Pebax®/TSIL blend thin film composite membranes for CO_2 separation

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In this study a thin film composite (TFC) membrane with a Pebax/Task-specific ionic liquid (TSIL) blend selective layer was prepared. Defect-free Pebax/TSIL layers were coated successfully on a polysulfone ultrafiltration porous support with a poly-dimethylsiloxane (PDMS) gutter layer. Different parameters in the membrane preparation (e.g. concentration, coating time) were investigated and optimized. The morphology of the membranes was studied by scanning electron microscopy (SEM), while the thermal properties and chemical structures of the membrane materials were investigated by thermo-gravimetric analyzer (TGA), differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). The CO_2 separation performance of the membrane was evaluated using a mixed gas permeation test. Experimental results show that the incorporation of TSIL into the Pebax matrix can significantly increase both CO_2 permeance and CO_2/N_2 selectivity. With the presence of water vapor, the membrane exhibits the best CO_2/N_2 selectivity at a relative humidity of around 75%, where a CO_2 permeance of around 500 GPU and a CO_2/N_2 selectivity of 46 were documented. A further increase in the relative humidity resulted in higher CO_2 permeance but decreased CO_2/N_2 selectivity. Experiments also show that CO_2 permeance decreases with a CO_2 partial pressure increase, which is considered a characteristic in facilitated transport membranes.

CO_2 capture, thin film composite membrane, task specific ionic liquids, Pebax, post combustion

1   Introduction

Carbon dioxide (CO_2) is a primary greenhouse gas generated by human activities such as the combustion of fossil fuels, deforestation, biomass burning and different industrial processes (e.g. the cement industry, the ammonia industry and the refinery industry) [1]. Among these, flue gas from fossil fuel power generation is the largest contributor to CO_2 emissions, and the capture of CO_2 from flue gas is one of the most important measures for greenhouse gas emission control [2]. However, the relatively low CO_2 partial pressure in flue gas (10–14 vol% CO_2) and the large volume of gas that needs to be treated makes the separation difficult and energy-intensive. More effective CO_2 capture technologies are needed to reduce the energy penalties and capture costs. Currently, there are several technologies that can be used for CO_2 capture from flue gas, including physical or chemical absorption, pressure/temperature swing adsorption, cryogenic separation and membrane separation [3,4]; among them chemical absorption is widely recognized as the most mature technology [5].

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Membrane separation technology is considered a promising alternative to traditional CO_2 absorption process, as it holds a number of advantages for CO_2 capture such as operational simplicity, low capital costs and environmental friendliness [3]. However, currently membrane technologies are not yet competitive compared with the chemical absorption process in CO_2 capture, as the separation performance of the most commercial CO_2 membranes is low.

The development of high-performance CO_2 separation membranes with both high permeability and selectivity has been a research highlight in recent years [6], while the use of ionic liquids (ILs) in membrane separation processes for CO_2 separation is one of the fastest growing research topics [7]. ILs have unique properties such as high CO_2 sorption capacity, tenable physical/chemical properties, extremely low vapour pressure and good thermally stability [8]; therefore, ILs are commonly applied in membranes to enhance gas separation properties. Task-specific ionic liquids (TSILs) are ILs with different functional groups; a specially designed TSIL can chemically interact with CO_2 and greatly enhance CO_2 solubility even in low CO_2 partial pressure conditions.

Many different IL-based membranes have been developed including supported ionic liquid membranes (SILMs), poly(ionic liquid) membranes (PILMs), poly(ionic liquid)-ionic liquid (PIL-IL) composite membranes, polymer-IL composite membranes and ion-gel membranes [9]. Among these methods, blending polymers with ILs to prepare blend membranes is a simple but effective way to improve the gas transport properties of the polymers. For example, when adding 70 wt% of [C₆mim][Tf₂N] into the poly (vinylidene fluoride)-hexafluoropropylene [P(VDF-HFP)] polymer matrix, an incredibly increased CO_2 permeability (almost one thousand times higher than that of the pure polymer, and one hundred times higher than that of the neat added IL) was documented [10]. Other polymers such as poly (vinylidene difluoride) (PVDF), polyimide (PI) and polyether-polyamide block-copolymer (Pebax®) have also been applied in polymer-IL composite membranes.

Commercially available polyamide-polyether block copolymers (Pebax®) with flexible polyether and rigid polyamide segments are known to be excellent materials for the separation of CO_2 from light gases [11–13]. Another important factor is that environmentally friendly solvents (e.g. ethanol and water) could be used during Pebax membrane preparation. A blend membrane of Pebax with an ionic liquid (1-butyl-3-methylimidazolium trifluoromethanesulfonate ([Bmim][TfO])) was applied using different grades of Pebax, as reported by Bernardo *et al.* [14]. The results show that the gas permeability and selectivity of Pebax®2533 are not notably affected by the addition of the IL, whereas the blend with Pebax®1657 shows a significantly increased gas permeability with a slight decrease in selectivity. 1-Ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) was also used to prepare Pebax/ILs blend membranes [15]. Similarly, the results show a remarkable increment in the per-

meation of all the tested gases, particularly CO_2, and the ideal selectivity of CO_2/H_2 is enhanced significantly.

However, composite membranes with a thin selective layer are generally desired for gas separation to reach a higher gas flux. For example, thin film composite (TFC) membranes with a selective layer below 1 μm dominate the gas separation market, and great efforts are still being made to reduce the thickness of the selective layer to enhance the gas flux (permeance) while maintaining the membrane stability [16]. In the past few decades, a great number of polymers have also been used to fabricate TFC membranes [17–19]. However, there are limited reports on ILs and polymer blend TFC membranes [20]. By fabricating a TFC membrane with a selective layer of about 100 nm, Noble and co-workers [20] reported a CO_2 permeance of 6000 GPU with a CO_2/N_2 selectivity of around 40, indicating that IL-polymer blend materials are a promising candidate for preparing TFC membranes.

