Blended Polybenzimidazole and Melamine-co-Formaldehyde Thermosets

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Abstract

Polybenzimidazole [PBI; poly-2,2'(*m*-phenylene)-5,5'-bibenzimidazole] is known to have excellent high temperature stability (up to 450 °C) and superb H₂/CO₂ selectivity compared to most high performance (HP) polymers. New blended thermosets were made with PBI and poly(melamine co-formaldehyde) [PMF] to produce stable thin-films after thermal processing at 220-250 °C. PBI film formation is difficult, because of challenging processing techniques. As a result, the film tends to fracture and fissure due to processing aids and stabilizers (salt/acid additives) that are found in PBI solutions above 10 weight percent. Therefore, PBI dense thin-films are fragile and prone to fracturing during film processing. The reported PBI-PMF blended thermosets do not have stabilizers, and can be made into dense thin-films. The PBI-PMF films were analyzed using pure and mixed gas permeability measurement techniques. At 250 °C, the

data show H₂/CO₂ gas selectivities greater than 13. Also from the gas permeation data, the energy of activation (E_p) of a mixed gas stream for PBI-PMF shows that hydrogen permeates more easily than the other gases, while the permeabilities for the larger kinetic diameter gases are greatly diminished. In addition, the FT-IR spectra show that the PBI-PMF films have changed from parent PBI after thermal processing, and PMF dominates the spectra even in minor percent compositions. Overall, the reported PBI-PMF thermoset films show good stability which can be used for high temperature gas separation.

Keywords: High performance polymers; synthesis; polybenzimidazoles; high temperature; gas permeation analysis

Introduction

Polybenzimidazole (PBI; poly-2,2'(*m*-phenylene)-5,5'-bibenzimidazole [Figure 1]) is a high performance (HP) polymer that has a thermal decomposition point greater than 500 °C and good chemical resistance towards common organic solvents.[1–4] However, PBI's film processing methods are less defined, and thin-film membranes have been difficult to form reproducibly from organic solvents. These solution processing problems are not trivial due to PBI's chemical structure, solvents, crosslinking agents, and additives. PBI is produced by a condensation polymerization (step growth) reaction, where the molecular weight is controlled (10,000-65,000 g/mol [32 to 208 repeat units]).[5–7] This low molecular weight resin can be dissolved in strong polar aprotic organic solvents, such as N,N-dimethylacetamide (DMAc) or N-methyl-2-pyrrolidone (NMP), to form solutions that can be thermally processed into fibers or membranes. For example, concentrated solutions (up to 26 wt% in DMAc) of PBI are made into

fibers and woven into textiles to form fire resistant fabrics (e.g. fireman suits withstanding 600°C).[8–10] Other applications include hollow fiber membranes for water purification,[11–13] gas separation,[14–20] and functionalized resin materials for liquid chromatography.[21,22] However, employing dense thin-film PBI membranes for gas separation is not easily done, especially at elevated temperatures (>150°C). Dense thin-films (<50 µm) of PBI are difficult to make due to its molecular interactions and how additives influence the polymeric structure. Therefore, new strategies are needed to form thin-film membranes with long-term structural reliability suitable high temperature gas separation applications.

Dense thin-films cast from PBI solutions with and without additives, such as mineral acids or lithium salts, tend to craze or crack during or after heat processing. It is noted that thermal processing of the low molecular weight polymer could prompt internal physical stresses as the condensation polymerization reaches completion.[23–26] This behavior is inherent to PBI's structure (rigid-rod), and the additives used to stabilize the polymer matrix. PBI's molecular structure is dependent upon hydrogen bonding with imidazole groups and/or possible aromatic Π - Π stacking (Figure 2). Disrupting these interactions result in defects that are pronounced after drying; therefore, additives or plasticizers are introduced to “stabilize” the polymer matrix. Most common stabilizers are sulfuric or phosphoric acids (and their organic derivatives). Concentrated acids soften and/or swell the polymer and protonates imidazole nitrogen on the polymer backbone. It is postulated that these acids penetrate into the PBI matrix; therefore, breaking up crystal packing or ordering, which gives a pliable polymer matrix that aids membrane formation. As a result, these acidic compounds tend to solubilize PBI as gels or dopes. These dopes are useful in constructing PBI hydrogen fuel cells (or similar devices),

where water is intimately integrated into the matrix and important for proton transport. In this application, the membranes are not allowed to dry out completely.

