Mechanically robust hollow fiber supported ionic liquid membranes for CO₂ separation applications

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Abstract

Polymeric hollow fiber supported ionic liquid membranes (SILMs) were fabricated utilizing Matrimid[®] and Torlon[®] as the supporting structure and the ionic liquid (IL) 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₆mim][Tf₂N]) as the gas transport media. This IL served as a baseline while the polymer and the fiber pore morphology were varied in order to optimize the support structure. By using sufficiently high fiber porosity, and thus maximizing the IL content of the membrane, it was found that the permeance and selectivity for CO₂/H₂ separation were comparable for both Matrimid[®] and Torlon[®] supports. However, the mechanical strength of Matrimid[®] supports was low when saturated with IL. Therefore Torlon[®] fibers were subsequently investigated because of the higher strength of this material. Molecular modeling was used to investigate the source of the increased strength of Torlon[®], and it was found that the polymer chains in Torlon[®] tend to interlock with each other to a greater degree than Matrimid[®]. Also, the IL [C₆mim][Tf₂N] has less interaction with Torlon[®] than with Matrimid[®]. In this work the permeance and selectivity for CO₂/H₂ of these hollow fiber SILMs are reported, as well as the tensile strength, Young's modulus, and glass transition temperature. Threshold image analysis was used to determine the volume fractions of polymer, macro-voids, and micro-voids. X-ray computed tomography scanning was used to non-destructively evaluate the location of IL within the fiber wall.

Key words: Torlon; Matrimid; hollow fiber; ionic liquid; strength

1. Introduction

Supported ionic liquid membranes have shown promise for gas separation applications such as carbon dioxide capture because of their high permeability and selectivity for carbon dioxide [1,2]. To date they are still only used experimentally due to concerns of the stability of the membranes [3,4]. An SILM consists of a porous support that is saturated with an IL, where the IL is suspended within the membrane by capillary forces. Traditionally SILMS are tested as flat sheets, but in order to further this technology towards commercial applications several groups including our own have recently begun testing SILMs in a hollow fiber format [5,6]. With the transition to SILMs as hollow fibers, practical concerns remain for the stability of the

IL component, the plasticizing effect of the IL on the polymer, and the location and migration of IL within the fiber wall.

CO₂ separation applications such as CO₂/H₂ separation of syngas produced from coal gasification or CO₂/CH₄ separation from natural gas sweetening are particularly demanding from a stability standpoint, requiring separation at high pressures and potentially high temperatures. The stability of the IL can be measured using the bubble point method, which measures the maximum transmembrane pressure that a supported liquid membrane can withstand before expelling liquid from the pores of the support. This behavior is modeled by the Laplace-Young equation, which shows that the critical displacement pressure is proportional to surface tension and inversely proportional to pore size [7,8]. In a study by Hopkinson and others, the bubble point was measured for the ILs 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₆mim][Tf₂N]) and 1-ethyl-3-methylimidazolium ethyl sulfate ([emim][EtSO₄]) on flat sheet supports of various materials, pore morphologies, and pore sizes [9]. Since bubble point is proportional to surface tension and inversely proportional to pore diameter, it was found that SILMs can be quite stable under pressure if the properties of both the support and IL are optimized appropriately.

In a previous study, we successfully demonstrated SILMs using Matrimid[®] hollow fiber supports with the IL 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C₆mim][Tf₂N]) [5]. These materials were studied because of their wide use in gas separation testing [1-4,10,11]. Although other materials may provide better gas separation performance, the primary objective of the study was to optimize the morphology of the support. It was found that increasing the porosity of the support also increases the CO₂ permeance and the CO₂/H₂ selectivity of the membrane because of the higher IL content in the micro-porous selective layer of the fiber. Both the polymer support and the IL contribute to the total permeance of the membrane, but the CO₂ and H₂ permeability of the IL are dramatically higher than for the polymer [5]. However, while a high porosity is beneficial to the gas transport properties of the membrane, it has a negative effect on the Young's modulus and tensile strength. This is because increasing the porosity causes a reduction in the polymer fraction of the membrane, which provides all of its structural stability. Also, some IL/polymer combinations are incompatible and result in severe plasticization of the polymer [9]. Therefore there is a need to better understand the interactions between the IL and the supporting polymer to provide guidance for future SILM designs.