In the present work, with the motivation of achieving high CO_2 flux and selectivity, a Pebax/TSILs blend TFC membrane has been developed. Pebax®2533 in combination with a triethylene tetramine (TETA)-based TSIL was used to fabricate the TFC membranes on porous polysulfone (PSf) supports. Highly permeable polydimethylsiloxane (PDMS) was used as the gutter layer between the selective layer and the porous support. The cations of the dopant ILs tend to complex with the ether oxygen of the polymer backbone, thus offering better membrane stability. The thickness of the membrane was minimized to about 200–500 nm to ensure high gas permeance. It is believed that with the presence of water vapor, the reactive amine groups in the TSILs could reversibly react with CO_2, thus serving as CO_2 selective facilitated transport carriers. Various properties of the Pebax®2533/TSIL blend TFC membranes were investigated by different technologies including scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), thermo-gravimetric analyzer (TGA) and differential scanning calorimetry (DSC). The membrane permeation properties were also evaluated using a CO_2/N_2 gas mixture. The CO_2 permeance and selectivity over N_2 were tested over a range of pressures and relative humidities to study the transport mechanism and effects of separation conditions.

2 Experimental

2.1 Materials

Pebax®-2533 (kindly supplied by Arkema, France) is a block copolymer containing 80 wt% poly(ethylene oxide) (PEO) and 20 wt% polyamide (PA12, nylon-12). It is referred to as "Pebax" in this paper. Triethylenetetramine (TETA) and trifluoroacetic acid (TFA) were purchased from Sigma (USA) and used without any further purifica-

tion. Ethanol (96 wt%), toluene and *n*-hexane were delivered by VWR (Norway). PDMS was supplied by Dow Corning GmbH (Germany) with the trade name of Cylgard 184. The gases used in the permeation tests were all delivered by Yara (Norway). The polysulfone (PSf) porous support membrane with a molecular weight cut-off of 20000 Da was purchased from Alfa Laval (Danmark). The PSf membrane was washed in warm tap water for 1.5 h, followed by a DI-water wash for 30 min.

2.2   Task specific ionic liquid synthesis

The TSIL triethylene tetramine trifluoroacetate ([TETA][Tfa]) was synthesized according to the procedure given by [21] (Figure 1).

Briefly, the TSIL used in this work was prepared by the neutralization of the TETA in water with an equal mole of trifluoroacetate. The reaction temperature was controlled by placing the flask in an ice-water bath at 0 °C under vigorous stirring. The TETA was firstly dissolved in an amount of water, and then the acid was added into the solution dropwise over a period of approximately 1 h. After the reaction had lasted for 4 h at 25 °C, the solvent was removed by evaporation under vacuum at 40 °C for 6 h.

2.3   Solution preparation

The procedure of the PDMS solution preparation is as follows: silicone elastomer and the curing catalyst were mixed in a beaker with weight ratio of 10:1, and the mixture was vigorously stirred for a few minutes afterwards. Then the solution was left for 3 h and diluted with a pre-calculated amount of *n*-hexane to form a 2.0 wt% PDMS solution. The partially cross-linked PDMS solution was kept in a fridge to inhibit further crosslink reaction.

The procedure of the Pebax solution preparation is as follows: a mixture of ethanol (96%) and Pebax was heated to 80 °C under reflux for 4–6 h under stirring. A homogeneous solution (0.25–2 wt%) without gelation was obtained. After cooling the Pebax solution to room temperature, calculated amounts of TSIL were added and stirred again for a further 2 h.

2.4   Pebax/TSIL blend TFC membrane preparation

The Pebax/TSIL blend TFC membranes were fabricated by a dip coating method similar to ref. [22]. In brief, the membrane was attached to a piece of glass and sealed with alu-

minum tape. The PSf porous support was first immersed in the gutter layer coating solution (PDMS) for 5 s. After 10 min, the PSf was coated with the PDMS solution for another 5 s. The gutter layer coated PSf porous support was dried for at least 24 h before coating the selective layer. The Pebax-TSIL solution was then coated twice (5 s each) onto the porous support with a gutter layer. Finally, the TFC membrane was dried for another 24 h at room temperature, followed by drying at 80 °C in a convective oven before testing the gas separation performance.

2.5   Membrane characterization

2.5.1   Scanning electron microscopy (SEM)
The thickness and surface of the composite membranes were studied using a Hitachi TM3030 and a S3400 scanning electron microscope (Japan). Samples of the cross-section were prepared by freeze-fracturing in liquid nitrogen. The samples were mounted in a sample holder and coated with a thin gold layer in order to make the samples electronically conductive.

2.5.2   Differential scanning calorimetry (DSC)
The thermal properties of the membrane materials were investigated using a differential scanning calorimeter (Q100, TA instruments, USA). A sample of about 10 mg was put in an aluminum pan covered with a proper lid together with a standard empty pan into the DSC sample holder and heated at a rate of 10 °C/min under an N_2 atmosphere.

2.5.3   Thermo-gravimetric analysis (TGA)
The thermal stability of the membranes and TSILs were investigated with a thermo-gravimetric analyzer (Q500, TA instruments, USA). Samples of 5–10 mg were placed in the sample pans and heated for 10 °C/min from room temperature to 550 °C. Nitrogen was used as both the balance and sweep gas, with flow rates of 10 and 60 mL/min, respectively.

2.5.4   Fourier transform infrared spectroscopy (FTIR)
The IR spectroscopy experiments were carried out with a Thermo Nicolet Nexus FTIR spectrometer (USA) with a smart endurance reflection cell. The experiments were carried out on the pure [TETA][Tfa], a pure Pebax membrane and Pebax membranes containing 10, 20 and 30 wt% [TETA][Tfa] in order to identify the bonds and the differences in composition.
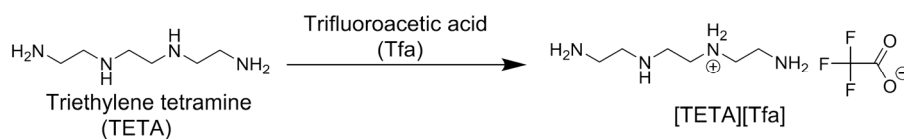

Figure 1   Schematic representation of [TETA][Tfa] synthesizing [21].

