

Effects of Blending on the Melting and Crystallization of Polyethylene and Polypropylene under High Pressure

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ABSTRACT: The melting and crystallization behavior of polyethylene (PE) and polypropylene (PP) blends under high hydrostatic pressures up to 500 MPa was studied by differential thermal analysis (DTA). These high pressure crystallized blends were also investigated at 1 atm by DTA, X-ray diffraction, and electron microscopy. The melting temperature T_m of PE in the blend under high pressure was determined from the peak temperature of a DTA curve of melting. The T_m versus pressure curve for PE in the blend shifts to the high pressure side with decreasing PE content. In the DTA curve of melting at 1 atm for a blend crystallized under 450 MPa, an endothermic peak that could not be assigned to the melting of folded PE chain crystals (FCC) appeared on the low temperature side of the melting peak for extended chain crystals (ECC), indicating that small PE crystals different from FCC were formed in the molten PP during crystallization. The X-ray diffraction pattern of this blend showed that no eutectic crystallization occurs even in the isothermal crystallization under high pressure. Electron microscopic observations of the fracture surface of the high pressure crystallized blend showed a clear boundary between the PE and PP domains, suggesting that no interdiffusion of the two polymers occurs.

KEY WORDS Blend / Polyethylene / Polypropylene / Melting / Crystallization / High Pressure / DTA / X-Ray / Electron Microscopy /

Many investigations on polyethylene (PE) and polypropylene (PP) blends have been carried out to improve the low temperature toughness or impact strength of PP.¹ Since it is fundamentally important to obtain information on the compatibility of polymer molecules in blends, many studies on the compatibility of PE and PP have also appeared. Some investigators²⁻⁴ made microscopic observations on the PE/PP boundary to see whether interdiffusion of the two polymers occurs to give an interphase layer.

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were used to study thermal behavior of PE/PP blends. Some authors¹⁻⁵ found in the DTA curve separate endothermic peaks corresponding to the melting of PE and PP.

The melting and crystallization of pure polymers under high pressure have been studied by many investigators.⁶ In the case of PE, it is widely known that extended chain crystals (ECC) are formed under high pressures above 300 MPa. The existence

of a high pressure hexagonal phase was confirmed in the past decade.⁷⁻⁹

For PP, melt-crystallization produces the triclinic γ form under high pressure,¹⁰⁻¹² and the monoclinic α form at 1 atm.

The pressure dependence of the cloud point in blend polymer systems has been studied recently,^{13,14} mainly in regard to the compatibility of amorphous and crystalline polymers or amorphous and amorphous polymers.

In this paper, the melting and crystallization of PE and PP in their blends under high pressure are reported. It is shown that the behavior of PE in the blend is different from that in the pure state. High pressure DTA measurements were performed on PE/PP blends of different composition. The boundary of the PE/PP phases in a sample was observed using an electron microscope. X-Ray diffraction measurements were performed on the same sample.

EXPERIMENTAL

The samples used in this study were commercial grade high density PE, Hizex 2200J, with a viscosity-average molecular weight $M_v = 40,000$, provided by Mitsui Petrochemical Industries Co. and isotactic PP, with a molecular weight $M_v = 420,000$, supplied by Mitsubishi Yuka Co. Mixed PE and PP pellets were dissolved in *p*-xylene at 135°C to make a solution with a concentration of 0.1%. Following slow cooling to room temperature at a rate of 1°C min⁻¹, the precipitated crystals were filtered and dried in a vacuum oven. The composition ratio (PE/PP) was changed from 80/20 to 5/95.

High pressure DTA measurement was performed using the apparatus reported elsewhere.¹² The heating rate was 6°C min⁻¹ and the cooling rate, 5°C min⁻¹ for all DTA measurements.

A sample for electron microscopy was prepared by the following procedure. A block of the blend obtained by filtration was covered by epoxy resin and placed in the DTA cell to crystallize from the melt under high pressure. The temperature of the sample was monitored by the DTA thermocouple. The sample crystallized under high pressure was cleaved in liquid nitrogen and was examined under an electron microscope using the two-stage standard replication technique with cellulose acetate and chromium metal. A Hitachi HS-7 electron microscope was used. X-Ray diffraction photographs were taken on a cylindrical camera with radiation of Ni filtered CuK α for 1 h.

