Preparation and Characterization of Several Types of Polyvinyl Butyral Hollow Fiber Membranes by Thermally Induced Phase Separation

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ABSTRACT: Hollow fiber membranes were prepared by thermally induced phase separation from three types of polyvinyl butyral (PVB) and a blend of two of these polymers. Although the difference in the chemical composition of the PVB polymers used was not remarkable, their respective membrane performances were quite different. With a high phase separation temperature the pore size of the prepared membrane was large, because structure growth occurred for a long time. Water permeability tests of the wet membranes showed the results that corresponded to the pore sizes of the membranes. By contrast, the results for the dried membrane appeared to be related to the hydrophilicity of the PVB polymer and independent of pore size in the wet condition. Although the membrane with high wettability had low mechanical strength, the membrane from the polymer blend of two different PVB polymers showed adequate wettability and mechanical strength. This produced a hollow fiber membrane with favorable characteristics for application in water treatment. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Recently, water shortages have become a severe problem worldwide because of population growth and an increase in the demand for high quality water. A possible solution to this problem is water purification by membrane technology, and this technique has attracted attention for wastewater treatment and production of drinking water. Many polymers have been investigated as membrane materials, including polyethylene, polypropylene, polyethersulfone, polysulfone (PSf), cellulose acetate, and polyvinylidene fluoride. Because each polymer is unique in terms of permeability, hydrophilicity, chemical resistance, mechanical strength, and fouling properties, membrane materials can be selected according to the application.

The main fabrication method for porous polymer membranes is phase separation. The thermally induced phase separation (TIPS) process is particularly attractive because of the high reproducibility it offers, and the fact it can be used with a variety of polymers. Novel polymers and various additives to improve membrane functionality have been adopted for the TIPS process. The polymers used in the TIPS process include polyethylene,[1,2] polypropylene,[3,4] cellulose acetate,[5] poly(ethylene-*co*-vinyl alcohol) (EVOH),[6,7] poly(vinyl butyral) (PVB),[8,9] polylactic acid,[10,11] polyvinylidene fluoride/polymethyl methacrylate,[12,13] PVB/EVOH,[14] polyethersulfone/polymeric surfactant,[15] and PVB/TiO$_2$.[16]

Membranes for domestic water purification need to completely exclude bacteria and have high antifouling properties. Although PSf is often used in domestic water purification, hydrophilic additives are usually required in the membrane preparation process to improve its hydrophilicity. Polyvinyl acetal is a potential candidate for membrane preparation that will not suffer from this disadvantage of PSf membranes. Polyvinyl acetal is obtained by partial saponification and subsequent acetalization of inexpensive polyvinyl acetate. The polymer has high resistance against acid and base, and high mechanical strength. A representative polyvinyl acetal is PVB, and this has been studied as an ultrafiltration flat membrane[17] and a microfiltration hollow fiber membrane. It has been reported that PVB is more hydrophilic than other polymers because of the vinyl alcohol group in its molecular structure.[8] In other studies, polymer blending with EVOH,[14] blending with surfactants,[9] and hydrophilization of the PVB membrane by HCl treatment[17] have been attempted.

In this study, hollow fiber membranes for water treatment were prepared from three types of PVB and their mixture. The molecular structures of the PVB polymers were investigated for
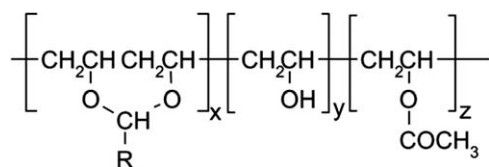
Figure 1. Molecular structure of polyvinyl acetal.

suitability for the membrane in terms of membrane performance and wettability.

EXPERIMENTAL

Materials

Polyvinyl butyral (6000C and 6000AS) and polyvinyl acetal (067) were obtained from Denki Kagaku Kogyo (Tokyo, Japan). The polymers of 6000C, 6000AS, and 067 are abbreviated as PVB-1, PVB-2 and PVB-3, respectively. Their structures are shown in Figure 1 and their chemical compositions are summarized in Table I. Polyethlene glycol (PEG) 200 and PEG 600 were purchased from Wako Pure Chemical Industries (Osaka, Japan). Polystyrene (PS) latex particles with diameters of 20, 50, 100, and 300 nm were purchased from Duke Scientific Co. (Palo Alto, CA). All the chemicals were used without further purification.