2.5.5   Contact angle test

The static contact angles of the PSf porous support, the PDMS coated support and the TFC membranes were measured using Attension tensiometers (Biolin Scientific, Sweden). DI-water was used as the liquid phase and the contact angle was determined from the average value of 5 measurements. The measurement error was ±3°.

2.5.6   Gas permeation test

The gas separation performances were measured using a constant pressure/variable flow method. Before the permeation test, all the membrane samples were carefully evacuated to remove previously dissolved species. The gas separation performance was investigated by measuring the steady state flux of two components in a mixed gas stream permeating through the membrane, where all the process variables such as pressure, the relative humidity (RH) of the gases, the gas flow rate, temperature and gas composition were continuously and simultaneously registered by a Lab View program. A mixed gas with a composition of 10% CO_2/90% N_2 was used as a feed gas and CH_4 was used as a sweep gas. The composition of the permeate gas was analyzed continuously by a micro GC Agilent 3000 (USA). All the mixed gas permeation experiments were performed at room temperature with a feed pressure of 1.7 bar and a sweep pressure of 1.1 bar if not particularly mentioned.

The mixed gas permeance of CO_2 and N_2 was calculated using a complete mixing model from the total permeate flow (Eq. (1)):

$$Q_A = \frac{J_A}{x_{fA}P_f - x_{pA}P_p} \tag{1}$$

where Q_A represents the permeance ($m^3_{STP}/(m^2$ bar h)) of component A (CO_2 or N_2), J_A is the flux ($m^3(STP)/m^2$ h), X_{fA} and X_{pA} represent the molar fraction of the component on the feed and permeate sides, respectively, and P_f and P_p (bar) are the absolute pressure on the feed and permeate sides. The CO_2/N_2 selectivity corresponds to the ratio of the CO_2 and N_2 permeances (Eq. (2)). In this study, the unit of permeance is converted to GPU for easier comparison, where 1 GPU=10^{-6} cm$^3_{STP}$/(cm^2 s cm$_{Hg}$)=$2.7×10^{-3}$ m$^3_{STP}$/(m^2 h bar).

$$\alpha_{A/B} = \frac{Q_A}{Q_B} \tag{2}$$

3   Results and discussion

3.1   Porous support and gutter layer selection

Porous support usually contributes significantly to the separation performances of the composite membrane; therefore, selecting a proper porous support is logically important for making an efficient composite membrane [23]. In general, a good porous support has the right pore size,

high porosity, good mechanical strength and a smooth surface; at the same time it should be able to maintain minimum gas transfer resistance.

In this study, PSf ultrafiltration membrane was chosen as porous support to prepare the Pebax/TSIL blend TFC membrane as it is one of the most commonly used substrate to prepare TFC membranes for gas separation [24,25]. Figure 2 shows the cross-section structure of the PSf support membrane. As can be seen, the PSf support shows a typical asymmetric structure with a less porous top layer.

A gutter layer is a highly permeable layer applied between the selective layer and the porous support. It can effectively prevent the diluted polymer solution from penetrating the porous structure, and thus reducing the possible membrane resistance. It was found that in this study a gutter layer is a prerequisite for achieving a thin defect-free selective layer when a low-concentration selective-layer cast solution is used. Highly permeable polymers such as PDMS and poly[1-(trimethylsilyl)-1-propyne] (PTMSP) are most commonly used to fabricate the gutter layer. However, PTMSP suffers from a physical aging problem and loses its high permeability in a relatively short period [22]. Partially cross-linked PDMS was therefore chosen as the gutter layer owing to its high gas permeability and reasonable long-term stability. Experiments showed that the gas permance of the PSf substrate itself is extremely high (over 5000 GPU), but with no CO_2/N_2 selectivity. The CO_2 permeance of around 1500 GPU with a CO_2/N_2 selectivity of approximately 10 were obtained in the PDMS/PSf membrane, demonstrating that the pores in the PSf substrate is completely covered by the PDMS gutter layer.

3.2   Effects of coating solution concentration

The concentration of the coating solution has a significant impact on the selective layer thickness and consequently the gas separation performance. In addition, the coating layer thickness is a function of soaking time, the viscosity of the liquid (mainly depending on the polymer concentration), the withdrawal speed of the support as well as the surface tension of the liquid [26]. In this study the soaking time of
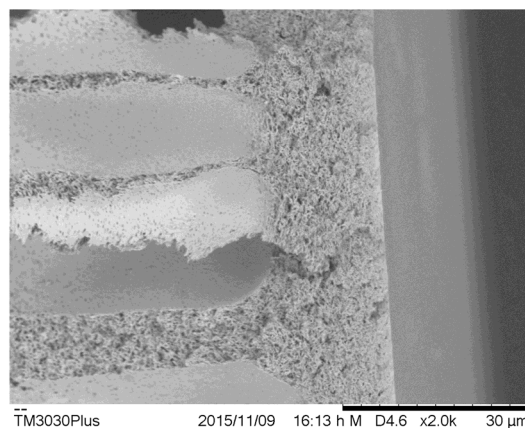

Figure 2   SEM images of the PSf porous support cross-section.

all the membranes is fixed to 5 s, and the surface tension of the liquid and the glass plate withdrawal speed are almost constant, therefore it was mainly by reducing the polymer concentration that a thinner selective layer was achieved.

Figure 3 shows the membrane structure after coating. The selective layer was successfully coated on the support, showing evidently smoother surface than the un-coated porous support (Figure 3(a)), and the selective layer (Figure 3(b)) has a thickness of around 0.5 μm (the concentration of the coating solution is 0.25 wt%).

