Crystallization, Melting Behavior, and Morphology of BPP/HDPE Blend

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ABSTRACT: The crystallization, melting behavior, and morphology of a low ethylene content block propylene–ethylene copolymer (BPP) and a high-density polyethylene (HDPE) blend were studied. It was found that the existence of ethylene–propylene rubber (EPR) in BPP has more influence on the crystallization of HDPE than on that of PP. This leads to the decreasing of the melting temperature of the HDPE component in the blends. It is suggested that the EPR component in BPP shifted to the HDPE component during the blending process. The crystallinity of the HDPE phase in the blends decreased with increasing BPP content. The morphology of these blends was studied by polarized light microscopy (PLM) and SEM. For a BPP-rich blend, it was observed that the HDPE phase formed particles dispersed in the PP matrix. The amorphous EPR chains may penetrate into HDPE particles to form a transition layer. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2469–2475, 1998

Key words: crystallization and melting behavior; morphology; block propylene–ethylene copolymer; high-density polyethylene; blend

INTRODUCTION

The properties of polymeric materials can be modified by changing their chemical structure. An alternative way is to mix two or more polymers into a physical mixture,[1] that is, a polymer blend, in which there are no covalent bonds between the components. The concept of physically blending two or more existing polymers to obtain new products or for problem solving has not been developed as fully as the chemical approach but is now attracting widespread interest and commercial utilization.

Within the last few decades, propylene and ethylene multiphase polymer systems including polymer blends have assumed considerable technological and commercial importance. Polypropylene (PP) and polyethylene (PE) blends have been widely investigated to improve the low-temperature toughness of isotactic polypropylene (i-PP). The success of blending depends upon some compatibility between the polymer components.

Lovinger and Williams showed that a distinct maximum in tensile strength and modulus occurs at a composition of about 80% PP. They discussed the relationships between the tensile properties and morphology of PP/high-density PE (HDPE) blends.[2] Noel and Carley carried out similar investigations with these polymer blends.[3]

The two polymers are thermodynamically immiscible, and this precludes generating a truly homogeneous product. This may not be a problem per se since often it is desirable to have a two-phase structure. However, the situation at the interface between these two phases very often can produce problems, in that there is a high interfa-

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cial tension and poor adhesion between the phases. This interfacial tension along with high viscosities led to an inherent difficulty in dispersing the components randomly in the mixtures and also to their lack of phase stability which leads to gross separation or stratification during further processing or use. Poor adhesion leads to the production of very weak and brittle (or cheesy) blends.

It is known that the presence of certain polymeric species, usually block or graft copolymers, suitably chosen, can minimize some of these problems, and it is generally believed that this is a result of their ability to alter the interfacial interaction. Such species, as a consequence, are often referred to as "compatibilizers."[4]

Ethylene–propylene copolymers have been used as compatibilizers for the blending of PP and PE.[5,6] In previous work,[7] the TREF fractionation showed that the block propylene–ethylene copolymer (BPP) contains about 15% amorphous ethylene–propylene rubber (EPR). In the present work, studies on the role and distribution of EPR in the blend will be investigated along with the crystallization and melting behaviors as well as an analysis of the morphology of the blend. BPP will be seen as two parts: i-PP and EPR. The crystallization and melting behavior of BPP/HDPE blends made by melt and solution mixing were studied.

EXPERIMENTAL

Both BPP and HDPE are commercially available from Solvay. The ethylene content in BPP was 7 mol %. Blends were prepared by solution mixing and also by melt mixing.

Solution Mixing

Polymer pellets were dissolved in *o*-xylene at 135°C for about 90 min with agitation. The solutions were subsequently precipitated into a large volume of methanol and filtered, and the blends washed with acetone. The polymer blends were dried at 60°C in a vacuum for 48 h.

Melt Mixing

Melt mixing was carried out on a Schwabenthan hot-roll mill. The temperature of the rollers and mixing time were 180°C and 15 min with a veloc-

Table I Crystallization Parameters of i-PP and BPP

Crystallization Parameters	i-PP	BPP
T_c (K)	385.74	383.34
T_{onset} (K)	395.59	389.51
ΔH_c (J g^{-1})	−91.18	−48.63

ity ratio of 1.2 : 1 to encourage shear mixing. The band of the polymer melt on the rolls was cut diagonally and folded repeatedly to improve the mixing.

RESULTS AND DISCUSSION

General Crystallization Characteristics

The crystallization behaviors of BPP, HDPE, i-PP, and HDPE/BPP blends at different compositions were investigated as a function of temperature. On cooling at 10 K min^{-1}, for both solution and melt-mixed blends, the temperature ranges in which the crystallization occurred decreased in the order of i-PP, BPP, the blends, and HDPE, but there was considerable overlap in the temperature range 390–370 K.

As shown in Table I, the presence of the EPR component in BPP results in a decrease in T_c, ΔH_c, and T_{onset} when compared with i-PP. A decrease in T_{onset} of the BPP blends clearly indicates that the inclusion of the rubber phase in PP results in delayed nucleation.

