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Novel thermally cross-linked polyimide membranes for ethanol dehydration via pervaporation

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ABSTRACT

In this work, two novel carboxyl-containing polyimides, 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-4,4'-diaminodiphenylmethane/3,5-diaminobenzoic acid (6FDA-MDA/DABA, FMD) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride-4,4'-diaminodiphenylmethane/3,5-diaminobenzoic acid (BTDA-MDA/DABA, BMD), are synthesized via chemical and thermal imidization methods, respectively, and employed as pervaporation membranes for ethanol dehydration. Chemical structures of the two polyimides are examined by FTIR and TGA to confirm the successful synthesis. A post thermal treatment of the polyimide membranes with the temperature range of 250 to 400 °C is applied, and its effects on the membrane morphology and separation performance are studied and characterized by FTIR, TGA, WAXRD, solubility and sorption test. It is believed that the thermal treatment of the carboxyl-containing polyimide membrane at a relative low temperature only leads to the physical annealing, while it may cause the decarboxylation-induced cross-linking at a higher temperature. In addition, the operation temperature in pervaporation is also varied and shown to be an important factor to affect the final membrane performance. Performance benchmarking shows that the developed polyimide membranes both have superior pervaporation performance to most other flat-sheet dense membranes. This work is believed to shed useful insights on polyimide membranes for pervaporation applications.

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1. Introduction

Pervaporation, which combines the permeation and evaporation processes of liquid components across the membrane, is a membrane-based separation technology for molecular-level liquid/liquid

Abbreviations: 6FDA, 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride; 6FDA-DAM/DABA, 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-2,4,6-trimethyl-1,3-diaminobenzene/3,5-diaminobenzoic acid; 6FDA-MDA/DABA, FMD, 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-4,4'-diaminodiphenylmethane/3,5-diaminobenzoic acid; 6FDA-NDA/DABA, 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-1,5-naphthalene diamine/3,5-diaminobenzoic acid; 6FDA-ODA/DABA, 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-4,4'-oxydianiline/3,5-diaminobenzoic acid; Ac₂O, acetic anhydride; BTDA, 3,3',4,4'-benzophenone tetracarboxylic dianhydride; BTDA-MDA/DABA, BMD, 3,3',4,4'-benzophenone tetracarboxylic dianhydride-4,4'-diaminodiphenylmethane/3,5-diaminobenzoic acid; DABA, 3,5-diaminobenzoic acid; DMF, N,N-dimethylformamide; FTIR, Fourier transform infrared spectroscopy; GPC, gel permeation chromatography; MDA, 4,4'-diaminodiphenylmethane; NMP, 1-methyl-2-pyrrolidinone; PAA, polyamic acid; TEA, triethylamine; THF, tetrahydrofuran; TGA, thermogravimetric analysis; UV, ultraviolet; WAXD, wide-angle X-ray diffraction

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separations, and has been commercialized in the modern industry over the past decades. Compared to conventional separation technologies, pervaporation presents many attractive advantages such as energy efficiency, environmental benignity and high separation efficiency especially for the separation of azeotropic liquid mixtures [1–3]. Based on the solution-diffusion transport mechanism, the membrane is the key factor in order to obtain a satisfactory pervaporation performance.

For bioalcohol dehydration, polymeric membranes are generally used because of their low cost and high processability as compared to inorganic membranes. In the early time, most researches were concentrated on the hydrophilic polymeric membrane materials such as polyvinyl alcohol, chitosan and sodium alginate etc. [4–7], all of which show high permeation flux and good selectivity towards water. However, grave limitations exist for the wide applications of above membrane materials due to their weak mechanical strength, poor stability and severe membrane swelling in the feed solutions.

Alternatively, polyimide, an excellent candidate as pervaporation membrane material, has drawn more and more attention in recent years because of their superior physicochemical properties

to most conventional hydrophilic polymer materials mentioned above [8–11], such as higher thermal resistance, greater mechanical properties and better operation stability. Polyimide is a typical glassy polymer usually prepared by condensation polymerization of dianhydride and diamine monomers. The facial routes of polyimide synthesis include two strategies based on its solubility in organic solvent [2,12]. For the synthesis of both soluble and insoluble polyimides, the first step is to form a polyamic acid precursor via addition polymerization of dianhydrides and diamines. Then the second step – imidization can be conducted with heating or chemical reagent to convert the polyamic acid to the corresponding polyimide. Obviously, the properties of the corresponding polyimide mainly depend on chemical structures of the reaction monomers. Therefore, the molecular design of the polyimide can be carried out via selection of suitable monomers, thus to further manipulate the separation performance of the polyimide membrane easily.

However, in spite of the low swelling property of most polyimide materials, it still remains a big problem to the membrane stability during the pervaporation process. Therefore, a number of modification methods of polyimide membranes have been exploited to improve their physicochemical properties and obtain a more stable separation performance of the membranes. One of the most efficient modifications is cross-linking, which can be implemented by irradiation, thermal treatment or a chemical crosslinker [13]. The selectivity of the resulted membrane is therefore improved, while the corresponding flux is reduced to some extent accordingly. The most common method for polyimide modification is diamino cross-linking, which has been extensively investigated and demonstrated to be a useful way to enhance the gas separation [14–16] and pervaporation performance [17,18] of polyimide membranes. In addition, diol [18–20] and thermal cross-linking [18,21–24] have also been reported to modify the carboxylic-containing polyimides efficiently.

