High-density Polyethylene (HDPE) Hollow Fiber Membrane via Thermally Induced Phase Separation. I. Phase Separation Behaviors of HDPE–Liquid Paraffin (LP) Blends and Its Influence on the Morphology of the Membrane

H. SUN,[1] K. B. RHEE,[1] T. KITANO,[2] S. I. MAH[3]

[1] National Institute of Technology and Quality, Joongang-Dong 2, Kwachon 327-010 Korea

[2] National Institute of Material and Chemical Research 1-1 Higashi Tsukuba, Ibaraki 305, Japan

[3] Inha University, YongHyun-dong 253, Nam-ku, Inchon 402-751, Korea

ABSTRACT: Phase separation behaviors of the blends that consist of high-density polyethylene (HDPE) and LP was investigated by means of thermal analysis. The miscibility of the two components was evaluated in terms of the Flory–Huggins interaction parameter, determined from the Hoffman–Weeks plot, gave a value of 0.36. This leads us to a conclusion that this blend system is applicable to the preparation of microporous hollow fiber membrane by melt spinning of the blend. The homogeneous blends in the molten state become heterogeneous systems to yield microporous HDPE membranes in the course of cooling due to thermally induced phase separation. The influence of the phase separation on the membrane morphology was also discussed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2135–2142, 1999

Key words: high-density polyethylene; phase separation; Hoffman–Weeks plot; Flory–Huggins interaction parameter; hollow fiber membrane

INTRODUCTION

The last several decades have witnessed a tremendous growth of synthetic polymeric membranes as a tool for the separation the component from the mixture. The search for the elucidating mechanisms of membrane function makes it possible to utilize various membranes for sophisticated applications, such as in membranes for reverse osmosis, ultrafiltration, dialysis, and electrodialysis.[1]

In terms of the cost and resistance to chemicals, polyethylene is the most advantageous as a material for the membrane; however, the phase inversion technique cannot be applied to polyethylene due to the lack of a suitable solvent. The preparations of the membranes having microporous structures from polymers like polyethylene (PE),[2,3] poly(vinylidene difluoride) (PVDF),[2] or polypropylene (PP)[4,5] have been studied by R. L. Douglas and his coworkers by a thermally induced phase separation technique (TIPS). Since then, a wide variety of the hollow fiber membranes are now being commercialized by this method.[6–9] This method is principally based on the dependence of the polymer solubility on the temperature. Membranes having a microporous structure are obtainable when the diluent is extracted from the heterogeneous thin film, which is the product of cooling of the homogeneous blend

Table I   HDPE Used

Melt Flow Rate[a] (g/10 min)	1	5	8	12
Number-average molecular weight (M_n[b])	22,381	12,502	12,441	9138
Weight-average molecular weight (M_w[b])	131,327	84,703	74,798	65,191
Poly dispersity index index M_w/M_n (PDI)	5.87	6.78	6.01	7.13
Density (g/cm^3)[c]	0.954	0.961	0.961	0.962

[a] Measured in accordance with ASTM D1238.
[b] Determined by high-temperature gel permeation chromatography (Milliore Co., Waters Chromatography Div.) using trichlorobenzen (TCB) as a solvent.
[c] Measured in accordance with ASTM D 1505.

in the molten state. However, the application of this method in commercial production of membrane is disturbed by the poor physical properties due to the honeycomb structure formation in the TIPS process.

In this article, we report the thermodynamic aspect of phase separation behaviors of the blend of high-density polyethylene (HDPE) and LP. And the effect of the several factors that affect the morphology of the HDPE hollow fiber membrane was also discussed.

EXPERIMENTAL

Materials

HDPE having four different melt flow rate values (Table I) (Honam Petrochemicals, LG Chemicals, and Korea Petrochemicals), technical-grade LP (Ducksan Petro-Chemicals; density ≥ 0.86 g/cm^3 at 25°C; viscosity, 23.1 cp. at 25°C, measured by a Brookfield viscometer); the reagent-grade Decalin (Aldrich) and n-hexane (Showa Chemicals) were used without further purification.

