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Pervaporation properties of EC membrane crosslinked by hyperbranched-polyester acrylate

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Abstract

An aliphatic type of hyperbranched-polyester (HBPE) that was synthesized from 2,2-dihydroxymethyl propanyl acid (DMPA) and 1,1,1-trihydroxymethyl propane (TMP) was end-capped with acrylic group, and the photo-polymerizable hyperbranched-polyester (AHBPE) was obtained. These AHBPEs were employed as the macromolecular crosslinking agents to enhance the pervaporation performance of EC membrane for the separation of benzene/cyclohexane mixtures. The effects of the content of AHBPE and benzophenone (BP) as well as the radiating time on the separation factor and the total permeate flux were investigated in detail. The results show that, the performance of EC membranes incorporating AHBPEs of higher generations exhibited much higher flux, with a comparison to the membranes modified by micromolecular crosslinking agent of ethylene glycol dimethacrylate (EGDM). The membrane with the total permeation flux of 42.5 kg μm m^{-2} h^{-1} and the separation factor of 6.82 was obtained at the AHBPE and BP content of 40 wt% and 10 wt%, respectively.

Keywords: Pervaporation; Benzene/cyclohexane; Hyperbranched-polyester; Acrylate; Ethyl cellulose

1. Introduction

Separations of azeotropic, close boiling, isomeric liquid mixtures by membrane-based pervaporation (PV) technique have been studied extensively because of the potential industrial utility of this approach [1]. Pervaporation is considered to be a promising technology in the separation of volatile organic compounds, for it is economical, safe and eco-friendly. In many cases, systems based on membranes combined with one or two of these more traditional techniques have been accepted as attractive options. Yet, the performance of the membrane is still the key in separating the liquid mixtures effectively.

In recent years, dendritic polymers have been employed as novel materials for membrane separation. It is generally accepted that dendritic macromolecules have unusual properties such as: less flexibility, lower entanglement degree, and significant chain end effect. Also, these polymers can hardly crystallize, and possess larger free volume than linear polymer with similar structure of unit. The study on gas separation of hyperbranched polyimide by Fang et al. [2] proved that, hyperbranched-polyimide membrane exhibited better gas selectivity and flux, with respect to linear polyimide. Xiao et al. [3] studied polyimide membranes crosslinked by dendimer with terminal amine group. The results indicated that the selectivity and flux of polyimide membrane could be enhanced simultaneously by controlling the crosslinking time. Cha et al. [4] prepared composite membranes of poly(dimethylsiloxane) films deposited with PAMAM layer containing silver salt, and the propylene permanence and ideal separation factor over propane of these membrane reached 34GPU(10^{-6} cm^3 (STP) cm^{-2} s^{-1} $cmHg^{-1}$) and 340, respectively, at high silver loading. Nagale et al. [5] have described the preparation and characteristics of hyperbranched-poly(acrylic acid) membranes on porous alumina supports.

To the best of our knowledge, however, the reports on the separation of organic mixtures by pervaporation have not been found in the past investigations of membrane containing dendritic polymer. In the last few years, the application of aliphatic HBPE acrylates in UV-curable coating system has been described extensively [6]. A series of hyperbranched-urethane–acrylates based on aliphatic HBPE and polyethyleneglycol acrylate were prepared and evaluated for use in UV-curable coatings. The hyperbranched-acrylates exhibited

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higher cure rate and lower shrinkage than the conventional polyester acrylates. The large amount of terminal groups as well as the pseudo-spherical structure of AHBPE intrigued us to employ them as crosslinking agents in membrane system, for the large molecular volume may impart the membrane to large free volume, which plays a significant role in affecting the permeate flux of membrane.

