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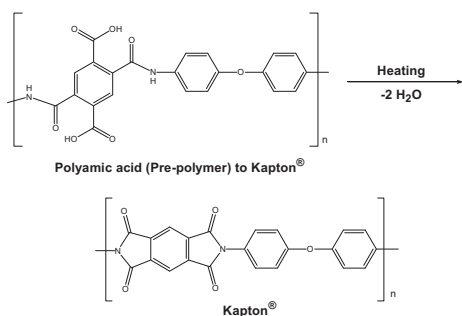
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Introduction

Polymer membranes are available for many commercial gas separations, like hydrogen recovery, air separation, and the removal of carbon dioxide (CO₂). These applications depend on polymer membranes for their high permeabilities and their excellent selectivities; however, most gas separation research has concentrated on the optimization of polymeric materials at or near ambient conditions. As a result, high temperature gas separations (> 150 °C) using polymer membranes has not been thoroughly researched; therefore, high performance polymer membranes provide a suitable means to evaluate gas permeability and selectivity at elevated temperatures.

High performance (HP) polymers are glassy polymers that are thermally stable and mechanically robust with high compressive strength, like polybenzazoles (polybenzimidazole (PBI)), polyimides (Kapton[®]) and polyamides (nylon). A number of HP polymers have decomposition temperatures 500 °C or higher. In addition, many HP polymers are resistant to many acids and bases and most organic solvents; therefore, they can tolerate chemical conditions that other organic polymers cannot. HP polymers can be prepared into various shapes or thin films, but they are required to be dissolved into polar organic solvents, such as N,N-dimethylacetamide (DMAc) and N-methyl-2-pyrrolidone (NMP). These solvents are not always the most advantageous for film processing, and our previous investigations with N-substitution of PBI has shown that synthetic modifications will increase the solubility of PBI in common organic solvents, like tetrahydrofuran and chloroform.¹ However, finding solvents that will dissolve an HP polymer and produce a good membrane is ultimately determined by its structural and physical characteristics.



Scheme 1. Polyamic acid condensation to the polyimide.

In these investigations, several polyimides (like Kapton[®]) were explored. Specifically, VTEC PI[®] series (VTEC) and Pyre-ML RC5083[®] (Pyre-ML) were selected, because they produce thin films that remain robust and flexible even after several thermal cycles. Remarkably, these polyimides were capable of being blended with

other polymers or additives without issues. Previous studies have shown that the VTEC polyimides were promising HP polymers that gave interesting results for high temperature gas separations.² It should be noted that polyimides start as polyamic acids in solutions, which are made into films by solvent evaporation. The resulting polyimides are formed as the polyamic acid films are heated (Scheme 1) to complete the condensation reaction, which will result in a highly heat-resistant, virtually insoluble film. In this work, VTEC and Pyre-ML were used with and without various additives to form polymer films for gas transport and positron annihilation lifetime analysis.

Experimental

Materials and Instrumentation. The polymer films investigated in this work reported here were: Kapton[®], Pyre-ML RC 5083 (polyimide from Industrial Summit Technology Co.), VTEC PI Series (polyimide from Richard Blaine Industries, Inc.), PBI (polybenzimidazole from PBI Performance Products, Inc.) and PBI-TMS (bis(trimethylsilylmethylene)polybenzimidazole, synthesized at INL¹). Thermal analyses were obtained using a Model 2950 thermogravimetric analyzer (TGA). Dynamic mechanical analysis (DMA) data was acquired using a TA Instruments Model Q800.

Polymer Film Processing. From our previous studies,² it was apparent that the polymer processing procedures for the membranes are critical. A heat treatment regimen was used, and the resulting membranes gave reliable gas permeation testing data. The regimen consisted of casting the polymer solution on glass plates and evaporating the solvent to give the polymer film. The polymer films were heated to 150 °C to remove additional solvent and water. Additional heating to 250 °C is required to completely cure the polyimide film. Afterwards, the films were lifted from the glass plates using water and dried again at 150 °C.

