Effect of Polymer Density on Polyethylene Hollow Fiber Membrane Formation Via Thermally Induced Phase Separation

Hideto Matsuyama,[1] Kentarou Hayashi,[1] Taisuke Maki,[2] Masaaki Teramoto,[1] Noboru Kubota[3]

[1]*Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan*
[2]*Department of Chemical Engineering, Kyoto University, Yoshidahonmachi, Nishi Kyo-ku, Kyoto 606-8501, Japan*
[3]*Asahi Chemical Industry Co., Ltd. 2-1 Samejima, Fuji, Shizuoka 416-8501, Japan*

Received 29 April 2003; accepted 13 February 2004
DOI 10.1002/app.20461

ABSTRACT: Microporous high-density polyethylene (HDPE) and low-density polyethylene (LDPE) hollow fiber membranes were prepared from polyethylene–diisodecyl phthalate solution via thermally induced phase separation. Effect of the polyethylene density on the membrane structure and performance was investigated. The HDPE membrane showed about five times higher water permeability than the LDPE membrane because it had the larger pore and the higher porosity at the outer membrane surface. The formation of the larger pore was owing to both the initial larger structure formed by spinodal decomposition and the suppression of the diluent evaporation from the outer membrane surface due to the higher solution viscosity. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 471–474, 2004

Key words: thermally induced phase separation; hollow fiber membrane; high-density polyethylene; low-density polyethylene; asymmetric structure

INTRODUCTION

The thermally induced phase-separation (TIPS) process is a valuable way of making microporous membrane.[1] In this process, a polymer is dissolved in a diluent at high temperature. Therefore, TIPS is applicable to a wide range of polymers, including those that could not be used in the immersion precipitation method of making microporous membranes due to the solubility problem. Such a typical polymer is polyolefin. Polyolefin is the material suitable for the microporous membrane because it has good thermal and solvent resistance as well as low cost. Thus, a lot of studies have been reported on the microporous polyolefin membrane formation via the TIPS process.[2–12] Li et al. investigated the formation of microporous polyethylene (PE) membrane via the TIPS process.[13] They used low-density polyethylene (LDPE) and high-density polyethylene (HDPE). The membrane structure depended on the kind of PE; that is, the spherulite was formed in the LDPE system, while HDPE led to the formation of leafy structure.

A hollow fiber membrane is one of the most useful membrane forms from the commercial application because it enables higher membrane area per unit membrane module volume.[14] Microporous hollow fiber membranes were prepared via the TIPS process of polypropylene/soybean oil mixture.[15] The effects of operation parameters such as the initial composition of the melt solution, the spinning temperature, and the melt–draw ratio on the membrane structure were investigated. Hollow fiber membranes were spun from solutions of poly(2,6-dimethyl-1,4-phenylene ether) (PPE) in cyclohexanol.[16] The membranes were used for the separation of oxygen and nitrogen. Sun et al. prepared the HDPE hollow fiber membrane by the polymer crystallization via the TIPS process.[17,18] The water permeability was discussed in connection with the membrane morphology. In our previous works, PE and poly(ethylene-*co*-vinyl alcohol) hollow fiber membranes were prepared by the liquid–liquid phase separation via the TIPS process.[19,20] Effects of polymer molecular weight, ethylene content of the copolymer, air gap distance, water bath temperature, and kind of diluents on pore size and water permeability were investigated.

In this work, HDPE and LDPE were used as membrane materials for the preparation of hollow fiber membrane. Membrane structure and performance were compared in the HDPE and LDPE membranes to clarify the effect of the PE density.

EXPERIMENTAL

Materials

HDPE (polymer density = 0.965 g/cm^3, M_w = 127,000, M_w/M_n = 7.6) was supplied from Asahi Chemical Industry Co., Ltd. LDPE (polymer density = 0.922

Correspondence to: Hideto Matsuyama (matuyama@chem.kit.ac.jp).

