

Melt-State Miscibility of Poly(ethylene-co-1-octene) and Linear Polyethylene

Kyusoon Shin,¹ Byeong Uk Nam,² Joon Bang,³ Jae Young Jho¹

¹School of Chemical and Biological Engineering, Seoul National University, Shinlim, Kwanak, Seoul 151-742, Republic of Korea

²Department of Applied Chemical Engineering, Korea University of Technology and Education, Chongnam, 330-708, Republic of Korea

³Department of Chemical and Biological Engineering, Korea University, Anam, Seoul 136-701, Republic of Korea

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ABSTRACT: On purpose to examine the effect of branch length on the miscibility of polyolefin blends, miscibility behavior of linear polyethylene/poly(ethylene-co-1-octene) blend was studied and compared to that of linear polyethylene/poly(ethylene-co-1-butene) blend. Miscibility of the blend was determined by observing the morphology quenched from the melt, and by using the relation between interaction param-

eter and copolymer composition. When the weight composition and molecular weight was the same, poly(ethylene-co-1-octene) was slightly more miscible with linear polyethylene than poly(ethylene-co-1-butene) was. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2584–2587, 2008

Key words: polyolefins; blends; miscibility

INTRODUCTION

Interaction parameter is the key parameter scaling miscibility between the two or more components in polymer blends. While small angle neutron scattering (SANS) has been the main experimental technique determining interaction parameter,^{1–3} isotope effect has been known to make the analysis complicated^{4,5} when specific interaction between the components was absent as in polyolefin blends. The interaction parameter has also been evaluated by measuring melting temperature depression.^{6,7} It has a limitation that at least one of the components should be crystalline, since the thermodynamics of melting point depression deals with melting transition.⁸

Rhee and Crist proposed a method estimating an interaction parameter of the blends containing random copolymers,⁹ based on the thermodynamic relation called “copolymer equation,”^{10,11} which described the relation between interaction parameter and copolymer composition. They applied the method to linear polyethylene/poly(ethylene-co-1-butene) blend, and the results were proved to be sound. As the method can be employed for any

blend containing random copolymer, the limitations of SANS and melting point depression measurement are overcome.

The present work was motivated by the interest in the effect of branch length on the miscibility of the polyolefin blends containing linear polyethylene and poly(ethylene-co- α -olefin). At a same mole composition, it is natural that, longer the branch length is, less miscible the blend is. The miscibility behavior of the blends at a same weight or volume composition, however, is yet to be compared. In the present study, employing the same procedure, miscibility behavior of linear polyethylene/poly(ethylene-co-1-octene) blend is investigated. The result is compared to that for linear polyethylene/poly(ethylene-co-1-butene) blend to examine the effect of branch length on the miscibility at the same weight composition.

EXPERIMENTAL

Poly(ethylene-co-1-octene)s (EOs) used in this study were supplied by Dow Chemical Company (Plaquemine, LA), and linear polyethylene (LPE) was supplied by Hanwha Chemical Corporation (Yeocheon, Republic of Korea). The structure of EOs was characterized with ¹³C NMR,¹² and the content of 1-octene comonomer was determined by ¹H NMR by counting the number of methyl protons, both using a JEOL Lambda 300 spectrometer. The samples were prepared in 1,2-dichlorobenzene with concentrations of 5 wt %, and deuterated benzene was used as locking agent.

Correspondence to: K. Shin (shin@snu.ac.kr) or J. Y. Jho (shin@snu.ac.kr).

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TABLE I
Characteristics of the Materials Used

Sample code	Trade name	1-Octene content (wt %)	M_w	M_w/M_n	Critical composition with LPE ^a (vol %)
LPE	7400	0.0	135,000	7.8	–
EO21	PF1140	21.0	130,000	2.6	54.8
EO29	CL8003	28.7	166,000	2.6	59.8
EO35	KC8852	35.1	134,000	2.4	59.0
EO38	EG8100	37.8	143,000	2.5	57.8
EO45	EG8842	45.0	152,000	2.5	57.0

^a Critical composition was calculated using eq. (2).

The weight-average molecular weights and molecular weight distributions were determined by GPC using a Polymer Laboratory 210 instrument at 140°C in 1,2,4-trichlorobenzene. The GPC data were calibrated with SRM 1483 or Easy-cal[®], which is the polyethylene standard supplied by NIST or Polymer Laboratory, respectively. The characteristics of the polymers are summarized in Table I.

EO was blended with LPE at its critical composition with LPE. The two polymers were solution-blended in xylene (1 wt %) at 140°C, precipitated in dry ice/acetone, filtered, and then dried in a vacuum oven at 60°C for 48 h. The blend samples were placed in a preheated DSC furnace at 150 or 200°C for 600 s, and quenched in a dry ice/acetone bath to preserve the melt-state morphology. Quench-crystallized samples were cut using a microtome at –100°C to observe the bulk morphology. The surface was etched with 0.4 wt % permanganic acid for 10 h, washed following the procedure known,¹² and the morphologies were observed with JEOL JSM-840A SEM.