Variations in the PBI structure allow the material to be dissolved in more common organic solvents. This can be accomplished by using different aromatic/aliphatic dialdehyde and tetraamine precursors (monomers) prior to the condensation polymerization.[27–32] Another synthetic method is N-substitution of PBI, which others have attempted with varying success.[33–36] Other PBI materials have been derived from synthetic techniques by crosslinking with other functionalized compounds, such as halogenated alkyl/phenyl compounds, aldehydes and alcohols. Additionally, blending methods can use pre-polymers, like polyamic acids, to give PBI composites after thermal processing.[37–44] At high PBI solution concentrations, thin-film formation remains problematic, and it is advantageous to include into the polymer matrix some solvent or additives to maintain stable films. Generally, most crosslinking methods were developed to make practical products, like fibers and structural composites. These methods led to numerous crosslinked blends with PBI by employing reactive polymers that could be incorporated resulting in a polymer thermoset after processing. However, there are few methods for making thin-film membranes for high temperature applications, such as gas separation. Moreover, many of the synthetic descriptions use custom synthesized variants of PBI, rather than utilizing the described commercial product. The rationale for these custom syntheses is to control the molecular weight of PBI and eliminate other possible insoluble fractions and/or need for additives.

To employ polymeric membranes for gas separation, rigid supports are required to dimensionally stabilize the selective films. Post thermal processing of PBI membranes on a structural support, such as porous metal, is difficult. Under extreme diligence, supported dense

PBI membranes have been developed for syngas gas applications, and these membranes have shown extraordinary H_2/CO_2 selectivity up to 40 at 250°C; however, PBI's stability as thin-film membranes are a problem that requires further development.[14,20,45]

In summary, many of the issues associated with formation and use of PBI membranes are a result of additives. In this paper, we report a new PBI polymer blend that produces thin-films without the need for additives. We also describe a thermally processing route for solutions of PBI with methylated poly(melamine-co-formaldehyde) [PMF]. The resulting PBI-PMF polymer can be isolated as free-standing, thin-films which are stable in the presence of water. Several different ratios of PBI and PMF were synthesized and characterized and the new blended PBI thermoset membranes have interesting gas permeation performance at high temperature.

Experimental

Materials and General Procedures. The thin-films investigated in this work include: Matrimid 5218 (polyimide from Huntsman Chemical); Ultem 1000 (polyetherimide from GE plastics), Kapton-HN (polyimide from Dupont), VTEC PI series (polyamic acid from RBI, Inc.), and PBI (polybenzimidazole from PBI Performance Products, Inc.). The VTEC PI series and Matrimid 5218 were solution cast into thin-film membranes and thermally processed. Ultem 1000 and Kapton-HN films were used directly from the manufacturer. The following reagents were received from Aldrich Chemical Co. and used without further purification: 80% by weight of methylated, poly(melamine-co-formaldehyde) in butanol [PMF; avg $M_n \sim 511$ g/mol]; anhydrous N,N-dimethylacetamide (DMAc); anhydrous N-methylpyrrolidone (NMP). Deionized water aided removal of membranes from glass plates used to form the films. Several different concentrations of PBI-PMF were made for attenuated reflectance FT-IR experiments.

Thermal Analyses. Thermal behaviors were analyzed by TA Instruments Model 2910 differential scanning calorimeter (DSC) and a Model 2950 dynamic mechanical analyzer (DMA). The samples were heated at 10 °C/min in both instruments while under nitrogen. The DSC was heated to a maximum temperature of 500 °C, and the TGA was heated to 550-600 °C.

Dissolution of Polybenzimidazole. Previous methods were used, where a 10 wt% parent PBI solution was made using anhydrous DMAc.[5] PBI (10 grams) as a fine powder (100-300 mesh) is placed into 250 mL round bottom flask. The flask was equipped with a water-jacketed condenser, gas inlet adapter and magnetic stir bar. This system was placed under vacuum for 4 hours and the system was then purged with nitrogen. Anhydrous DMAc (~100 mL) was transferred to the flask and the solution was heated to boiling with stirring for about 48 hours. The solution was allowed to cool to room temperature gradually becoming more viscous as the solution cools. Note: If particulates are seen, then these particles are left to settle or filtered. This amount was never directly measured because the small amount of fine powder (milligrams) can be easily suspended in the solution by the slightest agitation.