Journal of Applied Polymer Science, Vol. 93, 471–474 (2004)

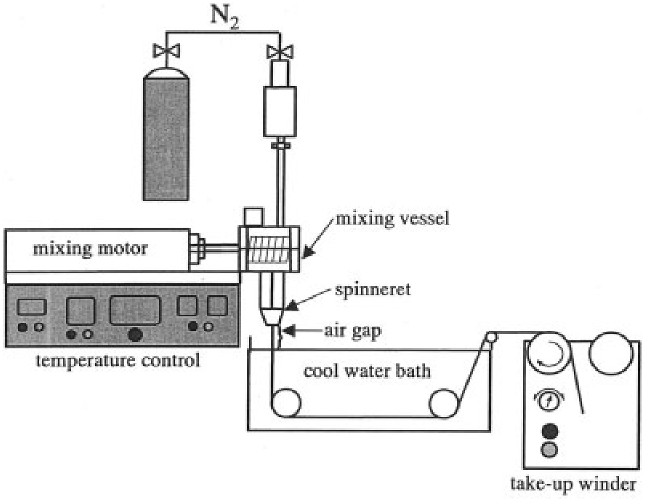

Figure 1 Schematic diagram of batch-type extrusion apparatus for hollow fiber membrane preparation.

g/cm^3, M_w = 111,000, M_w/M_n = 10.9) was purchased from Aldrich Chemical Co. The molecular weights of the two polymers were almost the same. Diisodecyl phthalate (DIDP, Wako Pure Chemical Industries, Osaka, Japan) was used as diluent without further purification.

Phase diagram and light-scattering measurement

Cloud point and crystallization temperature were measured by the method used previously.[12] Homogeneous polymer–diluent sample was placed between a pair of microscope coverslips. After the sample was heated on a hot stage (Linkam, LK-600PH) at 453 K for 3 min, it was cooled to 298 K at a controlled rate of 1 K/min. Cloud point was determined visually by noting the appearance of turbidity under an optical microscope (Olympus BX50). The crystallization temperature was determined by DSC (Perkin-Elmer, DSC-7) measurement. The solid polymer–diluent sample in an aluminum DSC pan was melted at 473 K for 3 min and then cooled at the rate of 10 K/min. The onset of the exothermic peak during the cooling was taken as the crystallization temperature.

The light-scattering measurement for the polymer solution was carried out with a polymer dynamics analyzer (Otsuka Electronics Co., Hirakata, Japan; DYNA-3000).[21] The sample with polymer concentration of 20 wt % was sealed with two coverslips and placed on the stage located between a He–Ne laser and a detector. After the sample was melt-blended at 453 K, it was cooled at the rate of 130 K/min. The structure growth behavior during the cooling was measured at the time interval of 0.1 s.

Membrane preparation

Hollow fiber membranes were prepared by a batch-type extruder (Imoto Co., Kyoto, Japan; BA-0) described in the previous work.[19] The schematic diagram of the extrusion apparatus is shown in Figure 1. PE and diluent was mixed in the vessel heated to 443 K for 20 min under a nitrogen atmosphere. The polymer concentration was 20 wt %. The homogeneous polymer solution was fed to a spinneret (outer diameter = 1.58 mm, inner diameter = 0.83 mm) by a gear pump under nitrogen pressure of 0.2 MPa. The diluent was introduced into the inner tube of the spinneret to make a lumen of the follow fiber. After the hollow fiber extruded from the spinneret entered the water controlled at 323 K to induce the phase separation, it was wound on a take-up winder. The remaining diluent in the membrane was extracted in ethanol. In both HDPE and LDPE systems, the following conditions were fixed. The air gap distance, which is the distance from the spinneret to the water bath, was 5 mm. The extrusion rate of the polymer solution and the flow rate of the diluent in the inner tube of the spinneret were 0.16 and 0.22 m/s, respectively. The take-up speed was 0.42 m/s.

SEM observation and water permeation experiment

After the hollow fiber membrane was immersed in water by the replacement of ethanol in the membrane to water, it was freeze-dried. The cross section and surface of the membrane were examined by SEM (Hitachi Co., Tokyo, Japan; S-800) with an accelerating voltage of 20 kV.

Water permeability through the hollow fiber membrane was measured by a method similar to that described by Saito et al.[22] Water was forced to permeate from the inside to the outside of the hollow fiber membrane. The water permeability was calculated on the basis of the inner surface area of the hollow fiber membrane.