RESULTS AND DISCUSSION

The critical point of miscibility for a blend is defined by critical interaction parameter, χ^c , and critical volume fraction, ϕ^c , which are given by the following equations,^{13–15} which can be applied to blend systems of homopolymer/homopolymer, homopolymer/random copolymer, or random copolymer/random copolymer with different compositions.

$$\chi^c = \left(N_{Az}^{-1/2} + N_{Bz}^{-1/2} \right) \left(N_{Az}^{1/2} N_{Aw}^{-1} + N_{Bz}^{1/2} N_{Aw}^{-1} \right) / 2 \quad (1)$$

$$\phi_B^c = N_{Aw} N_{Bz}^{1/2} / \left(N_{Aw} N_{Bz}^{1/2} + N_{Bw} N_{Az}^{1/2} \right) \quad (2)$$

Here, ϕ_B , N_{Bw} , and N_{Bz} are the volume fraction, weight-average degree of polymerization, and z-average degree of polymerization of polymer B.

Critical volume fraction is given by the molecular weights only, and those for the EOs, based on C₈ unit, are calculated and listed in Table I. Since the weight-average molecular weights and molecular weight distributions of EOs were kept nearly the same, the binary blends with LPE had similar ϕ^c around 57 wt % of EO. The deviations from the average do not exceed 3 wt %.

Critical interaction parameter is the χ at which phase separation just occurs, since a blend is miscible when $\chi < \chi^c$ and immiscible when $\chi > \chi^c$. In the present system, a series of poly(ethylene-*co*-1-octene)s with different composition is blended with LPE at ϕ^c , and χ^c can be determined at the composition where the system becomes unstable.

Rhee and Crist observed this critical point for linear polyethylene/poly(ethylene-*co*-1-butene) blend (LPE/EB).⁸ They further determined the parameter that directly described the miscibility of the blend using the following “copolymer equation,” which was proposed by Scott earlier.^{10,11}

$$\chi = CY_{br}^2 \quad (3)$$

where Y_{br} is the fraction of branched or comonomer units. The constant C was determined from χ^c and the critical 1-butene content where phase separation just occurred. C defines the miscibility between linear C₄ unit in LPE and branched C₄ unit in poly(1-butene). A series of separate SANS experiments with the same series of copolymers indicated that the copolymer equation correctly describes the relation between the interaction parameter and the composition of copolymer.¹⁶ Therefore, this method was thought to be used for the evaluation of interaction parameter of random copolymer blends.

The same approach was employed for LPE/EO blend system in the present study. The copolymers used were prepared by metallocene catalysts. For it has been known that metallocene catalysts produce the polymers with narrow molecular weight distribution ($M_w/M_n \approx 2$)¹⁷ and random comonomer distribution,¹⁸ the above equations could be applied to the present system.

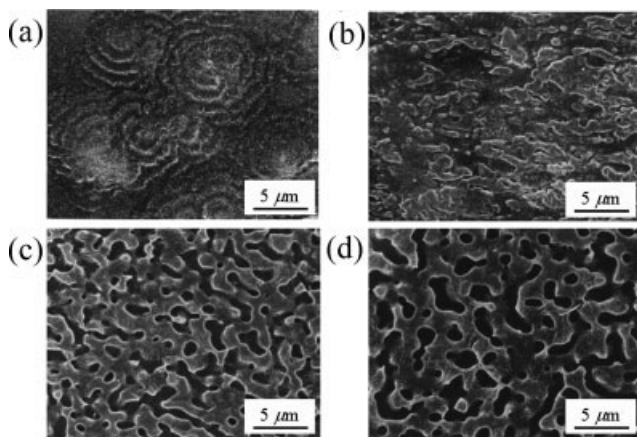


Figure 1 SEM images of the blends quench-crystallized from 150°C; (a) LPE/EO21, (b) LPE/EO29, (c) LPE/EO35, and (d) LPE/EO38. The blends were prepared at their critical compositions.

SEM images of etched surface of blend samples quench-crystallized from 150 and 200°C are shown in Figures 1 and 2, respectively. Figure 1(a) shows morphology of LPE/EO21 blend of banded spherulites with no sign of phase-separation, which indicates that the blend is miscible at 150°C. For the blends with EO containing 29 wt % or more of 1-octene, phase separation is evident. Figure 1(b–d) shows the morphology by spinodal-decomposition and subsequent removal of segregated EO-rich phase by etching. It is thus figured out that increasing the comonomer content from 21 to 29 wt % causes the blend system to become immiscible at 150°C. The constant C in eq. (3) is calculated to lie between 0.019 and 0.039 from χ^c s and $Y_{br,s}$ at Y_{br} between 0.21 and 0.29. C determined here represents the

