane was 49.3 ± 3.5 compared to 37 for a PEI dense film. Among the semi-IPN membranes, those with 5 wt% cardo-BMI exhibited better performance than the 1% and 10%.

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1. Introduction

The stringent regulations on the anthropogenic carbon emissions and increasing need for upgrading of natural gas and other renewable energy sources such as “bio-gas” warrants economical and energy efficient methodologies for carbon dioxide separation. Membrane technology is emerging as an alternative to conventional absorption, adsorption, and cryogenic distillation techniques [1–4]. Although membrane based gas separations are already commercialized in a few specific applications, their use in CO₂ separations is not as prevalent. Despite the surge in new membrane materials, few polymers are used in industrial installations [1]. These materials should combine higher selectivity and permeance along with material stability, easy processability, and be commercially attractive. Hence the engineering polymers like polyetherimides and polysulfones that offer higher thermal, mechanical and chemical stabilities are still predominantly used in the industrial sector [1]. Moreover, most of the reports on new membrane materials are based on dense film data with single gases. The behavior of these materials can be considerably different when made into thin film composites or asymmetric membranes

and operated at high pressures using mixed gases. Often these promising new materials are difficult to design into commercial membrane formats such as asymmetric hollow fibres/flat sheets and thin film composites, due to their inherent rigidity, hydrophilicity and poor thermal/mechanical/chemical stabilities. Therefore modification of commercial materials to improve permeance remains an attractive option.

Membrane performance improves with an increase in permeance and/or selectivity. The permeability, and in turn the selectivity, of the material is often expressed as a product of diffusivity and solubility [4]. In general, the rigid engineering polymers exhibit higher diffusivity selectivity [3]. Hence, numerous authors have reported varying the intrinsic free volume in the polymers by incorporating bulky groups in the polymer chain [3]. Recently, “Cardo groups”, which are non-planar aromatic bulky groups have been of increasing interest in polymeric membrane materials [5–12]. A wide range of polymers including polyamides, polyimides, polyethers, polycarbonates, polyethersulfones, and polyetherether ketones having cardo groups in the backbone were synthesized and evaluated for their gas transport properties [5–12]. These different cardo groups are often used to hinder the molecular packing and increase the fractional free volume and rigidity of the polymer chains. Among the cardo groups, those containing fluorene moieties are of particular interest [13–18] due to their higher solubility co-efficient for CO₂ [15,16]. Hence these fluorene based cardo groups increase both permeability and selectivity. Generally, the amino or hydroxyl

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Fig. 1. (a) Synthesis of cardo-BMI and (b) cross linking of cardo-BMI in PEI solution to form semi-IPN, no reaction with PEI.

terminated bisphenyl fluorene group is used as a monomer to synthesize polymers having “cardo” groups [13,18]. It would be advantageous and cost effective to incorporate cardo functionality with the commercial polymers via semi-IPNs rather than synthesizing tailor made polymers.

Polyether imides such as Ultem 1000, a well known class of engineering thermoplastic polymers, offer exceptional thermal, chemical and mechanical stability and available in large quantities [19]. Their cost is similar to other thermoplastic polymers that offer similar performance and significantly more economical than small batch thermoplastic polymers. Polyether imides have higher diffusivity selectivity due to their fused ring structure and rigid backbone. Their high glass transition temperatures allow higher pressure and temperature applications without plastic deformation. These are important parameters in designing polymeric membranes for gaseous separation. Hence polyether imides are one of the leading membrane materials. Despite these salient properties, the permeance of the polyether imides should be substantially increased in order to compete with conventional separation processes. Recently our group reported asymmetric semi-IPN membranes with increased permeance [20–22]. Semi-IPN membranes of thermoplastic polymer and bismaleimide (BMI) increased the permeance by a factor of 15 without compromising the selectivity [20]. The in situ polymerization of BMI led to the formation of thermoset BMI domains inside the polyimide matrix that gave rise to increased fractional free volume [20,21] resulting in higher permeances.