As mentioned before, different polymer concentrations in coating solutions result in different selective layer thicknesses. In principle, the selective layer thicknesses decrease with decreasing the solution concentration (Figure 4). A further reduction of the solution concentration leads to a thinner selective layer but it is found to be more difficult to maintain a defect-free coating layer. Compared with different coating solution concentrations, a concentration of 0.25 wt% was chosen as it resulted in a reasonably low selective layer thickness and maintained the selective layer as defect free.

3.3 Thermal property characterization

3.3.1 Thermo-gravimetric analysis

The thermal stability is studied by comparing the thermal

Figure 4 Variation in the coating layer thickness as a function of the pure Pebax concentration.

onset decomposition temperatures (T_{onset}), which can be determined from the intersection of the slopes before and after the decomposition starts in the TGA curve. The TGA study of pure Pebax, Pebax/TSIL blend material and pure TSIL is illustrated in Figure 5.

As can be seen from Figure 5, pure Pebax has the highest thermal stability among these samples with a T_{onset} of around 340 °C. The [TETA][Tfa] has a relatively lower thermal stability, which starts decomposing at around 160 °C. As expected, the properties of the blend material lie somewhere between their corresponding pure materials, and the curves show two decomposition temperatures. For the sample containing 30 wt% [TETA][Tfa], the thermo-gram curve shows that approximately 30% of the sample weight is lost before the T_{onset} of Pebax decomposition, which corresponds well with the amount of TSIL added to the Pebax solution during preparation. However, this material shows a reasonable thermal stability for post-combustion CO_2 capture, which normally has an operation temperature of around 80 °C.
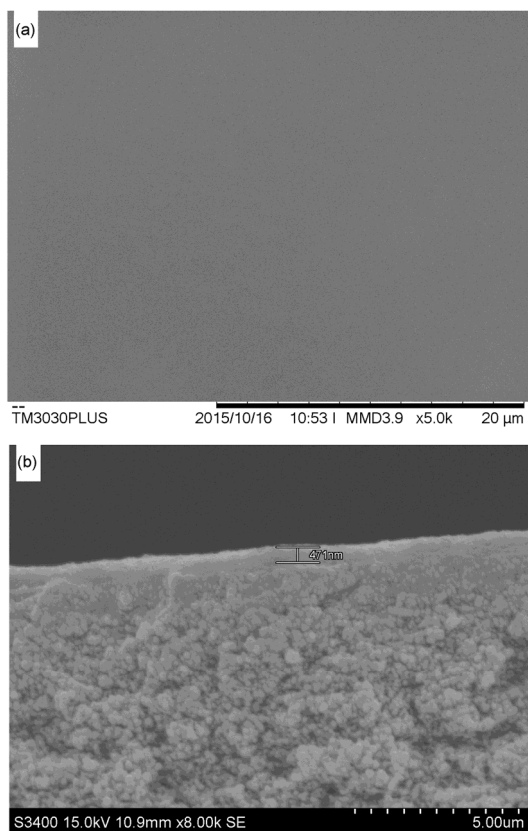
Figure 3 Morphology of the TFC membrane fabricated on a PSf porous support (a) surface and (b) cross-section, coating solution concentration 0.25 wt%.
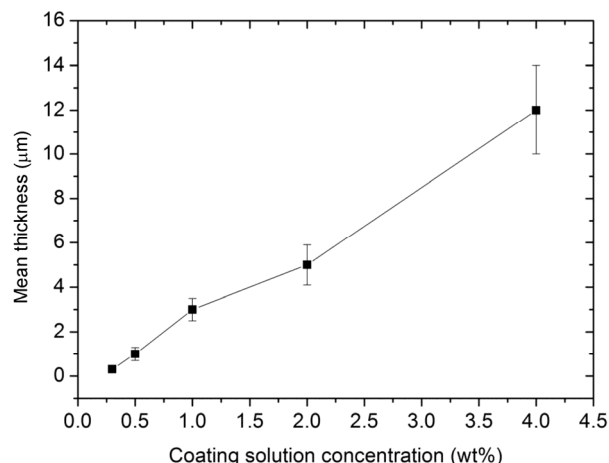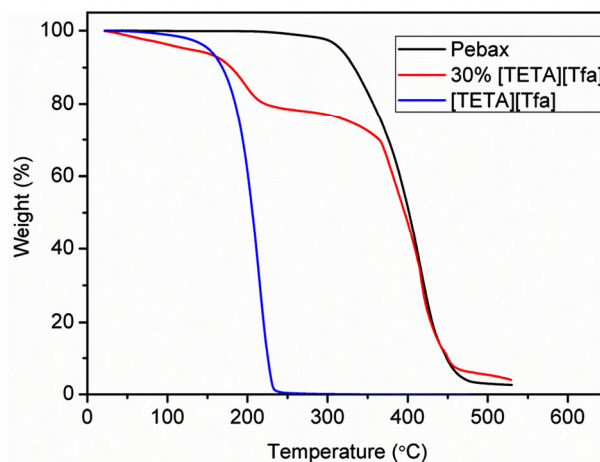
Figure 5 Thermal gravimetric analysis of Pebax, [TETA][Tfa] and Pebax/TSIL blend with 30 wt% [TETA][Tfa] (color online).

3.3.2   Differential scanning calorimetry

The thermal properties of the Pebax/TSIL blend materials were studied by DSC analysis. Figure 6 shows the second heating run of the DSC curves for pure Pebax, pure [TETA]-[Tfa] and the Pebax/TSIL blends consisting of 10, 20 and 30 wt% [TETA][Tfa].

