Transport and thermal properties of poly(ether imide)/acetylene-terminated monomer blends

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Abstract

Blends of an acetylene-terminated monomer (ATM) with a commercially available poly(etherimide) (PEI, Ultem™) were prepared, crosslinked, and characterized. Varying degrees of crosslinking were achieved through thermal treatment at 150–270 °C. Incorporation of the uncrosslinked additive into the PEI resulted in reductions in the glass transition temperature, gas permeabilities and selectivities, and thermal stability. These behavior are consistent with antiplasticization of the polymer host by the ATM additive. Crosslinking of the acetylene-terminated additive led to increases in thermal and chemical stability and improved gas selectivities as compared to the uncrosslinked blend. Gas transport properties are reported as a function of temperature. For the blend composition considered (9 wt% ATM in PEI), the fully crosslinked blend had transport properties which were essentially equivalent to the virgin PEI. Further, processing of the blend could be achieved in the same manner as for the virgin PEI. The resistance of the crosslinked blend to chemical dissolution or swelling was markedly improved as compared to PEI. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Crosslinking; Gas and vapor permeation; Polyimide

1. Introduction

Polymers employed for the separation of gases using membrane technology have not required significant chemical resistant. Polysulfone, one of the most widely used materials, is soluble in a wide range of organic solvents. Recently, chemically and thermally resistant polyimides, polyetherketones, and polyethersulfones have been developed and characterized [1–3]. These polymers have an attractive combination of properties; yet, they are difficult to process. Polyimides, for example, are frequently processed from the more soluble polyamic acid form and subsequently converted to the desired polyimide by thermal treatment. This conversion leads to the evolution of water, which increases the bulk density, causes bulk shrinkage, and can produce defects in the materials [4].

Manipulation of the chemical structure has resulted in a few polyimides that are solution processible in the fully imidized form. Use of these materials could exploit many of the advantages of polyimides with more facile processing. The aromatic poly(ether imide), Ultem™, is such a material. Considerable
research has been reported on the development of membranes for the separation of gases and liquids using Ultem™ for example, [5,6]. Ultem™ has separation selectivities that are sufficiently high for the majority of applications considered. Its use is limited by (a) low fluxes, (b) plasticization at high pressures (especially for carbon dioxide/methane separations), and (c) limited resistance to organics. The incorporation of an ATM into the blend provides an opportunity to stabilize this material through a solid-state crosslinking reaction. Such stabilization may allow for the use of thinner polymer layers in the ultimate membranes. Without stabilization, thin polymer layers are more susceptible to chemical attack. With a stabilizing additive, a thinner layer may provide sufficient chemical resistance while simultaneously achieving higher transport rates.

The curing behavior and the resultant properties of a series of blends of Ultem™ with low molecular weight acetylene-terminated imides (ATI) have been reported. Mercer et al. [7] have shown that blends containing 20 wt% ATI/80 wt% Ultem™ were readily processed either from solution or the melt. The blends could be thermally crosslinked at approximately 250°C. Crosslinking yielded tough, flexible films with improved solvent resistance and high-temperature mechanical properties. Choudhary and Pearce [8] examined the thermal reactivity of blends of Ultem™ with similar ATIs. They demonstrated that the solvent resistance of the crosslinked blends is markedly improved when compared to that of the virgin Ultem™. No transport data were reported for these blends.

This research examines the possibility of employing these stable polymer blends for membrane applications. The gas transport, chemical resistance, and bulk properties of a poly(ether imide)/ATM blends are examined as a function of crosslinking.

2. Background

In a previous study, we evaluated the influence of blending and crosslinking of low molecular weight acetylene–terminated diacetylene–functionalized oligomers (ATDFO) with a nonreactive host polyimide [9]. These oligomers differ from the simple ATMs reported in the literature in that they also contain reactive diacetylene groups in the oligomer backbone. Thus, two types of reactivity were possible; one through the internal diacetylene groups, and the other through the terminal acetylenes. The blends of the acetylene–terminated diacetylene–functionalized oligomers exhibited the following [9]:

- Increased chemical resistance with increasing content of the crosslinkable component.
- Decreased permeabilities and increased selectivities with increasing crosslinkable component content.
- For diacetylene-containing oligomer contents of 9 wt% and greater, dissolution in common organic solvents was not possible, although swelling was observed.
- Blends with greater than 35 wt% oligomer had insufficient cohesive strengths to be film forming.
- Crosslinking the blend materials resulted in enhanced chemical resistance and improved thermal stability with no measurable change in the transport of gases through the matrix.

