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This publication could be one of several versions: author's original, accepted manuscript or the publisher's version.

Publisher's version / Version de l'éditeur:
https://doi.org/10.1016/j.memsci.2006.01.024
Journal of Membrane Science, 280, pp. 234-244, 2006
Formation and thermal stability of BMI-based interpenetrating polymers for gas separation membranes

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Received 24 March 2005; received in revised form 6 January 2006; accepted 13 January 2006

Available online 17 February 2006

Abstract

Semi-interpenetrating polymer networks (semi-IPNs) were prepared by sol–gel technique through in situ polymerization of bismaleimide (BMI) in thermoplastic polyetherimide (PEI) as well as in polysulfone (PSF). This synthesis route allows arresting thermoset/thermoplastic phase separation at an early stage by solidifying the semi-IPNs through membrane phase inversion. The phase separation could be observed visually in the casting solution or by optical microscope on the surface of the produced membranes. These semi-IPNs with a density lower than their thermoplastic base polymer allowed easier water penetration during membrane phase inversion. This led to improved membrane morphology that was confirmed by scanning electron microscopy. Membranes fabricated from these semi-IPN materials had thinner skin layers and longer straight fingers perpendicular to membrane surface. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) showed that these semi-IPNs membranes have improved glass transition temperatures but a lower thermal stability. However, at ambient conditions, these membranes with their improved structure and morphology showed superior gas separation characteristics compared to base polymers. For example, the permeance was increased by 12–15 times without a significant decrease in the selectivity of oxygen over nitrogen in air separation experiments.

1. Introduction

Membrane-based separation is a rapidly growing green technology that has been commercially recognized in many industrial applications [1]. Most commercial asymmetric membranes are fabricated from engineering plastics using different techniques to obtain ideally ultra-thin skin layer having a high microporosity as well as selective gas permeation characteristics [2]. Additional requirements for membrane materials include ability to form flexible membranes, absence of defects, improved damage tolerance and durability under various operating conditions. It is hard to achieve all of the above characteristics and therefore improving membrane materials is still an active topic of research. In addition to this, the trade off between permeability and selectivity for most polymeric membrane materials has to be overcome to increase productivity of gas separation membranes especially in some applications such as separation of oxygen from air [3].

Generally, most of the polymers require incorporation of additives to achieve desired characteristics for material performance [4,5]. Interpenetrating polymer networks (IPNs) introduced in the early 1960s, were successful in creating polymeric nano-scale blends having new extraordinary properties as reviewed elsewhere [6,7]. The importance of IPN synthesis has been recognized in engineering literature, patents and commercialized products since 1951 [8,9]. The concept of in situ polymerization within and through the structure of another polymer network as well as stabilizing this multiphase system was based on creating interpenetrating (i.e. physical interlocked or/and catenated) networks having multi-domains at supramolecular levels [8,9]. It was recognized that phase separation at macro-scale level that may arise from the mutual incompatibility inherent in multipolymer systems should be prohibited during formation, post-treatment, processing or/and end-use application in order to enhance IPN composite properties [10,11]. This was...
achieved by slowing down phase separation at an early stage at the onset of de-mixing through highly viscous solution by gelation or vitrification [12]. It was also reported that timing the two phenomena of gelation and phase separation is very important for governing the size of each domain in the polymeric network [8]. The concept of synthesis of IPNs seems to be useful for development of nano-size multiphase polymeric materials for gas separation membranes as it provides a distinct possibility to control composite material properties and morphology. However, in situ structuring and interfacial tailoring of IPNs is necessary to obtain desired properties and to overcome challenges such as defects in the fine structure [13], phase separation and incompatibility [10,11].

Bismaleimide (BMI) has been used successfully with high performance thermoplastic polymers for forming semi-IPNs. For example, BMI/poly(sulfone) semi-IPN was prepared from a casting solution of BMI, poly(sulfone) and anionic initiator (1,4-diazabicyclo[2.2.2]octane) in N-methylpyrrolidione solvent. Thermal polymerization of BMI was achieved to gel the cast film. However, at magnification of 1200 the optical microscopy of the cured films showed phase separation [14]. This was attributed to heating the cast film above the glass transition temperature of PSF before and during polymerization of BMI that led to a brittle IPN material. The weight ratio of BMI to PEI or PSF in semi-IPN formation was kept below 11% because a higher concentration led to a brittle IPN material. The major disadvantage of their process was a challenge in producing membranes that had both high flux and a small molecular weight cut-off [17]. Therefore, to overcome this obstacle, a new route for semi-IPN synthesis combined with membrane formation to control thermo set/thermoplastic phase separation at different polymerization stages, is needed. The present work describes the synthesis of new semi-IPNs materials, formation of membranes and their characterization including microscopic, thermal and permeation studies.