Sample Preparation

Blending of HDPE with diluent was carried out at 100 psi using a high-pressure blending apparatus, built in our laboratory. The mixture of HDPE and LP was thoroughly mixed in a reactor, which is equipped with heating band and a mechanical solenoid stirrer at 190°C under a nitrogen atmosphere. The blends having different compositions were crushed to pellet form after cooling and fed to the side or main feeds of the extruder for melt spinning depending upon the density of the blend. The hollow fiber membrane was prepared by the

passing the molten blends through a tube in orifice spinneret having inner/outer diameters of 2/4 mm, respectively, at 180°C. The temperature of the orifice was kept at 160°C. Nitrogen gas was blown into the inner orifice to provide a room in the inner side of the hollow fiber. The membrane thickness of the fiber was adjusted by controlling the flow rate of the nitrogen gas. It was found that the thinner membrane is obtained as the flow rate of nitrogen gas increases. The hollow fiber was then wound to a bobbin after it passes successively through a cooling bath, filled with LP and a cleaning bath, and filled with n-hexane. Freon or n-hexane was not considered as a cooling agent because of environmental reasons.[10] LP contained in the hollow fiber was extracted by n-hexane. The solvent was removed from the hollow fiber by evaporation and recovered by condensing. The as-spun hollow fiber is immersed again in the bath with filled n-hexane for 24 h for the complete removal of LP from the fiber. The outer and inner diameters of the membranes, obtained via this process, lie in the range from 0.8/0.7 to 0.5/0.4 mm.

Thermal Analysis

The measurement of cloud point of the blend was carried out using system composed of a microscope, a hot stage (Mettler Toledo, FP85), and a central process (Mettler Toledo, FP90) with a photomonitor sensor that allows simultaneous observation and determination of the brightness of the image field. The cooling rate of the molten blend was controlled by the programmed temperature lowering of the hot stage, which was adjusted at 2°C/min; and the temperature at which the blend system looses its transparency, was detected by the photomonitor.

The isothermal crystallization behaviors of the blends were investigated by means of differential scanning calorimetry (DSC) (Shimazu DSC 50 and Perkin–Elmer DSC-7). The thermal hysteresis of the samples were eliminated by the processes as follows: heating to 160°C at a rate of 10°C/min, keeping for 10 min at that temperature, and cooling to desired temperature of supercooled state at a constant rate of 10°C/min. The samples for the isothermal crystallization were placed at the desired temperatures for 1 h after they were cooled down from 160°C at a rate of 10°C/min. The rate of temperature raising for the blend samples for melting point determination was 5°C/min. The equilibrium melting temperatures of the blends were determined by the calculation using data obtained from the intercepts of the Hoffman–Weeks plot.

Morphological Study

Morphology of the membrane was investigated using scanning electron microscopy (SEM) (Philips XL-30) under an accelerating voltage of 10–20 keV. Specimens for the cross-sectional SEM photographs were prepared by fracturing or cutting of the frozen membrane with microtome. Liquid nitrogen was used for the quenching of the membrane. The surfaces of the specimens were coated with gold–platinum (50 : 50 in wt %) for 120 s using plasma vacuum depositor.

RESULTS AND DISCUSSION

Miscibility of HDPE with LP

Light scattering techniques were applied to the detection of the cloud formation since the HDPE crystallite, being formed in course of cooling, acts as a source of scattering. Figure 1 shows the dependence of the cloud point temperature of the blend on the content of HDPE. It reveals that the cloud point temperature of the blend increases with increasing content of HDPE. The tendency of the cloud point temperature depression of HDPE–Decalin blend is more significant than that of HDPE–LP, which leads us to a conclusion that the miscibility of Decalin with HDPE is higher than that of LP. It is believed that the rate of phase separation in the less miscible blend system is higher than that in the more miscible system when we assume the separation proceeds via a solid–liquid (S–L) phase separation mechanism,

Figure 1   Cloud point temperatures of HDPE–LP and HDPE–Decalin blends as a function of HDPE content: (●) HDPE–LP blend; (□) HDPE–Decalin blend; HDPE having MFR value 8 g/10 min was used.

since the rate of nucleation that precedes the separation process decreases as the miscibility of the two components increases.