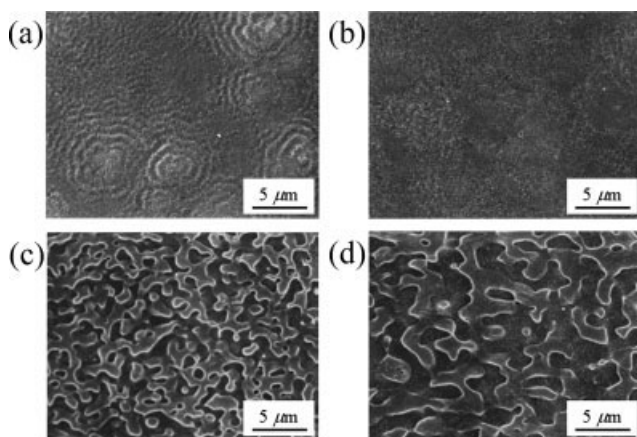


Figure 2 SEM images of the blends quench-crystallized from 200°C; (a) LPE/EO21, (b) LPE/EO29, (c) LPE/EO35, and (d) LPE/EO45. At this temperature LPE/EO29 that was not miscible at 150°C shows no sign of phase separation.

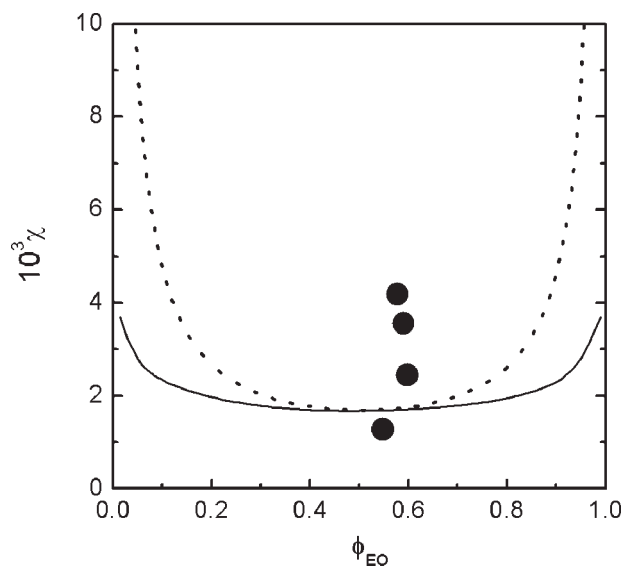


Figure 3 Calculated binodal (solid) and spinodal (dotted) curves for LPE/EO blends ($N_{LPE} = 1205$ and $N_{EO} = 1160$). Points represent blends of LPE and EO at 150°C.

interaction between the linear C_8 unit in LPE and the branched C_8 unit in poly(1-octene).

Figure 3 shows the phase diagram of LPE/EO blends. For binodal and spinodal curves, $N_{LPE} = 1205$ and $N_{EO} = 1160$ were used, which correspond to the LPE/EO21 blend. The estimated χ_c for blends in Figure 1 were located in this phase diagram. Since the polymers were assumed to be monodisperse in the calculations, the critical points in the experiments are different from those in the diagram. However, it is clearly shown that the LPE/EO21 blend is located at the miscible phase, while the others are within the window of phase separation, consistent with SEM images in Figure 1.

To elucidate the effect of branch length on the miscibility of branched PE to LPE, the result is compared with that of LPE/EB blend obtained by Rhee and Crist.^{9,16} Since their result is based on C_4 units, there needs a conversion of C_4 units to C_8 units for comparison. Converting two C_4 units to one C_8 unit corresponds to halving N , which is the number of monomeric units of the blend component. In the relation determining the phase separation, eq. (1), χ^c doubles by the halved N . At the same time, C in eq. (3) should be doubled by converting two C_4 units to one C_8 unit. The C converted is the χ parameter between two branched C_4 units in poly(1-butene) and linear C_8 unit in LPE.

C obtained by Rhee and Crist for the blends of LPE and hydrogenated polybutadienes by using the same method as the present study was 0.022.⁹ The converted value of 0.044 is a little larger than C of LPE/EO blends determined in the present study. It indicates that two C_4 branched units are less misci-

ble with linear C₈ unit than one branched C₈ unit is. It is therefore concluded that EB is less miscible to LPE than EO is, when molecular weight and weight fraction of comonomer are the same.

At an elevated temperature of 200°C, phase separation is observed for the blends of EO with higher branch content. As shown in Figure 2(b), LPE/EO29 blend that is phase-separated at 150°C is melt-miscible at 200°C. It is indicated that LPE/EO blends show upper critical solution temperature (UCST) behavior just as most polyolefin blends do.^{1,18} The constant *C* based on C₈ unit, calculated from the *Y*_{br} of 0.29–0.35, is 0.014–0.019, which is smaller than that at 150°C.

CONCLUSIONS

Based on the thermodynamics of homopolymer/random copolymer blend, the interaction parameter between the linear C₈ unit and the branched C₈ unit and its temperature dependency was evaluated. By comparing to the previously reported result, at the same weight fraction of comonomer, poly(ethylene-*co*-1-octene) appeared to be slightly more miscible with linear polyethylene than poly(ethylene-*co*-1-butene) was.

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