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# Pervaporation properties of EC membranes modified by aliphatic hyperbranched polyester

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ABSTRACT

Pervaporation membranes containing hyperbranched polymer were prepared from the blends of ethyl cellulose (EC) and hyperbranched polyester (HBPE). The FT-IR analysis indicated that the interactions between EC and HBPE decreased as increasing the generation of HBPE. The membrane containing HBPE (EC-HBPE) showed both higher sorption ratio and selectivity than pure EC membrane. The effects of HBPE content as well as temperature of feed solutions on the membrane performance were investigated in detail. The EC-HBPE membrane exhibited much higher permeate flux than the EC membrane, while the separation factor maintained at same level.

## 1. Introduction

Pervaporation (PV) is a membrane unit operation in which the separation of the desired component takes place through a dense membrane by a solution-diffusion mechanism. Extensive studies have been focused on the separation of organic liquid mixtures, especially for azeotropic and close boiling point solvents systems [1]. Like other membrane processes, the commercial applications of PV were also limited by the trade-off between selectivity and permeability. The selection of membrane materials is especially crucial for PV, because the PV performance can be highly affected by the affinity difference of components in feed solution with membrane.

In recent years, dendritic polymers became a novel type of membrane material [2–4]. Because of their highly branched structure, these polymers can hardly crystallize, and possess larger free volume than linear polymer with similar structure of unit. Zhao et al. [5] employed hyperbranched polyglycerol as pore-forming agent, and prepared porous membranes of PVDF via phase inversion process. The increasing content of HPG in the casting solution led to an increase in surface pore size and porosity of the membranes, which in return increased the pure water flux of the blend membranes.

However, these reports were mainly focused on the gas separation or ultrafiltration. Few reports have been made on the application of membrane containing dendritic polymer on the separation of organic mixtures by PV. The pseudo-spherical structure as well as the interior cavities of HBPE intrigued us to employ them as modification component of membrane materials, for this structure may impart the membrane on larger free volume and lower crystallinity (if any) than pure membrane material, which plays a significant role in affecting the permeate flux of membrane.

In our previous studies [6], hyperbranched polymers end-capped with acrylic groups were used as macromolecular crosslinking agents for EC membrane. Comparing to the micromolecular crosslinking agent, such as ethylene glycol dimethylacrylate (EGDM), the membrane incorporated with hyperbranched polymer exhibited both higher selectivity and permeate flux. And generally, membranes crosslinked by higher generation HBPs exhibited higher permeate flux than lower generation HBPs.

The aim of this work is to try another way of incorporating HBP into membrane that was simply prepared via blending HBPE with EC. EC is soluble in benzene, while insoluble in cyclohexane. The EC membranes swell heavily in case that benzene content in feed solution exceeded 20 wt%. Therefore, the pervaporation experiments in this work were performed at low benzene feed (the content of benzene in feed was around 10 wt%).

## 2. Experimental

### 2.1. Reagents

Ethyl cellulose (EC), and *p*-toluene sulfonic acid (*p*-TSA), ethylene glycol dimethacrylate (EGDM), benzophenone (BP), 2,2-

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dihydroxymethyl propanyl acid (DMPA), 1,1,1-trihydroxymethyl propane (TMP), benzene, cyclohexane are all from Beijing Chemical Agents Corporation, and were used without further purification.

### *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 is 10 cm. FT-IR measurements were performed on Nicolet 8700. X-ray diffusion (XRD) measurements were performed on D/max-2500. Differential scanning calorimeter (DSC) measurements were performed on SHIMAZU TA-60WS with a scan rate of 10 °C/min over the temperature range of 173–498 K. NMR spectrum was obtained from Avance 500.

### *2.3. Preparation of dense membrane*

The HBPEs were synthesized according to the method mentioned in literature [7]. The detailed characteristic results were reported in our previous work [6]. The membranes containing the 4th generation HBPE (*G*4HBPE) were chosen as a contrast to the EC membrane in sorption and pervaporation experiments. Specific amount of EC, HBPE, were solved in a blend of benzene and ethanol (benzene/ethanol = 1/1) in which the polymer concentration was 10 wt%. Then the solution was filtered by stainless steel mesh, and reposed 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 at room temperature for several hours. Then the membrane was peeled off and annealed at 80 °C for 2 h. The thickness of membrane is around 20–30 μm.