It has been known that the homogeneous blends in the molten state undergoes liquid–liquid (L–L) phase separation at an upper critical solution temperature in the course of cooling when the interaction of the two components is not so strong.[11–13] On the other hand, phase separation in the systems in which the concentration of the crystallizable component exceeds the monotectic composition, proceeds via a S–L separation mechanism due to the exclusion of noncrystallizable component from the crystals of the crystallizable component. It is worthwhile to mention that the monotectic point appears at lower concentration of the crystallizable component as the interaction between the two components increases. Since the concentration of HDPE in this investigation was always higher than that of monotectic composition, separation proceeds via S–L phase separation mechanism. Therefore, it is concluded that the range of the blend composition for the formation of the microporous structure becomes narrower as the interaction between the two components increases. As a diluent for HDPE, LP is better than Decalin for obtaining a microporous HDPE membrane via the TIPS process. This suggests that Flory–Huggins interaction parameter[13] is an index that is useful for the qualitative interpretation of the phase separation behaviors of the blend.

The dependence of the cloud point temperature of various HDPE–LP blends on LP content is

Figure 2 Dependence of cloud point temperature of HDPE–LP blends, prepared from HDPE having different MFR values. MFR values of HDPE used (in g/10 min): (●) 1; (□) 5; (▲) 8.

shown in Figure 2. The dependence of the cloud point temperature of the various blends on the composition, prepared from HDPE having different MFR values, were compared. The decreasing tendency of cloud point temperature of the blend with increasing LP content is more significant in the blend prepared from HDPE having higher MFR value. It is postulated that two different explanations can be given to this phenomenon. First, the interaction between two components, that is, the interaction between HDPE and LP increases as the MFR value increases. Secondly, the mobility of the crystallizable chain. It has been reported that the rate of crystallization of the polymer decreases as chain length increases,[14,15] as a result, which results in the lowering the cloud point temperature of the blend, prepared from HDPE having a higher MFR value.

Therefore, an attempt was made to evaluate the miscibility of HDPE with LP in terms of the Flory–Huggins interaction parameters using the data obtained from the Hoffman–Weeks plot. Figure 3 shows the dependence of the melting temperature of the blends of various compositions, on the isothermal crystallization temperature. HDPE having a MFR value of 8 was used for this experiment. The linear relationship is observed between the melting temperature of the blend and the isothermal crystallization temperature in both pure and blended polymer. It is also evident that the slopes of the curves, that is, the degree of dependence of the melting point on the isothermal crystallization temperature, is independent on

the blend composition. Since the crystallization of HDPE of the blend is conducted at finite rates, the deviation from the equilibrium results in a reduced thermodynamic stability of the crystallites. For polycrystalline substances, factors contributing to the reduced melting temperature arise from the finite size of the crystallites, their state of internal perfection, and the interfacial in the connecting regions. The melting temperature of a crystalline polymer is determined by the following equation[16,17]:

$$T_m = T_m^\circ \left[\frac{(\gamma - 1)}{\gamma} \right] + \frac{T_c}{\gamma} \qquad (1)$$

T_m°, T_m, T_c, and $\gamma = L/L^*$ denote the equilibrium melting temperature, the melting temperature observed, the crystallization temperature of the crystals, and the ratio of the final and initial thickness of growing crystals, respectively.

This equation is rewritten as

$$(T_m^\circ - T_m) = \phi(T_m^\circ - T_c) \qquad (2)$$

ϕ is a constant, defined as

$$\phi = \left(\frac{1}{2m} \right) \left(\frac{\sigma_e}{\sigma_e^*} \right) + \left(\frac{1}{n} \right) \left(\frac{\sigma_s}{\sigma_s^*} \right)$$

m and n represent the ratio of the actual crystallite dimension to that of critical size of nucleus, σ_e^* and σ_s^* are the surface energies of nucleus of

Figure 3 Hoffman–Weeks plots of HDPE–LP blends of various compositions, prepared from the MFR value of HDPE used (8 g/10 min). Compositions of the blends (expressed in the HDPE–LP weight ratio): (○) pure HDPE; (△) 8/2; (∗) 6/4; (◇) 5/5; (●) 4/6; (▲) 3/7.

