Preparation and Performance of Poly(vinyl butyral) Membrane for Ultrafiltration

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SYNOPSIS

Ultrafiltration membrane was prepared from poly(vinyl butyral). The effects of membrane thickness, polymer concentration, evaporation time, and evaporation temperature, etc., on the performance of the resulting membranes have been studied. Dimethylacetamide was used as a casting solvent. The membrane formed by casting the polymer from a 15 wt % solution and evaporation at 25°C for 30 s had a flux value of 250 cm^3/cm^2 h (4.8 kg/cm^2, 26°C) at 92.9% rejection level for dextran sodium sulfate (average mol. wt. 550,000) separation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Many functions of artificial membranes have been studied on various applications such as separation,[1,2] bioactive substance immobilization,[3,4] and transportation[5,6] by many researchers. Our group has also reported on the use of the poly(vinyl butyral) membrane in enzyme immobilization[7] and in biosensors.[8] In addition, researchers in many industrial fields have found that the membrane can be applied to reverse osmosis, ultrafiltration, and microfiltration as useful separation processes.[9,10] In the research presented in this paper, we applied the poly(vinyl butyral) membrane to ultrafiltration. Our report deals with the performances of the poly(vinyl butyral) membranes in a variety of prepared conditions to obtain fundamental data.

EXPERIMENTAL

Casting Solution Preparation

Poly(vinyl butyral) was purchased from Wako Pure Chemical Industries, Ltd. It consists of vinyl butyral, vinyl alcohol, and vinyl acetate moieties in the approximate ratio of 75 : 22 : 3, respectively. The casting solution was prepared by dissolving the requisite quantity of the polymer in dimethylacetamide with stirring at the room temperature until the polymer was dissolved completely.

Membrane Casting

The membranes were cast in the form of flat sheets. Membranes were cast by using a glass bar to spread the casting solution onto a glass plate. The membrane thicknesses were adjusted using a metal spacer of proper dimensions. After allowing the solvent to evaporate under various conditions of a set time and temperature, the glass plate was immersed in a bath of water at room temperature for about 24 h, at which time the membrane could be easily separated from the glass plate. The membrane was then preserved in distilled water until its use.

Membrane Thickness and Water Content

The water on the surface and back side of the membrane is wiped with the filter paper, and their thicknesses were measured with a microthickness gauge. The total water contained by the membrane was determined by weighing the membrane samples and then weighing them again after drying the membrane at 105°C to a constant weight. The formula for reaching the water content was
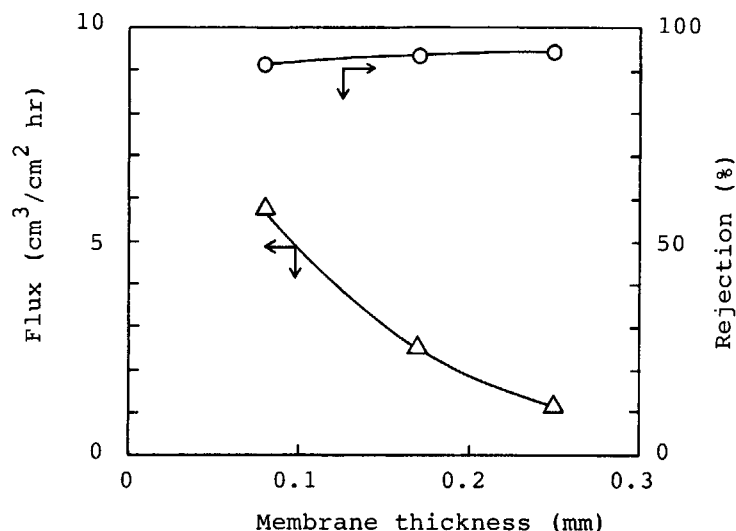
Figure 1   Effect of membrane thickness on membrane performance: polymer concentration, 15%; evaporation temperature and evaporation time, 25°C, 30 s; feed, 2.5% dextran sodium sulfate aqueous solution; operating conditions, 26°C, 4.8 kg/cm².

Water content (%)

$$= \frac{\text{wet weight} - \text{dry weight}}{\text{wet weight}} \times 100$$

All the determinations were carried out in triplicate and the average was calculated.

Scanning Electron Microscopy

The surfaces and the cross sections of the poly(vinyl butyral) membranes were observed through a Hitachi, S-415 scanning electron microscope. The cross section was obtained by breaking the membrane at the temperature of liquid nitrogen. The specimens were freeze-dried and then, using a vacuum metallizer, they were coated with a thin layer of gold.

