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Solvent and pH-stable poly(2,5-benzimidazole) (ABPBI) based UF membranes: Preparation and characterizations

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ABSTRACT

Poly(2,5-benzimidazole), commonly known as ABPBI, is an excellent thermo-chemically stable polymer that is widely evaluated as a proton exchange membrane material in a fuel cell. Its niche intrinsic characteristics could be highly useful in the membrane preparation for various separation applications, especially under harsher environments. To gain insights towards this feasibility, ABPBI based supported membranes were prepared by phase inversion method. Effects of the nonwoven porous support material (polypropylene/polyester), non-solvent (water/0.5 N NaOH) and polymer concentration (6 or 4 wt%) on the membrane properties (water flux, rejection and porosity) were investigated. The stability of these membranes towards common organic solvents, concentrated acid (25 N H_2SO_4), base (2.5 N NaOH) and an autoclave condition was analyzed. ABPBI membrane showed a pore collapse after drying. In order to avoid this, the glycerol treatment was not only found to be suitable but also repeatable, without significant deviations in the water flux.

1. Introduction

Excellent stability of polybenzimidazoles (PBIs and ABPBI) as a proton/hydroxide/Li-ion exchange membrane material under highly acidic/basic condition is well endorsed by their applications in fuel cells and Li-ion battery [1–5]. The potential of PBIs is also investigated for the separation applications such as ultrafiltration (UF) [6,7], nanofiltration [8–10], forward osmosis (FO) [11], reverse osmosis (RO) [12], gas [13–15] and chemodialysis [16,17]. These reports demonstrated the applicability of PBI-based membranes for the removal of solutes of different molecular weights and chemical nature.

Among all polybenzimidazoles (PBI), poly(2,5-benzimidazole) (ABPBI) could be a strong candidate as the membrane material for separation applications, owing to its niche characteristics. Most significantly, it is insoluble in common organic solvents such as chlorinated solvents, tetrahydrofuran (THF), dioxane, toluene, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), etc. It is known to be soluble only in strong acids such as sulfuric, formic, trifluoroacetic, phosphoric and polyphosphoric acid [2]. On the other hand, conventional PBI is soluble in the polar aprotic solvents such as DMF, DMAc and NMP [10]; which would enable them to be converted into membranes for separation applications by a phase inversion method. On the synthetic aspect, ABPBI is obtained by self-condensation of *3,4*-diaminobenzoic acid (DABA); a less expensive, non-carcinogen and readily available monomer [18]. Its synthesis is easy in comparison to other PBIs since polycondensation of only a single monomer is involved [2]. Moreover, the repeating unit of ABPBI contains only one benzimidazole moiety and thus have higher N-H group density [19] and lower flexibility than that of other PBIs. Owing to these structural properties, ABPBI has better thermo-chemical stability than the conventional PBI [20]. Even though ABPBI is well investigated as a membrane material for proton exchange membrane fuel cell (PEMFCs) [1,2,18], it is not demonstrated for the separation applications. It may be because of its poor solvent solubility, which is an essential criterion for membrane preparation by the phase inversion (a most suitable method of the membrane preparation).

There is an increasing demand for membranes that are stable to various solvents for niche separations in pharmaceutical, biotechnology, industrial wastewater treatment, food engineering, etc. The process, termed as the Solvent-Resistant Nanofiltration (SRNF) or Organic Solvent Nanofiltration (OSN) is widely reviewed in the literature, detailing various aspects of the membranes, processes, advantages and disadvantages [21–28]. The solvent stable membranes are gaining wide attraction due to their ability to do molecular separations, higher fluxes than RO, transmission of monovalent ions while retaining divalent ions and organic molecules [21]. They can be used in diafiltration mode to concentrate the solute and allow solvent recovery with an attractive energy economy [25,26]. For such applications, the membrane should be (i) stable in a wide range of organic solvents, (ii) show

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Nomenclature

A	Membrane area (cm^2)
σ	Surface tension ($dyne\,cm^{-1}$)
σ_p	Geometric standard deviation
P	Transmembrane pressure (bar)
R	Rejection (%)
Jw	Water flux ($l\,m^{-2}\,h^{-1}$)
L	Pore length (μm)
ρ_p	Density ($g\,cm^{-3}$)
d_s	PEG diameter (nm)
a	Stoke's radius (nm)
M	Molecular weight of PEG (Da)
θ	Polymer-water contact angle (°)
η	Viscosity of water (poise)
r_p	Pore radius (cm)
ε	Dielectric constant
$\eta_{solvent}$	Viscosity of solvent

high and reproducible performances on the long term and (iii) combining elevated solvent permeabilities and acceptable rejections for molecules in the 200–1000 $g\,mol^{-1}$ M mass range [25]. Many chemically stable polymers have been used to prepare solvent stable, asymmetric membranes via immersion-precipitation viz., poly(vinylidene fluoride), polyimide, polyamide, poly(etherimide), polybenzimidazole, etc., [25]. Recently, Organic-inorganic hybrids have been used as OSN membrane materials [27,28]. MOF-Based membranes, with the introduction of MOFs in the Polyamide layer, have demonstrated superiority in enhancing the OSN performance, compared to integrally-skinned asymmetric membranes [28]. Although ceramic membranes can be a better alternative, in terms of their thermo-mechanical and chemical stability, no compaction/swelling and easy cleanability; their up-scaling is difficult, they are expensive and brittle [25–27].