In this paper hollow fiber supports were optimized using both Matrimid[®] and Torlon[®] as the polymer support, while [C₆mim][Tf₂N] was used as the baseline IL. The focus of this work was to evaluate the effect of changing the polymer support material on both the gas transport properties and the mechanical properties, including the tensile strength, Young's modulus, and glass transition temperature. Since the purpose of this study was to optimize the support rather than the IL, only one IL was used that represents a typical commercially available material. A molecular dynamics model was used to provide further insight into the polymer-polymer and polymer-IL interactions that directly affect the mechanical strength of the membrane. Finally, the location of the IL within the fiber was evaluated non-destructively using X-ray computed tomography (CT) scanning by generating a three dimensional visualization of the fiber-IL structure.

2. Experimental Methods

2.1. Materials

Torlon[®] 4000T (Solvay Advanced Polymers) was chosen for the fabrication of polymeric hollow fibers due to its high glass transition temperature (~ 290 °C) and high neat tensile strength ~ 115 MPa), making it well suited for pre-combustion CO₂ capture [12]. Huntsman Matrimid[®] 5218 (D. H. Litter) was used to fabricate the control fibers [10, 11]. N-methyl-2-pyrrolidone (NMP, from VWR) was used as the solvent to prepare the polymer dope solutions. An additive, LiNO₃ (Sigma Aldrich), was also used to increase the fiber porosity. De-ionized water was selected as the non-solvent for the extraction of NMP. Methanol and hexane (VWR) were used during the solvent exchange to replace water from the hollow fibers. The hollow fiber pores were filled with the IL ([C₆mim][Tf₂N], from EMD Chemicals), which was used as the selective transport media for CO₂ separation. The chemical structures of Matrimid[®] 5218, Torlon[®] 4000T, and [C₆mim][Tf₂N] are shown in Figure 1. All of the membrane materials, solvents, non-solvents and additives were either in anhydrous form or of reagent grade. Gases for permeation testing were purchased from Matheson and were of purity 99.999% or greater.

Fig. 1. Chemical structure of **(top)** Matrimid[®] 5218, **(middle)** Torlon 4000T, and **(bottom)** ionic liquid [C₆mim][Tf₂N].

2.2. Preparation of the polymer solution

Solid polymer materials were kept in vacuum for more than 24 hours at 120 °C to remove any absorbed moisture. The polymer dopes were prepared by dissolving polymer material and additives with NMP followed by mixing on a roller at room temperature. Once the mixing process was completed, the polymer dope was transferred into a vacuum oven at room temperature and left until all of the dissolved gas bubbles disappeared. Later, the polymer dope was transferred to a syringe pump (Teledyne ISCO) and kept undisturbed at room temperature for another 24 hours to de-gas the polymer solution further. A mixture of water and NMP (4:96 wt%), which was used as the core fluid, was loaded into another syringe pump and kept

undisturbed at room temperature for 24 hours to de-gas. The composition of the bore fluid was determined using the cloud point technique [13].

Four different hollow fiber supports were fabricated using Matrimid[®] and Torlon[®] polymers at room temperature with the dope compositions shown in Table 1. Composition *a* used Matrimid[®] and served as a point of comparison for fibers *b*, *c*, and *d*, which were all made from Torlon[®]. Composition *b* was designed to have the same polymer concentration as type *a* fibers. Compositions *c* and *d* had a smaller polymer concentration than *b*, which was designed to further increase the fiber porosity. In all compositions, LiNO₃ was used as an additive because it forms a complex with NMP in the polymer dope, which increases the number of pore spaces after solvent extraction [14].

Table 1. Composition of the polymer dope.