Based on these observations, a substantial improvement in chemical resistance with limited reduction in permeability was achieved for blends with approximately 9 wt% crosslinkable component.

The use of ATMs instead of the low molecular weight oligomers (ATDFOs) has at least two potential advantages. First, production of the ATMs requires fewer synthetic steps than production of the ATDFOs. Second, the ATMs should produce miscible blends with a wider variety of polymers than the higher molecular weight ATDFOs. Finally, by evaluating the behavior of these blends which have a much more limited number of possible reactions, we can gain further insight into the reactions occurring and improved future polymeric system design.

3. Experimental

Blends of a commercially available polyimide with a crosslinkable ATM are prepared and evaluated. A blend composition of 9 wt% ATM and the balance poly(ether imide) was employed in the current study. The crosslink density was varied by control of the thermal annealing process used for crosslinking.
3.1. Materials

Poly(ether imide) (PEI, Ultem™ 1000, Fig. 1) was supplied in pellet form by the General Electric. PEI was dried under vacuum for 24 h at 80°C to remove moisture prior to use.

The crosslinkable acetylene-terminated monomer (ATM) used in this study was \(\text{N},\text{N'}\)-dipropargyl(4,4'-hexafluoroisopropylidene)bisphthalimide(1,1-6FDA–ATM, Fig. 2). This compound was prepared by reaction of propargyl amine with 4,4'-hexafluoro-isopropylidene bis(phthalic anhydride) (6FDA). The details of this synthesis have been provided [10]. The monomer, in the form of a white powder, was dried under vacuum at 40°C to a constant weight.

The 1,1-6FDA–ATM is soluble in a number of chlorinated and polar solvents including methylene chloride, chloroform, 1,1,2,2-tetrachloroethane, acetone, \(\text{N}\)-methyl-2-pyrrolidinone, dimethylacetamide, and dimethylsulfoxide. It is insoluble in alcohols and apolar hydrocarbons.

Pressurized gases were obtained from Air Products and used as received. Gas purity is as follows: helium, 99.997%; hydrogen, 99.995%; carbon dioxide, 99.0%; oxygen, 99.8%; nitrogen 99.999%; and methane, 99.0%.

3.2. Sample preparation and curing

Thick, isotropic films of pure PEI and a 9 wt% 1,1-6FDA–ATM/91 wt% PEI blend were cast. Solutions of the dried polymer or polymer/ATM mixture and methylene chloride were prepared and filtered (0.45 \(\mu\)m, Teflon) directly into a casting ring assembly maintained in a solvent-enriched atmosphere. Samples were allowed to dry in the solvent-enriched environment for approximately 6 h at which time they were removed to laboratory air and subsequently removed from the casting ring assembly by immersion in water. The materials were further dried under vacuum (see Table 1). The drying conditions were controlled to achieve both solvent removal and cross-linking. The “uncured” blend was dried at 100°C for 24 h to ensure removal of the casting solvents without activating the crosslinking reaction (see Fig. 3). The blend materials were dried at intermediate conditions which ensured solvent removal and varied the degree of crosslinking achieved. The thermal history of the blends were equivalent with the exception of the ultimate thermal cycle. Thus, internal comparison among the blend samples should be readily achieved.

The pure PEI was dried at a temperature approximately 10°C above its glass transition temperature. This removed all casting solvent and erased all prior thermal history, minimizing the impact of casting conditions on the measured material properties.

Sample thicknesses were on the order of 25–60 \(\mu\)m.

3.3. Characterization

Differential scanning calorimetry (DSC) was performed by heating samples at a rate of 15°C/min. from
20°C to 100°C. The sample was held at 100°C for 15 min to evaporate any moisture present. The sample was further heated from 100°C to 500°C at 15°C/min. DSC experiments were performed under a nitrogen purge of approximately 40 ml/min.

Thermogravimetric analyses (TGA) were conducted on a Setaram TG 111. TGA was performed on samples under inert (nitrogen) and oxidizing (air) atmospheres. The temperature profile for TGA experiments was identical to that employed for DSC. Purge gas rate was approximately 250 ml/min.

