Effect of UV crosslinking on transport properties of CO\textsubscript{2} and N\textsubscript{2} through poly(imide-siloxane) segmented copolymer

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Abstract

Crosslinkable segmented random copolymers are made by synthesizing a polyimide in the presence of bisaminopropyl dimethylsiloxane (PDMS) oligomers. The polyimide segments of these materials are composed of two different dianhydrides, 2,2'-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA), and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) with the base diamine, 2,4,6-trimethyl-1,3-phenylenediamine (DAM). Upon irradiation with UV light, the ketone group in BTDA can form radicals that crosslink with adjacent benzylic methyl groups on DAM. Thermal analysis reveals that siloxane-containing polyimide copolymer films are phase segregated, composed of a polyimide-rich continuous phase and dispersed PDMS phase. CO\textsubscript{2} and N\textsubscript{2} gas permeabilities of uncrosslinked and crosslinked samples were measured to investigate the effect of UV crosslinking on permeability and permselectivity. Incorporation of PDMS did not significantly change the transport properties of the membranes. Densification occurred as a result of UV crosslinking, which enhanced the size-sieving capability of the poly(imide-siloxane) segmented copolymer membrane.

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Keywords: UV crosslinking; siloxane-imide segmented copolymer; micro phase separation; permeability, permselectivity

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Introduction

For post-combustion CO$_2$ capture processes, membrane technology could potentially outperform amine absorption in terms of capital expense and energy requirement. However, conventional commercial membrane materials do not offer high enough CO$_2$ flux to compete effectively with amine absorption. In addition, membrane materials must be durable in the face of the aggressive thermal and chemical conditions of the feed [1]. Polyimides have been widely used in gas separation membranes owing to their outstanding permeselectivity, and their chemical and thermal stability [2]. However, polyimides often exhibit relatively low permeabilities and are less ductile than would be desirable. One approach to improve both transport properties and mechanical properties is to incorporate flexible, siloxane segments into the rigid polyimide [3,4]. Such poly(imide-siloxane) copolymer systems often exhibit a microphase-separated structure because of the low mixing entropy of the two components involved. The degree of phase separation is influenced by the siloxane composition, the segment length, and the sequence distribution. For low siloxane loadings, polymer films are composed of a continuous polyimide phase and a dispersed siloxane phase [5]. Siloxane microdomains provide highly permeable sites for gas molecules, which improves gas permeability. Permselectivity, on the other hand, is largely determined by the continuous polyimide phase [6]. Thus, transport properties improve in contrast with the pure polyimide, moving toward the upper-bound. The present work focuses on membranes made from UV-crosslinkable poly(imide-siloxane) copolymers. These copolymers were synthesized from 2,2'-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) in a 7:3 molar ratio, with 2,4,6-trimethyl-1,3-phenylenediamine (DAM) and varying amounts of siloxane oligomer ($<M_n> = 1000$ g/mol). Films were exposed to UV light to form crosslinks between the benzophenone moiety provided by the BTDA monomer, and benzyl methyl groups provided by the DAM monomer. CO$_2$ and N$_2$ permeabilities were measured to examine the effect of UV-activated crosslinking on siloxane-modified polyimide segmented copolymers with a variety of PDMS content.

1. Experimental

2.1. Polymer synthesis

Polymer samples were synthesized as follows: monomer-grade dianhydride was introduced to a three-necked flask equipped with a mechanical stirrer, nitrogen inlet, Dean-Stark trap and reflux condenser, and heated by an oil bath as described in earlier publication [7]. The dianhydrides, 6FDA and BTDA, were charged at 70/30 molar percentages, respectively. Then 9 mL of absolute ethanol per gram of dianhydride was introduced, and the Dean-Stark trap was filled with absolute ethanol and a catalytic amount of triethyl amine. The mixture was heated to 90 °C and allowed to reflux 45min, then the Dean-Stark trap was drained of ethanol. Stirring continued until the ethanol in the flask evaporated into the Dean-Stark trap, leaving a viscous solution of diester-diacid anhydride, and the trap was drained. Meanwhile, the diamine (DAM) was dissolved in dry N,N-dimethylacetamide (DMAc) and set aside. Bis-aminopropyl-terminated poly(dimethyl siloxane) ($<M_n> = 1000$ g/mol) was mixed with anhydrous tetrahydrofuran (THF) and combined with the diamine/DMAc solution. A cloudy mixture was apparent upon combination and the ratio of DMAc/THF was adjusted to create a clear, homogeneous solution; typically a 1:1 ratio of DMAc/THF was used. The diamine/PDMS mixture was introduced to the diester-diacid solution and diluted to a solids concentration of 30% (wt./vol.) with DMAc/THF. Anhydrous dichlorobenzene was added to the reaction vessel at 25% the volume of DMAc as an azo trope. The trap was filled with dichlorobenzene and then the reaction mixture was heated to 175 °C for 16-19 h. The polymer was allowed to cool, diluted to a solids content of 15% (wt./vol.) and then precipitated by slowly dripping the polyimide solution into stirred methanol in a large (2L) beaker. The polyimide was isolated by filtration, air-dried for 1-2h, and then vacuum dried at 140-160 °C for 24 h. Fig. 1 illustrates a general synthetic scheme for the ((6FDA/BTDA)-DAM)-(PDMS) segmented copolyimide.
2.2. Film casting