Permeability Gas Testing. Pure gas permeability results were obtained using the pressure-rise time-lag method.³ Membranes were exposed to individual gases, like hydrogen (H₂), methane (CH₄) and carbon dioxide (CO₂). In a typical experiment, both sides of the membrane are evacuated to an equal vacuum. The test cell is then isolated and the pressure at zero time is used as the baseline. The feed side is exposed to the test gas, and the pressure buildup on the permeate side of the membrane is recorded as a function of time. The two gas transport properties that are determined directly from the pure gas test system are time lag and permeability. The permeability is the rate at which the gas permeates through the membrane after the gas has come to equilibrium in the polymer. The time lag is the time it takes the gas to travel from the feed side of the membrane to the permeate side and can be used to calculate the diffusivity.

In the mixed gas analysis, permeation is determined analytically by gas chromatography rather than barometrically. The mixed gas experiment uses a 3% each of H₂, CH₄ and CO₂ along in helium as the analyte gas. The pure gas system can reach about 70 °C, whereas mixed gas system can achieve 400 °C. The high temperature gas permeation studies (greater than 70 °C) were conducted on the mixed gas system.

Positron Annihilation Lifetime method. The sample-source is prepared as a stack beginning with a substrate of titanium foil (0.7 mm), then a stack of polymer film, the source (NaCl between titanium film of 0.5 mil), another polymer stack (if enough sample is available), and a final titanium foil. The sample-source stack is held together with a small metal clip. The intention is that all positrons from the source annihilate in the source, the polymer sample, or the titanium substrate foil if the sample is too thin to stop the positrons.

The positron annihilation lifetime is measured with two Photonis XP2020/URQ photomultiplier tubes with Barium fluoride scintillators. The start and stop signals from the phototubes go to Ortec 583 constant fraction differential discriminators which are set to select the 1.27 MeV gamma ray from the Na-22 source for the start signal and the 0.511 MeV gamma ray for the stop signal. The singles go to an Ortec time to amplitude converter and then to an Ortec Trump Multi channel Analyzer (MCA) installed in a PC computer and operated with Maestro software. The Doppler broadening experiment is done with a liquid nitrogen cooled high purity germanium detector (hpGe) which is a 2 inch coaxial crystal with an aluminum cover. The output signal is processed by an Ortec 571 amplifier and then sent to a second Trump MCA. Data is typically collected for both the lifetime and Doppler broadening experiment at the same time.

Results and Discussion

The focus of this work was finding polymers both with and without additives that will enhance membrane performance for the next generation of the targeted membranes. The resulting membranes must achieve high selectivity, high permeability, chemical stability, and mechanical stability at elevated temperatures (> 150 °C). As compared to the previous data,² this research was able to provide several HP polymers that gave good gas separation factors at high temperatures, especially the polyimides like VTEC.

Table 1. Pure Gas Data Collected at 30 °C.^a

Polymer	Permeability (barrers) ^b						Selectivity α	
	H ₂	Ar	N ₂	O ₂	CH ₄	CO ₂	H ₂ /CO ₂	H ₂ /CH ₄
Kapton [®]	1.56	c	0.01	0.075	0.008	0.297	5.3	195.0
VTEC PI 80-851	3.56	0.20	0.06	0.19	0.03	0.48	7.4	121.6
VTEC PI 1388	3.97	0.06	0.04	0.17	0.05	0.53	7.5	30.8
Pyre-ML RC5083	5.32	c	c	c	0.144	2.35	2.3	36.9
PBI	4.6	c	0.12	0.29	0.13	0.85	5.4	35.4
Pyre-ML RC 5083 w/PBI-TMS	37.8	c	c	c	1.50	21.24	1.8	25.6

^aAll polymers in this table were heat cycled prior to testing.