Phase Diagram

Homogeneous polymer-diluent samples were prepared by mixing total 3 g of polymer and PEG 200 at 170°C for 10 min using a twin-blade mixer (IMC-119D, Imoto Co., Kyoto, Japan). A sample of the prepared homogeneous solution was placed between two coverglasses separated by a 100-μm-thick Teflon® sheet spacer. The sample was heated at 180°C for 2 min on a hot stage (HFS91, LINKAM) and then cooled at 10°C min^{-1}. The cloud point temperatures during cooling were observed using a microscope (BX50, Olympus). The measurements were repeated at least four times.

Hollow Fiber Membrane Fabrication

Hollow fiber membranes were prepared using a batch-type extruder (Imoto Co., BA-0).[1,6] Measured amounts of the polymer and PEG 200 were fed into the vessel with mass fraction of 20% the polymer, and then mixed for 60 min at 170°C. The sample was maintained at 170°C for 120 min, and then the homogeneous solution was fed to a spinneret by a gear pump under nitrogen pressure. The spinneret consisted of outer and inner tubes with diameters of 1.25 and 0.62 mm, respectively. PEG 600 was introduced into the inner tube to make a hollow fiber. The hollow fiber was extruded from the spinneret with an air gap of 0 mm and wound onto a take-up winder after entering a water bath at 10°C. The extrusion rate of the polymer solution and the flow rate of PEG 600 in the inner tube of the spinneret were fixed at 0.10 and 0.27 m s^{-1}, respectively. The diluent remaining in the hollow fiber membrane was extracted by immersing the fibers in water.

Differential Scanning Calorimetry Measurements of T_g of Membranes

Differential scanning calorimetry (DSC 8500, PerkinElmer, Waltham, MA) was used to evaluate the glass transition temperature (T_g) of blend membranes. The dried membrane piece was weighed before sealing the sample hermetically in an aluminum DSC pan. An empty pan with a lid was used as a reference. The samples were equilibrated at 70°C for 2 min and first heated up to 170°C at a rate of 10°C min^{-1}. After heating, the samples were cooled to 70°C and then heated up to 170°C again at a rate of 10°C min^{-1}.

Scanning Electron Microscope (SEM) Observation

To obtain dry hollow fiber membranes, the prepared membranes were freeze-dried (FD-1000, Tokyo Rikakikai, Tokyo, Japan). The dry hollow fiber membranes were fractured in liquid nitrogen and sputtered with Pt/Pd. The cross-sections and the surfaces of the hollow fiber membranes were examined using a SEM (JSM-5610LVS, Hitachi, Tokyo, Japan) with an accelerating voltage of 15 kV.

Water Permeability

Milli-Q water was forced to permeate from the outside to the inside of hollow fiber membranes. A transmembrane pressure (range 0.05–0.1 MPa) was applied by adjusting a pressure valve on the release side, and the pressure was averaged from the readings of the two pressure gauges. The water permeability was calculated based on the inner surface area of the hollow fiber membrane. Each datum of water permeability was the average of three measurements.

Mechanical Strength

The tensile stress of the hollow fiber membranes was measured using a tensile apparatus (AGS-J, Shimadzu, Kyoto, Japan). The membrane was fixed vertically between two pairs of tweezers separated by a gap of 50 mm, and extended at a constant elongation rate of 50 mm min^{-1} until it broke. Each datum of the tensile stress at the breaking point was the average of five measurements.

Exclusion of PS Particles and Bacteria

Filtration experiments were carried out using the same apparatus as that used in the water permeability test. The solutes used were monodisperse PS latex particles with diameters of 20, 50, 100, and 300 nm. The feed solutions were prepared by dispersing the PS latex particles in an aqueous nonionic surfactant solution [0.1% (mass fraction) Triton X-100]. The solute concentrations in the filtrate and feed solution were measured with an ultraviolet-visible spectrophotometer (U-200, Hitachi Co.) at 380 nm.