In general BMI and other vinyl groups are polymerized using thermal or ultra violet radiation. Due to the high reaction rate, it is very difficult to control the cross-linking density and the morphology of semi-IPNs. This often led to phase separation and inferior gas transport properties. Our group reported a novel synthetic route with increased control over the semi-IPN formation [20–22]. BMI was polymerized at ambient conditions in the presence of a proton donor, polar aprotic solvent and polyetherimide without the need for an initiator or catalyst [20,21]. At ambient conditions the polymerization occurs at a slower rate and hence it is possible to arrest the reaction at the required stage to control the phase separation

and morphology [20,21]. In this work, the synthesis of BMI with a bisphenyl fluorene group and its use to make novel semi-IPN asymmetric membranes with commercial PEI (Ultem® 1000) are reported. The chemical, thermal and gas permeation characteristics of these new materials are also presented.

2. Experimental

2.1. Materials

Aromatic PEI Ultem® 1000 was purchased from General Electric Plastics, USA in pellet form and was dried at 150 °C for 8 h before use to remove moisture. Anhydrous 1-methyl-2-pyrrolidinone (NMP) 99.5%, reagent grade (water <0.005%), tetrahydrofuran (THF), acetic anhydride, 9,9-bis(4-aminophenyl)fluorene, maleic anhydride, triethyl amine and sodium acetate were purchased from Aldrich Canada Ltd. Anhydrous ethyl alcohol was purchased from Greenfield Alcohols Inc., ON, Canada. Hexanes of ACS reagent grade were purchased from VWR, Canada. All solvents were used as supplied, under a dry nitrogen atmosphere. Ultra high purity N_2 , O_2 , bone dry CO_2 , and research grade CH_4 were purchased from BOC Gases Canada Ltd. and were used as received without further purification.

2.2. Synthesis of 9,9-bis(4-maleimidophenyl)fluorene (cardo-BMI)

The outline of the synthesis of cardo-BMI and its cross-linked structure is given in Fig. 1. The synthesis of cardo-BMI is a modification of the procedure reported earlier [23]. To a well-stirred solution of 9,9-bis(4-aminophenyl)fluorene (8.01 g solid) in freshly distilled tetrahydrofuran, 4.51 g of maleic anhydride was gradually added at 10 °C over a period of 30 min. The solution was stirred for an additional four hours at room temperature and the yellowish precipitate formed was filtered and purified by re-crystallization from a DMF/ethanol (50:50, w/w) solution. The amic acid intermediate was weighed into a three neck round bottom flask with 50 mL of THF. To the dispersion, 1.35 g of fused sodium acetate was

Table 1

Casting dope formulations for asymmetric membranes. Codes are assigned by wt% of cardo BMI in total solids.

S. no.	Membrane code	PEI (g)	Cardo-BMI (g)	NMP (mL)	EtOH (mL)
1	PEI (25)	25	0	62.5	12.5
2	Cardo 1%(25)	24.75	0.25	62.5	12.5
3	Cardo 5%(25)	23.75	1.25	62.5	12.5
4	Cardo 10%(25)	22.5	2.5	62.5	12.5
5	PEI (27)	27	0	61	12
6	Cardo 5%(27)	25.65	1.35	61	12
7	PEI (29)	29	0	60	11
8	Cardo 1%(29)	28.71	0.29	60	11
9	Cardo 5%(29)	27.55	1.45	60	11
10	Cardo 10%(29)	26.1	2.9	60	11

added and the solution was heated to boiling temperature. To this solution, 15 mL of acetic anhydride and 0.5 mL of triethyl amine were added and the reaction was carried out for another six hours. The reaction solution was cooled to room temperature and the pale yellow precipitate was filtered. The final product was washed three times in THF and again two times in 10% sodium carbonate solution. The precipitate was filtered and vacuum dried. The product yield was 85%.

