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Review

Polyimides membranes for pervaporation and biofuels separation

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ABSTRACT

Pervaporation is the most promising technology in the molecular-scale liquid/liquid separations existing in biorefinery, petrochemical, pharmaceutical industries, etc. for being highly selective, economical, safe and ecofriendly. However, the inadequacy of the existing polymeric membranes hinders the full exploitation of the application opportunities on the industrial-scale. This situation has motivated a substantial amount of work to explore diverse polymers and their efficiency in current and potential pervaporation fields. Due to the various attractive properties of polyimides as compared to other polymers, this review article is especially contributed to provide a comprehensive overview on the current state-of-art technologies for polyimides membranes in pervaporation. As an indispensible orientation for development of pervaporation, firstly the transport mechanisms and some other fundamentals of pervaporation were introduced.Thereafter, the pros and cons of the various facets of polyimides for pervaporation application, from polymer synthesis, modification to membrane formation were analyzed. Finally, the superiority of polyimides over other polymers in separation property was highlighted. In the light of the anticipated role of polyimides as distinguished materials for pervaporation, the future prospects were analyzed whereby to draw new guidelines for the further promotion of polyimides application in pervaporation.

Abbreviations: APD, alternating polyelectrolyte deposition; BAPP, 3,3-bis[4-(4-aminophenoxy)phenyl]phthalide; BATB, 1,4-bis(4-aminophenoxy)-2-*tert*-butylbenzene; BADTB, 1,4-bis(4-aminophenoxy)-2,5-*tert*-butylbenzene; BHTDA, 3,3′,4,4′-benzhydrol tetracarboxylic dianhydride; BMTC, 2,5-bis(methoxycarbonyl)terephthaloyl chloride; BPDA (BP), 3,3′,4,4′-biphenyltetracarboxylic dianhydride; BTDA (BT), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride; β-CD, β-cyclodextrin; CSP, ceramic supported polymer; CTC, charge transfer complex; CVDP, chemical vapor deposition and polymerization; DABA, 3,5-diaminobenzoic acid; DABC, trans-4,4′-diaminodibenzo-18-crown-6; DANT, 1,5-diaminonaphthalene; DAPy, 2,6-diaminopyridine; DBAPB, 2,2′-dimethyl-4,4′-bis(4-aminophenoxy)biphenyl; DBSA, 2,4-diaminobenzenesulfonic acid; DDBT, 2,8,(6)-dimethyl-3,7-diaminobenzothiophene-5,5-dioxide; DEB, 2,2′-diethynylbenzidine; DMMDA, 4,4′-diamino-3,3′-dimethyldiphenylmethane; DSDA, 3,3′,4,4′-diphenylsulfone tetracarboxylic dianhydride; EDA, ethylene diamine or 1,2-diaminoethane; EG, ethylene glycol; FPEI, fluorinated polyetherimide; HMDA, hexamethylene diamine; HQDPA, 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride; Kapton®, polyimide from pyrromellitic dianhydride and aromatic diamines (e.g., *m*-phenylenediamine, bis(4-aminophenyl)ether); Matrimid® 5218, polyimide of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride and diaminophenylindane; MDA, 4,4′-diaminodiphenylmethane or 4,4′-methylene diamine; MDMS, 1, 3-bis(3-aminopropyl) tetramethyldisiloxane; MgO, magnesium oxide; MTBE, methyl-*tert*-butyl-ether; ODA, 4,4′-diaminodiphenyl ether or 4-aminophenyl ether or 4,4′-oxydianiline; ODMS, α, ω-bis(3-aminopropyldimethyl)oligodimethylsiloxane; ODPA, 4,4′-oxydiphthlic dianhydride; PAA, poly(amic acid); PAI, polyamide-imide; PAN, poly(acryl nitrile); PAH, poly(allylamine hydrochloride); PBI, polybenzimidazole; PDMS, polydimethylsiloxane; PDADMAC, poly(diallyldimethylammonium chloride); PEBA, poly ether block amide; PEI, polyetherimide or polyethylenimine (polyions); PEO, poly(ethylene oxide); PES, polyethersulfone; PFDAB, 2-(perfluorohexyl)ethyl-3,5-diaminobenzoate; PI-2080, polyimid of benzophenone tetracarboxylic acid and a mixure of diisocyannates [(toluene diisocyanate + methylenebis (phenyl isocyanate)); PMDA (PM), pyrromellitic dianhydride; PPO, poly(propylene oxide); Psf, polysulfone; PSSA, poly(styrene sulfuric acid); PTFE, polytetrafluoroethene; PTHF, poly(tetrahydrofuran); PTMSP, poly[1-(trimethylsilyl)-1-propyne]; PUR, polyurethane; PUR-urea, polyurethanurea; PVA, poly(vinyl alcohol); PVDF, polyvinylidene fluoride; P84®, co-polyimide of 3,3′,4,4′-benzophenone tetracarboxylic dianhydride-methylphenylene diamine/methylene diamine; SIDA, siloxane diamine; SDPA, 4,4′-sulfonyl diphthalic anhydride; TCE, trichloroethylene; TCNE, tetracyanoethylene; TFC, thin film composite; TrMPD, 2,4,6-trimethyl-1,3-phenylenediamine; VOC, volatile organic compounds; 3MPD, 2,4,6-trimethyl-1,3-phenylenediamine; 4MPD, 2,3,5,6-tetramethyl-1,4-pphenylenediamine; 6FDA, 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride; 6FpDA, 4,4′-hexafluoroisopropylidene dianiline; *m*-PDA, meta-phenylenediamine or 3,5-diaminobenzene; *p*-PDA, para-phelenediamine or 1,4-diaminobenzene.