A bacteria exclusion test was conducted for the membranes using a suspension of *Brevundimonas diminuta* NBRC14213 (4 × 10^6 CFU/mL). The bacterial suspension was permeated

Table I. Copolymer Composition, Molecular Weight, and Water Contact Angle of the Three Types of PVB Polymers

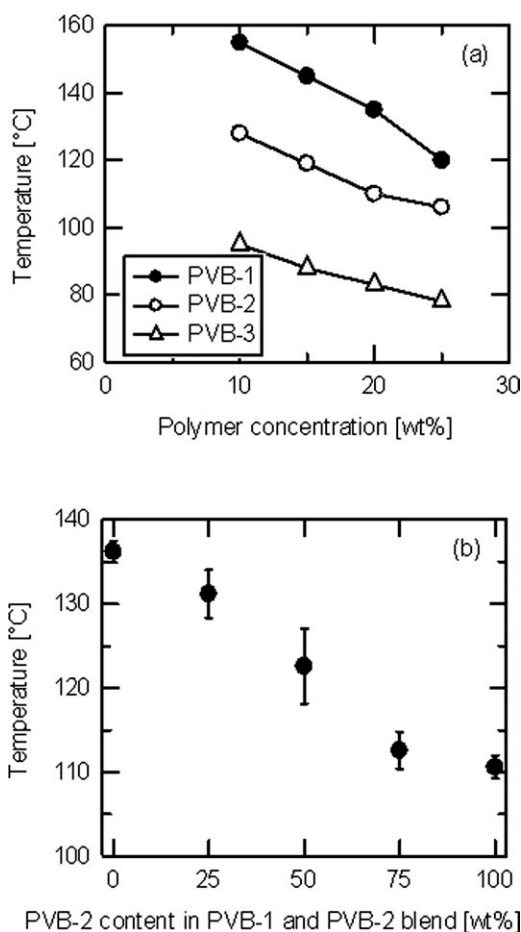| Polymer	Composition				M_w	Water contact angle (°)
	x	Y	z	R		
PVB-1	83	16	1	CH$_3$:C$_3$H$_7$	288,000	76
PVB-2	87	12	1	CH$_3$	190,000	71
PVB-3	85.4	13.5	1.1	CH$_3$	188,000	69

Figure 2. Phase separation temperatures of the PVB solutions. (a) PVB solution; (b) polymer blend solution of PVB-1 and PVB-2.

through the PVB membranes, and the number of bacteria in the permeate were counted according to the Japanese Industrial Standard (JIS K3835).

RESULTS AND DISCUSSION

Phase Diagram

The cloud point temperatures of the solutions with a PVB mass fraction of 10–25% were measured [Figure 2(a)]. The temperatures were in the order of PVB-1 > PVB-2 > PVB-3, which indicated that the chemical compositions of the PVB polymers affected the phase separation temperatures. The solubility parameters of the polymers and PEG 200 are shown in Table II. The difference between the solubility parameters of PEG 200 and PVB-1 was larger than those among PEG 200 and other PVB polymers. This meant that the cloud point temperature of the PVB-1 solution was highest, because it had the lowest compatibility between the polymer and the diluent. By contrast, the solubility parameter of PVB-3 was closest to that of PEG 200, and this solution had the highest compatibility. Thus, the cloud point temperature in this system was lowest.

The cloud point temperatures of polymer blend solutions containing PVB-1 and PVB-2 were also examined. The temperature decreased with an increase in the PVB-2 content [Figure 2(b)],

Table II. Solubility Parameters of the Three Types of PVB Polymers and the Diluent

	Solubility parameter (MPa$^{1/2}$)
PVB-1[a]	22.6
PVB-2[a]	22.9
PVB-3[a]	23.3
PEG 200[b]	24.3

[a]Estimated using Fedor method [18].
[b]Cited from Ref. [19].

because PVB-2 had higher compatibility with PEG 200. Because PVB-1 and PVB-2 are compatible with each other, the cloud point temperatures of the polymer blend solution gradually changed with its composition, and two cloud point temperatures were not observed.[14]

DSC Measurement

T_g measurement of the prepared membranes were carried out using DSC. Figure 3 shows the relationship between T_g of the PVB-1 and PVB-2 polymer blend membranes. The T_g measurement of each sample had only one peak and the T_g smoothly increased with the increase in the PVB-2 content. If the compatibility of the blend polymers is low, original T_g of each polymers appears even in the measurement of blend polymer. Therefore, this result clearly expresses that PVB-1 and PVB-2 polymers have high compatibility.