2.3. Preparation of polyether imide and cardo-BMI semi-IPN membranes

Asymmetric membranes of polyetherimide (PEI) with and without cardo-BMI were prepared as reported earlier [20,21] using the casting solution compositions given in Table 1. The calculated quantity of PEI was dissolved in anhydrous NMP by rolling the bottles at 60 °C. To the completely dissolved PEI solution, the calculated amount of anhydrous ethanol was added and mixed again until a homogeneous solution was obtained. To this, the synthesized cardo-BMI monomer was added and the solution was rolled at 60 °C. These solutions were used to prepare asymmetric membranes after an indicative color change from yellow to blood red and the onset of turbidity was observed. The turbidity is indicative of the formation of a cross-linked insoluble cardo-BMI, Fig. 1b.

Dense films of semi/pseudo-IPNs have been made of azide in 6FDA-NDA and 6FDA-TMPDA polyimides [24]. However, dense films of the cardo-BMI/PEI semi-IPN cannot be made due to phase separation. Removal of NMP, which was the only suitable solvent for the monomer, results in discrete PEI rich/PEI poor zones with obvious macro-defects. Removing ethanol will also prevent the formation of the semi-IPN given its role in the anionic polymerization reaction [20]. The homogeneous dopes were cast at room temperature on clean glass plates placed in a glove box purged with dry nitrogen. After casting each sample with a doctor knife having a gap of 250 μm , the plate was quickly immersed in distilled water at ambient temperature. The membrane films were left in water for 3 days, which was frequently changed then washed by immersing in ethanol for one day to exchange water and stored in fresh anhydrous ethanol bath for one more day. Membranes were subsequently washed and stored in hexanes for 2 days before leaving them in a fume hood for 1 day. Drying was carried out at 80 °C in an air purging convection oven for 1 day and finally in an oven at 80 °C and 96.7 kPa (725 mmHg) of vacuum for 2 days. Circular samples of 7.4×10^{-2} m diameter were cut from each sample to be used in the permeation test while the remaining material was used for thermal, microscopic and spectroscopic characterizations. The coupons of the membranes used in the permeation test were coated with silicone rubber. A solution of 3% Sylgard 184 with a catalyst to base rubber ratio of 1:10 in *n*-pentane was sprayed as a thin layer on the top surface of the membrane and the solvent was allowed to evaporate. Application of four coatings was found

to be adequate for making gas separation membranes. Finally, the silicon coated membranes were cured in an air purging convection oven at 80 °C for 1 day.

2.4. Measurements

Fourier transform infrared attenuated total reflection (FTIR-ATR) analysis was performed using a Super Charged ZnSe single-bounce ATR crystal with a tensor FT-IR spectrometer (Bruker IFS 66) in absorption mode. The spectra were taken with 200 scans at a resolution of 4 cm^{-1} in the range of $400\text{--}4000 \text{ cm}^{-1}$. The FT-IR-ATR background was performed at the same conditions without a sample in place. NMR spectra were obtained using a Varian Unity Inova spectrometer at a resonance frequency of 399.934 MHz for hydrogen and 100.563 MHz for carbon. A 5 mm indirect detection probe was used for acquiring 1D and 2D COSY (correlation spectroscopy), HSQC (heteronuclear single quantum coherence) and HMBC (heteronuclear multiple bond correlation) spectra. The NMR solvent DMSO- d_6 was used as the internal reference for ^1H (2.50 ppm) and ^{13}C (39.51 ppm).

A thermal analysis (TA) instrument model 2920 differential scanning calorimetry (DSC), calibrated with indium at 156.60 °C and with tin at 231.93 °C was used to measure the glass-transition temperature (T_g). Under a nitrogen atmosphere (50 cc/min), polymer samples were ramped to 350 °C at 5 °C/min. The T_g was calculated at the point of inflection of the DSC curve. A TA instruments, Model TGA 2950 was used for measuring the degradation temperatures by thermogravimetric analysis (TGA). Under a nitrogen atmosphere (50 cc/min), polymer samples were heated at 120 °C for 60 min to remove moisture, if any, cooled to 40 °C before heating to 1000 °C at the rate of 10 °C/min.