RESULTS AND DISCUSSION

Effects of Blending on the High Pressure Phase of PE

The DTA curve of pure PE under high pressure shows complicated features, because the orthorhombic to hexagonal phase transition occurs below the melting temperature at pressures above about 350 MPa. Figure 1 shows the high pressure DTA curves of pure PE and the blend of 40/60 in PE/PP. The DTA melting curve at 1 atm on the blend sample crystallized at 1 atm (curve d) shows two endothermic peaks corresponding to the melting of the FCC of PE at 132°C and the melting of the α form crystal of PP at 165°C. In the DTA curve of melting above 350 MPa of pure PE crystallized at 1 atm, three endothermic peaks and one exothermic

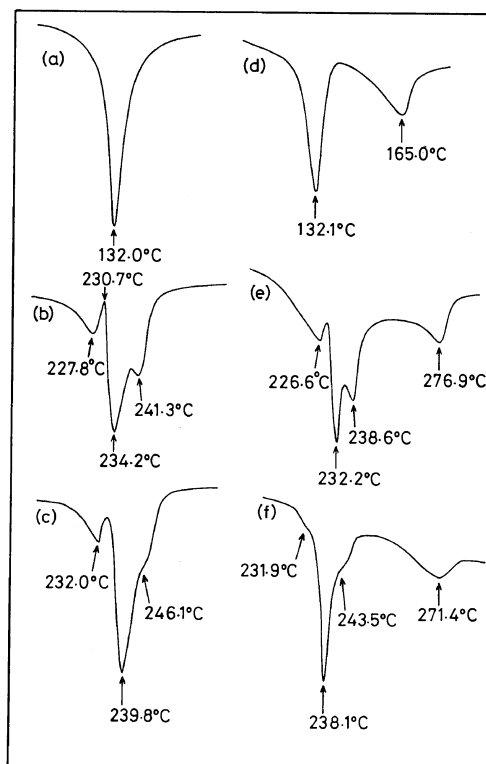


Figure 1. DTA curves of melting for pure PE and PE/PP blend of (40/60): (a), 1 atm DTA of PE melt-crystallized at 1 atm; (b), 458 MPa DTA of PE melt-crystallized at 1 atm; (c), 484 MPa DTA of PE melt-crystallized at 450 MPa; (d), 1 atm DTA of the blend melt-crystallized at 1 atm; (e), 450 MPa DTA of the blend melt-crystallized at 450 MPa; (f), 477 MPa DTA of the blend melt-crystallized at 450 MPa.

peak appear as shown in curve b. These peaks of pure PE under high pressure were assigned as follows.^{15,16} The 227.8°C peak is due to melting of FCC, the 230.7°C peak to recrystallization of the FCC melt, the 234.2°C peak to the transition from the orthorhombic to hexagonal phase, and the 241.3°C peak to melting of the high pressure hexagonal phase. The high pressure DTA curve of pure PE crystallized under high pressure (curve c) is somewhat different in shape from that of the sample crystallized at 1 atm. The peak and shoulder temperatures in curve c, 239.8°C and 246.1°C, agree with T_{tr} (*ortho*-hexa transition temperature) and T_m (melting temperature of the hexagonal phase), as determined by Bassett and Turner⁷ and Yasuniwa *et al.*¹⁵ within experimental error. However, the peak