Dynamic mechanical thermal analysis (DMTA) measurements were conducted on a Seiko DMS 210 tension module at a frequency of 1 Hz over the temperature range of 0–480°C. A nitrogen purge of 40 ml/min was employed for all measurements.

Permeation measurements were made using a constant-volume/variable-pressure apparatus [11] at 35°C. Permeabilities are reported at 10 atmosphere upstream pressure with a permeate pressure of less than 10 torr. The error of the permeability coefficient associated with the system was determined to be ±11% for the slowest gas. The largest sources of error were the measurement of the sample thickness and area. While thickness and area directly impact the measured permeability, they do not influence the selectivities reported here. Thus, the error associated with the selectivities is approximately ±2%.

The influence of temperature on the transport rates over the range 25–250°C is also reported. These measurements were made in a permeation apparatus of the same design in which the sample test cell was maintained in a heated oven.

The bulk densities of the polymer films were measured by flotation in a density gradient column at 23±0.1°C. Aqueous calcium nitrate solutions of varying density were employed.

4. Results

4.1. Density

The densities of the PEI and the blends are reported in Table 2. The fractional free volume of each material was calculated using the method of Lee [12,13]. A weight-averaged method was used for blend samples. No attempt to account for differences in chemical structure as a result of crosslinking was made. Densities increased when the additive was added to the original PEI. Crosslinking further increased the measured densities and decreased the fractional free volumes.
4.2. DSC

The glass transition temperature of the uncured and cured blends, and pure PEI as measured by DSC are presented in Table 2. The DSC exotherms of the blend components and blends cured under different conditions are shown in Fig. 3. The virgin PEI shows a distinct glass transition temperature at approximately 220°C. It has no other significant features. The virgin ATM shows a broad exotherm with an onset temperature of approximately 250°C. This exotherm has been attributed to an acetylenic crosslinking reaction. The uncured blend shows a glass transition temperature at approximately 150°C and a broad exotherm over the range from 200°C to at least 400°C. Increasing the curing temperature to 150°C results in an increase in the glass transition temperature (to 190°C) and a reduction in the crosslinking exotherm with an onset temperature of approximately 280°C. The blend cured at 270°C exhibits a subtle glass transition temperature at 210°C and no other distinct features. The energy released upon heating (as integrated from 185°C to 385°C) for each material is also presented in Table 2.

The extent of reaction can be roughly correlated with the residual exotherm [14]. If the “uncured” blend is deemed to be completely unreacted, then, the extent of reaction at each curing condition can be calculated from the ratio of the residual exotherm measured by DSC to the original exotherm of the “uncured” blend. The calculated extents of reaction are listed in Table 2. These values show that the material cured at 150°C can be considered only partially reacted while those cured at 230°C and 270°C are essentially completely reacted.

4.3. TGA

The PEI homopolymer was considerably more thermally stable than either the 1,1-6FDA–ATM or blends of these components. The behavior of these materials when exposed to both nitrogen and air atmospheres is detailed in Table 3. Following curing, the blend material was nearly as stable as the pure PEI homopolymer.

The ATM containing materials appear to be slightly less stable in the presence of air than nitrogen (as is

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature at 2% weight loss (°C)</th>
<th>Temperature at 5% weight loss (°C)</th>
<th>Residual mass at 485°C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 cured PEI/1,1-6FDA–ATM blend</td>
<td>255</td>
<td>450</td>
<td>93</td>
</tr>
<tr>
<td>230 cured PEI/1,1-6FDA–ATM blend</td>
<td>375</td>
<td>450</td>
<td>93</td>
</tr>
<tr>
<td>270 cured PEI/1,1-6FDA–ATM blend</td>
<td>460</td>
<td>&gt;485</td>
<td>97</td>
</tr>
<tr>
<td>Pure PEI film</td>
<td>475</td>
<td>&gt;485</td>
<td>97</td>
</tr>
<tr>
<td>Pure 1,1-6FDA–ATM</td>
<td>175</td>
<td>440</td>
<td>81</td>
</tr>
</tbody>
</table>