Membrane	Matrimid [®] wt%	Torlon [®] wt%	NMP wt%	LiNO ₃ wt%
<i>a</i>	18	18	78	4
<i>b</i>	0	18	78	4
<i>c</i>	0	16	80	4
<i>d</i>	0	14	82	4

2.3. Hollow fiber fabrication and post-treatment

Hollow fiber supports were fabricated as explained elsewhere using a single-layer spinneret at ambient conditions [5,15,16]. The core fluid, a mixture of NMP and water (96:4 wt%), and the sheath material, 18 wt% Matrimid[®], or 18-14 wt% Torlon were injected through core and sheath feed lines, respectively. Syringe pumps were used to control the core and sheath fluid flow rates during extrusion through the spinneret. The core fluid and polymer dope flow rates were maintained at 60 and 90 mL/hour, respectively, and an air gap of 2 cm was used for all experiments. A water container with a 2.2 m long non-solvent quench path was used for the phase separation. Upon entering the quench bath, the nascent fibers were phase separated and collected on the winding drum at a speed of about 6.75 m/min.

The residual NMP solvent in the fibers has the ability to plasticize the solidified polymer wall causing shape deformation. Therefore, collected fibers were rinsed in de-ionized water three times for 24 hours each time. The fibers were then rinsed in methanol three times for 30 minutes each time. Finally the fibers were rinsed with hexane three times for 30 minutes each time. After rinsing, fibers were transferred into a vacuum oven and dried at 30 °C for 24 hours.

After the fibers were dried, single fiber modules were prepared to facilitate gas transport testing. 10 cm long modules were prepared by mounting one hollow fiber in the center of a metal tube and using epoxy glue to seal it at each end. Next, IL was loaded into the shell side of the fiber module and kept at ambient conditions for another 48 hours and in vacuum at room temperature for 1 hour to achieve the maximum possible IL loading (total of 49 hours) and stored under ambient conditions to be used for testing. Previously, type *a* Matrimid hollow fibers were soaked in IL and the weight was recorded for several days. It was found that the maximum loading was approximately 80 wt% IL after a period of 24 hours [5]. After the initial loading of the membranes with IL, dry nitrogen gas was sent through the core of the hollow fiber at 3 SLPM for 3 hours in order to remove excess liquid (referred to subsequently as ‘cleaning’ the fiber).

2.4. Fiber imaging

Hollow fibers were examined under a Scanning Electron Microscope (SEM, Quanta 600F) to determine the morphological features and wall thickness. The SEM samples were prepared by shear fracturing of hollow fibers in liquid N₂ using tweezers and then sputter coating with palladium.

Fibers were also scanned using micro X-ray CT scanning. Micro CT scanning combines microscopy and X-ray technologies to form images based on X-rays transmitted by the sample. X-ray absorption increases with density and thickness, and it is generally higher for elements with a higher atomic number in the periodic table.

For the CT observations of this study, an Xradia Micro XCT-400 scanner was used which is equipped with an X-ray source (voltage of 40-150 kV and power of 4-10 W) and up to 40x magnification lenses. Its resolution can be less than 1 μm for a three dimensional field-of-view range of 0.7 mm. Three microfiber samples (dry fiber, IL saturated, and IL cleaned) were scanned by X-ray CT. Samples were placed in a plastic sample tube (ID = 1 mm, thickness = 0.5 mm) and then mounted on an aluminum rod, which was held by a pin vise sample holder. X-rays were generated with an 80 kV source voltage and 8 W power. Samples were scanned with 40x magnification lens at 12 seconds exposure time for 360 degrees and 16 projections per degree (total 5761 projections). The distances of the sample from the X-ray source and detector were 44.5715 mm and 6.4175 mm, respectively, resulting in a pixel resolution of 0.592 μm . A complete scan with reference projections took 22 hours. The acquired raw images were manually reconstructed to minimize beam hardening and center shift, and then compiled into a three dimensional volume image with XMReconstructor (Xradia). The images were further processed for representation using public domain image processing and analysis software ImageJ 1.47 [17].