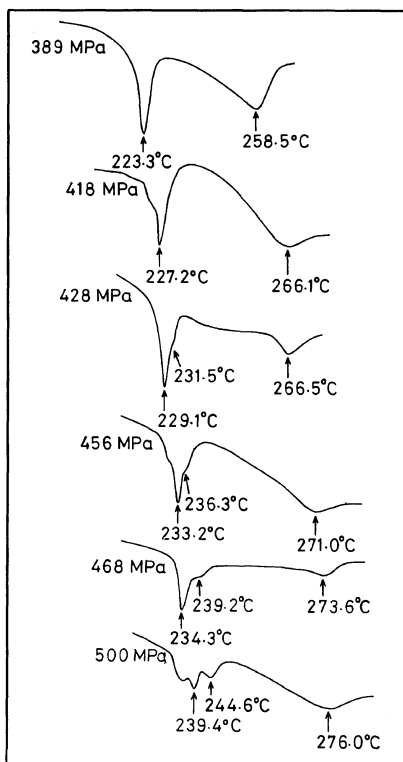


Figure 2. DTA curve of melting under high pressure for the blend (20/80) crystallized at 460 MPa.

temperature in curve b for the FCC sample is 234.2°C, which is about 2°C lower than the transition temperature T_{tr} at 458 MPa determined by these two groups. Therefore, an ECC sample was used to determine the phase diagram of PE.

The 450 MPa DTA curve for the blend sample crystallized at 1 atm shows three endothermic peaks around 230°C due to the transition and melting of PE and an endothermic peak of melting of the α form of PP at 276.9°C. The DTA curve of the blend sample crystallized under high pressure resembles that of pure PE crystallized under high pressure in the melting region of PE. The phase diagram of PE in the blend was also determined from the DTA curve for a high pressure crystallized sample, *i.e.*, for the ECC of PE in the blend.

The degree of depression of T_{tr} and T_m under high pressure increases with decreasing PE content. Figure 2 shows the change in the DTA curve for the sample of 20/80 in PE/PP crystallized under high pressure with the change in pressure. A small shoulder corresponding to the melting of the hexa-

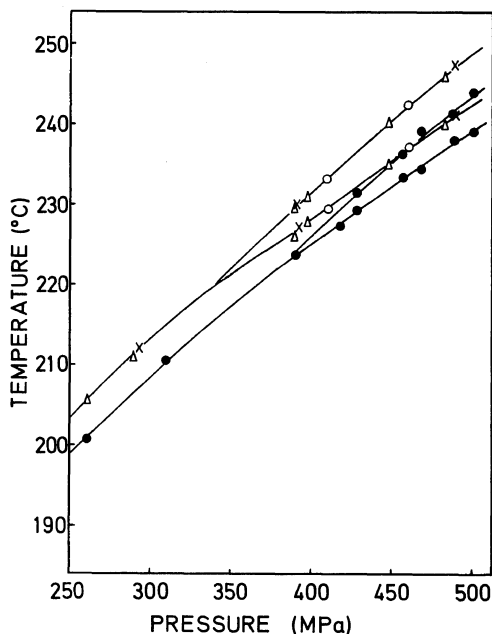


Figure 3. Phase diagram of pure PE and PE in the blend (20/80) at high pressure: O, Yasuniwa *et al.*¹⁵; ×, Bassett⁸; △, this work; ●, PE in the blend.

gonal phase appears on the high temperature side of the main peak above 428 MPa. In pure PE, the shoulder appears at 390 MPa. The temperature of the shoulder is plotted in Figure 3. The endothermic peak at 266.5°C is due to the melting of the γ form crystal of PP. Figure 3 shows the phase diagrams of PE above 250 MPa in the PE/PP (20/80) blend and pure PE. In this study, T_m of the ECC of pure PE at 1 atm was 140.8°C and T_m of the ECC of PE in the blend (20/80) at 1 atm was 140.2°C. The difference in T_m of ECC between pure PE and the blend PE increases with pressure, amounting to about 5°C at 300 MPa. The T_m versus pressure curve for the ECC of PE in the blend was formulated using the method of Wunderlich⁹ to obtain

$$T_m = A + BP - CP^2 \quad (1)$$

where P is the pressure in MPa and T_m , the melting temperature of the orthorhombic crystal. The coefficients were evaluated by the least squares method for all blends and are listed in Table I.