*not measured

Table 2
Physical properties of the polymers evaluated

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm³)</th>
<th>Calculated fractional free volume</th>
<th>Tg as measured by DSC (°C)</th>
<th>Tg as measured by DMTA (°C)</th>
<th>Heat releaseda (kJ/kg)</th>
<th>Extent of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEI</td>
<td>1.287</td>
<td>0.140</td>
<td>218</td>
<td>220</td>
<td>0</td>
<td>Not applicable</td>
</tr>
<tr>
<td>1,1 6FDA–ATM b</td>
<td>b</td>
<td>b</td>
<td>150</td>
<td>208</td>
<td>43.6</td>
<td>34</td>
</tr>
<tr>
<td>Blend: uncured</td>
<td>1.309</td>
<td>0.130</td>
<td>190</td>
<td>208</td>
<td>43.6</td>
<td>34</td>
</tr>
<tr>
<td>Blend: 150 cure</td>
<td>1.311</td>
<td>0.129</td>
<td>208</td>
<td>225</td>
<td>4.2</td>
<td>93</td>
</tr>
<tr>
<td>Blend: 270 cure</td>
<td>1.313</td>
<td>0.127</td>
<td>210</td>
<td>230</td>
<td>2.3</td>
<td>96</td>
</tr>
<tr>
<td>Blend: 9 wt% 1,1-6FDA–ATM/91 wt% PEI.</td>
<td>1,1-6FDA–ATM</td>
<td>bb</td>
<td>bb</td>
<td>b</td>
<td>315.8</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Blend: 9 wt% 1,1-6FDA–ATM</td>
<td>1.160</td>
<td>0.280</td>
<td>218</td>
<td>220</td>
<td>0</td>
<td>Not applicable</td>
</tr>
</tbody>
</table>

NOT: Exotherm integrated from 185°C to 385°C.

bNot measured.

Table 3
Stability of PEI/1,1-6FDA–ATM blends to temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature at 2% weight loss (°C)</th>
<th>Temperature at 5% weight loss (°C)</th>
<th>Residual mass at 485°C (%)</th>
</tr>
</thead>
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<td>255</td>
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<td>175</td>
<td>440</td>
<td>81</td>
</tr>
</tbody>
</table>
indicated by the lower temperatures required to achieve 2% and 5% weight loss). However, the differences are not large, and the residual mass at 485 °C is similar for both gases.

4.4. DMTA

The loss factor, tan delta, for each of the blend materials is shown in Fig. 4. DMTA was measured over the range from 0 °C to 480 °C. Only a single transition, the glass transition, was observed for each sample. Therefore, we have limited the temperature scale on Fig. 4 so that we might focus on the details of the influence of crosslinking on these peaks.

Examination of Fig. 4 indicates that the shape and location of the loss factor, tan delta, is a function of the cure temperature employed. As the temperature used to cure the blend samples increased, the tan delta peak decreases in height and shifts to higher temperature. The decrease in mechanical loss (represented by the decrease in tan delta) and the corresponding increase in T_g are consistent with an increase in crosslinking as the cure temperature is increased.

The relative order of the glass transition temperatures measured with DMTA is consistent with that measured by DSC. However, slight differences in the absolute values are observed. Such differences may be attributed to the different rates at which the glass transition was approached in these analyses. The numerical values of the T_g's of these materials are reported in Table 2.

While the thermal transitions of these polyimides are fairly subtle in the DSC, they are clear in the DMTA spectra. The presence of a single glass transition temperature (a single tan delta peak) is indicative of a homogeneous mixture of the ATM in the PEI matrix. Such homogeneity on mixing is to be expected for the mixture of these low molecular weight additives to a high molecular weight polymer.

4.5. Transport

4.5.1. Room temperature behavior

The permeabilities of gases through pure PEI, and cured blends of PEI and ATM are presented in Fig. 5. The values reported were measured at 10 atm feed pressure and 35 °C. Fig. 6 details the ideal selectivities for a number of gas pairs at these conditions. The transport properties for the PEI reported here are in acceptable agreement with those reported in the literature [15]. The helium permeability reported in the literature is somewhat higher than that reported here (9.4 vs. 6.1 Barrer). This may be the result of differences in the sample history of these materials. Many studies have shown that the permeabilities measured in polymer films can be dependent upon sample thickness, the solvent used for film casting, and the drying procedure employed [16]. Permeabilities for all other gases are in good agreement.

For a given gas, the permeabilities of the four materials evaluated (PEI and three blends cured at various conditions) are nearly equivalent within the experimental accuracy of the system. Variations in selectivity are obvious. The addition of ATM to the virgin PEI results in a marked reduction in selectivity. Crosslinking counteracts this drop and returns the selectivity to a level equal to or higher than the original PEI.