Glass transitions are second-order transitions that are characterized by a shift in the baseline. The glass transition temperature of [TETA][Tfa] is observed to be below −50 °C. The glass transition temperature of Pebax 2533 has been reported in the literature as −77 °C [27], which is close to the lower working limit for our instrument. Nevertheless, a clear shift of baseline can be found at the start of the Pebax curve in Figure 6. The blend samples, however, have no evident shift in the baseline representing the glass transition temperatures for either [TETA][Tfa] or Pebax. Two melting points can be observed for the Pebax-containing samples. The melting point of around 15 °C can be ascribed to the melting of the crystalline portions of the PTMO block, and the second peak can be ascribed to the crystalline polyamide block in Pebax, and is located at 140 °C for pure Pebax [28]. It can be seen that the first melting point increases slightly with the [TETA][Tfa] content, while the second peak moves to a lower value.

A slight reduction in the melting point peak of the PE block can be observed when the [TETA][Tfa] content is increased. This is reasonable due to the lower amount of Pebax in the blend. Overall, the DSC results show that the [TETA][Tfa] and Pebax have good miscibility, which ensures the mixture of [TETA][Tfa] and Pebax can be used as a coating material to prepare defect-free TFC membranes.

3.4   Chemical structure

FTIR spectroscopy was performed on the Pebax/TSIL blend material with various contents of [TETA][Tfa], and results are shown in Figure 7. The peaks for pure [TETA][Tfa]
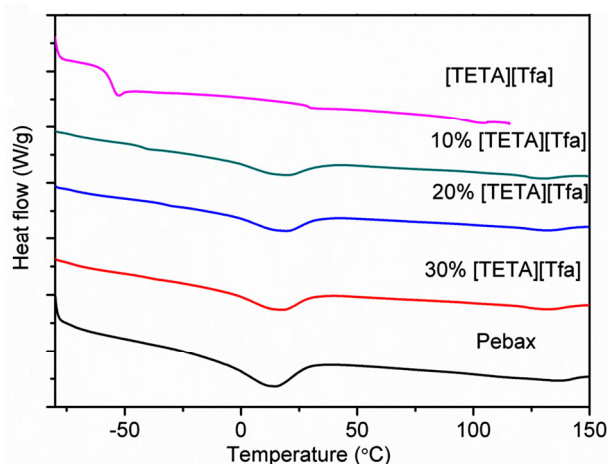
Figure 6   DSC analysis of the Pebax/TSIL blend materials with different [TETA][Tfa] contents. The curves are shifted vertically for clarity (color online).
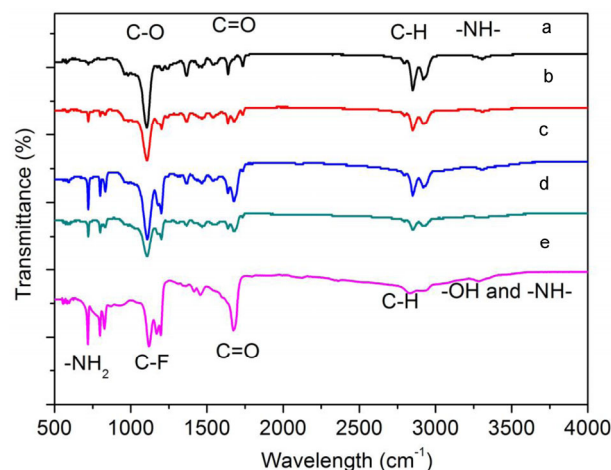
Figure 7   FTIR spectra of the pure Pebax (a), Pebax/TSIL blend materials containing 10 (b), 20 (c) and 30 wt% [TETA][Tfa] (d), and pure [TETA][Tfa] (e). The curves are shifted vertically for clarity (color online).

around 700–800 cm^{-1} are related to the effects from the amine groups. The peak at 715 cm^{-1} can be ascribed to –NH$_2$ wagging, while the peaks between 790–820 cm^{-1} can be ascribed to the wagging and twisting of –NH$_2$ [29]. It can be seen that the size of the peaks decreases with decreasing the concentration of TSIL in the Pebax/TSIL blend, and is not detectable for pure Pebax. The peak at 1200 cm^{-1} is attributed to the characteristic absorption range of the C–F bond, and the peak at around 1670 cm^{-1} can be assigned to the carbonyl group.

In terms of the pure Pebax samples, there are different distinct peaks that are characteristic of Pebax appearing. The ether stretching of the PEO block is present at 1106 cm^{-1} while nylon-12 gives a peak at 3300 cm^{-1} due to the N–H stretching, and a peak at 1640 cm^{-1} is related to the amide –C=O stretching [30,31]. Further, the peak at around 1740 cm^{-1} corresponds to the stretching of the PA-CO-O-PE carbonyl group [32]. There are two peaks around 2950–2850 cm^{-1}, which is within the characteristic absorption range of alkyl C–H stretch. The peaks are highest for pure Pebax and lowest for pure [TETA][Tfa], which is reasonable due to the many C–H bonds in the polymer.

For Pebax/TSIL blend materials, no peak shift was observed from the FTIR spectrum, denoting there is no chemical interaction between the [TETA][Tfa] and Pebax polymer. It can also be seen that the peak intensity is proportional to the TSIL content in the mixture.

3.5   Contact angle

As a porous support, the gutter layer and the selective layer are three different materials and thus they have different surface properties. Contact angle can be used as a simple but efficient way to quickly detect the defects of the composite membrane surface. As expected, the porous support,

the gutter layer and the selective layer exhibit different contact angles, as shown in Figure 8. In principle, if the coating layer is evenly distributed on a support without defects, the contact angle of the coating layer should be the same as the corresponding pure material. If there are defects in the coating layer, the surface underneath the coating layer will also contribute, which leads to a different contact angle. In this study, a Pebax layer coated only one time shows a relatively higher contact angle, implying the presence of defects in the coating layer; the underneath gutter layer, PDMS, which has a higher contact angle, also contributes and resulted in a higher contact angle. However, the Pebax TFC membrane by double coating shows a contact angle nearly the same as that of the dense self-standing Pebax membrane, indicating a defect-free Pebax layer has been formed on the PDMS gutter layer by double coating.