Synthesis of 10 weight% solution of PMF in PBI: The parent 10 wt% PBI solution in DMAc (10 mL; 0.0004 mol) was transferred by syringe into a 20 mL scintillation vial. Then, 0.128 g (10:1 mass ratio) of 80% by weight of methylated, poly(melamine-co-formaldehyde) in butanol is added directly into the PBI solution and mixed vigorously until homogeneous. This solution can be knife cast or solution cast on a polished glass slide/plate, where the solvent is carefully evaporated by a temperature controlled hot plate. A transparent, orange-brown film is produced on the glass slide that was then heated in a vacuum oven to 150°C for 24-72 hours. Additional heat processing in a convection oven (in air) is performed at 200-250°C for another 6-24 hours.

The orange-brown to brown film is slowly cooled to room temperature and is lifted from the glass plate by immersing it into distilled water. The free-standing film is heated again to 150°C to remove excess water. The resulting films were tested for their mechanical and thermal properties. Higher concentrations of PMF (20, 30, and 40 wt%) in PBI/DMAc solutions are made in a similar manner.

Gas Permeability Testing. Pure gas permeability results were obtained using the pressure-rise time-lag method.[46–48] Membranes were exposed to three individual gases: H₂, CH₄ and CO₂. The membrane surface area was 13.8 cm² using a circular flat sheet 47 mm modified filtration cell obtained from Millipore, Inc. Membrane thicknesses were determined by direct caliper measurement and ranged from 40 to 80 μm. The test gas pressure was 206.8 KPa and temperatures were varied from 20°C to 70°C. Permeabilities measured in Barrers which is (10⁻¹⁰)(cm³ x cm)/(cm² x sec x cmHg))

Mixed gas experiments have been carried out using a method previously described in the literature.[49–52] In the mixed gas procedure, permeation is determined analytically by gas chromatography. The feed gas was a mixture of gases (3% by volume) for H₂, CH₄ and CO₂ with helium making up the balance and was obtained from Scott Specialty Gases, Inc. Gas permeabilities for PBI-PMF were determined over a temperature range of 30°C to 200°C with a feed gas pressure of 206.8 KPa (absolute pressure).

Results and Discussion

Thin-film formation of PBI is challenging, due to additives found in parent polymer solutions. As a result, many processed PBI thin-films are fragile and easily fractured after thermal processing. Sometimes plasticizing compounds, such as phosphoric acid, are included to

provide some polymer matrix stabilization in the membranes. However, these additives tend to be hygroscopic which complicates film formation after the membrane completely dries. Therefore, these hygroscopic additives need to be restricted for thin film formation, especially for high temperature membrane applications that contain moisture.

The addition of the 10 weight percent (wt%) PMF into the PBI/DMAc solution produces a homogenous mixture without any visible precipitates; however a viscosity increase was observed. It is possible that the addition of PMF starts to crosslink with the PBI, but this reaction takes on the order of several weeks to result in a gel, depending on PMF concentration and storage temperature. The conceptual reaction schematic (Scheme 1) of the PBI-PMF condensation proceeds primarily with the reactive imidazole nitrogen (NH) on PBI; however, due to the high thermal processing temperatures, the reaction can produce random crosslinking at other possible reactive points, such as the aromatic rings on PBI. Also, self-condensation of PMF is possible. We postulate that PBI is reacting mainly with PMF's hydroxyl group and/or ether linkages to produce either water and/or methanol as a byproduct at the higher processing temperatures. The highest PMF concentrations were 40 wt% in solution.

PBI-PMF thermal processing times vary, due to the amounts of PMF that were used in the mixture. Larger amounts of PMF required relatively short thermal processing times, while lower concentrations of PMF required longer processing times. It was found that the 10 to 40 wt% PMF concentrations were optimal for consistent film formation. The most interesting feature of these films was their resilience towards moisture and water. After the PBI-PMF film was thermally processed on a glass slide, deionized (DI) water can be used to lift the membranes as free-standing films. As a comparison, parent PBI films shatter upon exposure towards DI

water. Before analyzing these films, they were heated to 150°C in a vacuum oven to dry for 24 hours to remove excess water.

