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Hydrophilic chitosan-modified polybenzoimidazole membranes for pervaporation dehydration of isopropanol aqueous solutions

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ABSTRACT

Surface-modification of polybenzoimidazole (PBI) membrane with chitosan chains has been performed using 4-isocyanato-4′-(3,3′-dimethyl-2,4-dioxo-azetidino)diphenylmethane (IDD) as a coupling agent to build up chemical linkages between the PBI membrane surface and chitosan chains. Incorporation of chitosan chains to PBI membrane surface increases its surface hydrophilicity and enhances its performance of pervaporation dehydration on isopropanol aqueous solutions. The surface chemical structure of the chitosan-modified PBI membrane (PBI-CS) has been characterized with attenuated total reflectance Fourier transform infrared and X-ray photoelectron spectroscopies. The scanning electron micrographs of PBI-CS indicate the surface reaction between PBI and IDD might take place at the top surface of the PBI matrix in a thickness of about 2 μm as the PBI membrane is swollen with the used solvent. PBI-CS is effective for pervaporation dehydration on isopropanol aqueous solutions in a wide concentration range from 30 to 90 wt%. The chitosan layer increases the dissolution rate of water into the PBI-CS membrane so as to simultaneously increase the water permeability and selectivity of the membrane. PBI-CS shows high pervaporation separation indexes which are about 3.9-fold of the value measured with the neat PBI membrane.

1. Introduction

Membrane-based pervaporation processes have shown attractive performance and operation convenience for the cases of liquid–liquid separation which could not be performed with the conventional distillation processes, such as azeotropic mixtures, thermally-unstable and thermally-sensitive products, and mixtures possessing components with close boiling points [1–4]. Compared to the conventional distillation processes, pervaporation processes are relatively energy-saving as only a small fraction of the feeding solution has been vaporized. Pervaporation units are easy for scale-up based on the well-designed membrane modules and could be used solely or integrated into the traditional chemical processes such as distillation [5] and membrane reactors [6,7]. Both polymeric and inorganic membranes have been developed for the pervaporation applications. The polymeric membranes are cheaper, easy for manufacturing, and less brittle compared to the inorganic ceramic analogs. The selection of polymers is dependent on the targets to be separated according to the solution-diffusion mechanism. The polymer having a relatively higher affinity to one of the components of the mixture to be separated is a suitable raw material for pervaporation application to show a high solution selectivity [8]. Introduction of β-cyclodextrin (β-CD) to polymeric membranes could increase the membrane selectivity on xylene isomer mixtures since β-CD has a molecular recognition for the xylene isomers [9]. Hydrophilic polymers, such as poly(vinyl alcohol) [10–12] and chitosan [13–15], have been widely used for pervaporation dehydration on various aqueous solutions of organic solvents. Recently, polyelectrolyte-based membranes also show great performance for pervaporation separation processes [16–18]. Most of the membranes exhibited high permeation fluxes and satisfied selectivity.

One of the major drawbacks for the hydrophilic polymer membranes for the pervaporation dehydration application is the relatively poor membrane stability, especially for the feeding solutions possessing high water contents. Many efforts, including crosslinking the membranes [15,19], formation of organic–inorganic composites [14], utilization of polymer blends [20], and formation of lay-by-layer membrane structures [21], have been reported to increase the membrane stability. Nevertheless, the approaches usually result in dramatic decreases in permeation fluxes and sometimes sacrifice the separation performance of the membranes. On the other hand, membranes fabricated with high performance polymers, such as polysulfone [22], polyethersulfone [23], polyamide [24], and polyimide [25,26], usually have excellent stability and could be applied for wide-range feeding solutions. Polymers with different chemical structures might show different

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Table 1
Pervaporation dehydration data for PBI and PBI-CS membranes on isopropanol aqueous solutions in different concentrations at 25 °C.

Membrane	Isopropanol concentration (wt%)	Water concentration at permeate side (wt%)	Permeability ($g\,h^{-1}\,m^{-2}$)	Selectivity
PBI	90	99.8	28	4276
PBI	80	99.0	75	384
PBI	70	97.6	80	95
PBI	50	94.8	83	18
PBI	30	95.8	158	10
PBI-CS	90	100.0	133	–
PBI-CS	80	98.2	150	221
PBI-CS	70	98.2	184	125
PBI-CS	50	98.2	200	54
PBI-CS	30	98.0	247	21

Table 2
Pervaporation dehydration data for PBI and PBI-CS membranes on 70 wt% isopropanol aqueous solution at different temperatures.