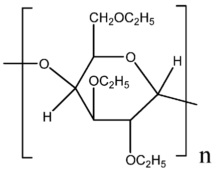
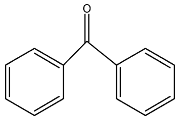
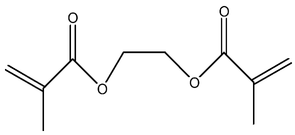
In this work, benzophenone (BP) was utilized as photosensitization-initiator, and the photo-polymerizable HBPE end capping with acrylic groups was used as crosslinking agent for EC dense membrane. The thread of selecting basic membrane material in this study is mainly based on the solubility parameter theory. According to this method, the calculated solubility parameter of ethyl cellulose is $20.91\,J^{1/2}\,cm^{-2/3}$, which is closer to benzene ($18.53\,J^{1/2}\,cm^{-2/3}$) than cylcohexane ($16.79\,J^{1/2}\,cm^{-2/3}$). Meanwhile, the amorphous structure of EC may result in good membrane permeability. The PV performances for the separation of benzene/cyclohexane (Bz/Cx) of the AHBPE modified EC membranes (EC–AHBPE) were investigated in detail.

2. Experimental

2.1. Reagents

Acrylic acid (AA) was distilled twice to remove inhibitor. The EC used in this study had the weight average molecular weight of 81,060 and the poly-dispersity index of 1.39. The DS (degree of substitution) of EC was 1.4. *p*-Toluene sulfonic acid (*p*-TSA), ethylene glycol dimethacrylate (EGDM), benzophenone (BP), 2,2-dihydroxymethyl propanyl acid (DMPA), 1,1,1-trihydroxymethyl propane (TMP), toluene, hydroquinone (HQ) are all purchased from Beijing Chemical Agents Corporation (Beijing, China), and were used without further purification. The structures and properties of EC, BP, and EGDM were listed in Table 1.

Table 1
Structures and properties of EC, BP, and EGDM

Materials	Structure	Properties
EC		T_g: 48 °C
BP		Melting point: 48.5 °C, boiling point: 305 °C
EGDM		Boiling point: 85 °C at 2 mmHg

2.2. Measurement

A high-pressure mercury lamp with power of 400 W was used to generate UV light, and the distance from the lamp to the position placing membrane was 10 cm. FT-IR measurements were performed on Nicolet 8700 (Thermoelectron). X-ray diffusion (XRD) measurements were performed on D/max-2500 (Rigaku). NMR spectrum was obtained from Avance 500 (Bruker), and the solvent of chloroform-D1 was adopted. The thermal analysis was performed on TA-60 (Shimazu).

2.3. Synthesis of HBPE and AHBPE

The synthesis of G1–G5 HBPE was undertaken according to the method described previously [7]. The number of hydroxyl and carboxyl group in HBPE was determined by titration with benzylformyl anhydride and $0.1\,mol\,L^{-1}$ NaOH aqueous, respectively.

The synthesis of AHBPE was synthesized from HBPE and acrylic acid via esterification reaction [8]. The modification degree of HBPE terminal groups was monitored by FT-IR and ^1H NMR. The glass transition temperatures (T_g) of the AHBPE with different generations were listed in Table 2.

2.4. Preparation of dense membrane

Specific amounts of EC, AHBPE or EGDM, and BP were solved in a binary solvent of benzene and ethanol in which the total weight fraction of polymer was 10%. The weight ratio of benzene to ethanol in solvent was 1:1; the weight ratio of BP to ABPPE (or EGDM) was 1:5; and the weight fraction of AHBPE in membrane was adjustable at the range of 0–40%. Then the solution was filtered and left to debubble at room temperature for 24 h. Membranes were prepared by casting these solutions on a clean and smooth glass plate. The solvent was allowed to evaporate for 6 h in a thermostatic oven. The temperature and pressure for evaporation was 30 °C and atmospheric pressure, respectively. Then the membrane was peeled off and radiated under UV light for certain time. The thickness of membrane was around 20–25 μm.

2.5. Sorption experiment

In sorption experiment, the mass weight ratio of AHBPE to EC in membrane was 1:5, and the thicknesses of membranes were controlled around 60 μm. The crosslinked membranes were tailored into strips with the same size. Then strips were

Table 2
The glass transition temperatures of AHBPE with different generations

Generation	T_g (°C)
G1	−30.5
G2	−23.1
G3	−7.8
G4	−8.3
G5	−2.3