^bPermeabilities measured in barrers: [(10⁻¹⁰)(cm³ (STP) x cm)/(cm² x sec x cmHg)]

^cnot tested

Another potential polyimide (Pyre-ML) was tested for its gas separations at high temperatures. The base Pyre-ML polymer has a similar structure as Kapton[®] after heat processing (see Scheme 1). Once it was fully processed Pyre-ML showed similar thermal stability as Kapton[®] and VTEC, suggesting that Pyre-ML was a good candidate for gas permeability testing. The pure gas permeation data at ambient temperatures (Table 1) revealed similar gas permeabilities for VTEC and Kapton[®] films, yet Pyre-ML showed better gas permeability than VTEC and Kapton[®]. The most interesting result showed that Pyre-ML has better CO₂ gas transport than Kapton[®] and VTEC at ambient temperatures. Also, Pyre-ML was blended with poly[bis(N-trimethylsilylmethylene)benzimidazole] (PBI-TMS) showed good gas throughput while retaining its selectivities at room temperature. At ambient temperatures, blended Pyre-ML with PBI-TMS revealed a 7-fold gas permeability improvement over the parent polyimide, which was exciting results for these high-temperature polymers. Our research has noted that VTEC polymers are not very good gas permeators at room temperature; however, these polymers are reasonable gas separators at 250°C (Table 2). Unfortunately, the mixed-gas data at high temperatures did not show complementary

results for Pyre-ML and its blend with PBI-TMS. The mixed-gas data for VTEC show good gas separations at 250°C (Table 2), while the data for Pyre-ML and Kapton[®] are much lower. Attempts to improve Pyre-ML performance, both at ambient and high temperatures, was performed through the inclusion of additives and cross-linkers.

Table 2. Mixed Gas Data Collected at 250 °C.^a

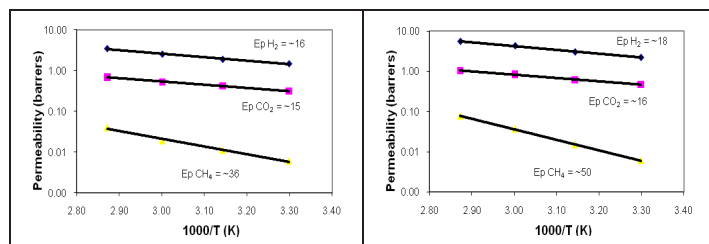
Polymer	Permeability (barrers) ^b				Selectivity α	
	H ₂	Ar	CH ₄	CO ₂	H ₂ /CO ₂	H ₂ /CH ₄
Kapton [®]	37.5	c	4.1	11.8	3.2	9.2
VTEC PI 80-851	83.0	3.1	2.3	9.3	8.9	36.1
Pyre-ML RC5083	45.1	c	6.5	16.6	3.1	8.1
PBI	33.1	c	1.69	4.7	7.1	2.8
Pyre-ML RC 5083 w/PBI-TMS	54.8	c	11.3	20.4	2.7	4.9
VTEC PI 851 w/PBI-TMS	99.9	c	6.9	11.5	8.7	14.5

^aAll polymers in this table were heat cycled prior to testing.

^bPermeabilities measured in barrers: [(10⁻¹⁰)(cm³ (STP) x cm)/(cm² x sec x cmHg)]

^cnot tested

An effort was aimed at making a Pyre-ML composite membrane that had similar gas separation properties to VTEC, especially at high temperatures, through the use of cross-linking agents to stabilize its final structure. From the mixed-gas at high temperature data (Table 2), it showed that Pyre-ML had better fluxes than Kapton[®] and VTEC, but the gas selectivity was not as good. From our initial trials, a cross-linking agent was identified to enhance Pyre-ML's thermal stability. It was found that large amounts of this cross-linker showed limited solubility in the Pyre-ML solutions. In addition, large amounts of cross-linker did not help with the stability and gave inconsistent membranes for gas permeability testing. We found that solutions with smaller amounts of cross-linker could give consistent films, and the resulting membranes were analyzed for both pure-gas (Figures 1–3) and mixed-gas permeability measurements.



Figures 1 and 2. Pure gas data for Kapton[®] (left) and Pyre-ML (right), heated to 75°C.