Figure 8 Contact angle of the porous support, gutter layer and selective layer (color online).

3.6 Gas permeation measurements

The CO_2 permeance and selectivity of CO_2 over N_2 were measured with 10% CO_2 and 90% N_2 gas mixture at room temperature with different feed pressures and relative humidity to evaluate the gas separation performance of the resulting Pebax/TSIL blend TFC membranes.

3.6.1   Effect of relative humidity

It is widely reported that water can greatly improve gas separation performances in many CO_2 separation membranes. The absorbed water in the membranes can to a certain extent lead to an enhanced polymer chain mobility, and in some membranes water benefits the facilitated transport of CO_2 [33,34]. The effect of RH on the gas separation properties for Pebax/TSIL blend TFC membranes was investigated, as shown in Figure 9.

For many hydrophilic membrane materials, a high relative humidity in feed gas enables a higher degree of membrane swelling, which favours the diffusion of gases in the membranes. As shown in Figure 9(a), for pure Pebax membranes, however, the relative humidity shows certain negative effect on CO_2 transport. When TSIL was embedded in the Pebax matrix, the CO_2 permeance was found to be strongly affected by the relative humidity as expected. For
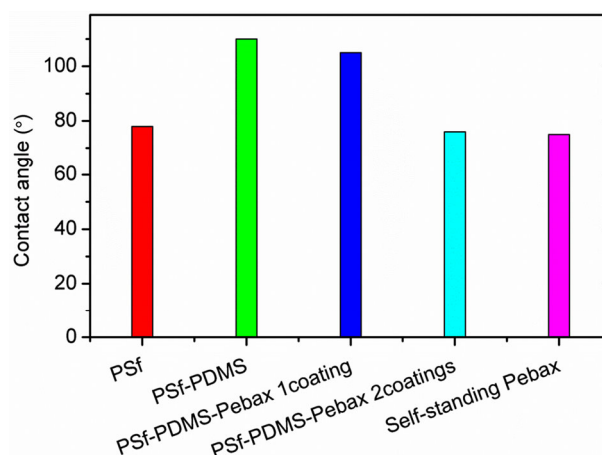
example, with RH increases from 0% to 100%, the CO_2 permeance of Pebax/TSIL blend TFC membrane containing 30 wt% TSIL increases from around 250 to 567 GPU, denoting that water vapor plays a positive role in gas transport in membranes containing TSIL. It can also be observed that CO_2 permeance in the Pebax/TSIL blend TFC membranes increases with increasing the relative humidity, and all the membranes exhibit the maximum permeance value at 100% RH. In addition, it is clear that with the presence of water vapour, the TSIL in the Pebax/TSIL blend TFC membrane can effectively promote CO_2 transport, as the increase in the TSIL content in the Pebax/TSIL blend TFC membranes (from 10 to 20 and 30 wt%) leads to the increasing CO_2 permeance. With the presence of water vapour, the primary and secondary amine groups in the TSIL function as facilitated transport carriers for CO_2 transport, resulting in a higher CO_2 permance compared to that of the pristine Pebax membranes. Similar mechanism has been reported in many water swollen facilitated transport membranes [35–38].

In terms of the CO_2/N_2 selectivity, it is clear that the addition of TSIL into Pebax can positively improve the selectivity; an increment of around 2–5 can be observed at dry conditions, and increasing the RH leads to a higher CO_2/N_2 selectivity, as shown in Figure 9(b). Many facilitated
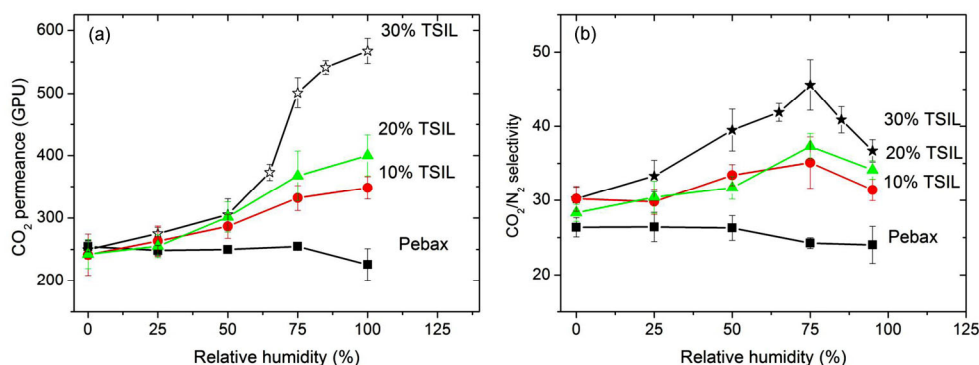

Figure 9   Effect of relative humidity (RH) on CO_2 permeance (a) and CO_2/N_2 selectivity (b). Feed gas pressure is 1.7 bar.

transport membranes have reported the best separation performances under maximum RH conditions [34,39]. However, in this study, all the Pebax/TSIL blend TFC membranes with different TSIL content show the highest CO_2/N_2 selectivity value at approximately 75% RH, and further increasing the RH tends to slightly reduce the selectivity. A possible explanation is that a higher RH increases the water-induced degree of swelling of the membrane materials, and triggers a considerable increase in N_2 permeance, thereby reducing the overall CO_2/N_2 selectivity. Similar results were reported for facilitated transport membranes containing functionalized carbon nanotubes (CNTs) for CO_2 separation [40].

3.6.2   Effects of CO_2 partial pressure in the feed

The CO_2 partial pressure has a significant influence on CO_2 separation performances in facilitated transport membranes, where the CO_2 permeance decreases with an increase in the CO_2 partial pressure, as a high CO_2 partial pressure on the feed side may saturate the facilitated transport carriers [39–41]. In this study, the effects of operation pressure on the gas separation performances were studied in a range of 1.7 to 5 bar to investigate the effects of pressure, as shown in Figure 10. As the Pebax/TSIL blend TFC membrane shows the best performances at 75% RH, the RH is fixed at 75% in these tests. Figure 10 presents the CO_2 permeance and CO_2/N_2 selectivity of the Pebax/TSIL blend TFC membrane at varied feed pressures and a comparison with the pure Pebax membrane.

