

Miscibility and Properties of cis-Polybutadiene/Ethyl-Branched Polyethylene Blends (II)

Ur-Ryong Cho

Department of Applied Chemical Eng., Korea Univ. of Technology and Education, Chonan 330-860, Korea

Received January 15, 2000

Abstract : Cis-Polybutadiene(cis-PBD) and the three polyethylenes(PE's) having different branch content were mixed to investigate crystallinity, thermodynamic interaction parameter(c), and diluents effect. Crystallinity of PE's decreased with increasing content of amorphous cis-PBD because of a decrease in both the degree of annealing and kinetics of diffusion of the crystallizable polymer content. The thermodynamic interaction parameter(c) for the three blend systems approximately equals to zero near the melting point. These systems were determined to be miscible on a molecular scale near or above the crystalline melting point of the crystalline PE's. From the measurement of T_m vs. T_c behavior, all the three blends showed a straight line for a plot of T_m vs. T_c . This result means that the melting behavior of PE is mainly due to a diluent effect of cis-PBD component.

Introduction

In the previous paper,¹ the three binary blend mixtures of cis-PBD with three different polyethylenes(PE's) differ in ethyl branch content. As published previously by U. R. Cho,² three kinds of PE's used for this research were obtained by hydrogenation of three polybutadienes which have vinyl unit of 2, 6 and 9%, respectively. According to the differences of the ethyl branch concentration by hydrogenation of vinyl unit, they were identified as PE(2), PE(6) and PE(9). In the previous work the melting point depression of polyethylene increases with the increase of branch concentration in PE. The measured dimensions of the unit cell of a semicrystalline polyethylene are not affected by the introduction of an amorphous component for three cis-PBD/PE blend systems. According to the measurement of T_g by dynamic mechanical thermal analyzer(DMTA) and the phase observation by transmission electron microscope(TEM), these blend systems were determined to be immiscible on a molecular scale at room temperature regardless of blend composition. The three blends showed a lin-

ear relationship between the density behavior and with change of blend ratio. This trend means that these blends have very weak or no interactions between the two component chain segments. From the measurement of stress-strain behavior for these blends, the breaking strength of cis-PBD/PE(2) and cis-PBD/PE(6) blends showed simple additivity effects. But cis-PBD/PE(9) yielded a rapid increase of the breaking strength, when using a polyethylene fraction of more than 0.5 because of the strain hardening effect. Especially, this remarkable result due to the strain hardening effect in the cis-PBD/PE(9) expects to be very useful for development of commercial products. As a successive work, crystallinity of three PE's with different ratio of cis-PBD was investigated by differential scanning calorimeter(DSC). Interaction parameter, c , for the these blend systems was calculated using Kwei and Frisch's Equation³ which extended Nishi and Wang's treatment⁴ by taking into account morphological effects. In addition to the above studies, to elucidate the role of cis-PBD for these blend systems, a plot of the crystallization temperature, T_c , versus observed melting point, T_m , was drawn by using DSC with respect to different blend ratio.

*e-mail : urcho@kut.ac.kr

Experimental

Materials. Cis-PBD(Goodyear, Budene 1208) was used as given. PE(2), PE(6) and PE(9) were obtained from hydrogenation of three polybutadiene; cis-PBD(Goodyear, Budene 1208), trans-PBD(Phillips, Tran-4), cis, trans-PBD(Scientific Polymer Products) which have vinyl unit of 2, 6 and 9%, respectively².

Blending. Cis-PBD was blended with various PE's, e.g., PE(2), PE(6), PE(9) to investigate their mutual compatibility. Samples of various compositions were prepared by solution blending in a mutual solvent(p-xylene) followed by solvent evaporation. The evaporation of solvent from the blend solution was carried out at 90 °C, at 10 in Hg in a vacuum drying oven to prevent polyethylene from precipitating due to crystallization.