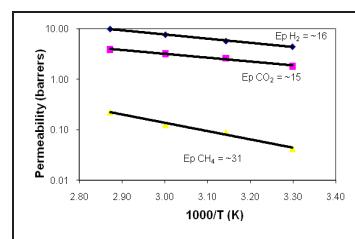


Figure 3. Pure gas data for Pyre-ML with cross-linker, heated to 75°C.

The activation energies of Kapton[®], Pyre-ML, and Pyre-ML with cross-linker (Figures 1– 3) were evaluated using pure-gas permeation analysis up to 75 °C. From each plot, the activation energies (Ep) for CO₂ and H₂ in all three membranes were similar,

however permeabilities for these two gases was higher in the membrane formed from Pyre-ML with the added cross-linker. The Ep data for methane (CH₄) was slightly lower in the modified membrane suggesting a modest change in transport mechanism. The exciting portion to this data was the CO₂/CH₄ separation factor (alpha), where Pyre-ML with cross-linker gave very good separations (alpha = ~17 at 75 °C).

At elevated temperatures (250 °C), the mixed gas permeation apparatus was used on Kapton® and Pyre-ML with cross-linker. The data largely correlated with the pure gas data; however, Pyre-ML with cross-linker showed better permeability and separation factor than Kapton®, suggesting that the Pyre-ML with cross-linker will perform gas separations, possibly even better at higher temperatures.

A key property of polymers that allows selective transport of small gases is polymer void volume. A method for measuring the voids inside the polymers is positron annihilation lifetime (PAL) spectroscopy. PAL spectroscopy uses the ortho positron (oPs) annihilation intensity and lifetime to determine void volumes. The main difference among the HP polymers was in the formation and trapping of positronium which manifests as a third, longer lifetime component in the lifetime spectrum. It is well known that positronium does not form in the polyimide structures such as Kapton®. Presumably the polyimide polymer chains were aligned such that there was not a large enough free volume void between the polymer chains to trap positronium. By N-substituting PBI with trimethylsilylmethylene (TMS) functional groups, some positronium can be trapped, presumably due to the voids created by the spacing with the TMS component. The results for the ortho positronium (oPs) annihilation intensity and lifetime for PBI-TMS and VTEC/PBI-TMS showed that positronium exhibited long (~1.5 - 2 ns) lifetimes. Tests concluded that the parent polyimide films of PBI, Kapton®, Pyre-ML and VTEC did not form positronium. These results were attributed to lower microporosity in these parent polymers, as compared to their corresponding blended or substituted polymers. This observation is significant since the gas permeation data for the parent polymers showed the lowest gas permeances, and the functionalized and/or blended polymers gave higher permeances.

Conclusions

Several polyimides (Kapton®, VTEC and Pyre-ML) and their blends were evaluated for high-temperature gas separations. Gas permeability data was collected for several polyimides including those that were blended with various polymers and additives, such as PBI-TMS and other cross-linkers. Many of these membranes gave excellent thermal stability and good gas permeabilities. Some of these blended polymers presented a great deal of promise for increased membrane fluxes while maintaining their good selectivities. From these, Pyre-ML and VTEC blended with PBI-TMS showed good selectivities and enhanced permeability for H₂ and CO₂. In addition, Pyre-ML offered good gas separations at ambient temperatures; however, it was a challenge to maintain Pyre-ML's thermal stability and gas separations at higher temperatures. Cross-linkers were used with Pyre-ML to thermally stabilize the films, and these membranes gave reasonable results on CO₂/CH₄ gas separations at high temperatures. An interesting note with the Ep data set is that Kapton® and Pyre-ML with cross-linker have similar values, pointing out that these two polymers exhibit similar gas transport mechanisms. Lastly, several of these polymers have been analyzed by PAL spectroscopy to measure the polymer's void volume. The PBI-TMS blended polyimides exhibited long positronium lifetimes thus having larger void volumes compared to the parent polyimides.

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