HDPE Hollow-Fiber Membrane via Thermally Induced Phase Separation. II. Factors Affecting the Water Permeability of the Membrane

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ABSTRACT: Some major factors of the melt spinning of high-density polyethylene (HDPE) and a liquid paraffin (LP) blend, which affect the water permeability of HDPE hollow-fiber membrane obtained therefrom, were investigated. The water permeability of the membrane was found to increase as the membrane thickness decreases and as the melt-flow-rate value of HDPE and the LP content of the blend increases. The dependence of the water permeability on the major factors is also discussed in connection with the morphology of the membrane. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 1235–1242, 2000

Key words: HDPE; liquid paraffin; membrane; water permeability; morphology; cutoff ability

INTRODUCTION

A subject of extensive study during last several decades has been to use a microporous polymeric membrane for separation purposes[1]; particularly, much attention has been paid to the possibility of the utilizing the membranes of hollow fiber for water purification by reverse osmosis (RO) or ultrafiltration (UF),[2] since the productivity and the efficiency of the separation process can be largely improved due to the large surface area per unit volume of the fiber form.[3,4]

The RO and UF membranes are distinctive in the dimension of the separated particle, and the dimension of the solid impurity separated by the membrane is determined by the pore size of the microporous membrane. The most important factor that influences the water permeability of the membrane is known to be the pore size of the membrane, which is determined in the phase separation or in the drawing process.[4] In our previous article,[5] we reported the thermodynamic aspects of the phase-separation process of the blend, which consists of high-density polyethylene (HDPE) and liquid paraffin (LP). It became evident that the interaction of the two components, evaluated in terms of the Flory–Huggins interaction parameter, is suitable for the preparation of the microporous membrane via a thermally induced phase-separation process. The value of the interaction parameter, 0.36, indicates that phase separation has taken place in the course of cooling to yield a membrane with a microporous structure after melt spinning of the blend.

Based on the facts mentioned above, we attempted to prepare a HDPE hollow-fiber mem-

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Table I Specimen Codes of the HDPE/LP Blends Prepared

M0164	M0155	M0146
M0564	M0555	M0555
M0864	M0855	M0846
M1264	M1255	M1246

Code of the blend specimens is composed of one letter and four figures. The first two figures denote the MFR value of the HDPE, expressed in g/10 min, and the last two figures denote the composition of the blend in the weight ratio of HDPE and LP, respectively. For example, M0146 means the blend consisting of HDPE : LP = 4 : 6 in a weight ratio prepared from HDPE having an MFR value of 1.

brane for ultrafiltration by melt spinning the HDPE/LP blend through an annular orifice. The major factors of the spinning process, which affect the water permeability of the membrane, were also investigated.

EXPERIMENTAL

Materials

HDPE, obtained from LG Chemicals and Korea Petrochemical, and LP, obtained from Ducksan Chemicals, were used without further purification. The specifications of the materials were given elsewhere.[5]

Blending and Melt Spinning

Totally, 12 different HDPE/LP blends containing three different LP contents were prepared using HDPE having four different melt-flow rate (MFR, expressed as g/10 min) values as shown in Table I. Blends in the pellet form were obtained by crushing the HDPE/LP blends precipitated from the HDPE/LP solution by cooling to room temperature, which were prepared by mixing the two components at 100 psi and 180°C while being drastically agitated.

Figure 1 shows a schematic diagram of the hollow-fiber spinning system from the HDPE/LP blend. The molten blend, supplied from the side feed extruder or main feed extruder depending on the density of the blend, changes its shape to hollow fiber by passing through a tube in an orifice spinneret whose inner and outer diameters are 2 and 4 mm, respectively. The rpm and the diameter of the screw of the extruder were 12.7 and 30 mm, respectively, and the temperature of the blend in the extruder was maintained at 160°C. Nitrogen gas was blown into the inner orifice of the spinneret to provide a inner space of the hollow fiber. Since the thickness of the hollow fiber membrane is sensitively affected by the flow rate of nitrogen gas, the flow rate was accurately controlled using a mass-flow controller in the range of 5–15 mL/min under constant pressure. The as-spun hollow fiber is wound on bobbin of the take-up device after successive passing through an air gap, a cooling bath filled with LP, and a cleaning bath filled with *n*-hexane. The dependence of the water permeability of the membrane on the nitrogen gas flow rate and the take-up speed was investigated in connection with the morphology change of the membrane. Finally, the