Instruments and Sample Preparation. The melting points of polymer blends were measured by differential scanning calorimeter(DSC, Dupont 9900 thermal analyzer) with disc memory. DSC analyses were carried out for each polymer sample by placing approximately 10 mg of sample into an aluminum sample pan.

Results and Discussion

Crystallinity. The degree of the crystallinity of the crystalline material in the polymer blends can be affected by several factors such as chemical compositions, crystallization temperature, pressure, orientation, molecular weight, and presence of a diluent. For the blends of cis-PBD/PE, understanding all of these variables is greatly simplified since all of the parameters except the effects of a diluent were kept constant. The heat of fusion in J/g for each blend composition was determined from DSC. The percent crystallinity was calculated from the ratio of the heat of fusion for 100% crystalline PE was selected as 70 cal/g.⁵ Figure 1 shows the plot of the heat of fusion, based on the potentially (stoichiometrically) crystallizable portion, against the volume fraction of cis-PBD. The level of crystallinity in the different cis-PBD/PE blends, as shown in Figure 1, is clearly a function of composition. As the rubber content in the blend increases, the crystallinity decreases in a mono-

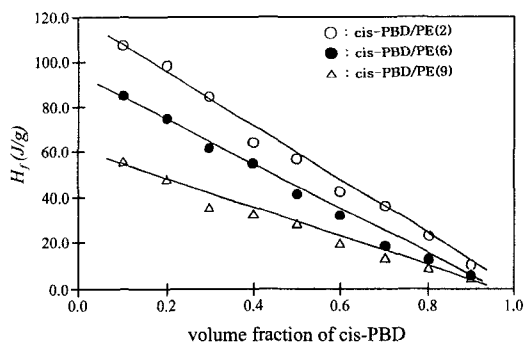


Figure 1. Observed heat of fusion for different cis-PBD/PE blends.

tonic fashion in all cases. The decrease of crystallinity with increasing rubber content can be explained in terms of both the degree of annealing and then decreasing the rate of crystallization. A decrease in average crystallinity may also result from a decrease in the crystallization kinetics. The kinetics of diffusion can be influenced by the presence of diluent. Thus, in the case of cis-PBD/PE blends, both of these effects may contribute to incomplete crystallization and thus to a decrease in crystallinity as the rubber content is increased. The viscous cis-PBD component reduces the rate of the segmental diffusion of the PE molecules to a growing crystal surface. In other words, the crystallization of PE segments is controlled by the segmental diffusion rate of the other PE chains which are randomly separated by the addition of the rubber content. The same trend in crystallinity has been observed in the other blend systems. Kwei³ and Natta⁶ reported a linear relationship between crystallinity and blend composition by measuring the heat of fusion in the poly(phenylene oxide)/polystyrene (PPO/PS). Nishi⁴ and Hoffman⁷ showed a linear dependence of crystallinity over the entire range of composition from the thermal analysis of solution cast mixture of poly(vinylidene fluoride)(PVF₂) and poly(methyl methacrylate)(PMMA).

Interaction Parameter. The thermodynamic interaction parameters for the cis-PBD/PE blends were obtained by analysis of the melting point depression. Nishi and Wang⁴ extended Flory's theory of the melting point depression by using Scott's expression for a binary polymer blend sys-

tem. The resulting Equation from their analysis of crystalline and amorphous polymers leads to the following an analytical expression of Equation(1).

$$\frac{1}{\Phi_1} \left(\frac{1}{T_m} - \frac{1}{T_m^0} \right) = - \frac{BV_3 \Phi_1 \chi_{23}}{\Delta H_m V_2} \quad (1)$$

where

- Φ_1 : Volume fraction of rubbery content.
- T_m : Absolute melting temperature.
- T_m^0 : Equilibrium melting temperature.
- B : Interaction energy density characteristic of polymer pair.
- V_2, V_3 : Molar volume of polymer 2 and polymer 3.
- χ_{23} : Interaction parameter between polymer 2 and polymer 3.
- ΔH_m : Enthalpy change of mixing.