2. Experimental

2.1. Materials

Aromatic polysulfone (Udel® P-1700 NT LCD) and aromatic polyetherimide (Ultem® 1000) were supplied in pellet form by Solvay Advanced Polymers, USA, and General Electric Plastics, USA, respectively. Both polymers were dried in an oven at 150°C for 8 h to remove any possible absorbed water vapors. Anhydrous 1-methyl-2-pyrrolidinone (Aldrich, 99.5%, reagent grade, water <0.005%), anhydrous isopropanol 99.5% and 1,1′-(methylene-4,1-phenylene) bismaleimide 95% were supplied by Sigma–Aldrich Canada Ltd. Anhydrous ethyl alcohol was received from Commercial Alcohols Inc., Ont., Canada. Hexanes of ACS reagent grade were supplied by VWR, Canada. All solvents were used as supplied under a dry nitrogen atmosphere. Ultra high purity Helium and medical air were supplied by BOC Gases Canada Ltd. and used as received without further purification.

2.2. Membrane preparation

Formulations of polyetherimide (PEI) as well as polysulfone (PSF) with and without 1,1′-(methylene-4,1-phenylene) bismaleimide (BMI) were used to prepare flat asymmetric membranes by sol–gel technique [18]. Polymerization of BMI monomer was carried out in polymeric solutions containing anhydrous 1-methyl-2-pyrrolidinone (NMP) as an aprotic dipolar solvent and one of the non-solvents, i.e. anhydrous ethyl alcohol (EtOH) or isopropyl alcohol (i-PrOH) [19]. Polyetherimide (Ultem® 1000) was selected as a high performance engineering amorphous thermoplastic polymer to impart strength and toughness with excellent thermal, mechanical and electrical properties [20]. The polysulfone Udel® P-1700 NT LCD was also selected as it provides very good control of pore size and pore size distribution, high membrane strength, good film-forming properties, good resistance to degradation, low cost and low content of cyclic dimer that may precipitate in the polymeric solutions. Both PEI and PSF have ether groups and an electron acceptor moiety such as phephalimide or sulphone. The two protic non-solvents were selected because they act as diluents for forming the porous structure [21] and as a proton donor to enhance BMI polymerization. In addition to these criteria, i-PrOH and EtOH have a different polarity and dielectric constant that may influence mechanism of BMI polymerization and semi-IPNs formation. The weight ratio of BMI to PEI or PSF in all formulations was kept below 11% because a higher concentration led to a brittle IPN material. The weight ratio of
the non-solvent was kept at one-fifth of NMP weight so that the final solution was close to its clouding point [19]. Based on these criteria nine different polymer solutions with compositions shown in Table 1 were prepared by mixing PEI or PSF and BMI in NMP. After PEI or PSF and BMI were completely dissolved, the non-solvent was mixed in this solution. Mixing of these solutions was continued under ambient light 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 silicone coated membranes were cured in air purging convection oven at 80 °C for one day.

2.3. Permeation test

A cross-flow test cell having an effective permeation surface area of 9.6 cm² was used. Medical air was used at feed pressure of 665 kPa gauge (6.65 × 10⁵ Pa) and the retenate was set at a flow rate of 400 ml/min. Permeate was discharged to atmosphere. The permeate flow rate for two days. Three circular coupons of 7.4 cm diameter were cut from each sample to be used in the permeation test while other pieces were cut from the same sample for characterization.

Membrane samples without coating by silicon rubber were prepared by cutting a strip from membrane, freezing in liquid nitrogen and fracturing to obtain a representative sample. They were mounted on carbon tape at 45° SEM stubs and sputter coated with gold. Photographs were taken at magnifications of 500, 2000 or 5000 times.

2.5. Thermal analysis

A TA instrument model 2920 Modulated differential scanning calorimetry, DSC V2.6 A, calibrated with Indium at 156.5985 °C and with Tin at 231.93 °C was used to measure the glass transition temperature (Tg). Under a nitrogen atmosphere, polymer samples were ramped to 50 °C at 1 °C/min, held isothermally for 10 min and then reheated to 350 °C at 10 °C/min. The Tg was calculated at the point of inflection of the DSC curve. A TA instruments, Model AutoTGA 2950HR V5.4A analyzer was used for measuring the degradation temperatures by thermogravimetric analysis (TGA). Under a nitrogen atmosphere, polymer samples were ramped to 40 °C at 1 °C/min, held isothermally for 60 min, and then heated to 800 °C at 10 °C/min.

3. Results and discussion

Surface of each membrane before silicon rubber coating was examined using a Leica DMRXE optical microscope (Leica Microsystems Wetzlar GmbH, Wetzlar, Germany) equipped for bright-/dark-field illumination. Microscope was set at reflected light mode using the reflected light bright-/dark-field objectives (Delta optics PL Fluotar series) at standard magnification of 50, 100, 200, 500 and 1000. Images were adjusted to be on a part of the surface that showed a thermoset/thermoplastic phase separation. These images were captured for magnification of 1000 times with Orthomat® E camera mounted on the microscope using Polaroid 72 black and white instant sheet films (ISO-400). An image of the microscope scale (graticule) was captured under identical conditions to scale all produced images.