4.5.2. Influence of temperature

The influence of temperature on the transport of gases through a dense polymeric network has been modeled using an Arrhenius-type relationship:

\[ P_A = P_{0A} \exp\left(-\frac{\Delta E_{pA}}{RT}\right), \]

where \( P_A \) is the permeability of gas A at any temperature, \( P_{0A} \) the pre-exponential factor for gas A,
The activation energy for permeation of gas A, $R$ the gas constant, and $T$ is the absolute temperature. Using this relationship, the activation energy for permeation of each gas was calculated and reported in Table 4. Fig. 7 provides an illustrative example of the influence of temperature on transport of gases through the blend cured at 230°C. The slope of the line represents the activation energy for each gas divided by the gas constant. Although the polymer thickness is known to increase with temperature, the thickness of the polymer at 25°C was used for determination of permeabilities at all temperatures. A more accurate measure of the activation energy for permeation would result if a measure of volume expansion on heating were incorporated.

The blends evaluated here were thermally reactive. While the permeation properties were measured to 300°C, calculation of the activation energies for all blends was limited to 150°C since changes in the material properties can result at higher temperatures due to additional crosslinking.

4.6. Chemical resistance

The resistance of these materials to solvation by methylene chloride was used as a qualitative measure of their chemical resistance. The original PEI (independent of the thermal history) rapidly dissolves in methylene chloride. The uncured blend also undergoes rapid dissolution. Following curing at 270°C, less than 30% of the mass is lost upon exposure to methylene chloride. This apparent steady-state mass loss was reached in a few hours. No additional mass loss was observed over 48 h solvent exposure. Thus, the incorporation of 9 wt% ATM into the polymer blend, followed by thermal crosslinking of these units, results in an improvement in the chemical resistance of the blend.

5. Discussion

The data will be evaluated in light of three comparisons. First, the role of additive addition of PEI will be examined. Here, the properties of the PEI will be compared with those of the uncured or lightly cured
blends. Some characterizations were not completed on the uncured blend because of the possibility of the presence of residual casting solvent in the material. To ensure the removal of this solvent, thermal treatment was employed which simultaneously lightly cross-linked the polymer. Second, the role of crosslinking on blend properties will be examined. Finally, a comparison of the properties of the pure PEI will be made with the fully crosslinked blend.

5.1. Additives in high Mw PEI

The addition of 9 wt% ATM to pure PEI resulted in an homogenous blend with the following properties:

- A glass transition temperature 50°C lower than that of pure PEI.
- Density higher than PEI (1.309 vs. 1.287 g/cm³).
- Reduced fractional free volume (0.130 vs. 0.140).
- Reduced permeation rates.
- Decreased gas selectivities.
- Reduced thermal stability (see Table 3).
- Activation energies for permeation slightly higher than those for PEI.

The reduction in thermal stability may be attributed to the presence of the more reactive aliphatic linkages present in the ATM [10].

The activation energies for permeation of the 150°C cure blend were higher for all gases than those for the PEI. This increase would suggest that over the range of conditions investigated, the blend is experiencing more significant molecular motions that the pure PEI. This increased molecular motion can be expected, at least in part, due to the reduced glass transition temperature of the blend.

Mercer [7] has reported that addition of 20% by weight of low molecular weight acetylene-terminated imide (ATI) to PEI reduced the \( T_g \) of the blend (188°C) nearly 30°C as compared to the pure PEI (215°C). This behavior is consistent with the results observed here. The larger reduction in glass transition temperature measured here for the PEI/ATM blends may result from the lower molecular weight of the ATM (518 g/mol) compared to Mercer’s ATI (1094 g/mol).

Low molecular weight compounds or plasticizers are often added to glassy polymers to lower their glass transition temperature and increase the flexibility of the material. While there is a continuous decrease in the glass transition temperature with addition of such miscible compounds, the frequency of the polymer segmental motions may not necessarily be increased. For relatively low concentrations of the order of 10–20% by weight, some low molecular additives appear to retard the segmental motions of the polymer. Increases in the modulus and a suppression or elimi-
ination in sub-$T_g$ transitions resulting in reduced elongations to break and impact resistance have been reported. These changes in mechanical properties are in direct opposition to what would be expected from plasticizing responses. This phenomenon has been termed antiplasticization. Numerous reports focus on mechanical properties and the elimination of sub-$T_g$ transitions as measured by dynamic mechanical spectroscopy [17]. Reduced molecular motion of phenyl rings in bisphenol-A containing polymers has been directly measured using NMR techniques [18,19].