From their studies on PVF₂/PMMA and PVF₂/PEMA mixtures, a plot of $\Delta T_m / \Phi_1 T_m$ versus $\Phi_1 T_m$ had straight line behavior with an intercept close to zero. Therefore, factors such as crystal imperfection and reduction in lamellar thickness were not considered to be major factors in the lowering of the melting point. Kwei and Frisch³ further extended Nishi and Wang's treatment⁴ by taking into account the morphological effects which may also contribute to the melting point depression. The numerical data of melting point in the cis-PBD/PE with blend ratio are listed in Table I. The resulting analytical expressions are shown in Equation(2) and Equation(3).

$$\frac{\Delta H_u (T_m^0 - T_m) / \Phi_1 (RT_m^0 - T_m) / m_1 - \Phi_1 T_m / 2m_2}{\Phi_1 T_m} = C/R - b\Phi_1 \quad (2)$$

$$\chi = a + b/T \quad (3)$$

where

- ΔH_u : Heat of fusion per mole of repeating unit of crystalline component.
- R : Gas constant.
- m_1, m_2 : Chain repeat lengths of polymer 1 and polymer 2.
- C : Proportionality constant.
- a, b : constants.
- T : Absolute temperature.

Table I. Observed Melting Point of Various cis-PBD/PE Blends

Composition (cis-PBD/PE)	T_m (°C)		
	cis-PBD/PE(2)	cis-PBD/PE(6)	cis-PBD/PE(9)
10/90	119.4	112.1	84.0
20/80	119.0	111.9	83.3
30/70	119.1	112.0	83.9
40/60	118.6	111.2	81.9
50/50	119.0	110.8	81.9
60/40	118.4	110.6	81.8
70/30	118.5	110.2	81.0
80/20	117.5	110.0	80.6
90/10	117.1	109.0	79.1

From a plot of the left hand side of Equation(2) vs. Φ_1 , they found a non-zero intercept for PPO /PS blends, an intercept value was found to increase with decreasing PS molecular weight. The authors concluded that the melting point depression is linked to the diluent effect as well as the morphological effect. In this study, the melting point data for each set of cis-PBD/PE mixtures were plotted in accordance with Equation(2). A value of $\Delta H_u = 70$ cal/g (980 cal per mole of -CH₂-unit) which was reported by Schultz⁵, is used in this analysis. The values of the interaction parameter, χ , for the polymer blends were computed by using a linear regression analysis on the data of Table I. The parameters C/R^* and b were determined from the computed intercept and slope values, respectively. The calculated values for the interaction parameter based on the depression of the melting point, as well as the critical interaction parameter determined using Equation(4) are compiled in Table II.

$$(\chi_{ab})_{cr} = \frac{1}{2} \left[\frac{1}{X_a^{1/2}} + \frac{1}{X_b^{1/2}} \right]^2 \quad (4)$$

Where $(\chi_{ab})_{cr}$ is the critical interaction parameter between polymer a and polymer b, X_a and X_b are the degree of polymerization in polymer a and polymer b. The results show that the interaction parameters for the different blend systems are in the range of 10^{-3} and no apparent differences were to be observed. One might imagine that the

Table II. Calculated Thermodynamic Interaction Parameter (c) and C/R^* for Different Blends from T_m Measurements

Polymer blend	C/R^* ($^{\circ}\text{K}$)	Slope ($^{\circ}\text{K}$)	$c(\text{at } T_m)$	c_{cr}
cis-PBD/PE(2)	2.583	0.786	0.002	0.0015
cis-PBD/PE(6)	6.353	0.539	0.001	0.0013
cis-PBD/PE(9)	9.474	0.256	0.0007	0.0012

