



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 wt%. 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.

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1. Introduction

Polybenzimidazole (PBI; poly-2,2'(*m*-phenylene)-5,5'-bibenzimidazole [Fig. 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 (Fig. 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

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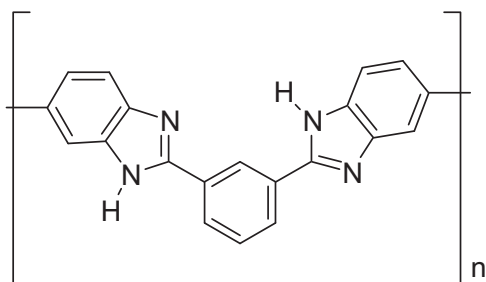


Fig. 1. Polybenzimidazole (PBI).

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.

2. Experimental

2.1. 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.

2.2. 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.

2.3. Dissolution of polybenzimidazole

Previous methods were used, where a 10 wt% parent PBI solution was made using anhydrous DMAc [5]. PBI (10 g) 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

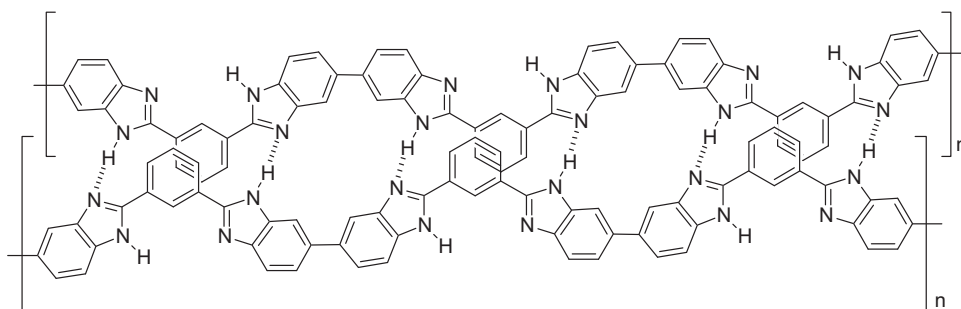


Fig. 2. Representation of PBI structural packing: π - π stacking and Hydrogen bonding.

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