The segmented copolymers make robust films which are cast from a 5-6 wt% solution in DMAc. The solutions were cast onto level 5" x 5" glass plates and initially dried under IR light for 18-24 hrs. The films were removed from the glass plates and submerged in deionized water for 24 hrs. The water bath also helped extract any remaining water-soluble organic solvent not removed by the IR light. The films were then dried in vacuo at 175 °C for 24 hrs.

2.3. UV crosslinking

UV crosslinking was performed in the solid state by passing a film through a "Fusion UV" 300 W mercury lamp UV chamber (Heraeus Noblelight Fusion UV Inc., USA). Films were exposed to 3 min of UV irradiation in air at broad spectrum of UV wavelength UV-V (100-200 nm); UV C (200-280 nm); UV B(280-320 nm); UVA (315 nm). The Thickness of the films was nominally 20 μm. The density of uncrosslinked and crosslinked samples was measured using a Mettler-Toledo benchtop density gradient kit (for AX/AT/AG balances Mettler Toledo, Greifensee, Switzerland) with n-heptane as a reference fluid.

2.4. Thermal analysis

2.4.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (Q500, TA Instruments, New Castle, DE) was used to investigate sample mass changes as a function of temperature and time. TGA scan was performed at 5°C/min for the temperature ramp over the range from 25 °C to 800 °C under nitrogen atmosphere. A nitrogen purge at flow rate 40 ml/min over the balance and 60 ml/min over the sample was used to maintain an inert atmosphere during the TGA experiments.
2.4.2. Dynamic mechanical analysis (DMA)

The glass transition temperature of the polymer systems was estimated by using dynamic mechanical analysis (Q800, TA Instruments, New Castle, DE) under nitrogen atmosphere and a frequency of 1 Hz. The scans were carried out from -150 °C to 550 °C at a heating rate of 2 °C/min using a film tension clamp. The specimen dimension was 6.3 mm x 19 mm of uniform thickness. The storage modulus (E'), loss modulus (E''), and damping factor (\(\tan \delta = \frac{E''}{E'}\)) were recorded during the DMA scanning. \(T_g\) values were determined from peaks in the tan \(\delta\) curve.

2.5. Gas permeation measurements

CO\(_2\) and N\(_2\) gas transport properties of these materials were measured using the constant volume, variable pressure method [8] at 35 °C with ultra high purity grade gases from Airgas (Radnor, PA, USA). A 1000 psig pressure transducer (Model STJE, Honeywell Sensotec, Columbus, Ohio, USA) was used to measure the upstream pressure in the system. A 10Torr capacitance manometer (Baratron 626 A, MKS, Andover MA, USA) was used to measure the downstream pressure, and downstream pressure was kept below 10 Torr with using a vacuum pump. All data were recorded using National Instruments Lab-VIEW software.

2. Results and discussion

3.1. Thermal properties

DMA was used to determine the glass transition temperature (\(T_g\)) of uncrosslinked and crosslinked PDMS-PI segmented copolymers as a function of siloxane content (wt%). Fig. 2 shows the temperature dependence of \(\tan \delta\) for uncrosslinked poly(amide-siloxane) copolymers. Peaks in the \(\tan \delta\) curves indicate glass transition temperatures. The \(T_g\) for the polyimide (0wt% PDMS) was 420 °C. PDMS has a \(T_g\) of -120 °C [9]. When a polyimide and PDMS are combined, the \(T_g\) of the mixture will reflect the nature of the mixture. For homogeneous mixing, a single \(T_g\) would be observed, as predicted by the Flory-Fox equation [10]:

\[
\frac{1}{T_g,\text{Fox}} = \frac{w_{\text{PDMS}}}{T_{g,\text{PDMS}}} + \frac{w_{\text{PI}}}{T_{g,\text{PI}}}
\]