RESULTS AND DISCUSSION

Figure 2 shows the phase diagrams in the HDPE and LDPE systems. Cloud point curve in the LDPE system

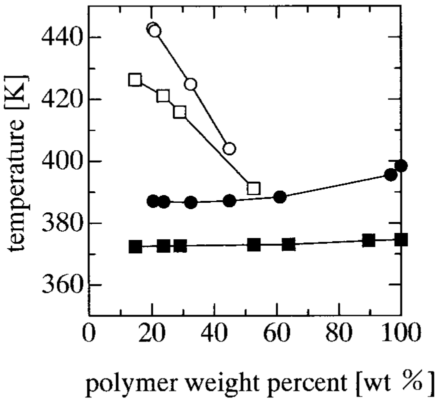

Figure 2 Phase diagrams in HDPE and LDPE systems. ○: cloud point in HDPE system; ●: crystallization temperature in HDPE system; □: cloud point in LDPE system; ■: crystallization temperature in LDPE system.

TABLE I
Crystallinity and Water Permeability

	Crystallinity (%)	Water permeability [$m^3/(m^2\ s\ Pa)$]
HDPE	52	5.52×10^{-9}
LDPE	20	1.06×10^{-9}

was lower than in the HDPE system. It is well known that HDPE is a linear polymer, whereas LDPE is a branched polymer.[23] Because of the increased entropy for the branched polymer, the cloud point in the LDPE system may be lowered. The crystallization temperature was also lower in the LDPE system. This is because crystallization is not likely to occur for the branched polymer. For the 20 wt % polymer solutions, the crystallinity obtained from the DSC measurement is listed in Table I. In the calculation of the crystallinity, the value of 289 J/g was used as the enthalpy of fusion of the perfect PE crystal.[24] The crystallinity in the HDPE system was about 2.5 times higher than in the LDPE system.

Figure 3 shows a light-scattering result by the phase separation of polymer solution during the cooling. The scattered light intensity I_s showed maximum in the plot of I_s against the scattered angle θ, which indicated that the phase separation occurred by the spinodal decomposition rather than the nucleation and growth mechanism.[25]

The interphase periodic distance Λ was calculated from the light-scattering result. Λ is related to the scattered angle θ where I_s shows maximum in eq. (1)

$$\Lambda = \lambda_0/[2n_0\sin(\theta/2)] \qquad (1)$$

Here, n_0 and λ_0 are the reflection coefficient and the wavelength *in vacuo* (633 nm), respectively.

The comparison in the time courses of Λ in both systems is shown in Figure 4. At the initial time, the LDPE system showed the smaller Λ. Λ is proportional to the polymer gyration radius R_g in the early stage of the spinodal decomposition.[26] Because the branched polymer has smaller R_g than the linear polymer,[27] the smaller Λ was obtained in the LDPE system. The difference in the growth of Λ was not remarkable in both systems. Thus, the smaller structure formed in the LDPE system at any time.

Figure 5(a, b) shows the whole cross-sectional struc-

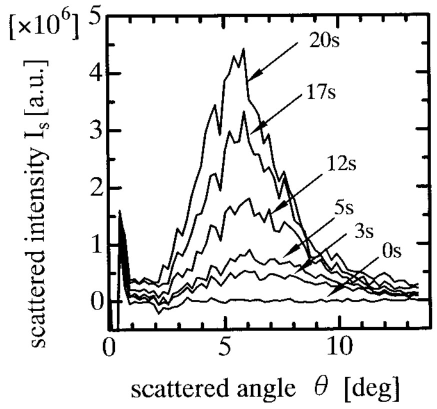

Figure 3 Light-scattering profiles for HDPE sample. Cooling rate = 130 K/min, polymer concentration = 20 wt %.

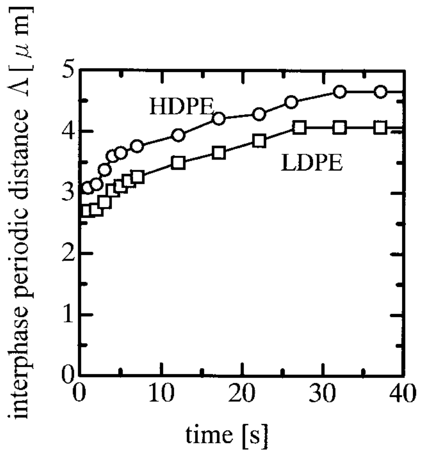

Figure 4 Time course of periodic distance Λ.