### *2.4. Sorption experiment*

In sorption experiment, the mass weight ratio of HBPE to EC in membrane was 10%, and the thicknesses of membranes were controlled around 60 μm. Membranes were all crosslinked by EGDM under UV light to maintain stable in higher benzene content [6], and tailored into strips with the similar size. Then these strips were immersed into various benzene/cyclohexane mixtures at 20 °C for various times, wiped quickly with tissue paper to remove liquid on membrane surface, and weighed at electric balance. After sorption reached equilibrium, membrane strips were placed into a dry flask connected to a cold trap and vacuum pump. The collected liquids were analyzed by gas chromatography (GC-14A, SHIMAZU).

### *2.5. Pervaporation experiments*

Pervaporation experiments were carried out in a batch stirred cell which had a thermostatic jacket, and the downstream pressure was maintained below 1 mmHg. The membrane area in contact with the feed solution was 19.6 cm$^2$. Permeates were collected in a cold trap, weighed, and analyzed using gas chromatography.

The permeation selectivity of benzene was calculated from the following equation:

$$\alpha = \frac{x_{\mathrm{Bz}}/x_{\mathrm{Ch}}}{y_{\mathrm{Bz}}/y_{\mathrm{Ch}}},$$

where $x_i$ and $y_i$ are the permeant contents in permeate and feed, respectively.

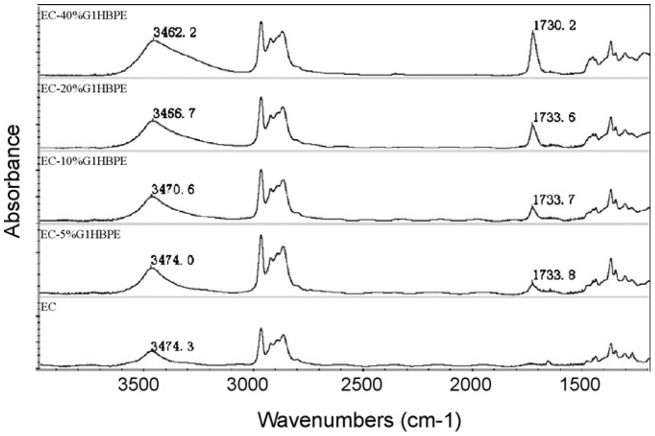

**Fig. 1.** Effect of the *G*1HBPE content on the IR spectra of the EC-G1HBPE membrane.

## 3. Experimental

### *3.1. Characterizations of EC-HBPE membranes*

#### *3.1.1. FT-IR*

FT-IR measurements were employed to characterize the interaction between EC and HBPE in membranes, for the interaction of two blend components may cause the position shift of certain peak [8].

The IR spectra of the membranes containing different amount of HBPEs were compared in Figs. 1 and 2. As shown in Fig. 1, the position of hydroxyl group peak of EC-*G*1HBPE membrane shifted from 3474.4 cm$^{-1}$ of pure EC to lower wave number as increasing the content of HBPE in membrane. And the carbonyl group peak of 1733.8 cm$^{-1}$ also moved toward lower wave number. Above indicated that hydrogen bonds formed between EC and HBPE, and leaded to the red-shift for both hydroxyl and carbonyl groups.

However, an interesting result was observed in the IR comparison of the membranes incorporating *G*3, *G*4 and *G*5HBPE with the EC-G1HBPE membrane. As for the *G*1HBPE, its hydroxyl value is 0.0125 mol/g which is higher than that of G3HBPE (0.0073 mol/g). That means the hydroxyl amount in the membrane containing 20 wt% *G*3HBPE is higher than that in membrane containing 10 wt% *G*1HBPE. However, for the EC-*G*3HBPE membrane (Fig. 2), there appeared to be no significant shift of the peak associated with

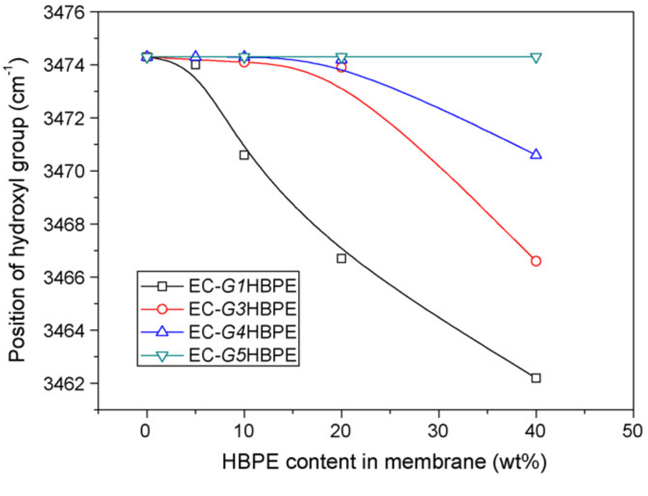

**Fig. 2.** Effect of HBPE content on the hydroxyl group position of EC-HBPE membranes.