2.5. Porosity measurements

The total porosity (also referred to as the bulk porosity), $v_{\text{void},\text{total}}$, was determined for each fiber composition by dimensional analysis using the relationship [5]

$$v_{\text{void},\text{total}} = 1 - \frac{1}{\rho_{\text{poly}}} \frac{4m}{\pi(OD^2 - ID^2)l}, \quad (1)$$

where ρ_{poly} is the density of the polymer, OD is the outer diameter of the fiber, ID is the inner diameter, m is mass, and l is length. The density of the neat Matrimid[®] and Torlon[®] polymers were measured using a pycnometer (AccuPyc II 1340, Micromeritics), and were found to be 1.30 and 1.41 g/cm³ respectively. The volume fraction of polymer, v_{poly} , was determined by

$$v_{\text{poly}} + v_{\text{void},\text{total}} = 1, \quad (2)$$

and the total volume fraction of voids can be further broken down into micro-voids, $v_{\text{void},\text{micro}}$, and macro-voids, $v_{\text{void},\text{macro}}$, according to

$$v_{void,total} = v_{void,micro} + v_{void,macro} \quad (3)$$

The volume fraction of macro-voids was determined using threshold analysis of SEM images [5,18,19]. SEM cross section images of the fibers were imported into ImageJ. A threshold gray level was determined by the Intermodes algorithm and used to distinguish between voids (dark areas) and the polymer (light areas) [20]. Images were converted into binary (black and white) to separate the two regions. Any dark region less than $10 \mu\text{m}^2$ in area was considered to be a micro-void, and was therefore excluded from the calculation of the macro-void area. Finally, the macro-void area and the total cross section area were used to calculate the fraction of macro-voids.

2.6. Gas transport measurements

The permeances and selectivities of mixed gas testing were determined using an isobaric system with constant flow (a schematic is shown elsewhere) [5]. The composition of both the permeate and retentate were measured using a gas chromatograph (Perkin Elmer ARNEL Clarus 500). The flow rate was measured using a digital bubble flow meter and the pressure with a pressure transducer (Honeywell TJE). Temperature was recorded using a type K thermocouple in contact with the surface of the fiber testing module. Fiber modules treated with IL were tested with the feed gas introduced through the core of the membrane and the sweep gas passing over the shell side. The feed gas composition was 20 mol% CO_2 , 20 mol% H_2 , and balance Ar, and had a flow rate of 12.4 mL/min. The sweep gas was pure Ar and had a flow rate of 3.2 mL/min. The feed pressure was 110 kPa and the permeate pressure was 103 kPa. After the introduction of the feed gas, the system was allowed to reach steady state (approximately 2 hours), and data was subsequently collected for at least another 2 hours.

In these measurements, the permeance, (P/l) , of a particular gas species i is defined as

$$\left(\frac{P}{l} \right)_i = \frac{Q_i}{A \Delta p_i} \quad (4)$$

where P is permeability, l is membrane thickness, Q is the flow rate, A is the membrane surface area (in this case the outside surface of the fiber), and Δp is the partial pressure difference across the membrane. Selectivity, α of gas species a with respect to species b is

$$\alpha_{a/b} = \frac{P_a}{P_b} \quad (5)$$

2.7. Dynamic mechanical analysis (DMA)

The mechanical integrity of the hollow fibers was investigated using a DMA (TA Instruments Q800). Glass transition temperature (T_g) was determined by applying a sinusoidal stress to the fibers with a frequency of 1 Hz and measuring dynamic modulus as a function of temperature. The T_g is taken as the peak of the resulting $\tan \delta$ vs. temperature curve, where δ is the phase lag between stress and strain [21]. Young's modulus and ultimate tensile strength were measured at a temperature of 30 °C by applying an increasing linear stress to the fibers at a rate

of 0.1 N/min until fracture occurred. Young's modulus was calculated as the ratio of stress/strain for the first 0.5% strain [22].