Infrared (FT-IR) was used to characterize PBI-PMF's physical properties. Figure 3 shows the changes in the FT-IR from the parent PBI resin (solid black) to various blends of PBI-PMF (solid gray), up to 40 wt% PBI-PMF (dashed gray). There are several changes from parent PBI (solid black line) to PBI-PMF polymers that are apparent in the spectra. The PBI resin has the most dominant absorbance at 3470 cm^{-1} , and PMF starts to dominate the PBI absorbencies at 1700 cm^{-1} as the PMF concentration increases. Interestingly, Ultem/PBI blended polymers show similar tendencies, where IR absorbances of Ultem are more intense than PBI.[53] Also, at 1550 cm^{-1} , the N-H stretches on PBI are not observed in PBI-PMF, whereas at 1493 cm^{-1} , the peak persists. In addition, the C-H stretch at 1327 cm^{-1} for PBI is more intense than the blends.[53–55] Dynamic Mechanical Analysis (DMA) has provided additional insight into the physical properties of PBI-PMF and its films. It is difficult to obtain an accurate glass transition (T_g) for PBI using differential scanning calorimetry (DSC). DMA was a more effective method. PBI is known to have a high T_g at about 425°C and the DMA reveals that the T_g for the 40 wt% PBI-PMF composite was about 350°C. The T_g is depressed due to the melamine co-formaldehyde component in the thermoset. The onset of decomposition is at 400 °C, which suggests that the PBI-PMF composites are not as thermally stable as PBI alone, which has a decomposition temperature at about 500°C.

Gas permeability analysis of the resulting PBI-PMF film showed good selectivities for hydrogen over carbon dioxide; however, in Table 1, measurement of permeability at lower temperatures proved to be difficult due to the low permeation rates of larger kinetic gas diameters, such as methane. At 30°C (pure gas), methane had long lag times (days) and never

reached steady state for the gas. It is proposed that methane does permeate through the membrane at this temperature, but it is below the detection limit of the instrumentation, which is ± 0.002 Barrers. Permeability and selectivity of the composites compared well to other glassy polymers, such as parent PBI and various polyimides. For our tests, an organophosphate additive was needed to stabilize the parent PBI film, and our data indicate that its permeability behaviors were influenced by this additive. In Table 2, higher temperature (220 and 250°C) permeability data reveals equally remarkable results for PBI-PMF compared to PBI and various polyimides. PBI-PMF gave high H_2/CO_2 selectivity of nearly 13, which is higher than the other tested polymers. The resulting PBI-PMF matrix is resilient even at high temperatures, when comparing the gas permeation data to ambient temperatures. Due to time limitations the other experiments on the various percentages of PBI-PMF were not completed.

To determine long term high temperature stability and gas separation performance, a 20 hour mixed gas permeability test was performed at 250°C on a film of PBI with a 40wt% PMF. In Figure 4, these data show that the membrane gives an excellent H_2/CO_2 selectivity ($\alpha = 9-13$), and CO_2/CH_4 selectivity between 6-7. An interesting result in the data is a slight increase in H_2 permeability from 37 to 56 Barrers after 6 hours, while the other gases remain about the same throughout the experiment (CO_2 and CH_4 were about 4 and 0.6 Barrers, respectively). Also, it is remarkable that the H_2/CO_2 selectivity increased to 13. Overall, the permeability results for the PBI-PMF membrane provide remarkable H_2 permeability and selectivity at high temperatures for extended periods.

Further analyses were performed on PBI-PMF to determine activation energies of permeation (E_p) using mixed-gas permeation analysis from 100 to 250°C (Table 3 and Figure 5). Tests below 100 °C were not conducted due to the difficulty in gas analysis for the larger kinetic

diameter gases. E_p for H_2 is relatively flat, Figure 5, compared to the other gases, whereas the E_p for CO_2 and CH_4 are higher. For comparison in Table 3, Kapton has slightly higher E_p for H_2 than PBI-PMF, but the other gases show similar E_p values between the two polymers. However, the gas selectivities for these polymers are vastly different at 200 °C: $H_2/CO_2(\alpha) = 15.6$ and $CO_2/CH_4(\alpha) = 9.6$ for PBI-PMF; and $H_2/CO_2(\alpha) = 3.5$ and $CO_2/CH_4(\alpha) = 5.5$ for Kapton. The advantage that PBI-PMF has is its low permeability of the larger kinetic diameter gases, while H_2 can permeate through the polymer matrix more easily with increasing temperature. This means that the voids and/or channels in the PBI-PMF are specific for small kinetic gas diameter molecules ($< CO_2$ at $3.3\text{\AA}$). In this respect, PBI-PMF is a superior polymer membrane for H_2 separation when compared to Kapton and many other glassy polymers, such as Matrimid and Ultem.