The morphology of the membrane samples was examined by scanning electron microscope (SEM, JEOL 840A) using an accelerating voltage of 10 kV. Samples were prepared by cutting a strip from the membrane, freezing in liquid nitrogen and fracturing to obtain a representative sample, then mounted on carbon tape at 45° on SEM stubs and sputter coated with gold.

A cross-flow test cell having a permeation surface area of $9.6 \times 10^{-4} \text{ m}^2$ was used. Pure O_2 , N_2 , CH_4 and CO_2 were used to obtain permeances and the pure gas selectivities of O_2/N_2 , CO_2/N_2 and CO_2/CH_4 gas pairs at a feed pressure of 0.69 MPa and 22 °C. Permeate was discharged to the atmosphere. The permeate flow rate was measured by a soap bubble flow meter. All membranes were conditioned for at least 12 h in each gas before measuring the permeance. The flux of a gas through asymmetric membranes (permeance) is generally reported in gas permeation unit (GPU) defined as the permeated volume of gas per unit area, per unit time, per unit pressure:

$$1 \text{ GPU} = 10^{-6} \text{ cm}^3 (\text{STP}) / (\text{cm}^2 \times \text{s} \times \text{cmHg}) \\ = 7.5 \times 10^{-12} \text{ m}^3 (\text{STP}) / (\text{m}^2 \times \text{s} \times \text{Pa}) \quad (1)$$

Fig. 2. ^1H (a) and ^{13}C NMR (b) spectra of 9,9-bis(4-maleimidophenyl) fluorene in $\text{DMSO}-d_6$.

while for a dense film the flux is normalized by the film thickness (permeability) and is reported in Barrers:

$$1 \text{ Barrer} = 10^{-10} \text{ cm}^3(\text{STP})/(\text{cm}^2 \cdot \text{s} \cdot \text{cm} \cdot \text{cmHg}) \quad (2)$$

The permeability of an asymmetric membrane's skin layer can be estimated by the product of the permeance and the skin layer thickness:

$$\text{Permeability (Barrer)} = \text{permeance (GPU)} \times \text{skin layer thickness } (\mu\text{m}) \quad (3)$$

3. Results and discussion

3.1. Characterization of 9,9-bis(4-maleimidophenyl) fluorene

9,9-bis(4-maleimidophenyl) fluorene (cardo-BMI) was prepared according to the reaction sequences shown in Fig. 1, and characterized by FT-IR, NMR, and DSC. Fig. 2 shows the ^1H and ^{13}C NMR spectra of cardo-BMI. Unambiguous assignment of several peak frequencies was done using 2D one bond and three bond hydrogen-carbon correlation spectra. The starting point for peak assignment was the only non-aromatic carbon, C7. Three bond coupling ($^3\text{JC}-\text{C}-\text{H}$) between C7-H5 and C7-H9 was observed on the HMBC spectrum (Fig. 3). The assignment of H-2, 3, 4 simply followed by identifying $^1\text{H}-^1\text{H}$ correlations from the 2D COSY spectrum (not shown). We were expecting H9 and H10 to appear as two different coupled doublets but instead they unusually appeared as a single frequency (7.25 ppm). That single proton peak shows couplings with two different carbon signals in HSQC ($^1\text{JC9}-\text{H9}$ and $^1\text{JC10}-\text{H10}$) as well as couplings with 5 different carbon signals in HMBC ($^3\text{JC7}-\text{H9}$, $^3\text{JC8}-\text{H10}$, $^3\text{JC9}-\text{H9}$, $^3\text{JC10}-\text{H10}$, $^3\text{JC11}-\text{H9}$). Finally, H13 appeared as a singlet at 7.08 ppm. Four carbon signals could not be formally assigned using 2D heteronuclear spectra due to H9 and H10 being the same frequency in ^1H NMR. Two of those peaks were C9 and C10 at 126.5 and 128.0 ppm. The two other carbon atoms were C8 and C11 which, unlike C9 and C10, could be assigned with the help of NMR prediction software because of their