Membrane samples without coating by silicon rubber were also examined by scanning electron microscopy (SEM) using JEOL 840A equipment at an accelerating voltage of 10 kV. Samples were prepared by cutting a strip from membrane, freezing in liquid nitrogen and fracturing to obtain a representative sample. They were mounted on carbon tape at 45° SEM stubs and sputter coated with gold. Photographs were taken at magnifications of 500, 2000 or 5000 times.

Table 1

<table>
<thead>
<tr>
<th>Samples</th>
<th>Composition (%, w/w) of the total solution</th>
<th>PSF</th>
<th>BMI</th>
<th>NMP</th>
<th>EtOH</th>
<th>i-PrOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-EtOH</td>
<td>19.5</td>
<td>67.2</td>
<td>0</td>
<td>13.3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>PEI-BMI-EtOH</td>
<td>17.6</td>
<td>67.2</td>
<td>1.9</td>
<td>13.3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>PEI-BMI-i-PrOH</td>
<td>28</td>
<td>60</td>
<td>1</td>
<td>11</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>PEI-BMI-EtOH</td>
<td>17.6</td>
<td>67.2</td>
<td>1.9</td>
<td>13.3</td>
<td>0</td>
<td></td>
</tr>
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<td>0</td>
<td>0</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
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<td>19.5</td>
<td>67.2</td>
<td>0</td>
<td>0</td>
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</tbody>
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2.4. Microscopy studies

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brightest color. After a long time (more than 80 days) both solutions started to be cloudy, less transparent with a decrease in the brightness and changing to a more brownish color. Phase separation was clearly observed through precipitation of one of the polymeric phases. This phenomenon is well known in literature for the phase separation of thermoset/thermoplastic polymeric blends particularly for BMI/PSF blends [14,22]. Through preliminary experiments, we found that membranes formed from those solutions, which had large separated phases did not have suitable gas separations characteristics.

Similar observations were made when isopropanol was used as a proton donor instead of EtOH. However, an increase in the brightness of yellow color was obtained. This may indicate that polymerization mechanism is different because it is known that purple or red color is obtained upon anionic polymerization of BMI that usually leads to a lower molecular weight polymer [23]. Absence of red or purple color in the case of isopropanol indicates that BMI probably underwent a free radical polymerization as reported elsewhere [24]. The chemical structures of modified BMI-PEI as well as modified BMI-PSF were analyzed by ATR-FTIR and XPS spectroscopy as found elsewhere [25,26].

In order to have a better understanding, additional experiments were carried out to polymerize BMI at the same conditions as discussed above but in the absence of PEI or PSF. There was no color change in the solution even after 100 days. This indicates that PEI or PSF in NMP has an important catalysis role in accelerating BMI polymerization. The catalysis role of PEI or PSF could be similar to the role of nano-crystalline titania [27]. We also found that polymerization of BMI at the above conditions did not occur in the absence of alcohol indicating the vital role of this proton donor in acceleration of BMI polymerization. As the above process required a long time, accelerating polymerization of BMI is necessary for economic reason. It is worth noting that the rate of polymerization of BMI is dependent on BMI and polymer concentrations as well as on solution viscosity and speed of mixing. Experimentally, we observe the change in the color would be faster for lower BMI concentration, lower viscosity and higher speed of mixing. We also found that increasing temperature to 60 °C during solution mixing lead to a decrease in the required time to change color to red (crimson) from 30 days to a less than 24 h. A significant decrease in solution viscosity and an improvement in the mixing were achieved when temperature was increased to 60 °C during solution mixing. It is worth noting that with increasing polymer concentration in the casting solution, it was possible to increase membrane gas selectivity but at the expense of membrane productivity.

3.1. Phase structure and morphology analysis

Surfaces of all membrane samples were examined by optical microscopy. Phase separation was not observed in PEI-BMI or PSF-BMI semi-IPN membranes that were cast after 30 days in the case of PEI and after 40 days for PSF. The appearance of the surface of these membranes was similar to surfaces of membranes prepared from PEI or PSF without adding BMI. Membranes containing BMI and cast after 80 days using PEI or after 100 days for PSF had brown to orange-red dispersed phase in some areas that represented thermoset BMI phase within a large area of continuous PEI or PSF phase. The dispersed phase might have circular or cylindrical shape and some of them could be seen with size that may exceed 10 μm (Fig. 1). The interface between two phases was observed to be more clear in membranes formed from isopropanol containing solution (Fig. 1(b and d)) while with ethanol (Fig. 1(a and c)) a diffused interface was observed. The dispersed phase in the PSF-based membrane prepared from solutions containing isopropanol (Fig. 1(d)) was shown to have a larger size than other membranes shown in Fig. 1(a-c). The phenomenon of phase separation influenced the membrane performance for gas separation as found through our preliminary experiments. We believe that polymeric solutions should be coagulated before the stage of significant thermoset/thermoplastic phase separation in order to form gas separation membranes.