As can be seen in Figure 10, the Pebax/TSIL blend TFC membranes with higher TSIL loading exhibit better separation performance, and all the Pebax/TSIL blend TFC membranes show better separation performance at lower pressures. The best performance (CO_2 permeance of 501 GPU and CO_2/N_2 selectivity of 46) is shown in the membrane with 30 wt% TSIL at 1.7 bar. In Figure 10(a), a decline in CO_2 permeance with the increasing feed pressure can be clearly observed. The membrane containing 30 wt% TSIL shows a CO_2 permeance decrement from 501 to 359 GPU with the increasing feed pressure from 1.7 to 5 bar. Membranes with 10 and 20 wt% TSIL content also exhibit evi-

dent declines in CO_2 permeance. This is recognized as the characteristic behaviour of a facilitated transport membrane due to "carrier saturation" [42]. At a low CO_2 partial pressure both solution-diffusion and facilitated transport (carrier-mediate transport) contribute to the CO_2 permeation through the membrane. However, by increasing CO_2 partial pressure the carriers gradually become saturated, which results in the loss of the facilitated transport effect and the decrease of CO_2 permeance. As N_2 transport exclusively through solution-diffusion, N_2 permeance does not change with the change in feed pressure, and hence the CO_2/N_2 selectivity also decreases with the increasing pressure.

The CO_2/N_2 selectivity of the Pebax/TSIL blend TFC membranes also decrease with the increase of the feed pressure (Figure 10(b)), while the feed pressure has limited effect on the pure Pebax membrane. Pebax/TSIL blend TFC membranes with 30 wt% TSIL shows a selectivity drop from 45 to 28 as the feed pressure increases from 1.7 to 5 bar. Similar trends have been reported for other facilitated transport membranes for CO_2 separation [34,43–45].

4   Conclusions

In the present study, Pebax/TSIL blend TFC membranes were fabricated and their CO_2 separation performance was studied under different conditions. [TETA][Tfa] was chosen as a compatible TSIL to blend with Pebax, and this blend was successfully used to form a TFC membrane with a selective layer of around 500 nm. A Pebax/TSIL blend with up to 30 wt% TSIL was coated onto the PSf porous substrates with a PDMS gutter layer. Both the SEM and contact angle results show a homogenous coating layer was fabricated on the substrate with no defects, while the thermal property analysis shows that the resulting membrane is stable in post-combustion CO_2 capture conditions. With the presence of water vapor, the reactive sites in [TETA][Tfa] can selectively react with CO_2 and promote CO_2 transport in the membranes, resulting in both improved CO_2 permeance and CO_2/N_2 selectivity. This membrane shows the best selectivity at an RH value of around 75%. The further in-
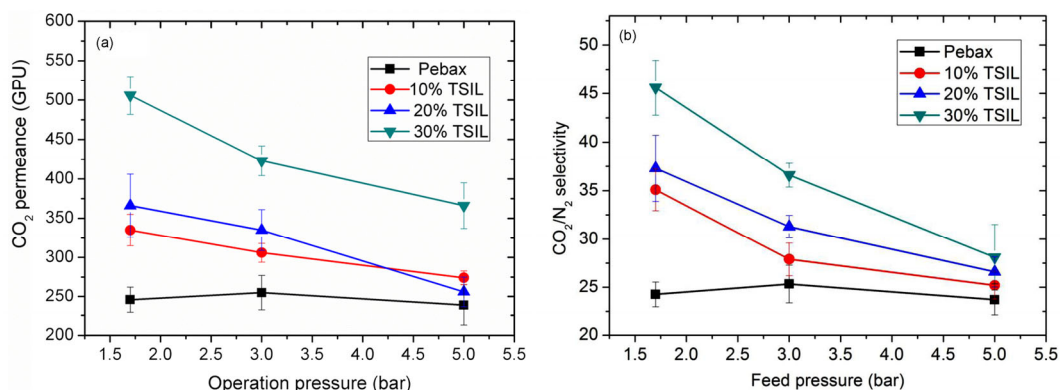

Figure 10   Effect of operation pressure on gas separation performances. (a) CO_2 permeance; (b) CO_2/N_2 selectivity.

crease in RH resulted in an increment in permeance but with a decreased selectivity. Similar to most of the facilitated transport membranes, the CO_2 separation performance is strongly pressure dependent, which exhibits a decline with increasing the pressure. This membrane shows better separation performance at low pressures (e.g., 1.7 bar), which is suitable for post-combustion CO_2 capture, as the post-combustion flue gas is normally at near atmospheric pressure with a CO_2 concentration of around 10%–15%, giving a CO_2 partial pressure of approximately 10–15 kPa. However, the long-term stability of the membrane, as well as the influence of different impurities in the flue gas such as SO_x and NO_x, should also be further studied. In addition, the highest TSIL content tested in this work is 30 wt%, as with a higher TSIL content, the coating of a defect free thin film composite membrane was not successful. Further optimization of the membrane preparation conditions may lead to membranes with a higher TSIL content and probably better separation performance.

Conflict of interest   The authors declare that they have no conflict of interest.