Fig. 3. 2D HMBC spectrum 9,9-bis(4-maleimidophenyl) fluorene in $\text{DMSO}-d_6$.

important difference in chemical shift (130.0 and 144.8 ppm). NMR prediction of molecule 9,9-bis(4-maleimidophenyl) fluorene using the ACD prediction software (Advanced Chemistry Development, C NMR predictor, version 12.01, November 2008) assigned C11 at 129.16 ppm and C8 at 135.04 ppm. The difference in chemical shift between the two peaks is more important in the experimental spectrum than in the calculated one, furthermore, it is the shift towards higher frequencies for C8 and lower frequencies for C11 that guided our assignment of both peaks.

The structure of cardo-BMI was also confirmed by FT-IR, Fig. 4. Cardo-BMI exhibited the characteristic absorptions of an unsaturated olefinic group at 3103 cm^{-1} ($=\text{C}-\text{H}$) [23] and 1608 cm^{-1} ($\text{C}=\text{C}$, olefinic bond) [23], which will be cured to form the semi-IPNs. The unique C-N-C absorption peak of maleimide was observed around 1149 cm^{-1} [25]. The imide absorptions around

Fig. 4. ATR-FT-IR absorption spectrum of 9,9-bis(4-maleimidophenyl) fluorene (shown as transmittance).

Fig. 5. DSC thermogram of 9,9-bis(4-maleimidophenyl)fluorene showing the melting point endotherm at 344.8 °C followed by an exotherm at 348.1 °C representing the self addition temperature.

1770, 1707 cm^{-1} ($\text{C}=\text{O}$, imide carbonyl group), 1370 cm^{-1} (C–N, imide group) indicated the completion of cyclization of amic acid.

The melting and self-curing behavior of the cardo-BMI was studied by DSC which is given in Fig. 5. The melting temperature of cardo-BMI appears as a sharp endotherm around 344.8 °C, which was in accordance with the reported value [23].

3.2. Characterization of semi-IPN membranes

3.2.1. FT-IR spectroscopy

The FTIR-ATR spectra of PEI and semi-IPN membranes are shown in Fig. 6a and b. The characteristic olefinic absorption peaks around 1608 cm^{-1} and 840 cm^{-1} were found to overlap with the peaks in PEI. The completion of crosslinking was confirmed using non-interfering peaks that are unique to maleimide. During polymerization, the maleimide is converted to succinimide moieties [25]. The FT-IR spectrum of pure cardo-BMI (Fig. 4) shows strong peaks at 3100 cm^{-1} due to a $\text{C}=\text{C}-\text{H}$ maleimide absorption and at 1149 cm^{-1} due to C–N–C maleimide absorption. Evidence for the cross-linking reaction is the diminishing peak at 3100 cm^{-1} , Fig. 6a, inset. The C–N–C maleimide absorption peak at 1140 cm^{-1} disappeared and a new peak at 1175 cm^{-1} corresponding to succinimide absorption appeared in the semi-IPN membranes, Fig. 6b [25]. This confirms the anionic polymerization of bismaleimide leading to the successful formation of the semi-IPN. The other characteristic absorptions of PEI at 1780 cm^{-1} ($\text{C}=\text{O}$, symmetric) and 1722 cm^{-1} ($\text{C}=\text{O}$, asymmetric), 1240 cm^{-1} (aromatic ether group Ar–O–Ar) indicates that the PEI is intact.