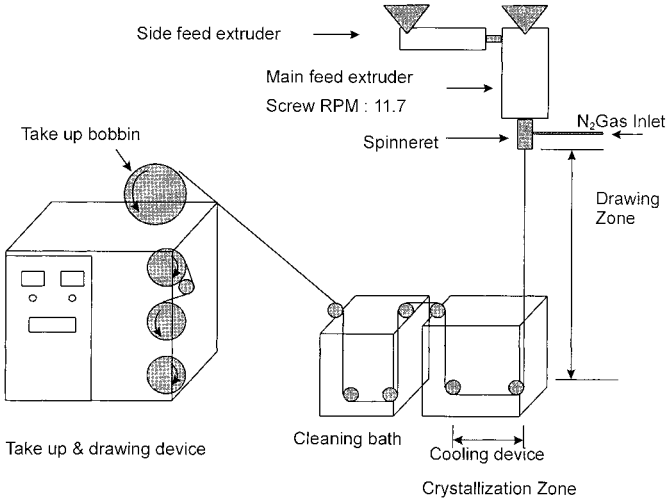

Figure 1 Schematic diagram of the melt-spinning system of HDPE hollow-fiber membrane from HDPE/LP blend.

hollow-fiber membrane was immersed in *n*-hexane for 24 h at room temperature just before use in order to assure the complete removal of LP.

Cold Drawing

Since water is impermeable to the membrane of the as-spun hollow fiber, the as-spun fiber was subjected to stretching at 25°C using an Instron Model 1011.

Analysis

Tensile Property of the Hollow-fiber Membrane

Mechanical properties including fiber strength and elongation were measured by the Instron Model 1011. The rate of extension was 5 mm/min for the specimen of 10 cm long.

Morphology of the Hollow-fiber Membrane

The morphology of the hollow-fiber membrane surface or cross sections, taken from the each step of the process, was studied using SEM and WAXD. The surfaces for the SEM photographs were treated with gold ion sputtering (1.2 kV, 5 mA) for 3 min. A rotating anode generator (20–60 kV and 10–80 mA) operating in the range of 2–3 degrees was used for measuring the X-ray diffraction intensity.

Determination of Water Permeability of the Membrane

The water permeability of the membrane was evaluated in terms of water permeability defined as

$$\text{Flux (L m}^{-2}\text{ atm}^{-1}\text{ h}^{-1}) = \frac{V_t}{2\pi RL\Delta Pt}$$

V_t is the volume of water permeated through the membrane (L); L, the measured fiber length (m); ΔP, the pressure difference at the flux test (atm); t, the test time (h); and R, the radius of the hollow fiber (m). The water permeability was measured at 25°C under various hydraulic pressures ranging from 2–3 atmospheres using a tester built in this laboratory. The water is supplied from the pump to the hollow-fiber membrane of 1 m long through a prefilter and a manifold. The membrane was installed in a module using epoxy resin (epoxy resin: crosslinking agent = 1 : 1 by weight) and the resin was cured at room temperature for 24 h. Then, the module was connected to a manifold, which is located between a set of a valve and a pressure gauge and another set of a vent valve and a pressure gauge. Accordingly, the hydraulic pressure applied can be controlled by the adjustment of the two valves and the pressure can be read from the pressure difference of the two pressure gauges.[6,7] The test specimen was immersed twice in *n*-hexane for 24 h before the test for the complete removal of LP.

Cutoff Test for the Hollow-fiber Membrane

The cutoff ability of the hollow-fiber membrane was evaluated by the ratio of the areas under the chromatographs of the original water sample containing 1% dextran having a number-average molecular weight of 75,000 and by its permeates of the hollow-fiber membrane, using gel filtration chromatography (GFC, Spectra System P1000). The water samples were introduced to the GFC in which columns of polystep 1000, 2000, 3000, and 4000 and a guard column were connected in series. Permeate was collected from a 1-m-long hollow-fiber membrane for 1 h under a pressure ranging 2–3 atm. The device was so carefully adjusted that the retention time of a peak appeared at around 50 min under the flow rate at 0.5 mL/min.