Membrane Testing

The membrane testing was carried out in a laboratory testing unit consisting of a feed solution tank, a pressurizing pump, a pressure gauge, and a stainless-steel high-pressure test cell. The effective membrane area set in the test cell was 9.62 cm², and this circle, together with the filter paper and the porous disk, was placed in the test cell with the air side (skin side) of the membrane always facing the feed solution. Dextran sodium sulfate (average mol. wt. 550,000), purchased from Kanto Chemical Co., was used as the feed solute. The four kinds of poly(ethylene oxide) purchased from Kanto Chemical Company were also used as feed solutes whose

average mol. wts. were 1000, 6000, 20,000, and 100,000, respectively. Feed solution containing 2.5% solute was circulated by a pressurizing pump, and the operating pressure in the system was controlled by a pressure gauge. In all the experiments, permeate was collected for analysis after 1 h of pressurization. The solute concentration in the feed solution and the permeate was determined by a TOC analyzer (Shimazu, TOC-10B). The amount of permeate collected in this set period was measured and the flux was calculated.

Membrane Performance

The performance of the membranes was measured in terms of flux and rejection, where flux was the ultrafiltrate (permeate) rate calculated as cm³/cm² h. The membrane rejection was calculated as

$$R\ (\%) = \frac{C_F - C_P}{C_F} \times 100$$

where R is the percent of solute rejection; C_F, the feed concentration; and C_P, the permeate concentration.

RESULTS AND DISCUSSION

Effect of Membrane Thickness on the Membrane Performance

The relationship between the membrane thickness and the membrane performance is shown in Figure

1, where the polymer concentration was 15% and the evaporation temperature and the evaporation time were kept at 25°C for 30 s, respectively. The operating pressure was 4.8 kg/cm². The feed solution contained 2.5% dextran sodium sulfate. The flux for aqueous solution of dextran sodium sulfate decreased with an increase in membrane thickness, while the rejection for dextran sodium sulfate increased slightly. The permeation characteristics for an aqueous solution of dextran sodium sulfate were a function of thickness of the resulting membranes. In view of membrane strength, it was thought that approximately 0.17 mm as the membrane thickness was suitable. Therefore, the same spacer was used in the all following experiments to obtain approximately 0.17 mm as the membrane thickness.

Effect of Polymer Concentration

The effect of poly(vinyl butyral) concentration on the membrane performance is shown in Figure 2, where the evaporation temperature and the evaporation time were kept at constants of 25°C and 30 s, respectively, and the polymer content in the casting solution changed within a range of 10–20 wt %. The operating pressure was 4.8 kg/cm². The feed solution contained 2.5% dextran sodium sulfate and the water content decreased with an increase slightly in the polymer concentration. These phenomena suggest that the membrane of higher polymer concentration is denser than that of lower ones.

Observation of Membrane Structure

The electron micrograph of poly(vinyl butyral) membrane prepared at each concentration is shown in Figure 3. The pore was not observed at high magnification (× 10,000) on the each membrane top surface. These electron micrographs revealed that the polymer density of the membrane increased with an increase in the polymer concentration. These membranes composed an asymmetrical membrane.