1   Boot-Handford ME, Abanades JC, Anthony EJ, Blunt MJ, Brandani S, Mac Dowell N, Fernandez JR, Ferrari MC, Gross R, Hallett JP, Haszeldine RS, Heptonstall P, Lyngfelt A, Makuch Z, Mangano E, Porter RTJ, Pourkashanian M, Rochelle GT, Shah N, Yao JG, Fennell PS. *Energ Environ Sci*, 2014, 7: 130–189

2   Kundu PK, Chakma A, Feng XS. *Int J Greenh Gas Con*, 2014, 28: 248–256

3   Luis P, van der Bruggen B. *Greenh Gases*, 2013, 3: 318–337

4   Pera-Titus M. *Chem Rev*, 2014, 114: 1413–1492

5   Budzianowski WM. *Int J Global Warm*, 2015, 7: 184–225

6   Mondal MK, Balsora HK, Varshney P. *Energy*, 2012, 46: 431–441

7   Noble RD, Gin DL. *J Membrane Sci*, 2011, 369: 1–4

8   Lei ZG, Dai CN, Chen BH. *Chem Rev*, 2014, 114: 1289–1326

9   Dai Z, Noble RD, Gin DL, Zhang X, Deng L. *J Membrane Sci*, 2016, 497: 1–20

10   Uchytil P, Schauer J, Petrychkovych R, Setnickova K, Suen SY. *J Membrane Sci*, 2011, 383: 262–271

11   Nafisi V, Hagg MB. *J Membrane Sci*, 2014, 459: 244–255

12   Yave W, Car A, Funari SS, Nunes SP, Peinemann KV. *Macromolecules*, 2010, 43: 326–333

13   Car A, Stropnik C, Yave W, Peinemann KV. *J Membrane Sci*, 2008, 307: 88–95

14   Bernardo P, Jansen JC, Bazzarelli F, Tasselli F, Fuoco A, Friess K, Izak P, Jarmarova V, Kacirkova M, Clarizia G. *Sep Purif Technol*, 2012, 97: 73–82

15   Rabiee H, Soltanieh M, Mousavi SA, Ghadimi A. *J Membrane Sci*, 2014, 469: 43–58

16   Baker RW, Low BT. *Macromolecules*, 2014, 47: 6999–7013

17   Xia JZ, Chung TS, Paul DR. *J Membrane Sci*, 2014, 450: 457–468

18   Shi YT, Burns CM, Feng XS. *J Membrane Sci*, 2006, 282: 115–123

19   Adzima BJ, Venna SR, Klara SS, He HK, Zhong MJ, Luebke DR, Mauter MS, Matyjaszewski K, Nulwala HB. *J Mater Chem A*, 2014, 2: 7967–7972

20   Zhou JS Mok MM, Cowan MG, McDaniel WM, Carlisle TK, Gin DL, Noble RD. *Ind Eng Chem Res*, 2014, 53: 20064–20067

21   Ren SH, Hou YC, Wu WZ, Tian SD, Liu WN. *Rsc Adv*, 2012, 2: 2504–2507

22   Chen HZ, Thong ZW, Li P, Chung TS. *Int J Hydrogen Energ*, 2014, 39: 5043–5053

23   Beuscher U, Gooding CH. *J Membrane Sci*, 1999, 152: 99–116

24   Li SC, Wang Z, Zhang CX, Wang MM, Yuan F, Wang JX, Wang SC. *J Membrane Sci*, 2013, 436: 121–131

25   Zhao YN, Ho WSW. *J Membrane Sci*, 2012, 415: 132–138

26   Maleki M, Reyssat M, Restagno F, Quere D, Clanet C. *J Colloid Interf Sci*, 2011, 354: 359–363

27   Bondar VI, Freeman BD, Pinnau I. *J Polym Sci Pol Phys*, 1999, 37: 2463–2475

28   Armstrong S, Freeman B, Hiltner A, Baer E. *Polymer*, 2012, 53: 1383–1392

29   Stuart BH. *Infrared Spectroscopy: Fundamentals and Applications*. Weinheim: John Wiley & Sons, Ltd., 2005

30   Sridhar S, Suryamurali R, Smitha B, Aminabhavi TM. *Colloid Surface A*, 2007, 297: 267–274

31   Le NL, Wang Y, Chung TS. *J Membrane Sci*, 2011, 379: 174–183

32   Sridhar S, Kalyani S, Ravikumar YVL, Muralikrishna TSVN. *Sep Sci Technol*, 2010, 45: 322–330

33   Deng LY, Hagg MB. *J Membrane Sci*, 2010, 363: 295–301

34   Deng LY, Hagg MB. *Int J Greenh Gas Con*, 2014, 26: 127–134

35   Deng L, Kim TJ, Sandru M, Hägg MB. PVA/PVAm blend FSC membrane for natural gas sweetening. Secondary PVA/PVAm blend FSC membrane for natural gas sweetening. In: *Proceedings of the 1st Annual Gas Processing Symposium*. Amsterdam: Elsevier, 2009. 247–255

36   Deng L, Hägg MB. *Ind Eng Chem Res*, 2015, 54: 11139–11150

37   Deng L, Hägg MB. *J Membrane Sci*, 2010, 363: 295–301

38   Sandru M, Haukebø SH, Hägg MB. *J Membrane Sci*, 2010, 346: 172–186

39   Deng LY, Kim TJ, Hagg MB. *J Membrane Sci*, 2009, 340: 154–163

40   Ansaloni L, Zhao YN, Jung BT, Ramasubramanian K, Baschetti MG, Ho WSW. *J Membrane Sci*, 2015, 490: 18–28

41   Liao JY, Wang Z, Gao CY, Li SC, Qiao ZH, Wang M, Zhao S, Xie XM, Wang JX, Wang SC. *Chem Sci*, 2014, 5: 2843–2849

42   Luangrujiwong P, Sungpet A, Jiraratananon R, Way JD. *J Membrane Sci*, 2005, 250: 277–282

43   Qiao ZH, Wang Z, Yuan SJ, Wang JX, Wang SC. *J Membrane Sci*, 2015, 475: 290–302

44   Saeed M, Deng LY. *J Membrane Sci*, 2015, 494: 196–204

45   Deng L, Kim TJ, Hagg MB. *Desalination*, 2006, 199: 523–524