interaction parameter would decrease with increasing branch concentration of PE. Since the melting point depression increases in the order PE(2), PE(6), PE(9) due to an increasing amorphous portion of PE, the more amorphous portion must increase the chain mobility between the crystalline and amorphous polymer molecules. Based on these findings, one may speculate that the interaction parameter decreases in order of PE(2), PE(6), PE(9). However, the existing data shows that these blends display no apparent dependence on the amount of the polyethylene branching, at least within the experimental limits of this technique. As shown in Table II, the slope is close to zero, or nearly so. Therefore the interaction parameter is very close to zero for all of these cis-PBD/PE mixtures regardless of the type of the blends. The interaction parameters calculated are the value given at the melting point of polyethylene. All three kinds of polyethylenes exist as a melted liquid state having no crystalline portion. This state doesn't make difference of crystallinity between PE's. The high mobility of chains in the melted state allows better interaction parameters (almost zero) at the melting point than at room temperature. If true, the different branch concentration of PE may all have roughly the same net thermodynamic interaction behavior with cis-PBD, namely, χ , is approximately equal to zero. These results agree with the data given by Schroeder¹⁵ using similar blend systems. The contribution of morphological effects on the depression of the melting point may be analyzed from the computed intercept values. The intercept values from the above plot is equal to C/R^* and is a linear function of the lamellar thickness. Results in Table II show that an apparent correlation appears to exist between different branch concentration PE and the crystal thickness. DSC measurements suggest that the crystallinity of PE decreases with

increasing branch concentration from which one may conclude that these effects are primarily due to a decrease in the crystal thickness. Upon inspection of the data, it is agreed that PE with low branching has a high melting point and high lamellar thickness. The decrease of C/R^* means that there is an increased contribution of morphological effects on the melting point depression. Therefore, the morphological effects increase in the order PE(2)>PE(6)>PE(9) according to the decreasing values of C/R^* value. Lin⁸ found that the ethylene content of the EPR component on morphological changes appear to be significantly influenced. He reported an intercept values of 7 for EPR-50 and EPR-60, and 20 for EPR-75 (The numerical suffix denotes mole percent of ethylene unit in ethylene-propylene rubber). Schroeder found that for that same blend system using higher molecular weight EPR, C/R^* values were in the range of 2-3. He did not find any relationship between the intercept value and ethylene content of the EPR for this higher molecular weight EPR, and attributed this phenomenon to the effect of the molecular weight of amorphous component. Likewise, for PPO/PS blends, Kwei¹⁰ found that C/R^* decrease with increasing molecular weight of PS, and he concluded that the melting point depression is almost entirely attributable to morphological effects at high molecular weight PS. Thus C/R^* as a linear function of lamellar thickness can be influenced by the molecular weight of the amorphous components as well as the chemical structure of the amorphous components. This study shows that the morphological effect on the melting point depression corresponds to the degree of crystallinity in PE with the same amorphous component.

Diluent Effect. Besides the calculation of an interaction parameter, one series of additional experiments was conducted to investigate further

the influence of cis-PBD on the melting behavior of PE and the experimental technique of melting point analysis. In this study the melting point measured after an isothermal crystallization from the molten state. Experiments were run after cooling the sample from the melt to a predetermined crystallization temperature below T_m for a period of 10 minutes using DSC only. A plot of the crystallization temperature, T_c , versus observed melting point, T_m , was then drawn. For binary polymer blends, the dependent on composition and can be more complicated than that observed for homopolymers. For those polymers which exhibit a melting point depression, the three fundamental types of behavior were illustrated in Figure 2. Various materials have been found to display a phase behavior similar to that illustrated. In case I, T_m is found to increase linearly with T_c . This type of behavior is often observed in semicrystalline homopolymers. The slope of the straight line is independent of composition and of T_c . As the concentration of the crystallizable component decreases, the extrapolation value of T_m also decrease (Figure 2A). In case II, T_m of the blend

increases linearly with T_c , but the lines extrapolate to the same equilibrium T_m value of the homopolymer and their slopes depend on composition (Figure 2B). In case III, T_m is a linear function of T_c only for a certain interval of T_c . Thereafter a non-linear trend is observed at high crystallization temperatures and the actual depression values are small and not dependent on composition (Figure 2C). The depression of the melting point for blends belonging to case I has been interpreted as being due to a diluent effect of the amorphous component. According to Hoffman⁷, a plot of the melting temperature T_m of the crystals against their crystallization temperature gives a straight line in accordance with the Equation (5).