SEM Observation

SEM observation of prepared membranes was carried out. Figure 4 shows the cross-section, outer surface, and inner surface of the hollow fiber membranes prepared from the three PVB polymers. The outer surfaces of all the membranes had obvious pores and their sizes were in the order of PVB-1 > PVB-2 > PVB-3. PVB-3 had a small porous structure on the outer surface, while PVB-1 and PVB-2 had rough outer surfaces. The inner surfaces of all the polymers had submicron size pores, and the sizes of these pores were in the same order as the pores on the outer surface. These tendencies can be explained in
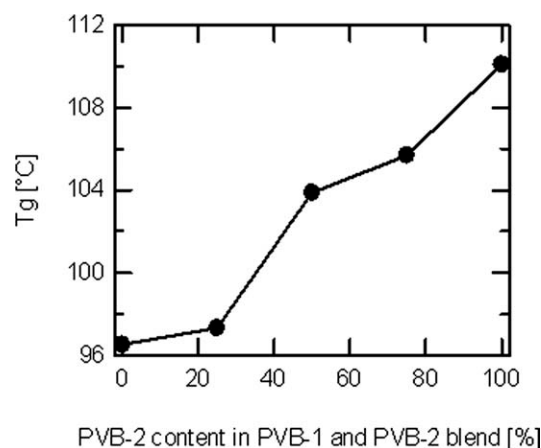

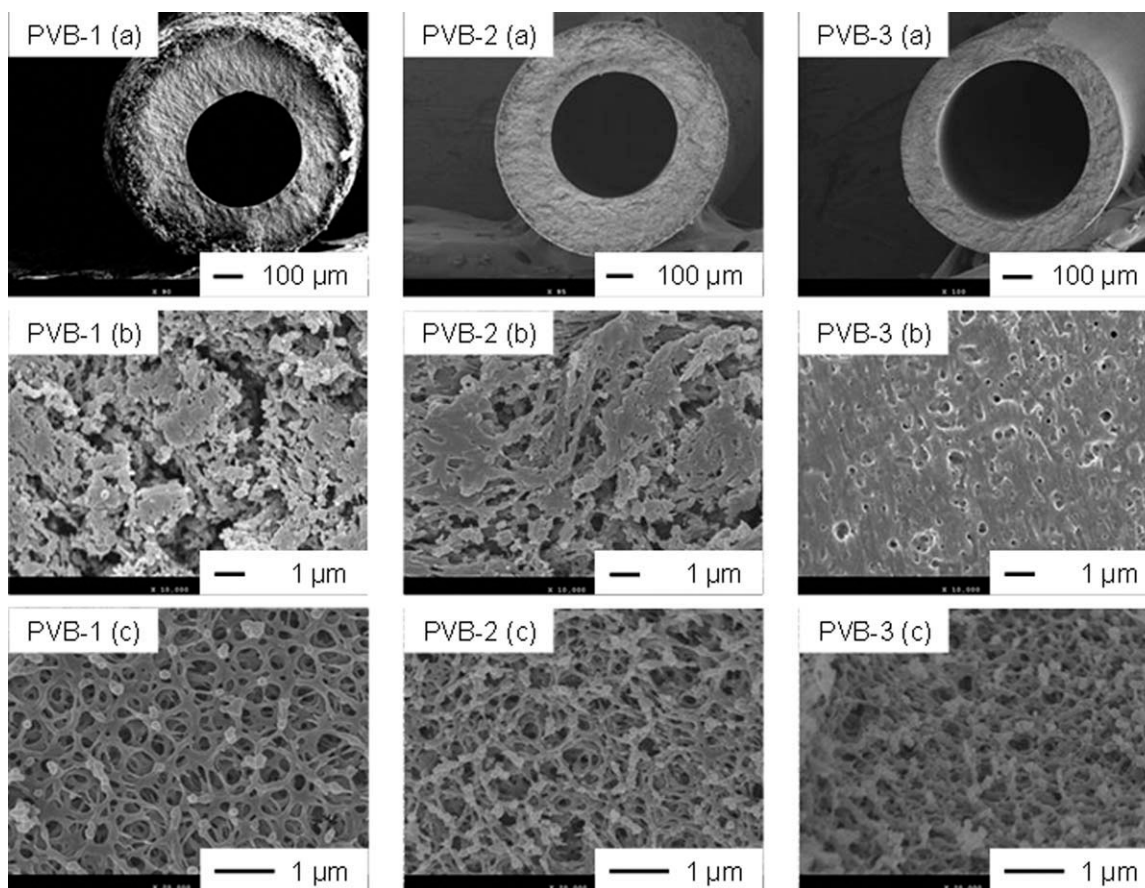**Figure 3.** T_g of the polymer blend membranes.