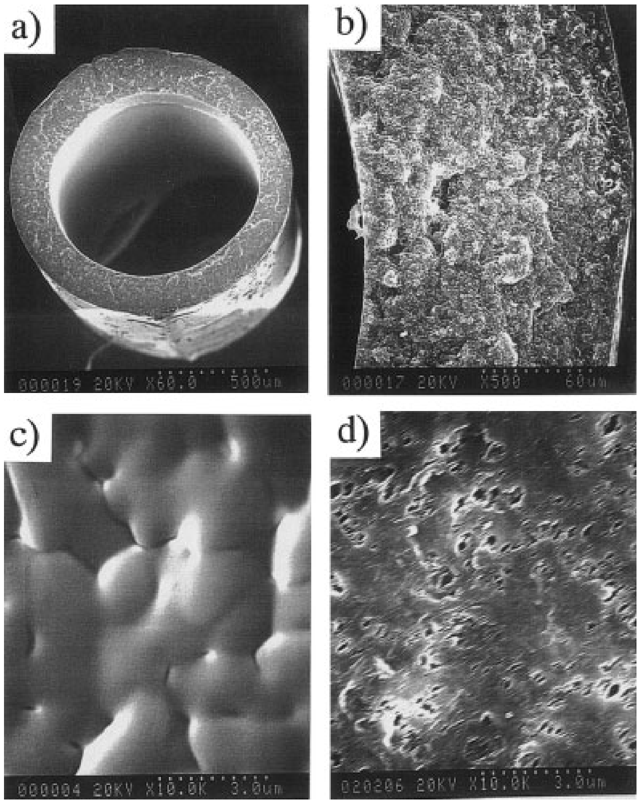

Figure 5 SEM images of the hollow fiber membranes. (a) Whole cross section (LDPE membrane); (b) enlarged cross section (LDPE membrane); (c) outer surface of LDPE membrane; (d) outer surface of HDPE membrane.

ture and the enlarged structure of the LDPE hollow fiber membrane. The outer and inner diameters of the membrane were 1280 and 900 μm, respectively. The membrane thickness was 200 μm. The HDPE membrane had almost the same geometry.

The water permeabilities of both membranes are listed in Table I. The HDPE membrane showed about five times higher permeability than the LDPE membrane. Thus, the PE density is one of the most important factors affecting the membrane performance. Figure 5(c, d) shows the outer surface structures of both membranes. The LDPE membrane had much smaller pores and lower porosity. This led to the lower water permeability. The pore sizes at the inner surfaces were larger than those at the outer surfaces in both LDPE and HDPE membranes, although these SEM micrographs are not included in Figure 5. Thus, the obtained membrane structures were asymmetric, which were similar to those in the previous work.[19] As described in the light-scattering result, the structure formed at the early stage of spinodal decomposition was smaller in the LDPE system. This is one reason for the smaller pore in the LDPE membrane. The diluent evaporates from the outer surface of the hollow fiber while the fiber moves from the spinneret to the water bath. This results in the higher polymer concentration at the outer surface. In the TIPS process, the higher polymer concentration brings about the smaller pore and the lower porosity.[9] Therefore, the asymmetric structure with the smaller pores at the outer surface was obtained, as described above. The viscosities of the polymer solutions with 20 wt % polymer concentration were measured at 473 K by a falling-sphere viscometer, by which the viscosity was obtained based on the falling rate of the sphere in the solution.[28] The viscosity of the HDPE solution was about eight times higher than that of the LDPE solution. Therefore, the evaporation of the diluent is more enhanced in the LDPE solution because of the lower solution viscosity, which leads to the higher polymer concentration at the outer surface. This is the other reason for the smaller pore and the lower porosity in the LDPE membrane surface.

CONCLUSION

The phase diagram of polyethylene–diisodecyl phthalate was clarified in both HDPE and LDPE systems. The cloud point curve and the crystallization temperature were lower in the LDPE system.

The phase-separation kinetics were measured by the light-scattering method. At the initial time, the structure formed by spinodal decomposition was smaller in the LDPE system. The difference in the structure growth rate in both systems was not remarkable.