Morphology of membranes was examined by scanning electron microscopy (SEM). The morphology of membranes prepared from solutions containing isopropanol was not significantly different from those obtained by using ethanol. Therefore, morphology analysis was conducted for only membranes produced from solutions containing ethanol. Membranes were labeled according to their solution composition. Symbols S and L refer to membranes coagulated after 30 and 60 days, respectively, for PEI and after 40 and 80 days, respectively, for PSF. SEM micrographs of cross-sections of PEI-EtOH, PEI-BMI-EtOH, PEI-BMI-EtOH-S and L are shown in Fig. 2. It was clear from micrographs (a) and (b) that the fingers penetrated along cross-section with changing direction between parallel and perpendicular to membrane surface. The beginning and end of these fingers were located at a distance far from both membrane surfaces and could be expressed, respectively, by top and bottom layers that were not penetrated by finger voids. The top layer thickness became smaller and the finger became straightforward and perpendicular to membrane surface as shown in micrographs (c) and (d) for membranes containing BMI. Although in both cases these fingers were well-developed but PEI-BMI-EtOH-L membrane (Fig. 2(d)) had slightly smaller top layer thickness and its finger started with a smaller diameter than those in PEI-BMI-EtOH-S (Fig. 2(c)). It was also clear that the diameter of the finger in the PEI-BMI-EtOH-L gradually increased towards the bottom of the membrane (Fig. 2(d)) while these fingers had approximately the same diameter along the cross-section of PEI-BMI-EtOH-S membrane (Fig. 2(c)). Although it was hard to see phase separation in L membranes within the resolution of optical microscope, the thermoset microphase domain might be larger than that in S membranes and could be responsible for a change in membrane morphology. The top homogenous layer thickness of PEI-EtOH membranes was significantly larger than 10 μm while it did not exceed 10 μm for PEI-BMI-EtOH-L membranes as shown in micrographs (e) and (f) in Fig. 2. We will discuss the correlation between membrane morphology and superior gas permeance for PEI-BMI-EtOH-L later on.

Scanning electron micrographs of PSF-EtOH and PSF-BMI-EtOH-L membranes are shown in Fig. 3. It is clear that in the absence of BMI, morphology of PSF-EtOH was different from that of PEI-EtOH membranes shown in Fig. 2. In contrast to
PEI, PSF had the ability to form a very thin top layer as shown in micrograph (a) of Fig. 3. A gradual increase in finger size was obtained for all membranes containing PSF; the penetration did not reach the bottom of the membrane and the thickness of bottom layer is significantly higher than 10 μm. For membranes containing BMI as shown in micrograph (b) of Fig. 3, the penetration of fingers might have reached the membrane bottom and the thickness of the bottom layer became very small. Using 5000 magnification the thickness of the top layer did not exceed 1 μm as shown in micrographs (c) and (d) in Fig. 3. It is hard to see significant differences in the top part of all membranes containing PSF as shown in Fig. 3. From these observations, we might expect gas permeance values for PSF-BMI-EtOH-L were higher than those for other PSF membranes which might be attributed to a thinner bottom layer. These results indicated that using PEI-BMI or PSF-BMI semi-IPNs as membrane materials led to a different membrane phase inversion and membrane morphology compared to using PEI or PSF alone as shown in Figs. 2 and 3.

3.2. Membrane thermal stability

Thermal stability of PEI, PSF and their BMI semi-IPNs was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Glass transition temperatures of PEI, PSF and their BMI semi-IPNs membranes were measured by DSC as listed in Table 2. The glass transition temperature \( T_g \) of PEI-BMI-EtOH-S membrane was found to be 199.7 °C, which was lower than \( T_g \) of PEI-EtOH by 13.7 °C. This could be attributed to weaker interactions between the thermoset BMI and thermoplastic PEI phases in the semi-IPN system than the inter chain forces in the individual polymers as reported elsewhere [28]. The large interface area between BMI and PEI was probably attributed to the small size of low-molecular-weight BMI oligomers. These oligomers might easily plasticize the imide-based polymer (PEI) caused by their higher dilution in the polymeric matrix as illustrated elsewhere [16, 29]. Similar observation was reported for the decrease of \( T_g \) of polyimide/BMI semi-IPN by 10 °C compared to free polyimides. This may also be accompanied by a decrease in the softening point \( T_{sp} \) of BMI phase by 10–60 °C compared to the neat BMI network [29]. However, as the BMI dispersed phase grew, a lower interfacial area and plasticizing effect might reduce the mutual influences Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_g ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-EtOH</td>
<td>213.4</td>
</tr>
<tr>
<td>PEI-BMI-EtOH-S</td>
<td>199.7</td>
</tr>
<tr>
<td>PEI-BMI-EtOH-L</td>
<td>216.1</td>
</tr>
<tr>
<td>PSF-EtOH</td>
<td>185.1</td>
</tr>
<tr>
<td>PSF-BMI-EtOH-S</td>
<td>182.9</td>
</tr>
<tr>
<td>PSF-BMI-EtOH-L</td>
<td>188.9</td>
</tr>
</tbody>
</table>
Fig. 2. SEM micrographs for the cross-section of membranes at 500 times magnification: (a and b) PEI-EtOH at different cross-section locations, (c) PEI-BMI-EtOH-S and (d) PEI-BMI-EtOH-L, in addition to 2000 times magnification: (e) PEI-EtOH and (f) PEI-BMI-EtOH-L.