Figure 4. SEM images of the hollow fiber membranes. (a) Cross-section; (b) outer surface; (c) inner surface.

terms of the phase separation temperatures of the PVB solutions shown in Figure 2(a). The high cloud point temperature for PVB-1 resulted in a long coarsening time for the structure and large pore size, while the short coarsening time for PVB-3 resulted in small pores.

Figure 5 shows the SEM images of the outer surfaces and cross-sections of the hollow fiber membranes prepared from the polymer blend of PVB-1 and PVB-2. The membrane structure became smaller as the content of PVB-2 increased, which corresponded to the lower cloud point temperature shown in Figure 2(b).

All the membranes prepared from the individual PVB polymers and the PVB blend had rough structure on the outer surface and small pores on the cross-section. Thus, the membranes prepared in the TIPS process had asymmetric structures. A skin did not form on the outer surface, because the air gap was 0 mm in the membrane preparation process. When the air gap is large, the solvent evaporates from the outer surface, which leads to formation of a skin on the outer surface.[6]

Water Permeability
Water permeability of the prepared membranes was investigated with wet membranes. Figure 6(a) shows that the water permeability was in the order of PVB-1 > PVB-2 > PVB-3 for the wet membranes. As was confirmed by SEM observation, PVB-1 had the largest pores and PVB-3 had the smallest. Thus, the

water permeability trend can be explained by the difference in the pore sizes. The water permeability was also measured after the membranes had been dried at 40°C for 24 h *in vacuo*. The dried PVB-2 membrane had a similar water permeability to the wet membrane, while the dried PVB-1 and PVB-3 membranes had negligible water permeability [Figure 6(a)]. SEM observation confirmed that the pore size of the PVB membranes did not change after the drying process, and the same trend in pore size was maintained for the three polymers. Surface tension determines the pressure needed to make water penetrate membrane pores. The pressure difference Δp can be expressed as follows:

$$\Delta p = 2\gamma/r \qquad (1)$$

where γ is the surface tension and r is the pore radius. Thus, the pore size and the hydrophilicity on the pore surface affect the water permeability of the dried membrane. Judging from the SEM image of the membrane, the PVB-3 membrane had much smaller pores on the outer surface than the other two membranes. Therefore, the dried PVB-3 membrane showed no water permeability, even though it had higher hydrophilicity. By contrast, the PVB-1 and PVB-2 membranes had large pores in the SEM observation, and the difference in the water contact angle was only 5° (Table I). This indicates that the difference in the membrane hydrophilicity between PVB-1 and PVB-2 is not
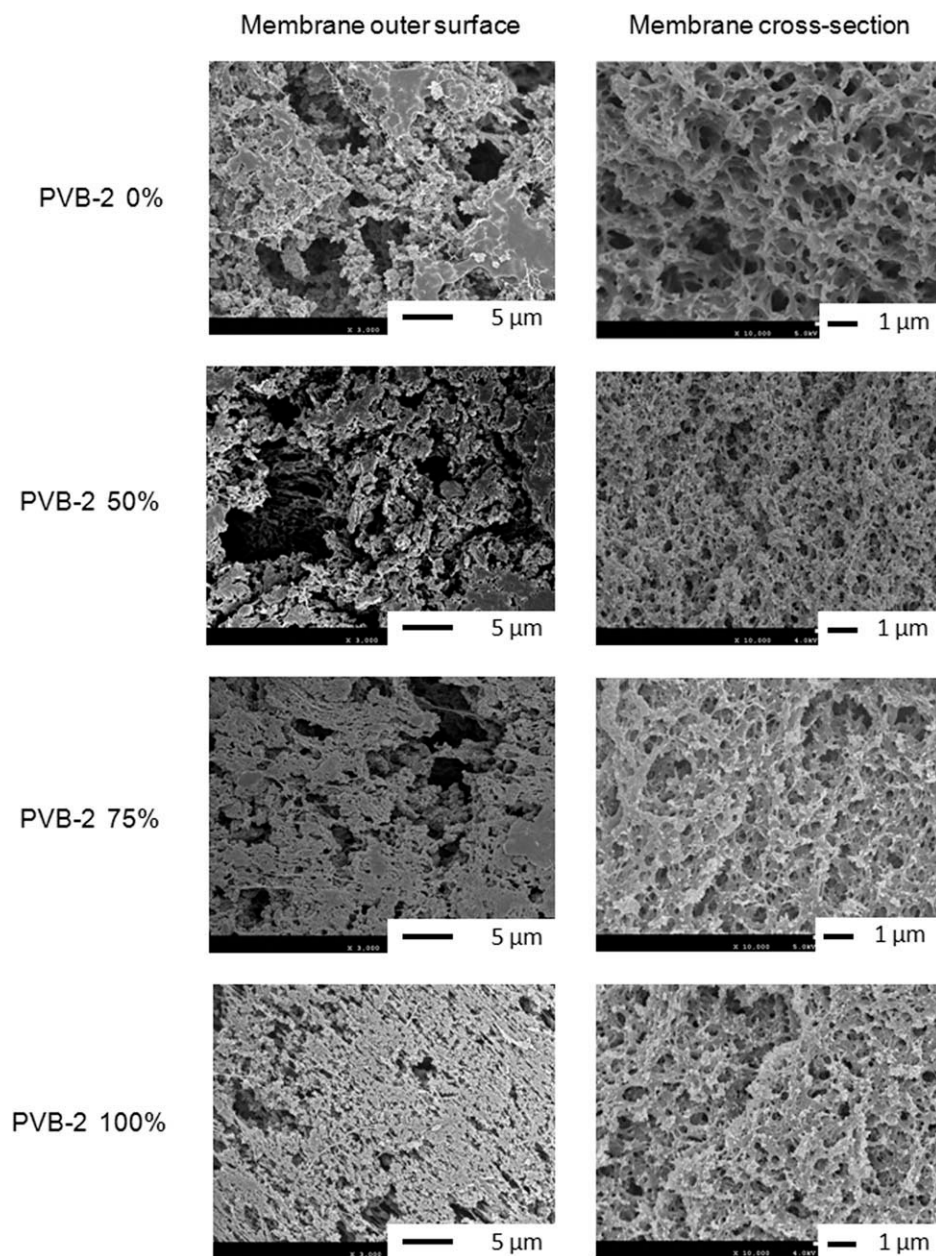
Figure 5. SEM images of the polymer blend membranes.

large. Because the dried PVB-1 membrane was not water permeable, a permeability test using aqueous isopropanol solutions was carried out to investigate the effect of surface tension and hydrophilicity. Aqueous solutions containing an isopropanol mass fraction of 2 and 5% gave permeabilities of 258 and 371 L/(m² h atm), respectively. Thus, the dried PVB-1 membrane showed high permeability with lower surface tension. This result implies that the difference in the hydrophilicity between the dried PVB-1 and PVB-2 membranes resulted in the difference in the water permeability of the two membranes, even though the difference in the hydrophilicity was not large.

Some dried membranes made with hydrophobic polymers are known to have low water permeability because of their low wettability. To give high wettability on the inner pore surface, it should usually be coated with a nonvolatile hydrophilic material before producing the membrane module. Thus, the high wettability of the PVB-2 membrane is a significant advantage over other hydrophobic membranes, because this coating process can be skipped.