RESULTS AND DISCUSSION

Effect of MFR Value of HDPE on the Water Permeability

Figure 2 shows the dependence of the water permeability of the membranes prepared from HDPE of two different MFR values (12 and 8) on the hydraulic pressure. The operating conditions of the spinning process were carefully adjusted so as to give membranes of the same thickness (0.21 mm) under a fixed draw ratio of 25%, irrespective of the blend composition.

Figure 2 reveals that the water permeability of the membrane prepared from HDPE having a higher MFR value is higher than that prepared from HDPE having a lower MFR value. Furthermore, it is recognized that the dependence of the water permeability on the hydraulic pressure is also higher in the membrane prepared from HDPE having a higher MFR value than that prepared from a lower MFR value. The water permeability of the membrane prepared from HDPE having a lower MFR value (8) is almost indepen-

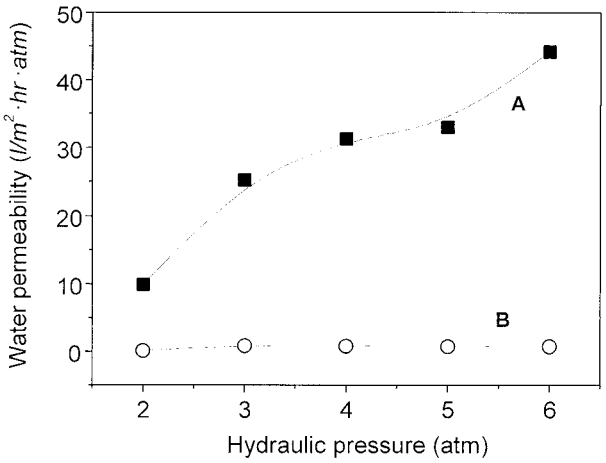

Figure 2 Comparison of the water permeability of the membranes as a function of the melt-flow rate of HDPE used. Membrane thickness: 0.21 mm; draw ratio: 25%; specimen code: (A) M1264; (B) M0864.

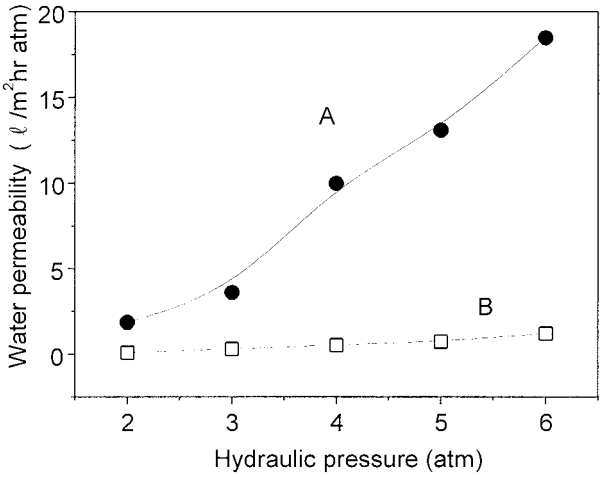

Figure 4 Comparison of water permeability of the hollow-fiber membrane prepared from the blends of different composition. Membrane thicknesses were 0.21 mm in (A) M1255 and (B) 0.20 mm in M1264.

dent on the hydraulic pressure applied. On the contrary, the water permeability of the membrane increases linearly with the hydraulic pressure in the membrane that was prepared from the HDPE having a higher MFR value (12).

Figure 3 shows the strain–stress curves of the as-spun hollow fibers whose spinning conditions and compositions of the blends are identical with those shown in Figure 2. It is revealed that the hollow-fiber membrane prepared from the HDPE having a higher MFR value is more easily deformed by the transmembrane pressure than that prepared from HDPE having a lower MFR value.