Membrane	Temperature (°C)	Water concentration at the permeate side (wt%)	Permeability ($g\,h^{-1}\,m^{-2}$)	Selectivity
PBI	25	97.6	80	95
PBI	40	98.0	95	117
PBI	55	97.4	123	86
PBI	70	97.8	137	106
PBI-CS	25	98.2	184	124
PBI-CS	40	97.5	209	91
PBI-CS	55	97.7	226	99
PBI-CS	70	97.9	250	108

separation performances. Nevertheless, most of the membranes suffer relatively low permeation fluxes due to their dense and hydrophobic features. Surface modification of the membranes is an effective approach to increase the solubility of the selective molecules in the membranes, so as to increase their permeation fluxes in pervaporation separation [27,28]. Meanwhile, the surface-modified membranes could maintain their bulk properties expected for pervaporation application. One example is incorporation of hydrophilic poly(styrene sulfonic acid) (PSSA) chains to poly(tetrafluoroethylene) (PTFE) membrane surface [29]. The PSSA surface layer increases the membrane permeation flux and the excellent stability of PTFE matrix warrants the membrane stability for various feeding solutions including high polar solvents.

Polybenzoimidazole (PBI) is a high performance polymer [30] and has been utilized in membrane technologies such as gas separation [31–33], proton exchange membrane fuel cell [34–36], and pervaporation [37–42]. For pervaporation separation, PBI was used as a modifier for polyimide membranes [37]. The hydrogen bonding between the two components stabilizes the membrane so as to increase the membrane selectivity. The membrane fabricated with the blend of PBI and polyimide has also been utilized for pervaporation dehydration on ethylene glycol aqueous solutions [38]. Chung and coworkers [39] prepared polyimide-PBI dual-layer hollow fiber membranes for pervaporation dehydration on tetrafluoropropanol aqueous solutions. The outer PBI layer serves as the selective part of the membrane due to its hydrophilicity and chemical resistance. The membranes have also been applied for dehydration on acetone aqueous solutions [40]. Nevertheless, crosslinking the PBI layer with dichlorobenzene is needed to improve the membrane stability in the feeding solutions. On the other hand, the stability of PBI membrane in acidic condition could be improved with sulfonation. Sulfonated PBI membranes have shown satisfactory stability and good separation performance in pervaporation dehydration on acetic acid aqueous solutions [41]. Moreover, a recent paper reported the preparation of mixed matrix membranes of PBI and zeolitic imidazolate frameworks and their pervaporation dehydration performance on various alcohol aqueous solutions [42]. Compared to the neat PBI membrane, the mixed matrix membranes showed enhanced permeation fluxes and good membrane selectivity. These previous works suggest that PBI could be a suitable material for pervaporation dehydration membranes. The major shortage to be improved is still the low permeation fluxes of the PBI membranes. As a result, this work reports an effective approach to incorporate hydrophilic moieties to PBI membrane surface so as to increase the surface hydrophilicity, water solubility, and permeation fluxes of the membrane. Chitosan has been selected for the hydrophilic chains to be grafted to PBI membrane surface, since chitosan-based membranes have been widely utilized for pervaporation dehydration processes [13–15,43]. The pervaporation dehydration performance of the chitosan-modified membrane has been studied and discussed using isopropanol/water mixtures as the feeding solutions.

2. Experimental

2.1. Materials

PBI was prepared in our laboratory using diaminobenzidine and isophthalic acid as the monomers according to the conventional method [44]. The yield is 80 wt% and the obtained PBI has an inherent viscosity of about 1.78 $dL\,g^{-1}$ (measured with a solution in N,N-dimethylacetamide (DMAc) at 25 °C). 4-Isocyanato-4′-(3,3′-dimethyl-2,4-dioxo-azetidino)diphenylmethane (IDD) was prepared in our laboratory according to the reported method (yield: 33%; purity $>99\%$) [45]. Chitosan with a molecular weight of about 600 k–800 k $g\,mol^{-1}$ and a degree of deacetylation of 85% was received from Acros Chem. Co. Reagent grade solvents were used as received.

2.2. Instrumental characterization

Fourier transform infrared (FTIR) spectra were obtained through the attenuated total reflectance method. A Perkin Elmer Spectrum Two FTIR equipped with a multiple internal reflectance apparatus and a ZnSe prism as an internal reflection element was employed. X-ray photoelectron spectroscopy (XPS) analysis was conducted with a VG Microtech MT-500 ESCA (British) using an Al-Kα line as the radiation source. Scanning electron microscopy (SEM) micrographs were recorded with a Hitachi S-4800 field-emission SEM. Water contact angles were measured with a First-Ten-Angstroms FTA-100 series instrument with pure water drops of about 5 μL.

2.3. Water absorption measurements

The weight of a dry membrane in about $2.0\times2.0\,cm^2$ was taken as W_{dry}. The membrane was immersed in pure water. After a certain period of time the membrane was drawn out, swept with a cleaning paper, and then weighed ($W_{wet,t}$). The water uptakes of the membrane at time t (W_t) is determined by $W_{wet,t}-W_{dry}$. The average values and the associating error were obtained with 4 measurements.

2.4. Pervaporation dehydration measurements

Pervaporation dehydration on isopropanol aqueous solutions was carried out with a conventional method reported in the previous work [16,46]. The membrane was clapped in a cell made