3. Results and Discussion

3.1 Fiber morphology

SEM images were used to study the pore structure of the four fiber types. Figure 2 shows the freeze-fractured cross section, the outer wall, and the outer surface of each fiber type. The cross section images reveal that each fiber consisted of finger-like macro-voids that extend from the inner surface, a micro-porous region that is between the outer surface and the macro-voids, and a dense skin layer that makes up the fibers' outside surface. However there are significant morphological differences between Matrimid[®] and Torlon[®] fibers. The Matrimid[®] fiber *a* has a very porous outer surface and a micro-porous region that is about 40 μm thick. Nearly all of the macro-voids are open to the inner core for this type of fiber. By comparison, the outer surface of type *b* and *c* fibers are very dense, with no visible pores at the magnification level that is shown. Some very small pores are visible in the outer surface of fiber *d*. All of the Torlon[®] fibers, *b*, *c*, and *d*, have a micro-porous region around 2 μm in thickness and some macro-voids that are open to the core, while others are not.

Fiber dimensions (outside diameter, *OD*; inside diameter, *ID*; thickness of the micro-porous region; $l_{\text{micro-porous}}$) and polymer and void fractions are given in Table 2. Fiber composition *b* had the lowest overall porosity, which is attributed to the use of a high polymer concentration. Porosity was increased in fibers *c* and *d* by decreasing the polymer concentration. By using SEM image analysis, it was also possible to determine the fraction of macro-voids and micro-voids. The micro-void region of the fiber is most likely to retain IL due to the higher capillary forces that are associated with small pores. From the Laplace-Young equation it is known that capillary pressure is inversely proportional to pore size [23]. IL that is initially contained in the macro-voids will become entrained in the feed (if fed from the bore side) or permeate (if fed from the shell side) gas stream and flow out of the membrane. To prevent this from happening during operation, excess IL was cleaned from the fibers after the loading procedure, as described previously.

Fig. 2. SEM images of the cross section (**top**), outer wall area (**middle**), and the outer surface (**bottom**) of each fiber type.

Table 2. Fiber dimensions and void/polymer volume fractions.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
<i>OD</i> (μm)	639 ± 57	545 ± 12	451 ± 08	590 ± 17
<i>ID</i> (μm)	357 ± 24	289 ± 18	263 ± 16	335 ± 10
<i>l_{micro-porous}</i> (μm)	41.2 ± 2.2	2.1 ± 0.1	2.1 ± 0.3	1.4 ± 0.4
<i>v_{poly}</i>	0.21±0.01	0.25±0.04	0.23±0.02	0.19±0.01
<i>v_{void,macro}</i>	0.33±0.05	0.36±0.03	0.37±0.06	0.52±0.04
<i>v_{void,micro}</i>	0.46±0.04	0.39±0.02	0.40±0.04	0.29±0.04
<i>v_{void,total}</i>	0.79±0.04	0.75±0.03	0.77±0.05	0.81±0.04

In order to determine where the IL resides in the cross section of the fibers after the cleaning procedure, X-ray CT scanning was used to non-destructively image the interior of the fiber. Other imaging techniques such as optical microscopy or SEM require cutting the fiber in order to view the cross section, which inherently causes a disturbance of the IL. X-ray CT scanning also has the advantage that it can be used to create a complete three dimensional mapping of the fiber. Three images are shown using fiber composition *d* as an example: a dry fiber without any IL, a fiber that was saturated with IL, and a fiber that was saturated with IL and subsequently cleaned (Figure 3). Because X-ray CT scanning discerns differences in density and the density of the IL (1.34 g/cm³) is close to that of the polymer (Torlon, 1.41 g/cm³), the contrast between the IL and the polymer is weak. However, by comparing the saturated fiber

with the dry fiber it is easy to see that all pores fill with IL after the fiber becomes saturated. Furthermore, after the fiber has been cleaned, many of the macro-voids become empty. The macro-voids that lose their IL during the cleaning process are all open to the inner core of the fiber, while macro-voids that are closed off from the inner core retain their IL.

From weight measurements, it is known that a fiber that is saturated with IL contains approximately 80 wt% IL, which corresponds to an amount that is necessary to fill all of the pores (note that the density of the polymer and the IL are approximately equal). Cleaning reduces that amount of IL by about 20 % after remeasuring the weight of the fibers, which corresponds to about half of the IL in the macro-voids. IL is retained in the micro-voids and in the macro-voids that are closed off from the fiber core. After cleaning IL from the macro-voids, the selective layer thickness becomes equal to the thickness of micro-void region, since many of the macro-voids are now empty. Gases can travel non-selectively through the empty macro-voids and separate only in the IL saturated micro-porous region of the fiber.