Effect of Evaporation Temperature

The relation between evaporation temperature in the range of 20–30°C and the membrane performance is shown in Figure 4, where the polymer concentration was 15% and the evaporation time was 30 s. The operating conditions were 26°C and 4.8 kg/cm². The feed solution contained 2.5% dextran sodium sulfate. The flux for aqueous solution of dextran sodium sulfate decreased with a rise of evaporation temperature, and the rejection increased
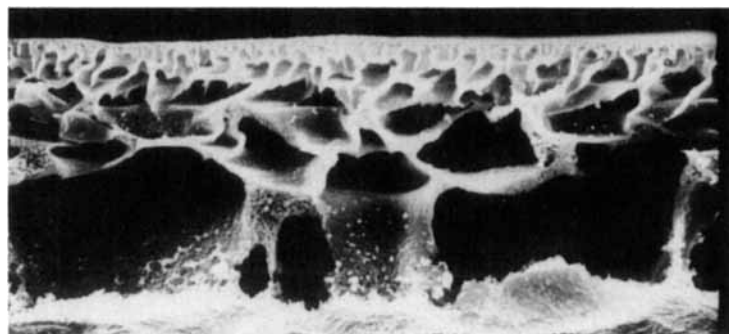
slightly with it. When the evaporation temperature is higher, the parts of crystalline structure in the membrane increased and the parts of noncrystalline structure in the membrane decreased. The decrease of the flux and the increase of the rejection with a rise of evaporation temperature were dependent on the above factors.
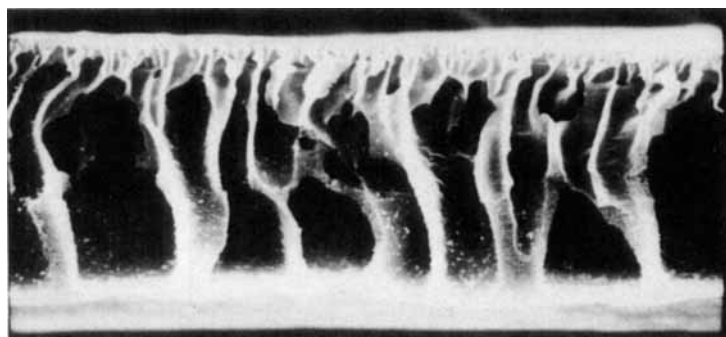
Effect of Evaporation Time

The effect of evaporation time in the range of 10–60 s on the membrane performance is shown in Figure 5, where the polymer concentration was 15% and the evaporation temperature was 25°C. The operating pressure was 4.8 kg/cm². The feed solution contained 2.5% dextran sodium sulfate. The flux for aqueous solution of dextran sodium sulfate decreased as the evaporation time increased, and the
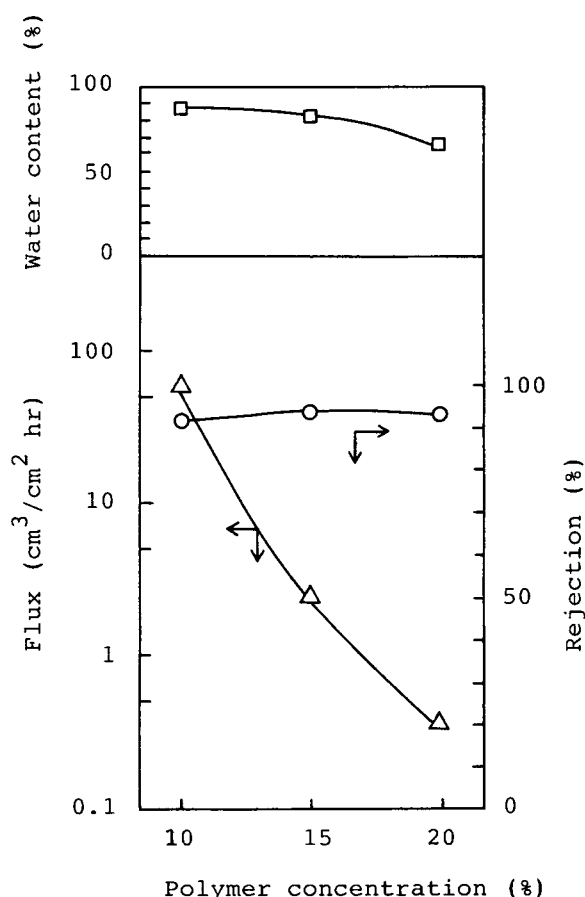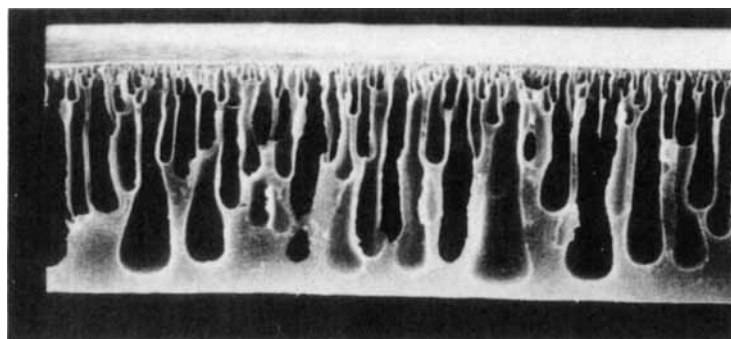