$$T_m = T_m^0(1-\gamma^{-1}) + \gamma^{-1}T_c \quad (5)$$

Where γ is a morphological factor that turns out to be almost independent of composition and of chemical structure. The behavior according to case I includes of PVF₂/PMMA⁶, PVF₂/PEMA¹⁰, and i-PP/EP¹¹. These systems have shown a linear type behavior with respect to composition. Paul and Altamiano¹² and Natov and coworkers¹³ interpreted case II to be due to morphological effects. These effects are considered to arise from the formation of smaller and less perfect crystallites by the addition of a non-crystallizable component especially. Blends of PEO/PMMA show a behavior similar to that for case III. This latter type of behavior has been interpreted by Martuscelli and Demma¹⁴ to be due to the occurrence of phase separation. For low T_c (the linear part of the T_m - T_c plot) the two components are completely miscible in the melt, and the non-crystallizing component acts as a diluent. At higher T_c the mutual solubility of the components decreases giving rise to the formation of a two-phase system. In these experiments the behavior of the observed T_m on the crystallization temperature for different cis-PBD/PE blends is shown in Figures 3 to 5. These blends display a straight line in plot of T_m vs. T_c . This implies that the melting behavior of PE is mainly due to a diluent effect of the cis-PBD component. In addition, each blend has a different equilibrium melting point depending on blend composition. Consequently, the two components must be miscible in the amorphous state for a

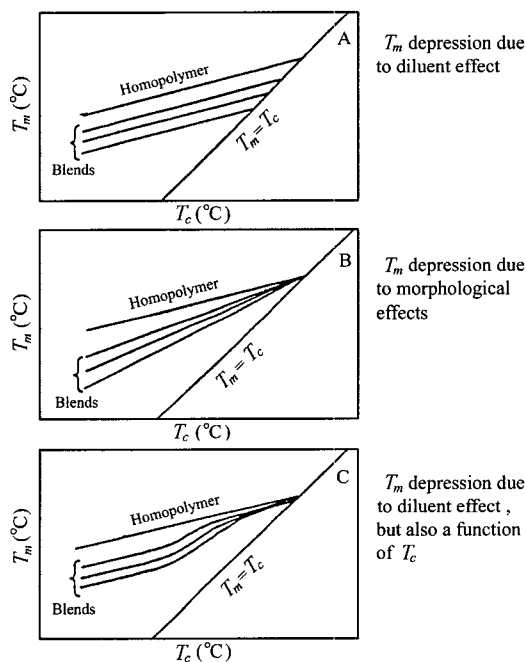


Figure 2. Schematic illustration of possible T_m vs. T_c behavior for semicrystalline blends.

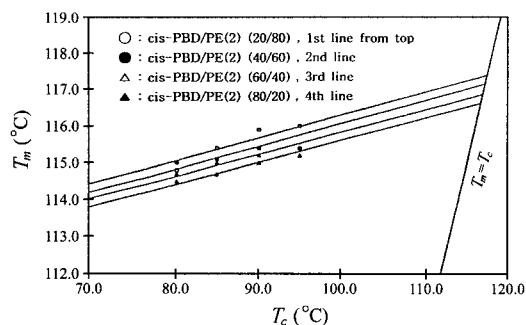


Figure 3. Observed melting point temperature vs. T_c for cis-PBD/PE(2).

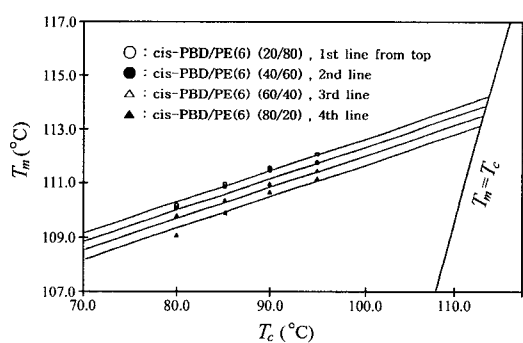


Figure 4. Observed melting point temperature vs. T_c for cis-PBD/PE(6).