Recyclability of solvents, separation of temperature sensitive solutes, lowering exhausts, low energy consumption although are major advantages of SRNF/OSN process, some important industrial solvents, such as THF, DMF, (dimethylsulfoxide) DMSO, NMP and (dichloromethane) DCM, are still critical for most currently available SRNF membranes [25]. It seems that no commercial membrane can withstand extreme pH conditions [21]. Realizing the potential of ABPBI, viz., (i) solvent stability in harsh solvents such as DMF, DMAc, NMP, DMSO, chlorinated solvents (ii) pH stability (except in concentrated inorganic acids) and (iii) thermo-chemical stability; properties of the porous ABPBI membranes is worth investigating. It could be anticipated that ABPBI based porous membranes would be applicable in harsher environments of organic solvents, acids or bases; and more importantly, without a need of cross-linking, unlike in the conventional PBI based diafiltration/ nanofiltration membranes. With this motive, present work reports, for the first time, preparation of the supported ABPBI based porous membranes by the conventional phase inversion method. Investigations towards fundamental membrane properties (flux, rejection and pore size) and their stability towards various solvents, autoclave condition and acid/base environments were performed as an initial study to unfold potentials of porous ABPBI based membranes. The membrane preparation parameters (viz., porous support, non-solvent and dope solution concentration) were varied to analyze their effects on the membrane performance. A capability of glycerol treatment was investigated towards prevention of the pore collapse observed even under ambient conditions.

2. Experimental

2.1. Materials

A *3,4*-diaminobenzoic acid (DABA) and polyethylene glycols (PEG) of different molecular weight were obtained from Aldrich Chemicals (USA). The polyphosphoric acid (PPA, P_2O_5, ca. 84% as phosphorus pentoxide) was procured from Alfa Aesar (USA). Other solvents and reagents, viz.; H_2SO_4 (98%), methanesulfonic acid (MSA), HCl, glycerol, *N,N*-dimethyl formamide (DMF), *N,N*-dimethyl acetamide (DMAc), toluene, chloroform ($CHCl_3$), hexane, isopropyl alcohol (IPA) and isobutyl alcohol (IBA) were procured from S. D. Fine Chemicals (India). All these chemicals were of AR/GR grade and were used without further purification. The non-woven porous support fabrics, viz., FO2470 and Viledon - H3160 were procured from Freudenberg (Germany); while Hollytex (grades: 3324 and 3265) were purchased from Ahlstrom (USA). The properties of these supports obtained from suppliers are given in Table 1.

Table 1
Properties of the porous supports.

Porous support	Material of construction[a]	GSM[a] ($g\,m^{-2}$)	Thickness (mm)	Air permeability[a] ($l\,m^{-2}\,s^{-1}$)	Water holding capacity (wt%)[b]
FO2470	Polypropylene (PP)	60	0.12	200	34.14
H3160	Polyester (PET)	60	0.07	30	23.08
3324	Polyester (PET)	99.9	0.13	72	29.12
3265	Polyester (PET)	81.2	0.13	160	28.26

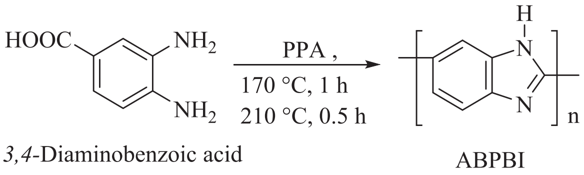
[a] Data specified by suppliers.
[b] Data generated by using the weight difference method [29].

2.2. Synthesis and characterization of ABPBI

ABPBI was synthesized by the polycondensation of DABA in PPA [2,19] as shown in Scheme 1 below.

A three-necked, 1-liter round-bottomed flask equipped with an overhead stirrer, an N_2 inlet and a $CaCl_2$ guard tube was charged with PPA (500 g) and heated up to 170 °C. A 25 g of DABA (0.1643 mol) was added while stirring and the heating was continued for an hour until its dissolution. The temperature was raised to 200 °C and stirred further for 30 min. The reaction mixture was precipitated into the stirred water. The obtained polymer was crushed in a blender and thoroughly washed with water until the filtrate was neutral to pH. The obtained polymer was suspended in 1% aqueous NaOH solution for 24 h while stirring. This was necessary in order to extract the acid that is bound to the N-H group of ABPBI. The polymer was finally washed with water, until the filtrate was neutral to pH. The collected polymer was soaked in acetone for 15 h in order to extract water from the polymer matrix and then dried in a vacuum oven at 80 °C for a week. It was preserved in the desiccator until use.

The inherent viscosity of the synthesized ABPBI was determined by using Ubbelhode viscometer (locally made) with 0.2 $g\,dL^{-1}$ solution in conc. H_2SO_4 at 35 °C. The FT-IR spectrum of ABPBI powder was performed on Perkin Elmer Spectrum One spectrometer (United Kingdom) (Fig. S1). The thermogravimetric analysis (TGA) of the polymer was performed by using Perkin Elmer TGA-7 (United Kingdom) under the



Scheme 1. Synthesis of ABPBI.