Figure 2 Effect of poly(vinyl butyral) concentration on membrane performance. The experimental conditions were the same as those in Figure 1 except for the membrane thickness (approximately 0.17 mm) and polymer concentration employed.
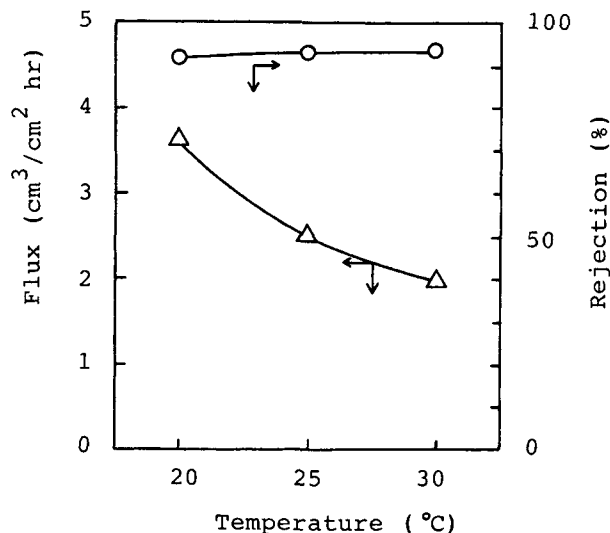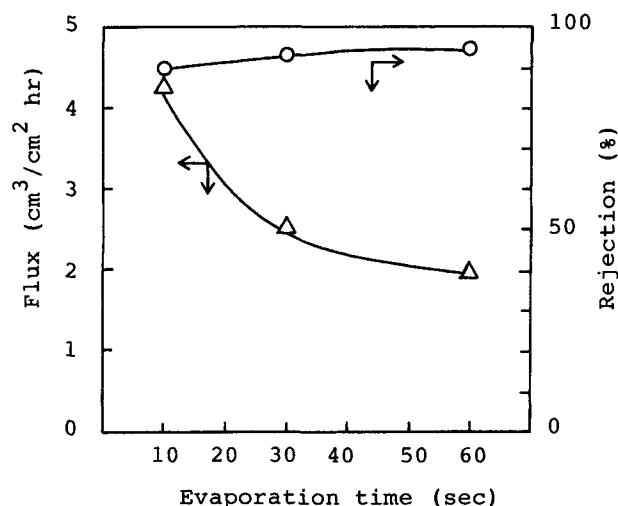
(a)

60 μm

(b)

(c)

Figure 3   Scanning electron micrograph of cross section of poly(vinyl butyral) membrane: (a) polymer concentration, 10%; (b) 15%; (c) 20%.
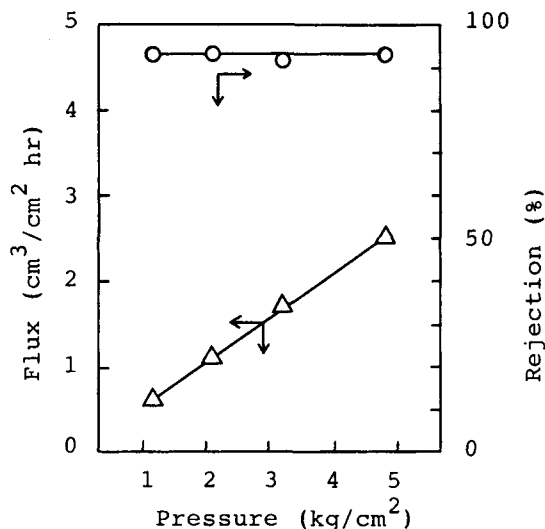
Figure 4 Effect of evaporation temperature on membrane performance. The experimental conditions were the same as those in Figure 1 except for the membrane thickness (approximately 0.17 mm) and evaporation temperature employed.
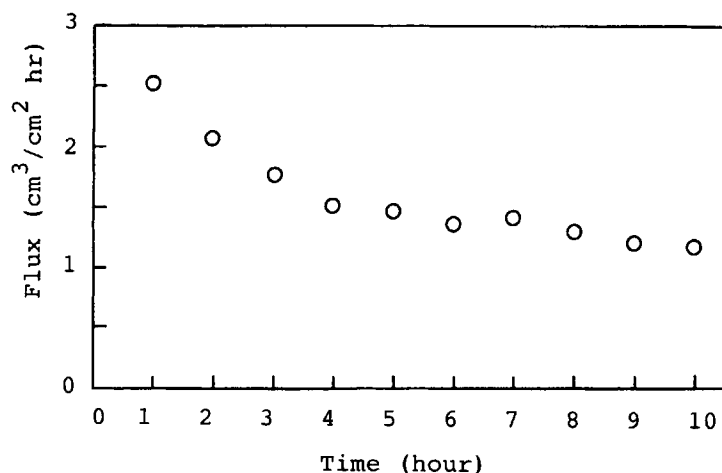

Figure 6 Effect of operating pressure on membrane performance. The experimental conditions were the same as those in Figure 1 except for the membrane thickness (approximately 0.17 mm) and operating pressure employed.

rejection increased with it. These results may be also attributed to the membrane structure. When the evaporation time is longer, the parts of crystalline structure in the membrane increase and the parts of noncrystalline structure in the membrane decrease.