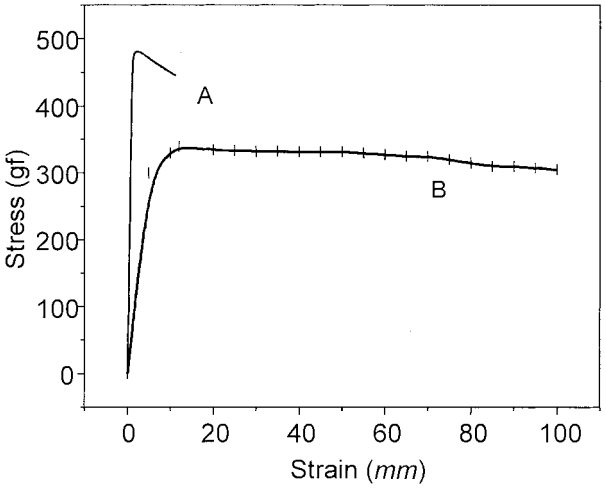

Figure 3 Comparison of stress–strain curves of the hollow-fiber membrane prepared from HDPE having different MFRs. Specimen code: (A) M0864; (B) M1264.

In other words, the pore of the membrane prepared from the HDPE of a higher MFR value is easily enlarged due to the drawing.

Effect of Blend Composition on Water Permeability

The dependence of the water permeability on the composition of the HDPE/LP blend was investigated by comparing the two kinds of membranes prepared from HDPE having the same MFR value (12) but different blend compositions. Figure 4 shows the water permeability of the membranes prepared from the blends having the compositions of 6/4 and 5/5 (expressed in the weight ratio of HDPE/LP). Although it is recognized that the water permeabilities of the two membranes increase with the hydraulic pressure applied, the slopes of the two curves are strikingly different. The higher degree of dependence observed in the LP-richer blend means that the pore of larger dimension is formed from the LP-richer blend in the phase-separation process.[8,9]

Stress–strain curves of the hollow-fiber membranes obtained from blends of different compositions are shown in Figure 5. It is important to mention that the hollow-fiber membrane obtained from the LP-richer blend (5/5) is more resistant to tensile stress than is that obtained from the HDPE-richer blend (6/4). It has been reported that the crazes are formed due to the generation of highly concentrated stresses during the mechanical loading of as-spun hollow fiber at the interface between the polymer-rich and the lean

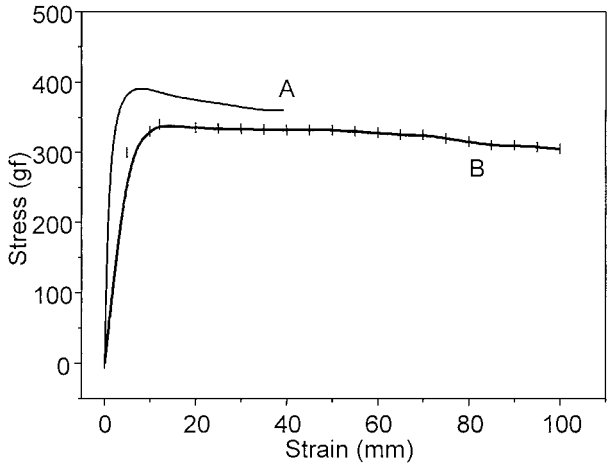

Figure 5 Comparison of stress–strain curves of the hollow-fiber membrane made from HDPE having different compositions Specimen code: (A) M1255; (B) M1264.

phase,[10,11] which is believed to be responsible to decrease the resistance to the tensile stress of the membrane obtained from the HDPE-richer blend.

Effect of Membrane Thickness on Water Permeability

Membranes with various thicknesses were prepared by control of the nitrogen gas flow rate in the melt-spinning process. The other conditions in the spinning and drawing processes were kept constant and the draw ratio was fixed at 25%. Figure 6 shows the water permeability of the

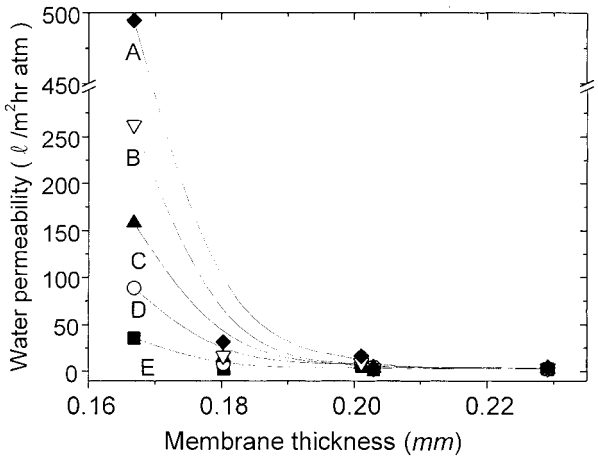

Figure 6 Water permeability as a function of thickness of hollow-fiber membrane prepared from M1264. Hydraulic pressure applied (atm): (A) 6; (B) 5; (C) 4; (D) 3; (E) 2.