Fig. 3. CT scan images showing the location of the IL in the fiber. (a) Fiber without IL. (b) Uncleaned fiber saturated with IL (c) Fiber that was saturated with IL and subsequently cleaned.

3.2. Gas transport properties

CO₂ permeance and CO₂/H₂ selectivity for the different hollow fiber types are shown in Figures 4 and 5. Both of these measurements were found to be strongly influenced by the pore structure of the fibers. First generation hollow fibers (type *a*) were prepared using an 18 wt% Matrimid[®] dope solution and second generation hollow fibers (type *b*, *c*, and *d*) were prepared using 18, 16, and 14 wt% Torlon[®] dope solutions respectively. As shown in Figures 4 and 5, the CO₂ permeance and CO₂/H₂ selectivity of type *d* fibers were comparable to type *a*, and high in comparison with types *b*, and *c*. Previously it was shown that hollow fibers with high porosity, such as fiber *a*, make excellent platforms for SILMs because they allow for a high IL content [5].

The second generation fibers (type *b*, *c*, and *d*) were prepared using Torlon[®]. Type *b* and *c* membranes showed poor transport properties compared to membrane type *a*. The observed low CO₂ permeance and separation factor were due to a lower porosity, which resulted in a low IL content [24,25]. Therefore the porosity of the Torlon[®] membranes was further increased by decreasing the polymer content to 14 wt% for type *d*. This membrane showed an improvement over *b* and *c* in CO₂ permeance. The CO₂/H₂ selectivity of type *d* membranes is higher than that of type *b* at low temperatures, but it is within the error bars of types *a* and *c*. Matrimid[®] type *a* membranes and the Torlon type *d* membrane have nearly the same total porosity and also very similar gas transport properties. This is because the polymer plays a negligible role in gas

permeation as compared with the IL, and the IL content is the same for fibers with a similar porosity. A dense Matrimid[®] film is inherently H₂ selective (for a Matrimid[®] film $P_{H_2} \approx 17.5$ Barrers and $P_{CO_2} \approx 7.2$ Barrers at 35 °C), but the overall gas permeability of the pure polymer is small when compared with the pure IL (for [C₆mim][Tf₂N] $P_{H_2} \approx 82$ Barrers and $P_{CO_2} \approx 744$ Barrers at 35 °C) [2]. Torlon[®] is an even stronger barrier for CO₂ and H₂ transport (for a Torlon[®] film $P_{H_2} \approx 4.4$ Barrers and $P_{CO_2} \approx 0.44$ Barrers at 35 °C). Therefore a higher porosity is favorable for CO₂ permeance and CO₂/H₂ selectivity due to the proportionally higher IL content in the membrane selective layer [5].

Fig. 4: CO₂ permeance of hollow fiber membranes saturated with IL.

Fig. 5. CO₂/H₂ selectivity of hollow fiber membranes saturated with IL.

3.3 Mechanical properties

Tensile strength and Young's modulus were measured at room temperature for each fiber with and without IL (Figures 6 and 7). Both of these values decrease with increasing bulk porosity. As the bulk porosity increases, the volume fraction of polymer decreases, negatively affecting the strength and stiffness because there is less polymer to provide support to the fiber. Fibers soaked in IL have a lower tensile strength than dry fibers. This is attributed to the plasticization effect that ILs can have on polymers. For Matrimid[®] fiber *a* with IL, the mechanical properties were too low to be measured. In comparing the mechanical properties of Matrimid[®] fiber *a* and Torlon[®] fiber *d*, which both had a similar level of bulk porosity, fiber *d* had a tensile strength that was approximately 4 times greater than fiber *a*. This increased strength represents a significant advantage for the commercial viability of this type of membrane. Young's modulus was also improved by about 1.5 times for fiber *d* over fiber *a*.