3.2.2. Thermal characterizations

The thermal stability of the semi-IPN membranes and PEI was measured by thermo-gravimetric analysis and the TGA results are presented in Fig. 7. The PEI membrane exhibited a two step degradation pattern whereas the semi-IPN membranes exhibited a single step degradation pattern. The onset degradation temperature was around 358 °C for the PEI membrane compared to 516 °C for neat PEI (no NMP). The two step degradation for PEI asymmetric membranes, agrees with our earlier work [20] where NMP and ethanol were shown to complex with PEI. The onset degradation temperature of the 1%, 5% and 10% cardo membranes were at 497 °C, 491 °C and 485 °C, respectively. The apparent increase in the thermal stability of the semi-IPN membranes over the parent PEI might be due to the formation of rigid interpenetrated network structure and are close to that of pure cardo-BMI. Also, it was reported [16] that the bulky fluoroenyl moieties restrict the chain mobility and

Fig. 6. (a) ATR-FT-IR absorption spectra of PEI and semi-IPN membranes (shown as transmittance) inset shows no absorbance at 3100 cm^{-1} ; (b) expanded view of 1100–1400 cm^{-1} .

may contribute to increased thermal stability. It can be seen that the percentage residue increases for the semi-IPNs from PEI. This might again be due to the higher crosslink density leading to higher char content.

The glass transition temperature (T_g) of the PEI and semi-IPN membranes was measured by DSC and a representative thermogram is given in Fig. 8. The T_g of the PEI membrane is 191 °C. There is a depression in the T_g of the pure PEI, even though the T_g was mea-

Fig. 7. TGA thermograms of unprocessed PEI (neat), PEI and semi-IPN membranes and cardo-BMI monomer.

Fig. 8. DSC thermograms of neat PEI, PEI membrane and semi-IPN membranes.

sured on the third run. The solvents ethanol and NMP were shown to form a complex with the PEI [20] and can act as a plasticizer to suppress the T_g . The two step degradation observed in the TGA might also be due to the presence of solvents that formed a complex with PEI. The T_g of 1%, 5% and 10% cardo semi-IPNs did not show any marked difference. The overall T_g of semi-IPNs increased when compared to PEI membrane which may be due to the formation of the network structure. In a semi-IPN, the molecular motion of each polymer is further restricted due to entanglements between the components leading to a higher T_g [26]. Also as discussed earlier, the bulky fluoroenyl group imparts rigidity to the system, which might also increase the T_g [16]. The complete reaction of cardo-BMI, forming a semi-IPN, is also evidenced from the absence of characteristic melting and curing peaks displayed by pure cardo-BMI around 342 °C.

3.2.3. Membrane morphology

Scanning electron micrographs of the semi-IPNs show the typical skin layer/spongy support and finger like voids of asymmetric membranes, Fig. 9. Phase separation was found to adversely affect the membrane performance for gas separation and hence the material composition was selected based on a previous work [21] to avoid phase separation. However, in the present study there was no obvious phase separation detected in microscopic and DSC studies.

3.2.4. Gas permeation studies

The pure PEI and cardo semi-IPN membranes were tested for gas permeation properties by measuring the pure gas permeance of O_2 , N_2 , CH_4 and CO_2 in triplicate. The ideal selectivities of O_2/N_2 , CO_2/CH_4 and CO_2/N_2 were calculated from the permeance of pure gases and are presented in Table 2. Oxygen and nitrogen are both categorized as non-interacting permanent gases. The O_2/N_2 selectivity mostly depends on the fractional free volume [16]. It can be seen from Table 2 that the 5 wt% cardo semi-IPN membranes exhibited higher selectivity and permeance than the parent pure PEI membranes. The casting solution compositions and gelation conditions are optimized for the cardo semi-IPN membranes, not for the pure PEI membrane. The control PEI membranes were made under the same conditions as the cardo semi-IPNs to highlight the effect of adding the cardo-BMI component. Under these conditions it was difficult to make asymmetric membranes having dense film O_2/N_2 selectivity of 8.0 [4]. Despite the loss in selectivity compared to the reported dense film value (8) [4], the PEI membranes still exhibited respectable selectivities of 5.5 ± 2.1 and 4.1 ± 0.9 .