Microporous HDPE and LDPE hollow fiber membranes were prepared via TIPS process. The HDPE membrane showed about five times higher water permeability than the LDPE membrane. This was attributable to the larger pore and the higher porosity at the outer membrane surface.

References

1. Castro, A. J. U.S. Pat. 4,247,498, 1981.
2. Hiatt, W. C.; Vitzthum, G. H.; Wagener, K. B.; Gerlach, K.; Josefiak, C. in Microporous Membranes via Upper Critical Temperature Phase Separation; Lloyd, D. R., Ed.; ACS Symposium Series 269; American Chemical Society, Washington, DC, 1985; p 229.
3. Lloyd, D. R.; Kinzer, K. E.; Tseng, H. S. J Membr Sci 1990, 52, 239.
4. Lloyd, D. R.; Kim, S.-S.; Kinzer, K. E. J Membr Sci 1991, 64, 1.
5. Kim, S.-S.; Lloyd, D. R. J Membr Sci 1991, 64, 13.
6. Lee, H. K.; Myerson, A. S.; Levon, K. Macromolecules 1992, 25, 4002.
7. Vadalia, H. C.; Lee, H. K.; Myerson, A. S.; Levon, K. J Membr Sci 1994, 89, 37.
8. Matsuyama, H.; Berghmans, S.; Lloyd, D. R. Polymer 1999, 40, 2289.
9. Matsuyama, H.; Yuasa, M.; Kitamura, Y.; Teramoto, M.; Lloyd, D. R. J Membr Sci 2000, 179, 91.
10. Yang, M. C.; Perng, J. S. J Membr Sci 2001, 187, 13.
11. Matsuyama, H.; Okafuji, H.; Maki, T.; Teramoto, M.; Tsujioka, N. J Appl Polym Sci 2002, 84, 1701.
12. Matsuyama, H.; Maki, T.; Teramoto, M.; Asano, K. J. Membr Sci 2002, 204, 323.
13. Li, W.; Yuan, Y.; Cabasso, I. Chin J Polym Sci 1995, 13, 7.
14. Zeman, L. J.; Zydney, A. L. Microfiltration and Ultrafiltration; Marcel Dekker: New York, 1996.
15. Kim, J. J.; Hwang, J. R.; Kim, U. Y; Kim, S. S. J Membr Sci 1995, 108, 25.
16. Berghmans, S.; Berghmans, H.; Meijer, H. E. H. J Membr Sci 1996, 116, 171.
17. Sun, H.; Rhee, K. B.; Kitano, T.; Mah, S. I. J Appl Polym Sci 1999, 73, 2135.
18. Sun, H.; Rhee, K. B.; Kitano, T.; Mah, S. I. J Appl Polym Sci 2000, 75, 1235.
19. Matsuyama, H.; Okafuji, H.; Maki, T.; Teramoto, M.; Kubota, N. J Membr Sci 2003, 223, 119.
20. Shang, M.; Matsuyama, H.; Maki, T.; Teramoto, M.; Lloyd, D. R.; Kubota, N. Polymer 2003, 44, 7441.
21. Matsuyama, H.; Kudari, S.; Kiyofuji, H.; Kitamura, Y. J Appl Polym Sci 2000, 76, 1028.
22. Iwata, H.; Saito, K.; Furusaki, S.; Sugo, T.; Okamoto, J. Biotechnol Prog 1991, 7, 412.
23. Okiyama, T. Plastic Film, 2nd ed.; Gihodo Publishers: Tokyo, 1995.
24. Domszy, R. C.; Alamo, R.; Edwards, C. O.; Mandelkern, L. Macromolecules 1986, 19, 310.
25. Nunes, S. P.; Inoue, T. J. Membr Sci 1996, 111, 93.
26. Lal, J.; Bansil, R. Macromolecules 1991, 24, 290.
27. Okamura, S.; Nakajima, A.; Onogi, S.; Kawai, H.; Nishijima, Y.; Higashimura, T.; Ise, N. Introduction to Polymer Chemistry, 2nd ed.; Kagakudojin: Kyoto, 1981.
28. Matsuyama, H.; Teramoto, M.; Kudari, S.; Kitamura, Y. J Appl Polym Sci 2001, 82, 169.