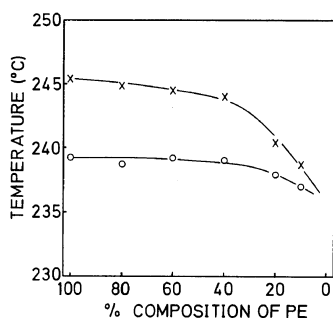
The triple point in the phase diagram shifts to the high pressure side with decreasing PE content in the blend, *i.e.*, from 350 MPa for pure PE to about 400 MPa for the composition 20/80. Table II lists

Table I. *A*, *B*, and *C* coefficient values in eq 1

PE/PP	<i>A</i>	<i>B</i>	<i>C</i>
	°C	°C MPa ⁻¹	°C MPa ⁻²
100/0	140.7	0.30	1.94 × 10 ⁻⁴
80/20	140.7	0.29	1.85 × 10 ⁻⁴
60/40	140.6	0.29	1.79 × 10 ⁻⁴
40/60	140.3	0.29	1.74 × 10 ⁻⁴
20/80	140.2	0.27	1.43 × 10 ⁻⁴

Table II. *T_m* and *T_{tr}* under high pressure for various composition in PE/PP blend

PE/PP	1 atm	150 MPa	300 MPa	450 MPa	
	<i>T_m</i> /°C	<i>T_m</i> /°C	<i>T_m</i> /°C	<i>T_{tr}</i> /°C	<i>T_m</i> /°C
100/0	140.8	181.1	212.7	235.6	240.4
80/20	140.8	180.6	212.1	235.3	239.6
60/40	140.6	180.0	211.5	234.8	239.0
40/60	140.3	179.5	210.8	234.4	238.5
20/80	140.2	177.4	208.1	232.5	235.0

**Figure 4.** Composition dependence of *T_m* and *T_{tr}* of PE in the blend at 480 MPa: ○, *T_{tr}*; ×, *T_m* of the hexagonal phase.

the values of *T_m* and *T_{tr}* in the blend at various pressures. Tables I and II show that the shift of *T_m* is remarkable at low content of PE. Figure 4 shows the changes in *T_{tr}* and *T_m* with change in composition in the blend at 480 MPa. The reduction in *T_{tr}* and *T_m* is remarkable at 20/80 in PE/PP. The shift of the triple point in the phase diagram for PE to the low pressure side has been reported by Oyama *et al.*¹⁷ on γ -ray irradiated pure PE. Shifting in the blend, occurs in the opposite direction.

Two different origins may be considered for the shifting of the triple point in the case of blend PE. One is the effect of blending with PP. Some compatibility effects on the boundary of two polymer crystals have been reported. Kryszewski *et al.*⁴ considered the possibility of the interdiffusion of PE and PP molecules at the boundary of the two polymers in the melt. Lovinger and Williams⁸ found a maximum in the tensile modulus versus PE/PP composition curve at about 20% of PE in the blend, and ascribed this mechanical behavior to a reduction in spherulite size and an increase in the concentration of intercrystalline links.

The other cause for the shift of *T_m*, *T_{tr}* and the triple point to the high pressure side may possibly be that the crystal size of the ECC of PE becomes smaller with decreasing PE content. The X-ray diffraction pattern taken at 1 atm on a high pressure crystallized blend showed a mixture of diffraction lines from PE and the γ -form crystal of PP. The intensity changed linearly with change in content of the constituent polymers. No such lines suggestive of alloy crystals of PE/PP as observed in annealed IPB-1 (isotactic polybutene-1)/PP blend¹⁹ were observed. The electron micrograph showed a clear boundary at the interface of two polymers, as shown below. The shift of *T_m* and *T_{tr}* of PE in the blend may occur as a result of the size effect of PE crystals in the PP matrix. Confirmation of the above results will require additional research on PE blended with different crystalline polymers under high pressure.

The *T_m* of PP in the blend was measured under high pressure, but no notable difference was observed.