Maeda and Paul [20–22] have examined the influence on gas transport of blending antiplasticizing additives with bisphenol-A polysulfone and poly(phenylene oxide). They concluded that the permeability of a polymer would initially decrease as additives were added to the matrix, go through a minimum and then increase. If a blend could be prepared with very high additive concentrations, the permeability of this blend would be expected to be significantly higher than that of the glassy polymer. This behavior is depicted in Fig. 8.

The precise response of the permeability to blend composition is dependent upon the penetrant gas and the chemical nature of the additive. Therefore, the ideal gas selectivities can increase or decrease. Maeda and Paul observed mostly increases for the polysulfone systems and decreases for the poly(phenylene oxide) systems.

While we have not measured the low temperature modulus of these blends, PEI modulus data are available [23]. The PEI exhibits a $T_g$ transition at approximately $-90^\circ$C [23]. This transition is believed to be the consequence of 1,4 phenyl ring flips of the bisphenol-A unit in the backbone [23]. Similar $T_g$s have been reported for bisphenol-A polycarbonates and polysulfone [24–26]. Suppression of this molecular motion would result in the decreased permeabilities observed here.

5.2. Influence of crosslinking on PEI/ATM blends

Mercer et al. [7] and Choudhary and Pearce [8] have shown that in the curing of PEI/ATI blends, reactions only occurred within the ATI phase. The ATI polymerizes and undergoes thermal rearrangement to form a crosslinked polyimide yielding a semi-interpenetrating network structure with a single $T_g$ [7]. No reactions between the PEI and the ATI were documented. Our data support this conclusion. The width of the loss factors for these blends (Fig. 4) are all approximately equal indicating that the distribution of molecular motions contributing to this loss remains constant with crosslinking. If reactions between the phases were occurring, one would expect a increased distribution of molecular motions being probed resulting in a broadening of the loss peaks [27].

At intermediate crosslinking, the system may be viewed as a three component blend consisting of PEI, a newly formed high molecular weight polymeric material, and the unreacted ATM. Following complete crosslinking, the system is a semi-interpenetrating polymer network.

The exact nature of the crosslinking reactions occurring in these ATM systems remains the subject of debate. It was initially proposed that chain extension in these imide ATMs occurred by trimerization of the ethynyl groups [28], but later work on model compounds revealed the greater complexity of the reaction [29]. A part of the acetylene-terminated monomers trimerize to form a benzene ring. However, the major part dimerizes to form an enyne structure.
which is believed to cyclo aromatize on further heating [29,30]. Significant differences from system to system are to be expected due to differences in (a) the steric hindrances of the ATM, (b) the densities of end-groups and (c) the mobility of the monomers. Dilution of the ATM by blending it with PEI could limit the number of reactions possible by limiting the availability of reactants.

We have measured the transport properties of the polymer produced by oxidatively coupling the 6FDA–ATM monomer analyzed here (details of synthesis [31], transport properties [32]). This high molecular weight polymer (termed 1,1-6FDA–DIA to refer to the presence of symmetric methylene spacers (1,1) and internal diacetylene units) was crosslinked at 205 °C prior to analysis. The single gas permeabilities at 35 °C and 10 ATM feed pressure were roughly three times higher than those of PEI (see Table 5).

If one analyzes the crosslinked system as a blend of two polymers, the slight increase in permeabilities with increased crosslinking is to be expected from the higher inherent permeability of the crosslinked 1,1-6FDA–DIA present in the blend. This analysis, however, has assumed that the nature of the crosslinked structure which results from curing the ATM has properties similar to those of a crosslinked polymer produced from this monomer. Future evaluation of the nature of these reactions (through NMR and IR) are on-going and should establish the validity of this assumption.

The properties of blends of PEI with a polymer of 1,1-6FDA–DIA (approximate degree molecular weight 40 000) have been analyzed [33]. Unfortunately, these two polymers are completely immiscible. Therefore, the measured properties are complicated by the presence of significant phase separation. Apparently, the in situ polymerization completed through the blending and curing of ATMs has overcome this problem.