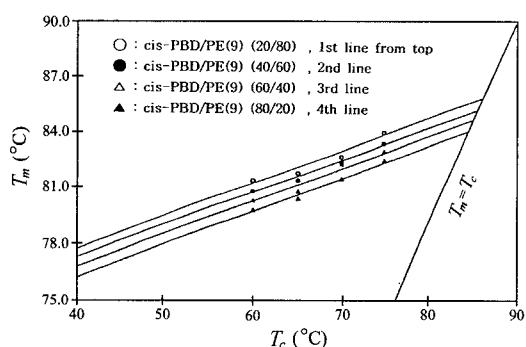


Figure 5. Observed melting point temperature vs. T_c for cis-PBD/PE(9).

temperature higher than that of crystallization.

Conclusion

The measured heat of fusion for the different polymer blend systems shows a decrease in per-

cent crystallinity with increasing content of the amorphous constituent. This decrease in crystallinity is explained by a decrease in both the degree of annealing and kinetics of diffusion of the crystallizable polymer component. The thermodynamic interaction parameter, χ , for different binary polymer mixtures was determined by an analysis of the phase diagram near the melting point. Results for cis-PBD/PE blends yield a value for the interaction parameter approximately equal to zero. As a result, these polymer systems were determined to be miscible on a molecular scale near or above the crystalline melting point of the crystallizable component. These findings are supported, at least for the blends studied, from both the isothermal crystallization melting point results conducted in this study and also from the recent studied of Lin⁸ and Schroeder¹⁵ using similar materials. From the measurement of T_m vs. T_c behavior for cis-PBD/PE blends. All the three blends showed a straight line in a plot of T_m vs. T_c . This implies that the melting behavior of PE is mainly due to a diluent effect of cis-PBD component. In addition, each blend has a different equilibrium melting point depending on blend composition. Consequently, the two components must be miscible in the amorphous state for a temperature higher than that of crystallization.

References

- (1) U. R. Cho, *Korea Polym. J.*, **7**, 196 (1999).
- (2) U. R. Cho, *Polymer(Korea)*, **19**, 535 (1995).
- (3) T. Kwei and H. Frisch, *Macromol.*, **11**, 1267 (1978).
- (4) T. Nishi and T. Wang, *Macromol.*, **8**, 909 (1975).
- (5) J. Schultz, "Polymer Materials Science", Prentice Hall, Inc, New Jersey, 1974.
- (6) G. Natta, P. Corradini, D. Sianesi, and D. Morero, *J. Polym. Sci.*, **51**, 527 (1961).
- (7) J. D. Hoffman, *Soc. Plast. Eng. Trans.*, **4**, 315 (1964).
- (8) W. Y. Lin, Ph.D. Dissertation, Univ. of Akron, 1983.
- (9) G. Allegra and I. Bassi, *Adv. Polym. Sci.*, **6**, 549 (1969).
- (10) T. Kwei, G. Patterson and T. Wang, *Macromol.*, **9**, 780 (1976).
- (11) E. Martuscelli, C. Silvestre and G. Abate, *Polymer*, **23**, 229 (1982).
- (12) D. Paul and J. Altaminano, *Am. Chem. Soc. Adv.*

U. R. Cho

- Chem. Ser.*, **142**, 371 (1975).
- (13) M. Natov, L. Peeva and E. Djararova, *J. Polym. Sci.-Part C*, **16**, 4197 (1973).
- (14) E. Martuscelli and G. Demma, "Polymeric Blends : Processing-Morpology and Properties", ed., E. Martuscelli, R. Palumbo and M. Kryszewski, Plenum Press, N. Y., 1990.
- (15) John R. Schroeder, Ph. D. Dissertation, Univ. of Akron, 1990.