According to the TREF analysis of BPP,[7] it was found that BPP is composed of EPR and PP as well as a series of crystallizable propylene–ethylene copolymers. On crystallization of BPP, the presence of EPR leads to the formation of some defective PP crystals, while for crystallizable propylene–ethylene copolymers, the uncrystallizable units exist as defects in the crystals. So, there is a larger decrease in ΔH_c for BPP (ΔH_c for BPP is −48.63 J g^{-1}) compared to i-PP (ΔH_c for i-PP is −91.18 J g^{-1}), even on subtracting the weight percentage of EPR rubber in the BPP blends and recalculating ΔH_c only on the weight percentage of the PP component.

Table II shows the heat of crystallization of HDPE/BPP blends both melt- and solution-mixed and the ΔH_c decreased with increasing BPP con-

Table II Crystallization Heat of HDPE/BPP Blends

Crystallization Parameters	Ratio of HDPE/BPP						
	0/100	10/90	30/70	50/50	70/30	90/10	100/0
$-\Delta H_c$ (J g^{-1}) melt-mixed	48.63	55.09	67.40	74.94	87.69	101.44	116.04
$-\Delta H_c$ (J g^{-1}) solution-mixed	48.63	49.69	54.52	60.95	70.40	94.39	116.04
Calculated ΔH_C	48.63	55.37	68.86	82.34	95.82	109.30	116.04

tent. Calculating the ΔH_c values according to the following additive equation:

$$\Delta H_c = x_1 \Delta H_{c1} + (1 - x_1)\Delta H_{c2} \qquad (1)$$

where x_1 is the weight percentage of the component with the crystallization enthalpy ΔH_{c1}, it can be seen that the experimental values are somewhat additive, which suggests that both PP and PE components in these blends crystallize independently of one another. However, the experimental values are lower than the calculated values (Fig. 1). If PP is the dominant phase, then it will crystallize with HDPE dispersed in it as droplets. Nucleation may then limit the extent of crystallization which develops within the HDPE and vice versa. The experimental values are then lower than the calculated values by the amount uncrystallized.

Overall Crystallization Kinetics

The overall crystallization rates of the blends were studied isothermally and analyzed using the
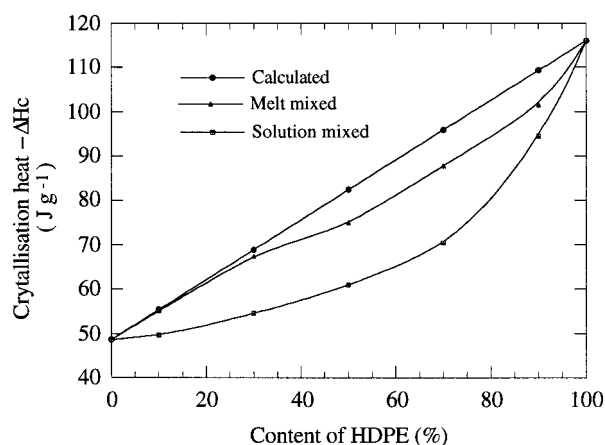

Figure 1 Variation of crystallization heat with content of HDPE.

Avrami equation. The half-lives of the crystallization of BPP and HDPE have a different temperature dependence (see Fig. 2). It can be seen that for melt-mixed blends the crystallization temperatures are between BPP and HDPE, while for solution-mixed blends, the crystallization temperature has shifted to lower temperatures. The HDPE-rich blends crystallized at similar rates to those of HDPE, while the BPP-rich blends crystallized at similar rates to those of BPP. It is apparent that provided the BPP forms a continuous phase the crystallization rate is essentially that of the BPP component and those blends exhibited a similar crystallization rate to that of BPP. However, when HDPE formed the continuous phase, the crystallization rate approached that of the bulk HDPE.

Melting Behavior

The melting curves for BPP, HDPE, and their blends crystallized from 470 to 320 K at a 10 K min^{-1} cooling rate are shown in Figure 3. Two well-separated melting peaks are present, corresponding to the melting of BPP and HDPE. This means that the BPP/HDPE blend system contains two distinct phases. Even for the 90 : 10 and the 10 : 90 HDPE/BPP blends, two melting peaks corresponding to PP and PE melting, indicating that both PP and PE crystallized in these blends, were present. Comparing the melting temperatures of the blends with those of BPP and HDPE, the melting temperatures of the PE component is shifted to lower temperatures with increasing BPP content, while the melting temperatures of the PP components in the blends shifted a little to higher temperature. χ_{AB} was used to evaluate the compatibility between the EPR and the amorphous part of PE and PP. According to Krause's method,[8] the δ values for PE, PP, and EPR are 8.31, 7.82, and 8.36 (cal/cm^3)$^{1/2}$, respectively, and χ_{PE-EPR} and χ_{PP-EPR} are 0.0368 and 0.0486, re-