High Pressure Crystallization of PE/PP Blend

The pressure dependence of the crystallization temperatures *T_c* of pure PE and PP was determined independently by high pressure DTA.^{12,15} *T_c* increased with pressure for both PE and PP, but the curvature of *T_c* versus pressure was different. The two curves crossed at 250 MPa. At 1 atm, *T_c* of PP was higher than that of PE, but above 250 MPa, *T_c* of PE was higher than that of PP. In the cooling process, the DTA curve of the blend showed two exothermic peaks and the peak temperatures corresponded to the crystallization temperatures of pure PE and PP. Therefore, it was concluded that PE crystallizes in the PP melt above 250 MPa and

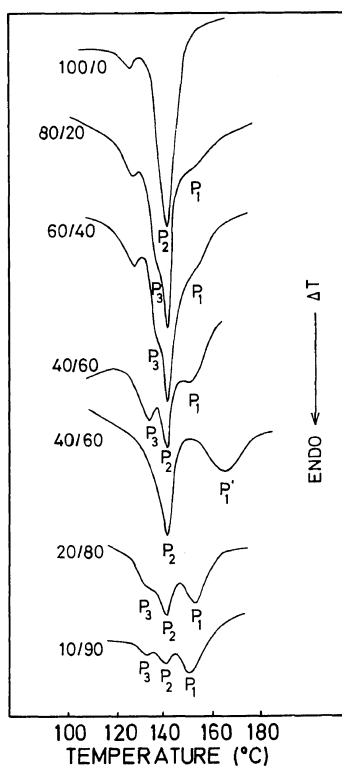


Figure 5. DTA curves of melting at 1 atm for pure PE and blends of different composition crystallized at 450 MPa. Composition is indicated in the figure. P_1 and P_1' are the melting peaks of PP γ -form crystal and α -form crystal, respectively. P_2 peak is due to melting of ECC of PE. The lower curve for 40/60 was obtained on the sample prepared by crystallizing only PE and not melting PP crystal under high pressure. The other curves were obtained on the sample crystallized by cooling from a temperature above T_m of PP.

crystallizes in the solid PP below this pressure.

High pressure crystallized PE/PP blends of different composition were investigated at 1 atm by DTA, electron microscopy, and X-ray diffraction. Figure 5 shows a series of DTA curves at 1 atm for these blends crystallized from the melt at 450 MPa. The P_1 peak at 151°C and the P_1' peak at 165°C correspond to the T_m of the γ -form and α -form crystals of pure PP at 1 atm, respectively. In the DTA curve of pure PE, a sharp endothermic peak corresponding to the melting of ECC was observed at 140.7°C (P_2 peak) and a small peak corresponding to the melting of the FCC of PE at 132°C. The change in peak temperature with com-

position was only 0.6°C, from 140.7°C for 100/0 to 140.1°C for 10/90 in PE/PP. In the blend crystallized under high pressure, a shoulder (P_3 peak) appeared on the low temperature side of the P_2 peak. The temperature of the P_3 peak decreased with decreasing PE content, from 139.1°C for 80/20 to 134.1°C for 10/90. In the sample crystallized at 1 atm, the P_3 peak did not appear at 1 atm, as already shown by curve d in Figure 1. To see the difference in melting behavior at 1 atm between PE crystallized in the molten PP and the solid PP under high pressure, melt-crystallization of only PE in the blend was performed at 460 MPa by cooling the sample from a temperature just above T_m of PE (242.3°C) to a temperature below T_m of PP. In this process, PP in the blend did not melt. The T_m of PE in this sample was 140.6°C, so that ECC of PE was formed in the solid PP by crystallization from the melt under high pressure. Taking this into account, we may conclude that the P_3 peak is associated with the melting of PE crystals formed near the boundary of the two polymers. These PE crystals may be formed in the molten PP. During the crystallization of PE, molten PP molecules are considered to interfere with crystallization to the ECC form. As the PE content decreases, the interference effect may become stronger and the thickness of the crystals may decrease, leading to a depression of T_m . The fact that the P_3 peak height decreases by isothermal crystallization at T_c of PE under high pressure supports the above argument.