Figure 5 Effect of evaporation time on membrane performance. The experimental conditions were the same as those in Figure 1 except for the membrane thickness (approximately 0.17 mm) and evaporation time employed.

Effect of Operating Pressure

The relation between the operating pressure within the range of 1–5 kg/cm^2 and the membrane performance is shown in Figure 6. The polymer concentration of the membrane used was 15%. The evaporation temperature and the evaporation time were 25°C and 30 s. The feed solution contained 2.5% dextran sodium sulfate and the feed temperature was 26°C. The flux for aqueous solution of the dextran sodium sulfate increased linearly as the operating pressure increased. The rejection, however, was independent of the operating pressure. It was thought that this membrane kept a stable structure under the general pressure of ultrafiltration.

Effect of Operating Time on Membrane Flux

The effect of operating time on the membrane performance is shown in Figure 7. The membrane used was the same as in the above experiments. The feed solution contained 2.5% dextran sodium sulfate and the feed temperature was 26–28°C. The operating pressure was 4.8 kg/cm^2. The feed solution was recirculated and the experiment was conducted over a period of 10 h. There was a decline in flux of approximately 50%. The decline in flux is attributed to the increased feed concentration as a result of the removal of permeate and the increased hydraulic

Figure 7 Effect of operating time on membrane flux. The experimental conditions were the same as those in Figure 1 except for the membrane thickness (approximately 0.17 mm), operating time, and operating temperature (26–28°C) employed.

resistance of the gel layer formed on the membrane surface.

Relation between Molecular Weight and Rejection

The relation between the molecular weight of feed solute and the rejection is shown in Figure 8. The membrane used was the same as in the above ex-

periments. The feed solution contained 2.5% of each solute. The operating pressure was 4.8 kg/cm², which shows that the "cutoff" level for this membrane has the order of 300,000–400,000 mol. wt. This cutoff level is found in few other substances other than the PVA membrane and is useful in several industrial fields.

In conclusion, it has been revealed that the poly(vinyl butyral) membrane can be used as the
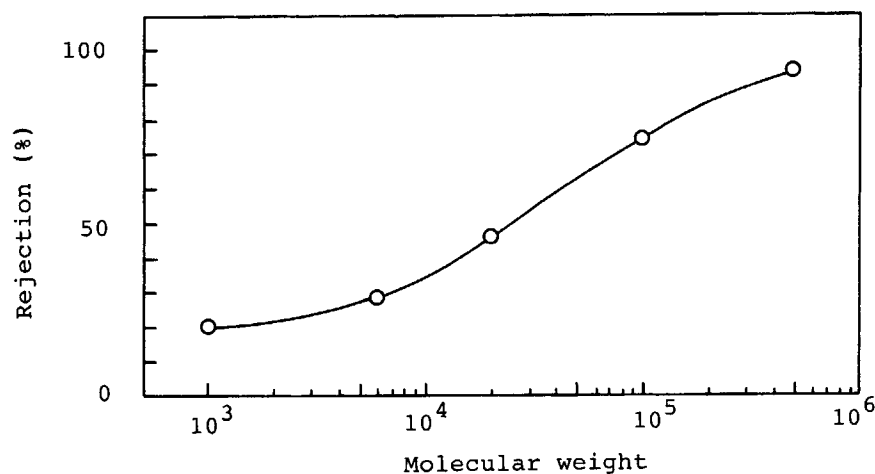
Figure 8 Relation between molecular weight of feed solute and rejection. The experimental conditions were the same as those in Figure 1 except for the membrane thickness (approximately 0.17 mm) and solute employed: feed, 2.5% each solute aqueous solutions, poly(ethylene oxide) (average mol. wt. 1000, 6000, 20,000, 100,000), dextran sodium sulfate (550,000).

membrane for ultrafiltration. This membrane can be applied to the separation, concentration, and purification processes in many industrial fields.

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