where \(w_{\text{PDMS}}\) and \(w_{\text{PI}}\) are the weight fractions and \(T_{g,\text{PDMS}}\) and \(T_{g,\text{PI}}\) are the glass transition temperatures of the PDMS and polyimide phases, respectively. For a completely phase-segregated morphology, two \(T_g\) values would be observed with the same values as the individual components [11]. In the present study, we observe two distinct \(T_g\) values for the PDMS-containing copolymers, indicating that phase segregation has occurred. However, as the amount of PDMS was increased systematically, we also observed a downward shift in the upper (polyimide phase) \(T_g\). The decrease in \(T_g\) is much less than what would be expected for homogeneous mixing of polyimide and PDMS. We attribute the depression in the polyimide phase to partial phase mixing at siloxane-imide interphase [12]. There also appeared a decrease in the polyimide phase peak intensity and an increase of the PDMS peak intensity with increasing siloxane content, which is consistent with an increase in the proportion of the PDMS phase in the film. For uncrosslinked and crosslinked poly(amide-siloxane) copolymers, \(T_g\) values for the polyimide phase along with Flory-Fox predictions for homogeneous polyimide-PDMS mixtures are presented in Table 1.

Thermal stability of uncrosslinked and crosslinked samples was characterized by TGA under a nitrogen atmosphere. Table 1 contains the 5% weight loss temperatures, \(T_{d,5}\), for uncrosslinked and crosslinked siloxane segmented polyimide copolymers. Thermal degradation was not observed for any samples below 300 °C. \(T_d\) is slightly lower for the siloxane-containing segmented copolymers than for the polyimide. This is attributed to the higher number of weak siloxane linkage in the polymer backbone [13]. Similar degradation temperatures were observed for uncrosslinked and crosslinked samples, indicating thermal stability is not impacted significantly by UV crosslinking.
Table 1. Physical properties of the polymers.

<table>
<thead>
<tr>
<th>(70/30)6FDA/BTDA-DAM</th>
<th>Irradiation time (min)</th>
<th>Density (g/cm³) at 25(°C)</th>
<th>DMA $T_g$ (°C)</th>
<th>$T_{g_F}$ (°C)</th>
<th>$T_d$ (°C) 5% wt. Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>[0 wt.% PDMS]-</td>
<td>3</td>
<td>1.336</td>
<td>1.407</td>
<td>420</td>
<td>494</td>
</tr>
<tr>
<td>[3 wt.% PDMS]-</td>
<td>3</td>
<td>1.308</td>
<td>1.335</td>
<td>394</td>
<td>481</td>
</tr>
<tr>
<td>[8 wt.% PDMS]-</td>
<td>3</td>
<td>1.277</td>
<td>1.306</td>
<td>368</td>
<td>469</td>
</tr>
<tr>
<td>[13 wt.% PDMS]-</td>
<td>3</td>
<td>1.267</td>
<td>1.292</td>
<td>340</td>
<td>460</td>
</tr>
</tbody>
</table>

a Measured glass transition temperature of the polyimide phase
b Flory-Fox equation prediction for a homogeneous mixture of polyimide and PDMS

3.2. Gas permeation properties

Fig. 3 shows the CO₂ and N₂ permeabilities of linear and crosslinked PDMS-PI segmented copolymers as a function of siloxane content. In materials with phase-segregated morphology, with a low-permeability continuous phase and a high-permeability dispersed phase, gas permeability usually increases as the quantity of the high permeability component increases [6]. However, in the present work, incorporation of PDMS did not substantially change the transport properties in contrast with pure polyimide films. The reason for this discrepancy is not fully understood, but one possibility is that the partial phase mixing observed in the continuous polyimide phase could result in a decrease in free volume within polyimide phase, thus reducing permeability for this phase. Such a reduction in permeability could potentially offset the increase in permeability afforded by the dispersed siloxane. Further investigation will be required in order to fully understand these phenomena.
Density measurements, listed in Table 1, indicate that densification occurred as a result of UV crosslinking. CO₂ and N₂ permeabilities, presented in Fig. 3, are depressed for crosslinked samples, most notably for larger molecules such as N₂. In addition, CO₂/N₂ selectivity values increased for crosslinked samples, as shown in Fig. 4. It has been reported that gas solubilities of crosslinked polymers are relatively unchanged except for very high degrees of crosslinking [14]. This suggests that the observed changes in transport properties for crosslinked polymers are predominantly due to a decrease in diffusivity associated with a decrease in polymer free volume.

4. Conclusions

Crosslinkable (70/30)6FDA/BTDA-DAM polyimide was synthesized in the presence of PDMS (\(<M_n> = 1000\) g/mol) oligomer with PDMS content ranging from 3 to 13 wt%. Films were subsequently crosslinked by exposing them to broad-spectrum UV irradiation for 3 minutes. Microphase separation was observed to with increasing partial phase mixing between siloxane-imide interphase as the PDMS content was increased. Both uncrosslinked and crosslinked poly(amide-siloxane) copolymers are thermally stable up to 300 °C. CO₂ and N₂ permeabilities did not substantially change as the PDMS content was increased. Densification occurred as a result of UV crosslinking, which reduced the free volume of the polymer, and enhanced its size-sieving capability of the polymer.

Acknowledgements

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References