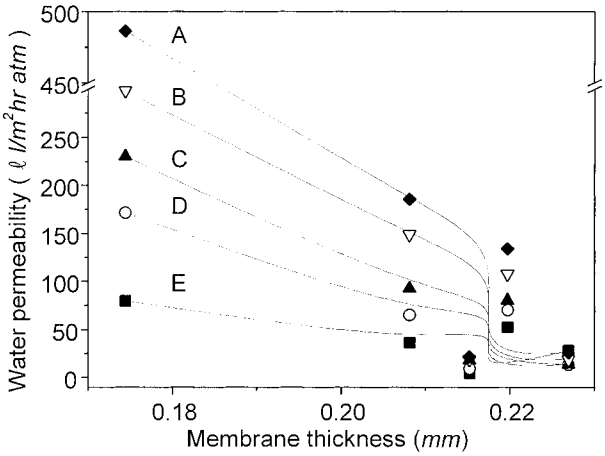

Figure 7 Water permeability as a function of thickness of hollow-fiber membrane prepared from M1255. Hydraulic pressure applied (atm): (A) 6; (B) 5; (C) 4; (D) 3; (E) 2.

membrane, prepared from the HDPE-richer blend (6/4), as a function of membrane thickness. The water permeability of the membrane increases with increasing hydraulic pressure applied in the range where the thickness of the membranes are small; however, the membrane becomes impermeable when the membrane thickness is larger than 0.2 mm—even the hydraulic pressure increases to 6 atm. Measurement of the water permeability of the membranes at hydraulic pressure higher than 6 atm was not carried out due to rupture of the membrane.

The effect of the membrane thickness on the water permeability for the membrane prepared from the LP-richer blends (5/5) is shown in Figure 7. Comparison of the data with those given in Figure 6 reveals that the membrane obtained from the LP-richer blend is more water permeable and has a higher dependence of the water permeability on the hydraulic pressure when compared with those membranes prepared from the HDPE-richer blend. It is evident that an abrupt decrease in the water permeability is observed at a certain value of the membrane thickness—0.22 mm is the value where an abrupt decrease in the water permeability is observed, which implies that there are some macrostructural factors, such as the regularity of the pore dimension and the shape of the spherulite, which affect the water permeability of the membrane.

Effect of Take-up Speed on Water Permeability

Membranes of different thicknesses can also be prepared by controlling the take-up speed. Mem-

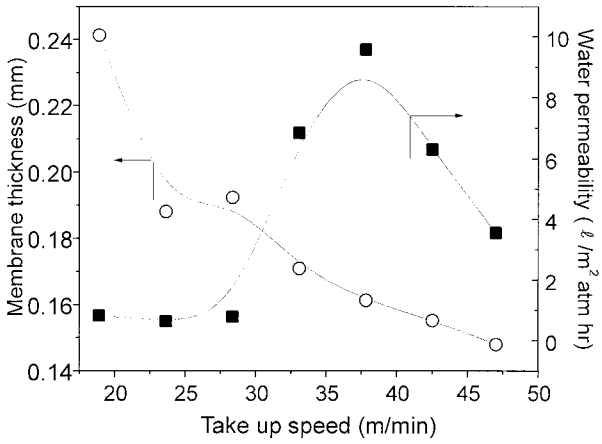

Figure 8 Dependence of water permeability and membrane thickness of HDPE (M1264) hollow-fiber membrane on take-up speed. Hydraulic pressure applied: 5 atm.