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1. Introduction

The polyimide family has become increasingly important in the past two decades for gas separation and then pervaporation. It belongs to the class of high-temperature polymers with balanced chemical and mechanical properties in addition to superior film-forming properties. Most importantly, some polyimides possess impressive separation properties for gas separations, liquid/liquid separation and biofuels separation. Therefore, polyimides have great potential to be the membrane materials for CO_2 capture to lower climate change, concentration and recovery of alcohols from biomass as energy sources, removal of volatile organic compounds (VOCs) from waste effluents, and separation of aliphatic and aromatic isomers as feedstock for the chemical industry. The versatility of polyimide chemistry, easy synthesis, and simple modification provide polymer and membrane scientists with powerful tools to tailor the polyimide molecular structure with desirable physiochemical properties and separation performance for the aforementioned applications. Hence, molecular architecture, modification and membrane structural design to improve separation performance of polyimides membranes for various liquid/liquid separations and biofuels separations via pervaporation are the main focuses of this review article. Biofuels consist of biodiesel, bioalcohol, biogas and some other minor components. Bioalcohol is one of the main biofuels capable of substituting petroleum usage globally and has received significant attention by both academia and industry. The separation of bioalcohol (especially bioethanol and biobutanol) from fermentation broths by pervaporation has been widely studied in recent years. This review targets polyimides specifically using pervaporation for liquid/liquid separation and bioalcohol separation. The polymer science and membrane development toward biodiesel separation are rather limited and therefore not included in this review.

Pervaporation is a technology combining membrane permeation and evaporation for molecular-scale liquid separation [1]. When a liquid stream containing two or more components is placed in contact with one side of a non-porous polymeric membrane or molecularly porous inorganic membrane, the components will sorb into/onto the membrane. The penetrants will diffuse through the membrane and evaporate as the permeate because of the chemical potential difference across the membrane induced by vacuum or gas purge [2]. The separation of different components is achieved when some of the components preferentially diffuse across the membrane.

The phenomenon of pervaporation was first observed by Kober et al. in 1917 [3], and it was the work of Binning et al. in 1956 that established the basic principles and potential of pervaporation technology [1]. The breakthrough of pervaporation in industrial applications was made in 1980s by GFT (Gesell-schaft für Trenntechnik, Hamburg, Germany) with the development of a series of poly(vinyl alcohol)–poly(acryl nitrile) (PVA–PAN) composite membranes for the dehydration of alcohol/water azeotropic mixtures [4]. From then on to 1996, more than 90 industrial pervaporation units were installed worldwide [5]. During almost the same period of time, around 200 European and US patents about pervaporation were publicized. As far as industrialization is concerned, the choice of pervaporation-based hybrid systems is indispensable at the present stage [6,7]. This is due to the fact that, with current limitations of membrane materials and lack of commercially available pervaporation membranes, pervaporation alone cannot replace as well as compete with distillation over a wide spectrum of feed compositions. The latter is a well-established and better-understood separa-