and magnitude of change in $T_g$ of two phases. The $T_g$ of neat BMI resin was reported to be 399 $^\circ$C [29]. The $T_g$ of the PEI-BMI-EtOH-L membranes was measured to be 216.1 $^\circ$C, which was slightly higher (by 2.7 $^\circ$C) than the $T_g$ of PEI-EtOH. This might be attributed to the formation of a rigid microphase of BMI resin with a higher softening point, $T_g$, than the $T_g$ of PEI that might restrict chain mobility of PEI. A similar explanation might also be given for PSF-BMI semi-IPN membranes. The measured $T_g$ of PSF-EtOH was 185.1 $^\circ$C, which was equal to the $T_g$ of this polymer as reported elsewhere [14,30]. The $T_g$ of PSF-BMI-EtOH-S was measured to be 182.9 $^\circ$C, which was lower than the $T_g$ of PSF by only 2.2 $^\circ$C. Considering that the amount of this decrease was lower than that for PEI-BMI-EtOH-S (i.e. 13.7 $^\circ$C) it indicates that plasticizing effect of BMI on PSF was less than that on PEI. On the other hand, the $T_g$ of PSF-BMI-EtOH-L was measured to be 188.9 $^\circ$C, which was higher than the neat PSF by 3.8 $^\circ$C. This increase in $T_g$ was slightly higher than that in the case of PEI and might be attributed to same reasons as for PEI. It was clear that the $T_g$ of base polymer could be improved through synthesis of PEI-BMI and PSF-BMI semi-IPN. This improvement might depend on the formation of rigid microphase dispersed in a base polymer such as PEI or PSF. The size of this microphase might have an important role on the properties of thermoset/thermoplastic composites. In case microphase comprised a low-molecular-weight BMI oligomer, it might act as a plasticizer that led to a decrease in the $T_g$, however if the microphase was large enough to form rigid domain, it might act as reinforcing particle that led to increase $T_g$ compare to $T_g$ of base polymer. In both cases, the microphase domain size should not exceed the resolution of optical microscope in order to maintain interpenetrating interactions of different components within the network. Also, a larger size for the thermoset phase would lead to a traditional polymer blend losing the beneficial features of IPN.

Thermal stability and heat resistances of PEI, PSF and their BMI semi-IPNs membranes were measured by TGA as shown in Fig. 4 for PEI as a base polymer and in Fig. 5 for PSF as a base polymer. From these figures, we will evaluate the thermal resistance of membranes through degradation temperatures at 2%, 10%, 20% and 50% weight loss and residual weights at 800 $^\circ$C or temperature at complete degradation if it was less than 800 $^\circ$C as summarized in Table 3. As shown in Fig. 4, the
thermal degradation of PEI-EtOH membranes took place in two stages that agrees well with the TGA obtained for polyetherimide in nitrogen illustrated elsewhere [31]. For PEI-BMI-EtOH-S membrane, the thermal degradation weight loss of the first stage was at lower temperatures than that for PEI-EtOH membrane while in the second stage they were located at higher temperatures. For instance as seen in Table 3, at 2% weight loss, the degradation temperature was lower by 75 °C while in the second stage and at 20% loss, it was higher by 5 °C. A relatively low thermal stability of BMI/polyimides semi-IPN compared to the free linear polyimide was attributed to the less stable polymerized maleimide structures as illustrated and reported elsewhere [29]. The increase in the thermal stability at higher temperatures within the second degradation stage was attributed to the BMI network as reported elsewhere [32]. The thermal degradation of PEI-BMI-EtOH-L membrane appeared at much lower temperatures compared to the other two membranes within the total range of the two stages (Fig. 4). The lower degradation temperature of this membrane might be attributed to the chemical structure of composite material which contained amic acid groups resulted from imide cleavage, substituted ethoxy moieties and complex NMP as was determined by a separate FTIR
other hand, the decomposition of ethoxy group may also occur and XPS analysis for PEI-BMI-EtOH-L membrane [25]. A ta