The cardo 5%(25) membrane achieved a selectivity of 9.1 ± 1.3 , slightly higher than the dense film value of PEI but not significant given the reported error. Increasing the total solids content from 25% to 27% with 5% cardo-BMI resulted in a minor decrease in the O_2 permeance and selectivity, however these changes were not statistically significant. Further increasing the solids content to 29%, a value typically used for hollow fibre spinning, resulted in a significant decrease of the O_2 permeance to 1.7 ± 0.2 GPU with a decrease in selectivity to 7.2 ± 0.5 , which was not statistically different.

The O_2 permeance of the cardo-BMI 5%(25) membrane was 4.1 ± 1.2 GPU, with an approximate skin layer thickness of 2 μm , which corresponds to an apparent O_2 permeability of 8.2 Barrers using Eq. (3). Kazama et al. [16] reported an O_2/N_2 dense film selectivity of 9.2 and O_2 permeability of 0.125 Barrers for one of their linear polyimides with the bisphenyl fluorene cardo group in the backbone (PI-BAFL/HMDA (50/50)-BTDA). The O_2 permeability for a PEI dense film is 0.41 Barrer [4]. The incorporation of the cardo-BMI in the semi-IPN morphology increased the permeability by a factor of 10 over the dense film permeability of PEI.

The performance trends of the semi-IPN membranes for the CO_2/N_2 gas pair are similar to that of O_2/N_2 , Table 2. The highest selectivity was observed at 5 wt% cardo-BMI at any total solids concentration. The selectivity at 25, 27 and 29% total solids was 32.6 ± 4.3 , 39.2 ± 3.0 and 35.7 ± 1.3 , respectively. The selectivity was statistically similar and these values were clearly greater than the reported dense film properties of pure PEI (27.2) [4] and the PEI membranes used in this study (12.6 and 21.6).

The permeance of the 5% cardo-BMI membranes was 13.9 ± 2.5 , 18.3 ± 4.0 and 8.0 ± 0.6 GPU for 25, 27 and 29% total solids. Although

Fig. 9. SEM images of a semi-IPN prepared from a solution of 25% total solids with 5% cardo BMI, solution #3 in Table 2, showing the overall morphology (a) and a close up of the skin layer (b).

Table 2

Pure gas permeation properties of cardo-BMI/PEI semi-IPN asymmetric membranes.

S. no.	Membrane	Permeance (GPU) ^a		Selectivity		
		O ₂	CO ₂	O ₂ /N ₂	CO ₂ /N ₂	CO ₂ /CH ₄
1	PEI (25)	–	–	–	–	–
2	Cardo 1%(25)	11.3 ± 3.4	35.8 ± 13.2	5.5 ± 0.9	17.7 ± 1.4	14.6 ± 1.6
3	Cardo 5%(25)	4.1 ± 1.2	13.9 ± 2.5	9.1 ± 1.3	32.6 ± 4.3	48.1 ± 13.7
4	Cardo 10%(25)	72.8 ± 12.3	334.0 ± 51.3	2.3 ± 0.1	11.2 ± 0.3	4.4 ± 0.1
5	PEI (27)	2.6 ± 0.7	7.4 ± 3.5	4.1 ± 0.9	12.6 ± 5.5	14.4 ± 7.4
6	Cardo 5%(27)	4.0 ± 0.6	18.3 ± 4.0	7.9 ± 0.4	39.2 ± 3.0	49.3 ± 3.5
7	PEI (29)	0.1 ± 0.03 ^b	0.5 ± 0.1	5.5 ± 2.1 ^b	21.6 ± 4.1	40.5 ± 13.2
8	Cardo 1%(29)	1.0 ± 0.3	2.6 ± 1.2	3.3 ± 0.4	10.0 ± 4.4	4.8 ± 3.4
9	Cardo 5%(29)	1.7 ± 0.2	8.0 ± 0.6	7.2 ± 0.5	35.7 ± 1.3	50.3 ± 9.0
10	Cardo 10%(29)	46.4 ± 9.8	242.6 ± 35.4	2.9 ± 0.2	18.1 ± 1.4	7.1 ± 1.4