Curing blends of PEI/ATM resulted in a more chemically resistant and thermally resistant material with a significant increase in the glass transition temperature of the material. Density of the blends increased in a small, but measurable manner from 1.309 to 1.313 g/cm³ upon increasing the curing temperature from 150°C to 270°C.

The gas transport of the materials increased slightly as the cure temperature increases from 150°C to 270°C. The selectivities of all gas pairs increased with increasing cure temperature. The trend of increasing ideal selectivity with increases in the degree of crosslinking (as indicated by increased density) has been previously observed [34]. The biggest increases in selectivity appear to be for fast/slow (or small/large) gas pairs. The selectivity for the hydrogen/methane gas pair nearly doubled whereas, the carbon dioxide/nitrogen selectivity increased by less than 20%.

The thermal resistance, as measured by weight loss upon heating, was markedly improved following high-temperature curing. After curing at 150°C, the PEI/ATM blend experienced 5% weight losses at 452°C. Following curing at 270°C, this temperature increased to greater than 485°C. Further, the residual mass at 485°C increased from 93% for the uncured blend to 97% for the cured sample.

The activation energies for permeation through the blend materials are highest for the blend cured at 150°C. The activation energies for permeation through the blends cured at 230°C and 270°C are essentially equivalent and lower than those for the 150°C cured blend. The similarity between 230°C and 270°C cured blends is to be expected in light of the similar crosslink densities indicated by differential scanning calorimetry. These blends have less molecular mobility (as demonstrated by the higher $T_g$) than the blend cured at 150°C and thus, would be expected to have lower activation energies. Indeed, Costello and Koros [25,35] have shown that, for a given polymer family, the activation energy for permeation is inversely related to the molecular motion of the polymer as monitored by $T_g$, $T_B$, and $T_R$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>H₂</th>
<th>He</th>
<th>N₂</th>
<th>CO₂</th>
<th>CH₄</th>
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<tr>
<td>PEI</td>
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<td>6.1</td>
<td>0.054</td>
<td>1.01</td>
<td>0.028</td>
</tr>
<tr>
<td>150 cure</td>
<td>4.3</td>
<td>5.7</td>
<td>0.048</td>
<td>0.68</td>
<td>0.035</td>
</tr>
<tr>
<td>230 cure</td>
<td>5.7</td>
<td>6.1</td>
<td>0.049</td>
<td>0.81</td>
<td>0.034</td>
</tr>
<tr>
<td>270 cure</td>
<td>6.0</td>
<td>7.6</td>
<td>0.052</td>
<td>0.89</td>
<td>0.025</td>
</tr>
<tr>
<td>1,1-6FDA–DIA [32]a</td>
<td>31.4</td>
<td>41.9</td>
<td>0.19</td>
<td>3.9</td>
<td>0.18</td>
</tr>
</tbody>
</table>

1 Barrer = 10⁻¹⁰ cm³ (STP) cm/cm² s cm Hg.

*Crosslinked at 205°C prior to analysis.
5.3. Comparison of PEI properties to those of fully cured blend

The addition of 9 wt% ATM followed by thermal curing resulted in a material with transport properties nearly identical to the original PEI but with improved chemical resistance. The chemical resistance of the fully cured blend is markedly improved when compared to the original PEI (71% mass retention in methylene chloride as compared to complete dissolution for the PEI). Thus, the incorporation of a small quantity of acetylene-terminated monomer in a PEI matrix followed by crosslinking may provide a mechanism to improve chemical resistance without significantly changing the transport behavior of the polymer.

6. Conclusions

Incorporation of a thermally-reactive acetylene-terminated monomer in a poly(ether imide) base results in a homogeneous blend with a depressed glass transition temperature and reduced transport rates. Following curing, the blend exhibits a glass transition temperature that is slightly higher than the virgin PEI and markedly higher than the uncured blend. Transport rates are not markedly influenced by crosslinking over the range of conditions investigated here. Nevertheless, the resistance of the blends to dissolution in methylene chloride is improved. These materials may prove useful for the separation of hydrogen from hydrocarbons in environments in which chemical resistance is a concern. By controlling the degree of curing of the ATM, the chemical resistance of the blend can be modulated between those of the pure PEI and the fully cured material while the transport properties remain relatively constant.

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References