<table>
<thead>
<tr>
<th>Sample</th>
<th>Degradation temperatures (°C) at different percent weight loss</th>
<th>Residue at 800 °C or temperatures at residue of 0%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2%</td>
<td>10%</td>
</tr>
<tr>
<td>PEI-EtOH</td>
<td>449</td>
<td>510</td>
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<tr>
<td>PEI-BMI-EtOH-H</td>
<td>574</td>
<td>589</td>
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<td>PEI-BMI-EtOH-L</td>
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<td>467</td>
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<tr>
<td>PSF-EtOH</td>
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<td>504</td>
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<tr>
<td>PSF-BMI-EtOH-H</td>
<td>403</td>
<td>479</td>
</tr>
<tr>
<td>PSF-BMI-EtOH-L</td>
<td>361</td>
<td>472</td>
</tr>
</tbody>
</table>

Thermal stability of PEI, PSF and their BMI semi-IPNs membranes as measured by TGA at heating rate 10 °C/min in nitrogen

Table 3

was clear from Table 3 that PEI-BMI-EtOH-L membrane had a higher degradation temperatures within the first stage as seen at 2% and 10% weight loss that might be attributed to loss of solvent as well as water resulting from imidization of amic acid as was illustrated to be in the range of 200–325 °C and also reported elsewhere [33]. A polymer containing amide group is usually less thermally stable than the one that has same structure but containing imide instead of amide group [34]. On the other hand, the decomposition of ethoxy group may also occur at 250–350 °C [35] or at a maximum temperature of 270 °C [36]. It was clear from Table 3 that PEI-BMI-EtOH-L membrane had a better thermal resistance than PSF-BMI semi-IPN membranes that might be attributed to the presence of less stable polymeric BMI as illustrated elsewhere [14]. In the second stage, thermal degradation was slowed for semi-IPN membranes between 530 and 580 °C and then a higher rate of degradation than that for a base PSF membrane was observed. The differences between the degradation temperatures of PSF-BMI-EtOH-S and PSF-BMI-EtOH-L at 2% weight loss as shown in Table 3 was 42 °C, which indicated that BMI microphase growth had smaller impact on the IPN structure in the case of PSF as a base polymer than the case of PEI where this difference was 125 °C. This also agreed well with the larger difference in $T_d$ values between S and L membranes in case of PEI compared to those of PSF as discussed above. Comparing both base polymers, PSF-EtOH membrane had higher degradation temperatures within the first stage as seen at 2% and 10% weight loss in Table 3 but lower degradation temperatures than PEI-EtOH membrane within the second stage as seen at 20% and 50% weight loss. High thermal stability of PSF polymer within the first stage could be attributed to its strong chemical moieties such as aromatic, sulfone and ether as illustrated elsewhere [37] while it was lower for imide-based polymer particularly for incomplete imidization or hydrolysis imide that condensed within this first thermal degradation stage. However, in the second stage, rearrangement, condensation and cyclization products from imide-based polymer, such as naphthalene, anthracene and phenanthrene might be responsible for its higher degradation temperatures [38] compared to PSF-based polymer. For this reason, the residual weight at 800 °C for PEI was higher than that of PSF base membranes (Table 3). For PSF-BMI-EtOH S and L, there was no residue at temperatures 795 and 797 °C, respectively. The decrease in these temperatures for complete degradation was due to the lower stability of polymerized BMI and perhaps to the relatively low molecular weight of the BMI resin. The influence of molecular weight and its distribution on thermal stability of polymers was illustrated elsewhere [39]. On the other hand, it was interesting to see that PEI-BMI-EtOH-S membrane had the same residue of 19% at 800 °C as the one without BMI although the polymerization time of BMI was shorter than that for PEI-BMI-EtOH-L membrane. It appears that the low-molecular-weight BMI oligomer had higher interactions with PEI network that led to plasticization with the ability to condense or possibly crosslink with PEI that maintained a 19% residue at 800 °C. However, growth of BMI resin to a relative larger size as in PEI-BMI-EtOH-L membrane would decrease the area available for interactions with PEI and therefore the thermal degradation of BMI phase might take place independently. The presence of a less stable BMI resin led to a complete thermal degradation of PEI-BMI-EtOH-L membrane (0% residue) at 721 °C.

It was clear from the above results that formation route of PEI or PSF semi-IPN had significant influence on the glass transition temperature as well as the thermal stability of final polymer networks. Both thermoset micro-domain size and the ability to interact with the base thermoplastic polymer in IPN were found to be responsible for changing the composite properties. The PEI-BMI-EtOH-L membrane was suitable for gas separation application at ambient temperature but not at elevated temperature because the onset thermal degradation might occur at temperatures as low as 135 °C (see Fig. 4). Both permeance and selectivity of this membrane for air separation did not vary more than 1% in one month, which indicated a reasonable stability at ambient temperature.