Water permeability was also measured for the PVB-1 and PVB-2 polymer blend membrane. The water permeability of the wet membrane decreased with an increase in the PVB-2 content of the polymer blend [Figure 6(b)]. However, for the dried membrane, membranes with a PVB-2 mass fraction <50% had little water permeability. The dried membrane had higher water permeability when the PVB-2 content of the membrane was higher. Thus, the water permeability of dried membranes increased as the hydrophilic PVB-2 content increased.
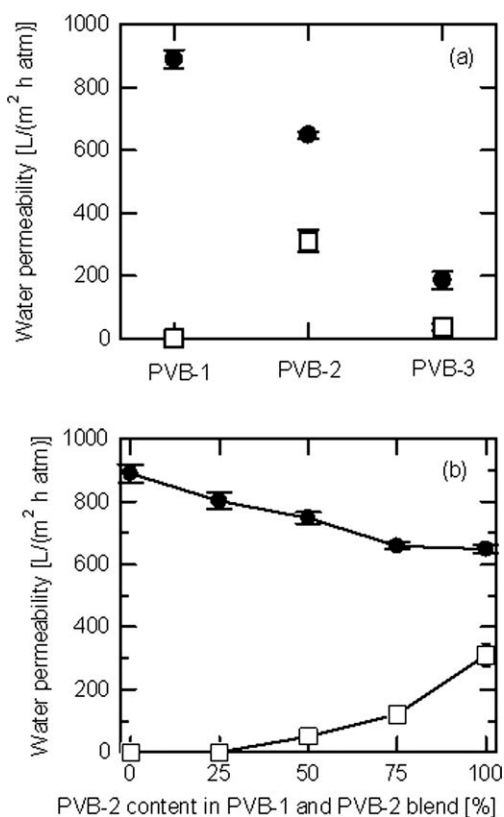
Figure 6. Water permeability of the prepared membranes. (a) PVB membrane; (b) polymer blend membranes. Solid circles, wet membranes; open squares, dry membranes (40°C, 24 h).

PS Particles and Bacteria Exclusion

Exclusion of PS particles was measured to investigate the pore size. The particle exclusion R is defined as follows:

$$R = 1 - C_f / C_0 \qquad (1)$$

where C_0 and C_f are the particle concentrations in the feed and the filtrate, respectively. The effect of the PVB species on the exclusion is shown in Figure 7. All the PVB membranes showed
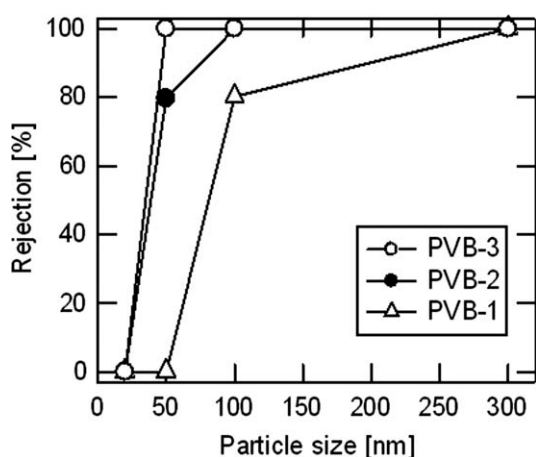

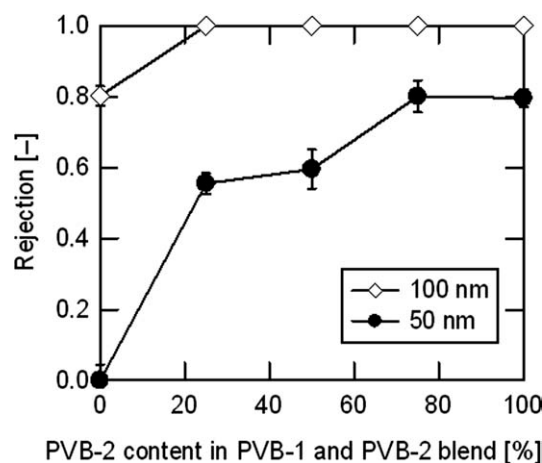**Figure 7 .** PS particle rejection by the PVB membranes.

Figure 8. Effect of polymer blend composition of the PVB-1/PVB-2 membrane on PS bead rejection.

100% exclusion of the PS particles with a 300 nm diameter and almost no exclusion for the particles with a 20 nm diameter. PVB-3 showed almost 100% rejection for the particles with diameters of 50 and 100 nm, while PVB-1 showed lower exclusion for these particles than PVB-3. These results are in good agreement with the SEM observations (Figure 4), which showed that PVB-1 had large pores compared with the other membranes.