The glass transition temperature (T_g) for the dry Matrimid[®] fiber was about 326 °C, while dry Torlon[®] fibers had a lower T_g of about 278 °C. As can be seen by comparing Torlon[®] fibers *b*, *c*, and *d*, glass transition temperature is independent of the fiber morphology. This behavior was also observed previously for Matrimid fibers, which also had a T_g that was insensitive to fiber morphology [5]. The T_g of both types of fiber was reduced when the polymers were

saturated with IL, although the reduction in T_g was slightly less for Torlon[®] fibers. To gain a better understanding of the structure-property relationships that cause this behavior, atomistic modeling was conducted for each of these intra- and inter-molecular species.

Fig. 6. Ultimate tensile strength of dry hollow fibers and fibers saturated in IL at 30 °C.

Fig. 7. Young's modulus of dry hollow fibers and fibers saturated in IL at 30 °C.

Table 3. Glass transition temperature of dry fibers and fibers that are saturated with IL.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
$T_{g,dry}$ (°C)	325.8 ± 1.4	283.4 ± 0.8	285.0 ± 4.0	267.0 ± 2.7
$T_{g,wet}$ (°C)	282.6 ± 1.7	252.8 ± 2.4	253.0 ± 5.6	246.8 ± 0.6

3.4 Atomistic simulations of polymer and ionic liquid interactions

Employing a simple model and atomistic force field molecular dynamics, the affinity between the polymers (Matrimid[®] or Torlon[®]) and IL ([C₆mim][Tf₂N]) was investigated. As shown in Figure 8, there are two possible states, herein referred to as (a) separated polymer-polymer and IL-IL complexes and (b) polymer-IL complexes, which may be adopted by the polymer/IL system when they are mixed. E_1 is the system energy of (a) in separated states between polymer and IL, E_2 is the system energy of (b) in a mixed state between polymer and IL and the energy difference ($\Delta E = E_1 - E_2$) is the transition energy from state (a) to state (b) [26]. Here, the values of E_1 and E_2 are not important, but the energy difference ΔE is the key in determining the system stability. When $\Delta E < 0$, state (a) is more energetically favorable. Conversely, $\Delta E > 0$ suggests that state (b) is more favorable.

Fig. 8. Schematic representation of transitions of different states in polymer/IL systems. (a) separated polymer-polymer and IL-IL complexes; (b) polymer-IL complexes.

In each simulation, 6 ns molecular dynamics with a time step of 0.5 fs was used to reach equilibrium in the canonical NVT ensemble at 298.15 K, was followed by an additional 4 ns of molecular dynamics simulation to record energies and trajectories for the system every 1 ps. CVFF (Consistent Valence Force Field) and CHARMM (Chemistry at HARvard Molecular Mechanics) based force fields were employed for Matrimid[®], Torlon[®] and IL [27,28]. All of the simulations were carried out using Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) in a large cubic simulation box (dimension of 250 Å) with periodic boundary conditions. For each scenario, three independent simulations with different initial configurations have been carried out, and the average results were calculated and listed in Table 4. The transition energy for Matrimid[®] from state (a) to (b) is -2.6 kcal/mol whereas for Torlon[®] it is -66 kcal/mol. Therefore, the Torlon[®] system has a more negative transition energy compared to the Matrimid system, is more stable, and hence prefers to stay in state (a).

Table 4. System energies (kcal/mol) between different polymer/IL states. E_1 : The combined system energy of a state in which polymer and IL are separated; E_2 : The system energy of a state in which polymer and IL are mixed; ΔE : Transition energy from a separated state to a mixed state.