3.3. Gas transport characteristics

The novel PEI-BMI and PSF-BMI semi-IPN membranes were characterized by a gas permeation test. Gas permeance and $O_2/N_2$ selectivity for separation of oxygen from air were shown in Table 4 and compared with literature [40–42]. It is well-known that cost-effective use of membranes would not only depend on membrane selectivity but also on its permeance. As a thick bulk film, material performance could be evaluated by both permeability and selectivity through 1991 Robeson upper bound trade off as shown elsewhere [43]. For homogeneous film, the flux is multiplied by the film thickness so that its permeability value would be independent of the thickness of the tested film. However, in commercial asymmetric membranes, gas permeance (pressure normalized flux) that could be increased by decreasing the thickness of the selective skin layer and the gas transport resistance of the sub-layer is an important factor that should be considered. Unfortunately, as the thickness of the selective layer (skin in asymmetric membranes or thin coated layer in compos-
Composite membranes

Polymeric PDMS/MDK [40] – 126 2.0
EC/PAN [40] – 74 3.0
PVTMS [40] – 219 3.5
PSf-BMI-EtOH-S 153 103 2.1
PEI-BMI-EtOH-2-L 9 7.9 7.2
PEI-BMI-EtOH-L 505 341 2.1
PEI-BMI-EtOH-S 126 87 2.2
PEI-EtOH 33 23 2.3

Comparison of permeance (total gas and oxygen) and O2/N2 selectivity for air separation with a reasonable permeance of 9 GPU as shown in Table 4. However, in order to obtain a permeance, which is significantly higher than 9 GPU, it was necessary to use diluted casting solutions. It was an objective in this study to increase membrane permeance as much as possible without decreasing membrane selectivity below the intrinsic selectivity of coating silicon rubber. It is clear from Table 4 that membranes produced from blends of polyethersulfones with aromatic polyimides, polyamides or polyamide-imides reported in a European Patent have an O2/N2 selectivity of 6.9 and O2 permeance of 12 GPU while at O2 permeance of 127 GPU, the O2/N2 selectivity decreased to 1.5 which is less than the intrinsic selectivity of silicon rubber [41].

We used Sylgard 184 silicon rubber coating technique [45], the BMI/PEI semi-IPN membrane showed air separation performance that was comparable to a recent US Patent [42], which was aimed at developing the coating technique but not the membrane materials. The PEI-BMI-EtOH-L membrane has O2 permeance of 341 GPU that is higher than that reported for composite membrane, which was prepared with polysulfone with a Teflon AFTM 1600 coating and dried for 75 s (334 GPU) in the above mentioned US Patent while the O2/N2 selectivity was comparable in two cases. The possibility of having very high O2 permeance for composite membranes was reported to be 826 GPU at similar O2/N2 selectivity (i.e. 2). However, the significant drop of O2 permeance upon increasing drying time from 30 to 75 s might be questionable. It is not clear from this patent if membranes having a high gas permeance are stable and do not need an additional drying. Although, the novel Teflon coating was applied on optimized membranes which is not the subject of this study, the gas permeance for PEI-BMI-EtOH-L was 505 GPU (341 GPU of pure oxygen in the mixture) with a calculated selectivity of 2.1 as shown in Table 4. Both PEI-BMI-EtOH-L and PSF-BMI-EtOH-L membranes had 12–15 times higher permeances, we might rule out the possibility of increasing pore size (or in other words the presence of large defects) especially in the top membrane skin. Therefore, increasing permeance might be attributed to an increase in material microporosity, which resulted from microphase separation or/and a decrease in the thickness of the top and bottom layers. The first possibility could be supported by SEM analysis as discussed in this work. The permeance of PSF-BMI-EtOH-L membrane was higher than that for PEI-BMI-EtOH-L membrane as listed in Table 4 due to PSF’s ability to form ultra-thin skin layer not exceeding 1 μm as shown in micrographs (c) and (d) in Fig. 3.

Table 4. Comparison of permeance (total gas and oxygen) and O2/N2 selectivity for air separation with different membranes