Conclusions

A new melamine/polybenzimidazole-based polymer thermoset has been developed for producing stable, flat-sheet films. The PBI-PMF thermoset is based on cross-linking melamine co-formaldehyde and PBI using similar high temperature processing methods applied to other high performance polymers. The novelty to the new PBI-PMF thermosets is that there are no additives (such as lithium salts or acids) used in the polymer solutions. Thin-films of PBI-PMF are characterized by thermal analysis, IR, and gas permeability. PBI-PMF is capable of high temperature applications up to 300°C and longer term operation at 250°C. The most interesting feature of PBI-PMF is its pure and mixed gas permeability results. A comparison of parent PBI and the other polyimides reveals that PBI-PMF has substantially increased H_2/CO_2 and CO_2/CH_4 selectivities. Also, long term mixed gas permeabilities at high temperatures show promising

H₂/CO₂ and CO₂/CH₄ selectivities, which is due to temperature induced increase in hydrogen permeability with increasing temperature. Overall, the described PBI-PMF blending and processing methods provide a reasonable pathway making free-standing films without additives for high temperature applications which will be able to withstand exposure to moisture.

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Scheme 1. Postulated Reaction for PBI-PMF.

Figure 1. Polybenzimidazole (PBI)

Figure 2. Representation of PBI structural packing: Π - Π stacking and Hydrogen bonding.

Figure 3. FT-IR of PBI and PBI-PMF composites.

Figure 4. Continuous 20 Hours Mixed Gas Permeation Analysis at 250°C for PBI-PMF.

Figure 5. Activation Energy (E_p) Plots for PBI-PMF using Mixed-Gas Permeation Analysis.

Table 1. Pure Gas Permeability of Glassy Polymers at 30°C.

Polymer	Permeability (Barrers) ^a			Selectivity α	
	H ₂	CH ₄	CO ₂	H ₂ /CO ₂	CO ₂ /CH ₄
VTEC PI 80-051	3.56	0.03	0.48	7.4	16.0
VTEC PI 1388	3.97	0.05	0.53	7.5	10.6
Kapton [®] -HN	1.56	0.008	0.297	5.3	37.1
Ultem 1000	12.85	0.026	1.8	7.1	69.2
Matrimid 5218 (from NMP)	15.42	0.181	6.16	2.5	34.0
Polybenzimidazole (PBI) with additives	4.6	0.13	0.85	5.4	6.5
PBI w/ 20wt% PMF	2.07	0.002 ^b	0.08	25.8	40

^a Permeabilities measured in Barrers: $[(10^{-10})((\text{cm}^3 \times \text{cm})/(\text{cm}^2 \times \text{sec} \times \text{cmHg}))]$

^b Detection limit of the instrument

Table 2. Mixed Gas Permeability of Glassy Polymers at 220 and 250 °C.

Polymer	Permeability (Barrers) ^a			Selectivity α	
	H ₂	CH ₄	CO ₂	H ₂ /CO ₂	CO ₂ /CH ₄
VTEC PI 80-051 (250°C)	83.0	2.3	9.3	8.9	4.0
VTEC PI 1388 (250°C)	66.8	0.85	9.2	7.3	10.8
Kapton [®] -HN (250°C)	37.5	4.1	11.8	3.2	2.9
Matrimid 5218 (220°C)	90.6	8.94	17.2	5.2	2.6
Ultem 1000 (220°C)	77.4	2.99	18.9	4.1	6.3
PBI w/additives (250°C)	33.1	1.69	4.7	7.1	2.8
PBI w/ 40wt% PMF (250°C)	56.8	0.69	4.4	12.9	6.4

^a Permeabilities measured in Barrers: $[(10^{-10})((\text{cm}^3 \text{ (STP)} \times \text{cm})/(\text{cm}^2 \times \text{sec} \times \text{cmHg}))]$

Table 3. Energy of activation (E_p) for Kapton-HN and PBI-PMF in Mixed Gas Streams.

Gas	Energy of Activation [kJ/(mol · K)]	
	Kapton-HN	PBI w/ 40wt% PMF
H ₂	14.1	7.7
CO ₂	17.4	17.0
CH ₄	34.3	31.4

Abstract

A new thin-film thermoset was made with polybenzimidazole (PBI) and poly(melamine co-formaldehyde) (PMF) and it produced stable thin-films after thermal processing at 220-250 °C. Parent PBI has issues with thin-film formation; however, the reported PBI-PMF membranes show good film formation compared to the parent PBI membranes. The FT-IR spectra of the PBI-PMF membranes show a dominance of the PMF structures compared to PBI. In addition, the mixed gas permeability of PBI-PMF gave good selectivity of hydrogen over carbon dioxide at 250 °C, even after several hours of exposure to these conditions.