^a Gas permeation unit, GPU = 1 × 10^{−6} cm³ (STP)/(cm² s cmHg).^b Values obtained from air permeation.

the CO₂ permeance decreased significantly for the 29% total solids, it is still well above the PEI values. For example the reported dense film CO₂ permeability of the PI-BAFL/HMDA (50/50)-BTDA [15] and PEI [4] are 0.54 and 1.33 Barrers, respectively, whereas the apparent CO₂ permeability of the cardo 5%(25) membrane was 13.9 ± 2.5 Barrers. Since the cardo represents only 5 wt% of the semi-IPN material, the higher permeance and selectivity for both the O₂/N₂ and CO₂/N₂ gas pairs must be due to both the cardo-BMI and the unique semi-IPN morphology.

The suitability of the semi-IPN membranes for upgrading natural gas and bio-gas was evaluated by CO₂/CH₄ permeation properties, Table 2. The selectivity of the Cardo 5% semi-IPNs (48.1 ± 13.7, 49.3 ± 3.5 and 50.3 ± 9.0) are statistically similar and are higher than a PEI dense film (37) [4] and the PEI membranes used in this study (14.4 ± 7.4 and 40.5 ± 13.2). The selectivity values are higher than the bisphenyl fluorene based cardo polyimide hollow fibre membranes (37) [27,28] for the CO₂/CH₄ gas pair. Again the 5% cardo-BMI exhibited higher selectivity than the 1% and 10% cardo-BMI concentrations.

At lower polymer concentrations (25 and 27 wt%) the effect of adding cardo-BMI at 1 wt% to the casting dope is primarily to reduce the number of defects and increase the selectivity. The reduction of defects can be attributed to an increase in viscosity of the dope and/or entanglement of the PEI and cross-linked cardo-BMI [24]. When the cardo-BMI content is increased from 1% to 5% at 25 wt% polymer, there is a greater reduction of defects as noted by the further increase in selectivity for all three gas pairs and a permeance reduction. At 29% total polymer, increasing the cardo-BMI content from 1 to 5% increases both the permeance and selectivity. The permeance of the control PEI (29) membrane is very low, at 5% cardo-BMI the increase in permeance can be due to the cardo-BMI disrupting the packing of PEI and increasing the FFV [24]. When the cardo-BMI is increased to 10%, the selectivity decreases are attributed to phase separation.

It should be noted that these semi-IPNs reported here are prepared by modification of a commercial polymer and hence the material is relatively inexpensive and the cardo-BMI can be easily synthesized. Also the amount of synthesized cardo-BMI used to obtain the best performance is merely 5 wt%.

4. Conclusions

Bis (4-maleimidophenyl) fluorene monomer was successfully synthesized from 9,9-bis(4-aminophenyl)fluorene and maleic anhydride, the structure of which was confirmed by spectroscopic and thermal characterizations. This monomer and commercial PEI (Ultem® 1000) formed a semi-IPN, which was found suitable for making asymmetric membranes. The formation of semi-IPN was confirmed by the absence of olefinic absorptions (of cardo-

BMI monomers) in ATR-FTIR spectra. The thermal stability and glass transition temperature of the semi-IPN membranes were significantly higher than pure PEI. An increase in cardo-BMI concentration in semi-IPNs did not change the thermal stability and glass transition temperature appreciably. Membranes showed a typical asymmetric morphology as displayed in SEM images. There was no obvious phase separation between the thermoplastic PEI and thermoset Cardo-BMI networks in the composition range used in this study. The CO₂/N₂ and CO₂/CH₄ selectivity values were higher than the PEI dense films and the PEI membranes used in this study, yet the CO₂ permeance of the semi-IPNs was at least double that of the control PEI membranes. The semi-IPNs prepared with 5% cardo-BMI composition exhibited better performance than those prepared with 1% and 10%. The formulations with solid contents of 25 and 27% gave better performance than that of 29%. These membranes would be highly suitable for industrial application for upgrading biogas and capturing of CO₂ from flue gases.

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