	Matrimid [®] /[C ₆ mim][Tf ₂ N]	Torlon [®] /[C ₆ mim][Tf ₂ N]
E_1 (kcal/mol)	1287.9	1345.1
E_2 (kcal/mol)	1290.5	1411.1
$\Delta E = E_1 - E_2$ (kcal/mol)	-2.6	-66.0

The representative snapshots in Figure 9 also show differences in the way Matrimid[®]/IL and Torlon[®]/IL tend to assemble. In Figure 9 (a) the interaction between a Matrimid[®] chain and a IL molecule are shown, and Figure 9 (b) is the same for Torlon[®] and IL. In Figure 9 (c) the interaction between two Matrimid[®] chains is shown, and Figure 9 (d) shows two Torlon[®] chains. While the IL becomes wrapped in the Matrimid[®] chain (Figure 9 (a)), it remains at the exterior of a Torlon[®] chain (Figure 9 (b)). This is another indication that Torlon is immiscible with IL. These results may explain the difference in mechanical performance when the two polymers are soaked in IL. Since there is a relatively weak transition energy barrier to the formation of a Matrimid[®]/IL complex, the Matrimid[®] fiber is more easily plasticized by IL compared with the Torlon[®] fiber. Therefore, introducing IL can reduce the mechanical properties of Matrimid[®] fiber more than Torlon[®] fibers, which has also been observed in experiments.

In Figure 9 (c), two Matrimid[®] chains maintain an extended conformation, but in Figure 9 (d) two Torlon[®] chains are coiled due to the more flexible backbone in Torlon[®] chains. The different trends in tensile strength and glass transition temperature between the two polymers may seem to be in conflict with each other, since Torlon[®] has a higher tensile strength but lower T_g than Matrimid[®]. However, these two properties are not only dependent on the rigidity of polymer chains, but also determined by the interaction and conformation between polymer chains. The difference in chain flexibility between Matrimid[®] and Torlon[®] results in the higher T_g of Matrimid[®] over Torlon[®], as this material property is dominated by local cooperative internal motion like functional group rotation. On the other hand, Matrimid[®] has a smaller tensile strength than Torlon[®]. When two Torlon[®] chains are allowed to assemble together, they interlock with each other as shown in Figure 9 (d). Matrimid[®] chains tend to remain extended and exhibit less interlocking behavior, as in Figure 9 (c). Therefore, more energy is required to separate Torlon[®] chains than Matrimid[®] chains, which leads to a higher tensile strength in Torlon[®].

Fig. 9. Representative snapshots of self-assembly between Matrimid[®], Torlon[®] and IL by atomistic molecular dynamics. In order to distinguish the different molecules, IL is represented by a bead-rod model and the polymer is represented by a rod model in (a) and (b). One polymer is represented by a bead-rod model and the other polymer is represented by a rod model in (c) and (d). (a) IL-Matrimid[®] complex; (b) IL-Torlon[®] complex; (c) Matrimid[®]-Matrimid[®] complex; (d) Torlon[®]-Torlon[®] complex. White: H; Red: O; Grey: C; Yellow: S; Light blue: F; Blue: N.

4. Conclusion

Hollow fiber SILMs were fabricated using both Matrimid[®] and Torlon[®] fiber supports. X-ray CT scan images were successfully used to show the location of IL within the pore structure of the fibers. It was found that after the fibers were saturated with IL and then underwent a cleaning procedure, that the IL only occupied the micro-porous region of the fiber and the macro-pores that were closed to the fiber core. Because of this, the selective layer thickness becomes the thickness of the micro-porous region since macro-pores that are not filled with IL do not provide any resistance to gas permeation. When comparing fibers that have a similar porosity, the CO₂ permeance and CO₂/H₂ selectivity are roughly the same regardless of the type of polymer that is used for the support. This results from the relatively small co-permeance contribution of the polymer compared with the IL. Torlon[®] fibers have improved mechanical strength when compared with Matrimid[®], but also have a lower glass transition temperature. Tensile strength is roughly 4 times greater for Torlon[®] than it is for Matrimid[®], and Young's modulus is 1.5 times as large. Furthermore, molecular simulations indicate that Torlon's[®] increased strength is associated with an interlocking of polymer chains that does not occur in the Matrimid[®]. This mechanism has the added benefit that it may prevent IL ions from interspersing within polymer chains, which would disrupt inter-chain molecular bonding and decrease mechanical strength. The reduced glass transition temperature in Torlon[®] is a result of its more flexible backbone chain structure.

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