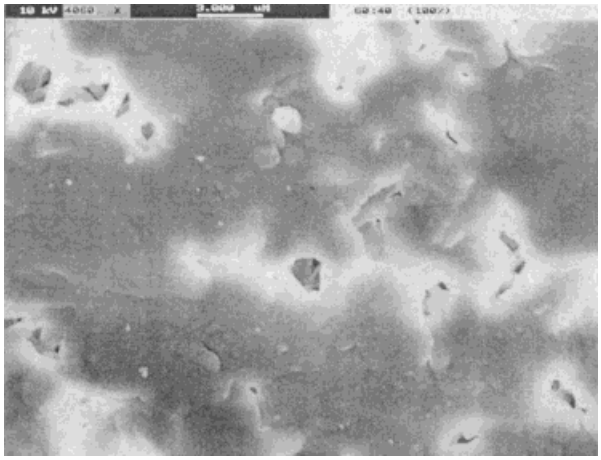

Figure 9 SEM micrograph of the surface of as spun hollow-fiber membrane.

branes with thinner walls are obtained at higher take-up speeds. The dependence of the water permeability of the membrane on the take-up speed was investigated. The results are shown in Figure 8, where the water permeability is expressed not only as a function of take-up speed but also as a function of membrane thickness which was measured using an image-analyzer system (Olympus microscope connected to a video camera). The figure clearly shows that the water permeability of the membrane increases as the take-up speed increases and the membrane thickness decreases. However, it is interesting to note that the dependence of the water permeability on the membrane is not so simple that a maximum value in the water permeability is observed at a certain value of take-up speed. When the extrusion rate is kept at a constant value, the membrane thickness decreases monotonously as the take-up speed increases.

The striking difference of the water permeability between the membranes where thickness is controlled by the nitrogen gas flow rate and take-up speed also suggests that there are some factors which affect the water permeability of the membrane other than the membrane thickness. This can be explained when we assume that the shape of the pore formed is sensitively influenced by the direction of the stress applied to the membrane during the processing. The pores formed by phase separation have shapes enlarged to the transverse direction due to the deformation given to the membrane by a nitrogen gas flow and those given by the take-up have shapes enlarged to the longitudinal direction. Therefore, the pores formed by the nitrogen gas are enlarged by the drawing; however, the pores enlarged in the longitudinal direction are collapsed due to the severe drawing which results in decrease in the water permeability.

An SEM micrograph of the as-spun membrane prepared from a 6/4 blend under the take-up speed of 40 m/min is shown in Figure 9 and that of the membrane obtained by phase separation in the absence of the deformation is shown in Figure 10. It is evident that a fibrillar structure is formed due to the drawing; no fibrillar structure is observed in the membrane obtained from the same blend formed by phase separation in the absence of deformation. Therefore, it is concluded that the

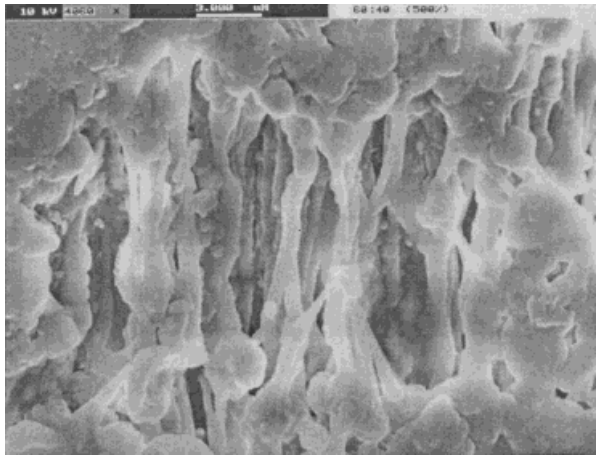

Figure 10 SEM micrograph of the surface of drawn hollow-fiber membrane after cold drawing. Draw ratio: 25%.