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Total permeance (GPU)</th>
<th>Oxygen permeance (GPU)</th>
<th>O2/N2 Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI-EtOH</td>
<td>33</td>
<td>23</td>
<td>2.3</td>
</tr>
<tr>
<td>PEI-BMI-EtOH-L</td>
<td>126</td>
<td>87</td>
<td>2.2</td>
</tr>
<tr>
<td>PEI-BMI-EtOH-L</td>
<td>9</td>
<td>7.9</td>
<td>7.2</td>
</tr>
<tr>
<td>PEI-EtOH</td>
<td>44</td>
<td>29</td>
<td>1.9</td>
</tr>
<tr>
<td>PEI-BMI-EtOH-S</td>
<td>153</td>
<td>103</td>
<td>2.1</td>
</tr>
<tr>
<td>PSE-BMI-EtOH-L</td>
<td>553</td>
<td>366</td>
<td>1.6</td>
</tr>
<tr>
<td>PVTMS [40]</td>
<td>–</td>
<td>219</td>
<td>3.5</td>
</tr>
<tr>
<td>EC/PAN [40]</td>
<td>–</td>
<td>74</td>
<td>3.0</td>
</tr>
<tr>
<td>PDMS/MDK [40]</td>
<td>–</td>
<td>126</td>
<td>2.0</td>
</tr>
<tr>
<td>Aromatic polyamide [40]</td>
<td>–</td>
<td>24</td>
<td>3.0</td>
</tr>
<tr>
<td>Polymeric</td>
<td>–</td>
<td>12</td>
<td>6.9</td>
</tr>
<tr>
<td>blends</td>
<td>–</td>
<td>121</td>
<td>2.1</td>
</tr>
<tr>
<td>membrane²</td>
<td>–</td>
<td>127</td>
<td>1.5</td>
</tr>
<tr>
<td>Composite membrane³</td>
<td>–</td>
<td>266-426</td>
<td>2.0-2.1</td>
</tr>
<tr>
<td>Composite membrane³</td>
<td>–</td>
<td>143-334</td>
<td>2.2-2.3</td>
</tr>
</tbody>
</table>

² Blends of polyethersulfones with aromatic polyimides, polyamides or polyamide-imides.
³ Polyether sulfone membrane coated with Teflon polymer.

ite membranes) decreases, the influence of material defects on gas selectivity becomes more prominent.

The intrinsic O2/N2 selectivity and O2 permeability values for a dense PEI film, at 35 °C were 57.0 × 10−16 and 3.0 × 10−18 m2 s−1 Pa−1 and (7.6 and 0.4 Barrer) [44] whereas for a dense polysulfone film these values were 45.0 × 10−16 and 9.0006 × 10−18 m2 s−1 Pa−1 (781 Barrer). Although these numbers might provide an idea about material performance, the ability to form ultra thin film with less and/or smaller defects and good mechanical properties is a challenge for producing commercial membranes. Belyaev et al. [40] tested four commercial O2-enriched-air membranes PVTMS, EC/PAN, PDMS/MDK and aromatic polyamide. The O2/N2 selectivity and O2 permeance of these commercial membranes were shown in Table 4.

It is clear that the O2/N2 selectivity of polydimethylsiloxane PDMS in commercial membranes is less than its intrinsic selectivity due to challenge in obtaining a homogenous ultra thin layer of silicon rubber. On the other hand, aromatic polyamide membranes have O2/N2 selectivity of 5 but Belyaev et al. [40] confirmed experimentally that this membrane was not economically suitable to produce O2 enriched-air used in coal gasification process.

In one experiment where casting solution (PEI-BMI-EtOH-2) contained higher percentage of PEI than others listed in Table 1. We observed that the PEI-BMI-EtOH-2-L had an O2/N2 selectivity of 7.2, which is close to the intrinsic selectivity of bulk PEI with a reasonable permeance of 9 GPU as shown in
Skin with thickness lower than 1 μm is more prone to defects leading to a decrease in the PSF-BMI/EoH-L selectivity to 1.6 that is lower than the intrinsic selectivity of 2.22 for silicon rubber. It is clear from our data that there is a limitation for increasing membrane permeance and for reducing gas transport resistance of sub-layers. This limitation occurs when the defects become large enough so that it is not possible to be sealed by silicon coating layer.

4. Conclusions

It was concluded that PEI-BMI or PSF-BMI semi-IPN membranes could be synthesized and assembled through in situ polymerization of BMI in PEI/NMP or PSF/NMP solutions at ambient conditions without the need for an initiator. Structure and properties of semi-IPN membranes could be varied by controlling the thermoset BMI micro-domain size interpenetrating within a thermoplastic polymer network. The size of this micro-domain depended on the polymerization time of BMI and the degree of thermoset/thermoplastic phase separation. Furthermore, for preparing suitable material the growth of micro-domain and phase separation should be arrested at an early stage when the phase separation in the casting solution was not visible. Both PEI-BMI and PSF-BMI semi-IPN membranes showed improved structures and morphology compared with the ones obtained from the corresponding base polymer. It was also concluded that the semi-IPN membranes showed an improved glass transition temperature but a decrease in their thermal stability. At ambient temperature, it was possible to increase the permeance of semi-IPN membranes by 12–15 times higher than membranes produced from the corresponding base thermoplastic polymer without sacrificing membrane gas selectivity at the same conditions. These semi-IPN membranes could be used for O₂-enriched-air applications where high selectivity is not required but membrane productivity should be as high as possible.

Acknowledgements

Authors are thankful to Mr. David Kingston and Dr. Jim Tunney for their help with SEM experiments and optical microscopy, respectively.

References