Figure 4 Hoffman–Weeks plots of HDPE–LP blends of various LP contents, prepared from the MFR value of HDPE used (5 g/10 min). Compositions of the blends: (○) pure HDPE; (△) 7/3; (∗) 6/4; (◇) 5/5; (●) 4/6; (▲) 3/7.

critical size, and σ_e and σ_s are the surface energies of actual crystal, respectively. Assuming $m = 1$, $n \gg 1$, and $\sigma_e^*/\sigma_e = 1$, that is, crystal grows mostly to transverse direction of the lamella, then ϕ approaches to a value of $\frac{1}{2}$; therefore, the equation is finally rewritten as

$$(T_m^\circ - T_m) = \frac{1}{2}(T_m^\circ - T_c) \qquad (3)$$

As shown in Figure 3, the slopes of the curves are independent on the LP content of the blend. This suggests that the HDPE crystal formed has a perfect crystalline structure, which is free from any defect, and crystal growth proceeds mainly to a direction that is perpendicular to lamellae thickness, while the thickness of the lamellae is kept constant.

Figure 4 shows the Hoffman–Weeks plot of the HDPE–LP blend, prepared from HDPE having a MFR value 5. It is evident that the slope of the curves in this case is less dependent on LP concentration when we compare it with that of the blend, prepared from HDPE having the MFR value of 8.

Based on the data obtained from the Hoffman–Weeks plot, the Flory–Huggins interaction parameter of this blend system can be estimated.[12] For those systems in which diluent is excluded from the crystalline phase, the problem is greatly simplified since the diluent is prevented from entering the crystal lattice for steric reasons. This

corresponds to binary liquid mixtures in which only one of whose component crystallizes over the complete composition range. Under such circumstances, the equilibrium established between the two phases requires, in addition to the equality of the temperature and pressure, that the difference of chemical potential of the crystallizing component in the two phases is zero. The basic equation, proposed by Flory for the depression of the melting temperature with added diluent, is

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = \left(\frac{RV_u}{\Delta H_u V_1}\right)(\phi_1 - \chi\phi_1^2) \qquad (4)$$

T_m, T_m°, ΔH_u, V_1, χ, and ϕ_1 are the melting temperature, the equilibrium melting temperature, the enthalpy change of mixing of repeating unit of the polymer, the molar volume of the repeating unit of polymer, the molar volume of the diluent, the Flory–Huggins interaction parameter of the polymer–diluent pair, and the volume fraction of the diluent, respectively. The value of the interaction parameter was calculated from the slope of the curve of the plot of $1/T_m^\circ - 1/T_m$ versus ϕ_1^2, as shown in Figure 5, which gives a value of 0.36. The values, 3289 J/mol for ΔH_u, and 16.37 and 28.1 cm³/mol for molar volume of LP and HDPE, were used for the calculation.[9] The comparison of the values of interaction parameters of the HDPE–LP blend (0.36) and the HDPE–Decalin system (0.07) gives an explanation why microporous HDPE membrane is obtained from more wide range of blend compositions of the HDPE–LP blend than that of the HDPE–

Figure 5 Comparison of plots of $1/T_m - 1/T_m^\circ$ versus ϕ_{12} for HDPE–LP blends, prepared from MFR values of HDPE used (in g/10 min): (■) 8; (●) 5.

Figure 6 SEM photograph of hollow fiber membrane surface. Composition of the blend used, 5/5; MFR value of HDPE used, 12 g/10 min.

Figure 7 SEM photograph of hollow fiber membrane surface. Composition of the blend, 5/5 blend; MFR value of HDPE used, 8 g/10 min.

Decalin blend in the TIPS process. The value reported for the interaction parameter for the HDPE–Decalin blend system lies in the range of 0.05–0.07 at 149°C.[18] The homogeneous HDPE–LP blend in the molten state becomes heterogeneous due to the S–L phase separation in a wide range of the blend composition when the temperature is lowered down to the crystallization temperature of HDPE. The deviation from the linear relationship between $1/T_m^o$ − $1/T_m$ versus ϕ_1^2, in the high-molecular-weight range of HDPE, however, suggests that the phase separation behaviors of HDPE–LP blend are not fully explainable with this simple thermodynamic approach. The decrease in the miscibility of the two components with increasing chain length of HDPE can be explained in terms of the free volume effect.[19]

Morphology of the Membrane

The morphology of the hollow fiber membrane, prepared by the melt spinning of the molten HDPE–LP blend through an annular spinneret, was studied by means of SEM. The specimens for the morphological study was drawn to 1.5 times after melt spinning since water is not permeable to the membrane of the as-spun fiber.