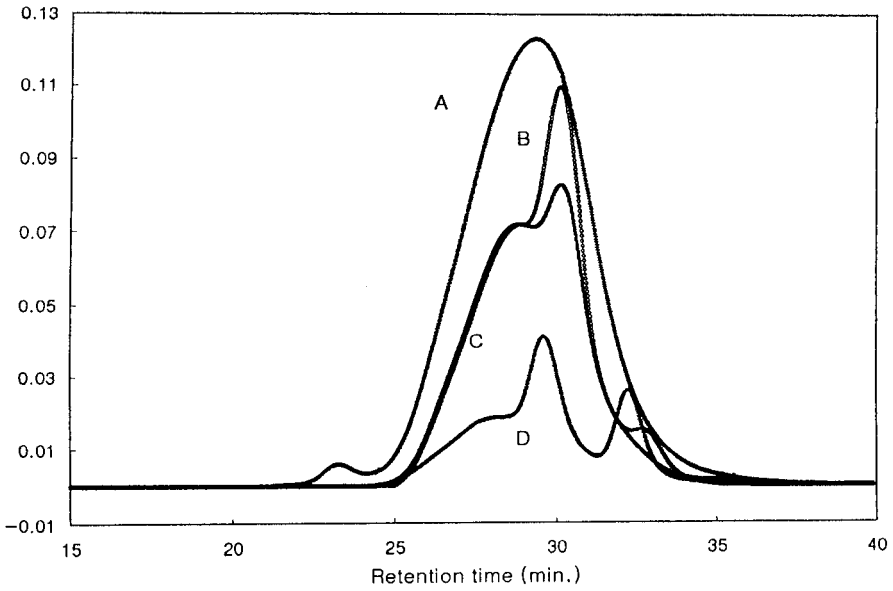

Figure 11 Gel filtration chromatographs of permeates of the HDPE hollow-fiber membrane and original water sample, containing 1.% dextran having number-average molecular weight of 75,000. (A) Original water sample; (B) permeate from M1264G9; (C) permeate from M1264G7; (D) permeate from M1264G5. G No means the nitrogen gas flow rate in the spinning process.

increase in the water permeability with increasing take-up speed is ascribed to the enlargement of the pore accompanied by the formation of a fibrillar structure due to the longitudinal deformation given to the hollow-fiber membrane in the take-up process.[12,13] However, the existence of a maximum in the water permeability at a certain value of the take-up speed indicates that the severe drawing results in the collapse of the pore already formed.

The cutoff ability of the membrane, which is defined as the percent rejection of particles of larger dimension, was evaluated using GFC. GFC of the original water sample containing 1% dextran having a number-average molecular weight of 75,000 is shown together with those of permeates from the various membranes in Figure 11. Membranes having almost the same thickness, controlled by careful adjustment of the extrusion rate and nitrogen gas flow rate, were used. Comparison of the chromatographs reveals that the dextran of the higher molecular weight portion is efficiently cut off by the membranes and the upper limit of cutoff is shifted toward to lower mo-

Table II Results of Cutoff Test of the Membrane, Expressed as Percent Rejection of Dextran, Having Number-average Molecular Weight of 75,000

	Specimen Code		
Results	M1264G5	M1264G7	M1264G9
N_2 gas flow rate (mL/min)	5	7	9
Membrane thickness (mm)	0.2252	0.2145	0.2041
Water permeability ($L\ atm^{-1}\ h^{-1}\ m^{-2}$)	2.8	3.8	7.6
Rejection (%)	76.8	39.9	37.2

Conditions of membrane preparation: MFR value of HDPE, 12; blend ratio, HDPE/LP = 6/4; extrusion rate, 77.9 g/10 min; take-up speed, 28.4 m/min; draw ratio, 50%. The thickness of the membrane was adjusted by controlling of the flow rate of nitrogen gas into the inner orifice.

lecular weight side with increasing nitrogen gas flow rate, irrespective of the membrane thickness. Considering the facts that the water permeability increases monotonously with decreasing membrane thickness, the relationship between the cutoff range and water permeability of the membrane is not so simple. The percent rejection, calculated from the ratio of the area under the chromatograph of the permeate and the original water sample, is summarized in Table II.

$$\text{Rejection } (\%) = 1 - (C_{\text{permeate}}/C_{\text{original}}) \times 100$$

C_{permeate} and C_{original} denote the concentration of dextran of the permeate and the original water sample, respectively, and the value of $C_{\text{permeate}}/C_{\text{original}}$ was determined by the ratio of the areas under chromatographs of the permeate and that of the original water sample.

CONCLUSIONS

The dependence of the water permeability of HDPE hollow-fiber membrane on the major factors in the melt-spinning process of the HDPE/LP blend was investigated. It was found that the water permeability of HDPE hollow-fiber membrane is sensitively influenced by the factors that govern the thermally induced phase-separation process of the HDPE/LP blend. The water permeability of the membrane increases with decreasing MFR values of HDPE used in the blending, increasing the LP content in the blend and decreasing the membrane thickness. However, it becomes also clear that there are some macrostructural factors other than thickness which affect not only the water permeability but also the cutoff ability of the membrane.

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