Among them, thermal crosslinking is particularly attractive since no external cross-linker is employed, where it involves a decarboxylation-induced cross-linking reaction at a relative high temperature. To our best knowledge, only a few researches on thermally cross-linked polyimide membranes have been investigated for the membrane separation. And systematic studies on the effect of thermal cross-linking temperature on the membrane morphology and separation performance of carboxyl-containing polyimide membranes are also limited [22–24]. Koros and co-workers developed 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-2,4,6-trimethyl-1,3-diaminobenzene/3,5-diaminobenzoic acid (6FDA-DAM/DABA) membranes for gas separation and found that membranes can be thermally cross-linked at a high temperature (15 °C above glass transition temperature) within a short time [21] or at low temperatures (much below the glass transition temperature) for a period long enough [22,23]. Maya et al. found that 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-4,4'-oxydianiline/3,5-diaminobenzoic acid (6FDA-ODA/DABA) membranes could be thermally cross-linked during the pyrolysis process at temperatures above T_g , resulting in an enhanced permeability and an improved plasticization resistance to CO₂ [24]. On the other hand, Le et al. employed the thermally-cross-linked 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride-1,5-naphthalene diamine/3,5-diaminobenzoic acid (6FDA-NDA/DABA) as pervaporation membranes for ethanol dehydration, and achieved a high flux and a comparable separation factor [20].

In this work, two novel polyimides with similar chemical structures, i.e., 6FDA-MDA-DABA and BMD-MDA-DABA polyimides, are synthesized via chemical and thermal imidization methods, respectively, and employed as pervaporation membranes for ethanol dehydration. Their chemical structures are characterized by FTIR and TGA to confirm the successful synthesis.

Effects of further thermal treatment temperature with a range of 250 to 400 °C are investigated on the morphology and performance of the polyimide membranes and characterized by FTIR, TGA, WXR, solubility and swelling test. The impact of operation temperature is also carried out. We believe this work could make important contributions to the fabrication and modification of polyimide membranes.

2. Experimental

2.1. Materials

2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) was purchased from Aladdin and purified by vacuum sublimation. 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) from Shanghai Flute Cypress Chemical Technology Co., Ltd. was purified by recrystallization from acetic anhydride (Ac₂O) and dried in a vacuum oven at 180 °C. The diamine monomers, 4,4'-diaminodiphenylmethane (MDA) and 3,5-diaminobenzoic acid (DABA), provided by Aladdin, were purified via recrystallization from ethanol and vacuum sublimation, respectively. All of the above monomers were used immediately for polyimide polymerization after purification. 1-methyl-2-pyrrolidinone (NMP) and Ac₂O were evaporated and subsequently dehydrated with 4 Å molecular sieves prior to use. Triethylamine (TEA), N,N-dimethylformamide (DMF) and methanol of analytical grade were supplied by Sinopharm Chemical Reagent Co., Ltd. and used as received. The deionized water was supplied by Wuhan PinGuan.

2.2. Preparation of nascent polyimide dense membranes

2.2.1. Preparation of 6FDA-MDA/DABA polyimide dense membrane

6FDA-MDA/DABA polyimide was synthesized by a two-step route via chemical imidization (Fig. 1) according to the previous literature [25]. In brief, one diamine, MDA, was completely dissolved in NMP under mechanical agitation, followed by the addition of the stoichiometric amounts of another diamine, DABA, and the dianhydride, 6FDA with the MDA/DABA/6FDA mass ratio of 7/3/10. Then the addition polymerization was conducted with stirring for 24 h to form a 15 wt% polyamic acid (PAA) solution. Subsequently, TEA and Ac₂O (with a molar ratio of 1:4 to 6FDA), acted as the catalyst and dehydrating agent respectively, were added to the solution, and subsequently stirred for another 24 h to produce polyimide. The whole synthesis process was carried out at ambient temperature under nitrogen protection. The resulted polyimide solution was precipitated in methanol solution, collected by filtration, washed with water, and dried in a vacuum oven at 200 °C for 24 h to obtain FMD solid.

6FDA-MDA/DABA dense membrane (denoted as FMD-origin) was fabricated by using a 15 wt% 6FDA-MDA/DABA polyimide solution in DMF. The prepared solution was filtered to remove any existing impurities in order to obtain defect-free membranes, degassed for overnight to remove bubbles, and then cast onto a glass plate with a casting knife at the thickness of 200 μm. The as-cast membrane was then placed in a vacuum oven at 50 °C for 18 h to evaporate the solvent slowly. Subsequently, the temperature was increased to 200 °C at a rate of 2.5 °C/min, maintained for 4 h to remove the residual solvent, and naturally cooled to room temperature. The resulted FMD membrane was peeled off from the glass plate carefully by being immersed in hot water and further dried at 80 °C for 24 h under vacuum. The thickness of as-fabricated FMD-origin membranes was about 13–17 μm measured by a Mitutoyo micrometer.

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