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Development of crosslinked plasma-graft filling polymer membranes for the reverse osmosis of organic liquid mixtures

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Abstract

We have prepared crosslinked pore filling-type membranes using a plasma-graft polymerization technique to carry out the reverse osmosis (RO) of organic liquid mixtures. The grafted methyl acrylate (MA) polymer was crosslinked to improve the pressure durability. Vinyl acrylate (VA) and *N*,*N*′-methylene bis(acrylamide) (MBAAm) were used as the crosslinkers. In the RO of a conventional non-crosslinked HDPE-g-MA membrane, the permeation rate continued to increase with operating time, and the separation factor decreased to unity (i.e., no separation occurred). The HDPE-g-MA/VA membranes showed an RO separation capability, but this deteriorated after the RO experiments were repeated several times. The HDPE-g-MA/MBAAm membranes exhibited an improved stability and a reasonable separation performance at pressures as high as 12 MPa. We show that pore filling-type membranes are applicable to the RO process using crosslinked grafted polymers. The separation performance and pressure durability can be improved on if the factors influencing the membrane are optimized, e.g., the chemical structure of the crosslinker and the composition of the monomer/crosslinker mixture.

Keywords: Reverse osmosis; Pervaporation; Crosslinked membranes; Plasma-graft filling polymerization; Organic liquid separation

1. Introduction

In the application of polymeric membranes in the separation of organic liquid mixtures, control of the membrane swelling is important in the optimization of the membrane performance. For this purpose, we have proposed the concept of using a pore filling-type membrane to control membrane swelling [1–4]. In this process, the pores of a porous substrate are filled with a grafted polymer, and the substrate material must be inert to all organic liquids. The swelling of the grafted polymer is suppressed by the matrix of the substrate. Pore filling-type membranes have been prepared using the plasma-graft polymerization technique. Pore filling-type membranes show excellent separation performance in the pervaporation of organic liquid mixtures [1–5].

Plasma-graft filling polymerization has become an important membrane preparation technique, and it has been applied in molecular recognition microcapsules [6], molecular recognition ion gating membranes [7,8], organic/inorganic composite membranes [9], and in fuel cell applications [10,11]. Research and development based on this concept has been reported by several other research groups [12–20]. Childs and co-workers applied this concept to the nanofiltration/reverse osmosis of aqueous solutions [14–17]. They succeeded in preparing a pore filling-type membrane using a crosslinked polyelectrolyte, and their membrane showed good separation performance at pressures up to 6 MPa.

Reverse osmosis (RO) and pervaporation (PV) are the two major membrane separation processes used in liquid separation. The RO technique has an advantage over the PV technique in that it requires less energy, because the separation is conducted without a phase transition occurring [21]. Reverse osmosis is already used commercially in the

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separation of aqueous solutions, such as in desalination and in the concentration of fruit juices. However, it is difficult to apply the RO technique to organic liquid separation systems, such as ethanol/water mixtures, due to the high osmotic pressure of these separation systems. In general, the separation performance (i.e., the permeation rate and separation factor) of the RO technique is usually lower than in the PV technique due to the osmotic pressure. It has been suggested that an RO system at infinite pressure will attain the separation performances of a PV system [22]. However, from the process simulation, it was suggested that RO has an advantage over the PV technique even in the case of organic liquid separation, provided that the membrane possesses the enough pressure durability [21]. So, the key issue is the pressure durability of the membrane under swollen state in organic liquid mixtures.

We decided to investigate whether pore filling-type membranes are applicable to the RO separation of organic liquid mixtures. Since a high operating pressure is required to overcome the osmotic pressure of the feed solution, the membranes used were required to be stable at high pressures. From the work by Childs and co-workers [14–17], it was suggested that pressure durability for organic liquid mixtures in the high RO pressure range (>8 MPa) could be attained by crosslinking the grafted polymer, if an appropriate crosslinker was selected, and if the crosslinking conditions were optimized. However, it has not been reported whether crosslinked pore filling-type membrane can be stable and show separation performance in the organic liquid mixtures.

In this work, we report on the preparation of crosslinked pore filling-type membranes and their separation performances in the PV and RO of organic liquid mixtures. We demonstrate that crosslinked pore filling-type membranes show RO separation of chloroform/*n*-hexane mixtures at pressures up to 12 MPa.

2. Experimental

2.1. Materials

Porous high-density polyethylene (HDPE) flat-sheet membranes were supplied by the Tonen Chemical Co. Ltd., Japan, and these were used as the porous substrate. The thickness of the substrates was 5 μm, and the pore diameter was 0.02 μm. The substrates had a symmetrical structure.

The methyl acrylate (MA), vinyl acrylate (VA) and *N*,*N*′-methylene bis(acrylamide) (MBAAm) used were purchased from the Wako Chemical Co., Japan, and these were used as the monomer and crosslinkers (MA, and VA and MBAAm, respectively). The MA and VA were purified by distillation under vacuum, and the MBAAm was used as received. Water was used as the solvents for the monomer solution and total monomer and crosslinker concentration was 3 wt% (only in Fig. 5, 20 wt% methanol aqueous solution was used and total monomer and crosslinker concentration was 5 wt%). The monomer solutions were degassed by repeated freezing and thawing under vacuum.

2.2. Plasma irradiation and graft polymerization

The plasma-graft polymerization procedure used has been described in detail elsewhere [1], but in brief, an HDPE substrate was placed in a glass tube, and was irradiated with an RF-plasma (power, 10 W and pressure, 10 Pa) in an argon atmosphere for 1 min. Then, the plasma-irradiated substrate was contacted with the monomer aqueous solution under argon atmosphere at $P = 10$ Pa. Graft polymerization was conducted in a shaking bath at $T = 30\,^{\circ}$C. The grafted membranes were then rinsed in toluene overnight to remove the homopolymer and any non-reacted monomer. The membranes were then oven-dried at 40 °C. The degree of grafting was calculated being the weight of grafted polymer per unit surface area of the substrate. The crosslinker ratio in the grafted polymer in the HDPE-g-MA/MBAAm membranes was estimated from N/C analysis.

2.3. Pervaporation

Pervaporation experiments through the prepared membranes using a chloroform/*n*-hexane mixture (72/28 wt%) were carried out using membranes with an effective membrane area of 19.6 cm^2, and the feed solution was maintained at $T = 25\,^{\circ}$C. A chloroform/*n*-hexane mixture (72/28 wt%) was chosen as the feed solution for comparison with the previous study [2]. In the experimental apparatus, the downstream compartment was evacuated, and the permeate was collected in a vacuum trap condenser that was cooled using liquid nitrogen. The feed and permeate concentrations were determined using gas chromatography. The separation factor, α, was defined as:

$$\alpha = \frac{y(100 - x)}{x(100 - y)} \tag{1}$$

where x is the concentration of chloroform in the feed mixture (wt%), and y is the concentration of chloroform in the permeate mixture (wt%).

2.4. Reverse osmosis

Reverse osmosis experiments on chloroform/*n*-hexane mixtures (72/28 wt%) through the prepared membranes were conducted. A schematic diagram of the RO apparatus is shown in Fig. 1 (for pressures up to 8 MPa), and in Fig. 1b (for pressures up to 12 MPa). In Fig. 1a, the feed solution was pressurized by N_2 gas from a cylinder. In Fig. 1b, the feed solution was pressurized using a pressure valve and a circulation pump that maintained a constant flow rate. In both systems, the effective membrane area was 19.6 cm^2, and the temperature of the feed solution was maintained at $T = 25\,^{\circ}$C. The permeate was collected in a collecting bottle cooled by