Electron microscopic observations were performed on the fracture surface of blends crystallized from melt under high pressure. Figure 6(a) shows the fracture surface of the blend (5/95) crystallized at 440 MPa. A stacking of long thin bands of ECC can be seen. Usually, small blocks of aggregated ECC of PE were observed to disperse in the PP matrix of the blend containing a small amount of PE. The average width of the band was about 3,000 Å. An isolated single crystal of ECC was seldomly observed even at a small content of PE (5%). On the fracture surface of the high pressure crystallized blend of (10/90), a PE block consisting of ECC was also observed. Figure 6(b) shows the fracture surface of the blend (20/80) crystallized under high pressure. A flat portion with a globular area of PP and a band of the ECC of PE can be seen. The globular area in high pressure crystallized pure PP has been reported by Sauer and Pae.²¹ The

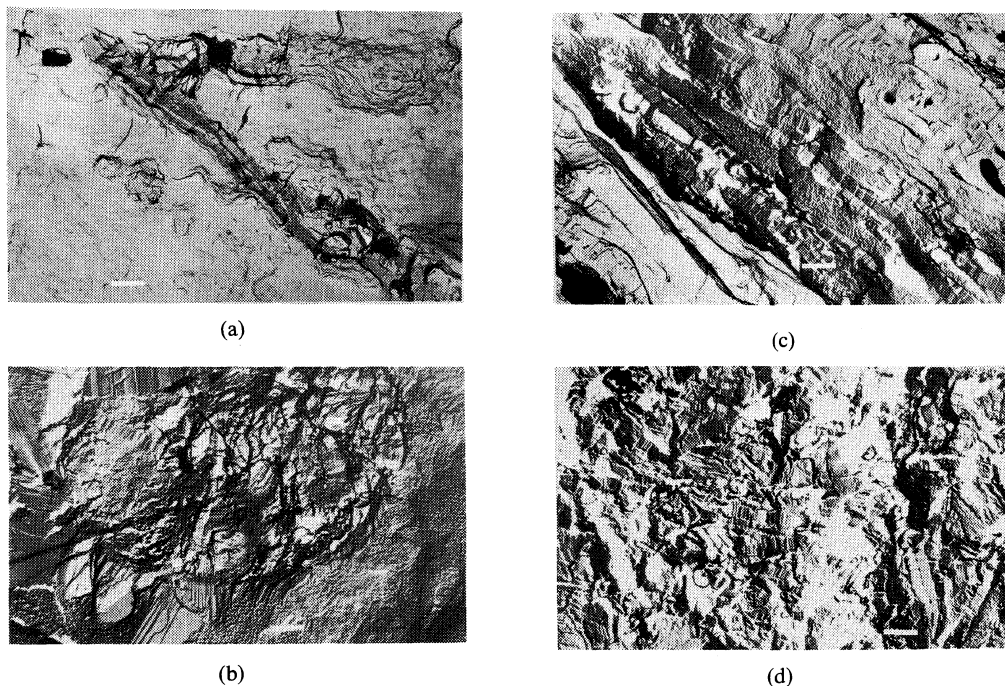


Figure 6. Electron micrograph of the fracture surface of high pressure crystallized blend. Scale bar means $1\ \mu\text{m}$: (a), 5/95; (b), 20/80; (c), 60/40; (d), 80/20.

flat area is characteristic of the band of PE/PP crystallized from melt under high pressure, and corresponds to the crystal which shows an endothermic shoulder (P_3 peak) in the DTA curve at 1 atm shown in Figure 5. In the blend of (60/40), a sandwichlike pattern consisting of the band of ECC of PE and the globular area of PP appeared as shown in Figure 6(c). The average width of the PE band was about $0.5\text{--}1\ \mu\text{m}$, but a band thicker than $1\ \mu\text{m}$ was also observed. The block of ECC of PE increased with increasing PE content. The boundary of the PE band and the globular PP was clear, and no interdiffusion of these two molecules likely. Figure 6(d) shows the fracture surface of the blend (80/20) crystallized under high pressure. In this sample, a small area of globular PP was dispersed between ECC of PE. These electron microscopic observations may be summarized as follows. ECC of PE is formed on melt-crystallization of PE/PP blends under high pressure even at a PE content as small as 5%, irrespective of whether PP is molten or solid. The size of the block of ECC of PE increases with increasing PE content in the blend.

This is also the case with the width of the band.

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