Particle exclusion measurements were also carried out for the PVB-1 and PVB-2 polymer blend membrane. As shown in Figure 8, exclusion of the PS particles increased with the PVB-2 content in the polymer blend. Exclusion of the 50 nm diameter particles was >80% for polymer blend membranes with a PVB-2 mass fraction >75%.

A bacterial exclusion test was also conducted for these membranes because the complete exclusion of bacteria is important for membrane water purification. Membranes with PVB-2 mass fractions of 75% and 100 % completely excluded *B. diminuta* (Table III). This result indicates that these membranes are suitable for drinking water treatment.

Mechanical Strength

Figure 9(a) shows the tensile stress at breaking point of the wet PVB hollow fiber membranes. PVB-1 showed significantly higher tensile stress than the other membranes, while its elongation was the lowest. Because the three PVB polymers have similar chemical structures, the higher tensile stress of PVB-1 is probably because of its molecular weight (Table I). A high

Table III. Number of Bacteria in the Filtrate After the Bacterial Exclusion Test

PVB-2 content	(wt %)	0	25	50	75	100
Number of bacteria	(CFU/mL)	n.d.	n.d.	4.0×10^5	0	0

n.d.: not determined.
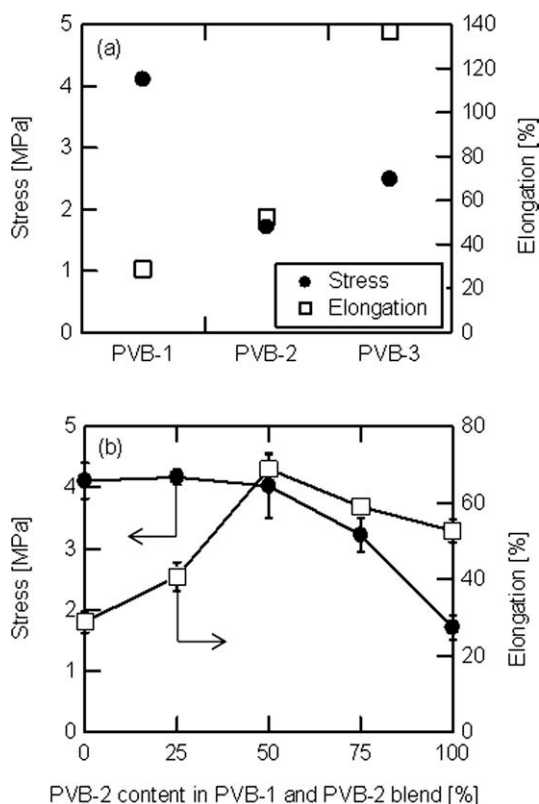Initial bacteria number: 1.7×10^6 CFU/mL.

Figure 9. Mechanical strength at breaking point of the prepared membranes. (a) PVB membrane; (b) polymer blend membranes.

polymer molecular weight results in high tensile stress of the membrane.

Tensile stress was also measured for the polymer blend membrane. Figure 9(b) shows that the membranes with a PVB-2 mass fraction of up to 50% had high tensile stress (>4 MPa), which gradually decreased with higher PVB-2 mass fractions. By contrast, elongation of the obtained membranes increased with PVB-2 mass fractions up to 50%, and slightly decreased with higher PVB-2 mass fractions.

CONCLUSION

Several hollow fiber membranes were prepared via the TIPS process from three types of PVB polymers and a polymer blend of two of these polymers. These PVB polymers have similar chemical structures, but different compositions.

The cloud point temperatures were measured in all three PVB systems, and the trends could be explained by the compatibility between the PVB polymer and diluent. The PVB system with a high cloud point temperature had a long structure growth period, which resulted in large pores in the membrane. The water permeability trend for the wet membranes corresponded to the trend for the cloud point temperatures of the PVB solutions. By contrast, the water permeability of dried membranes was independent of the pore size. For example, permeability of the dry PVB-2 membrane was half that of the wet membrane, while the PVB-1 membrane had a large pore when dry and almost no permeability. The permeability in the dry state could be explained by the membrane wettability, which was related to both the porous structure and hydrophilicity of the membranes. Furthermore, the effect of blending the two polymers on the membrane structures and performance was investigated. The membrane performance was easily controlled by changing the blend ratio. The membrane containing 75% (mass fraction) PVB-2 had high membrane wettability and high strength.

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