Figures 6–8 show SEM photographs of the membrane surface, prepared from HDPE having MFR values of 12, 8, and 5, respectively. The comparison of the photographs reveals that the more porous membrane is produced from the blend containing HDPE having lower MFR value. It is believed that the pore size of the membrane is closely related to the lamellar organization,

which is dependent on the free energy of nucleus formation of critical size and activation energy for transport process at the S–L interface.[20] Accordingly, it is thought that the larger domain size and the more significant depression of cloud point temperature of the blend, prepared from HDPE having a lower MFR value, is attributed to the larger rate of nucleation as well as the lower chain mobility. This is in good agreement with the results given in Figure 2.

SEM microphotographs of the membranes, obtained from the blends having compositions of 6/4 and 5/5, are shown in Figures 9 and 10, respectively. It is evident that the size of the spherulite obtained from 5/5 blend is larger than that ob-

Figure 8 SEM photograph of hollow fiber membrane surface. Composition of the blend, 5/5; MFR value of HDPE used, 5 g/10 min.

Figure 9   Cross-sectional SEM photograph of hollow fiber membrane, perpendicular to the fiber axis. Composition of the blend, 6/4; MFR value of HDPE used, 8 g/10 min.

Figure 11   Cross-sectional SEM photograph of drawn hollow fiber membrane, parallel to the fiber axis. Composition of the blend, 6/4; MFR value of the HDPE used, 8 g/10 min; draw ratio, 25%.

tained from 6/4 blend. It was reported that the size of the spherulite is dependent on the number of nucleus and the rate of the crystal growth.[19] This gives an explanation why the spherulite of a larger size is obtained from the 6/4 blend rather than the 5/5 blend. The nucleation density and the number of spherulites per unit volume of the 6/4 blend is larger than that of the 5/5 blend because it is believed that the nucleation density and the number of spherulite decrease as the content of LP increases. Furthermore, the spherulite size is also dependent on the rate of cooling. It is well known that spherulite of smaller size is obtained when the rate of cooling

becomes higher. It is thought that the growth rate of the spherulite of 5/5 blend is higher than that of 6/4 blend, owing to its lower cloud point temperature if the cooling of the molten blend is carried out under the same thermal treatment program. In such a case, the spherulite of smaller size is obtained from 5/5 blend because of the higher cooling rate (refer to Fig. 2, which shows that the most significant depression in the cloud point temperature is observed at the composition of 5/5).

Figure 11 shows SEM photographs of a cross section, perpendicular to the fiber axis. The as-spun fiber was drawn 1.25 times at room temperature after it passed through the cleaning bath. It clearly shows that the pore is enlarged and water paths, which pierce the membrane, is developed by the cold drawing. It is noteworthy to point out that water is not permeable to the membrane of the as-spun hollow fiber. The membrane becomes water-permeable after cold drawing. This reveals that the pores that are responsible for the water permeability of HDPE membrane is formed in the cold drawing process, and the water permeability of the membrane is primarily dependent on the formation of pores that pierce the membrane.

CONCLUSIONS

The thermodynamic aspect of the thermally induced phase separation of HDPE/LP blend has been investigated.

Figure 10   Cross-sectional SEM photograph of hollow fiber membrane, perpendicular to the fiber axis. Composition of the blend, 5/5; MFR value of HDPE used, 8 g/10 min.

The miscibility of HDPE and LP, estimated in terms of the Flory–Huggins interaction parameter, gave a value of 0.36. This indicates that microporous membranes of HDPE can be obtained in a wide range of the blend composition, which consists of HDPE and LP via a thermally induced phase separation process. It was found that the MFR value of HDPE used and the LP content in the blend are the major factors affecting the morphology of the membrane. A membrane having the largest spherulite size is obtained from 5/5 blend, and a membrane becomes water permeable when the pores that pierce the membrane is formed due to the drawing.

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