(a) Melt-mixing.
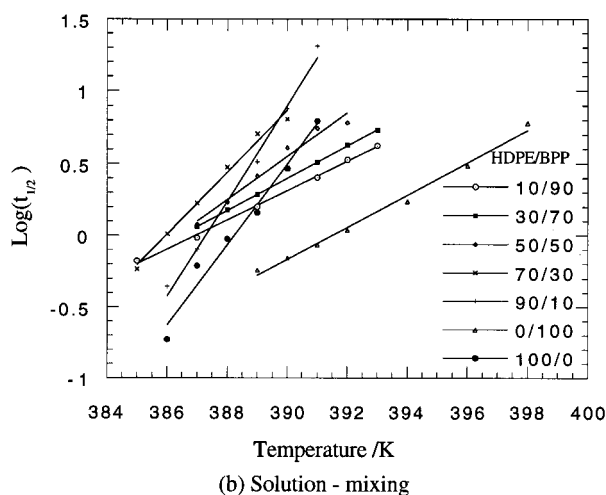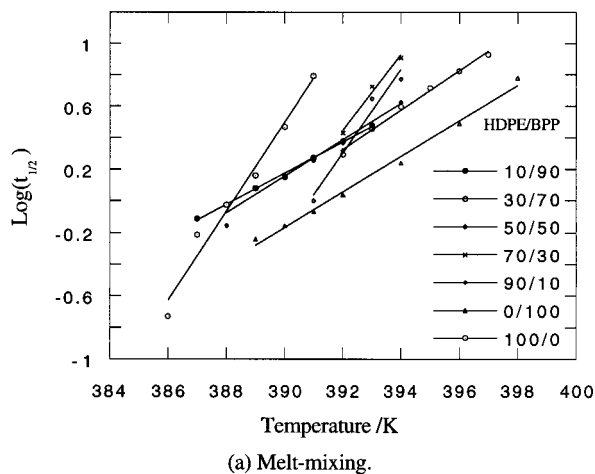

(b) Solution - mixing

Figure 2 Relationship between log ($t_{1/2}$) and crystallization temperature.

spectively, which demonstrated that the compatibility between PE and EPR is better than that between PP and EPR. On blending, the EPR component in the BPP dissolves in PE and, on cooling, alters the crystallization of PE, leading to some defects in the PE crystals and a decrease in the PE melting point.

The crystallinity was calculated from the DSC melting curves using the relationship

$$\% \text{ Crystalllinity} = (\Delta H_f^{obs}/\Delta H_f^0) \times 100 \quad (2)$$

where ΔH_f is the heat of fusion. The value of ΔH_f^0 for the 100% crystalline PP homopolymer was taken to be 209 and 293 J g^{-1} for PE. Figure 4 shows the degree of crystallinity, as measured by DSC, which develops in the blends with the com-

position assuming a two-phase morphology of PP and PE domains only. It can be seen that the crystallinity of the HDPE phase in the blends decreased with increasing BPP content, indicating that PP and EPR were present in the phase and altered the degree of perfection of the PE crystals.

A plot of the T_m against T_c for the PP component of each blend shows that T_m varied with T_c in accordance with the Nishi and Wang equation[9]:

$$T_m = \Phi T_c + (1 - \Phi)T_m^0 \quad (3)$$

where Φ is a stability parameter which depends on the lamellae thickness and T_c is the crystallization temperature. Φ is assumed to have values
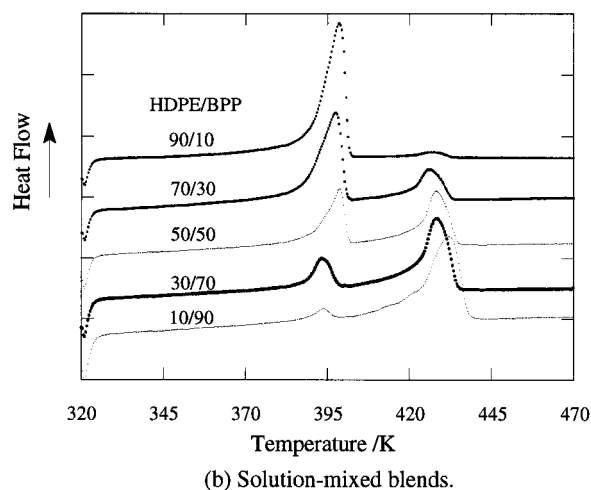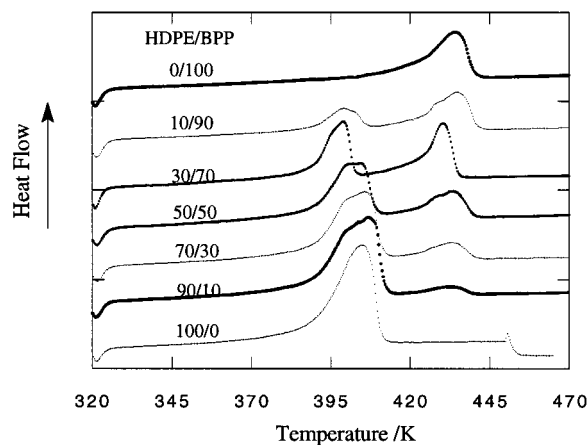

(a) Melt-mixed blends.

(b) Solution-mixed blends.

Figure 3 Melting curves of HDPE/BPP blends.

(a) Melt-mixed blends.
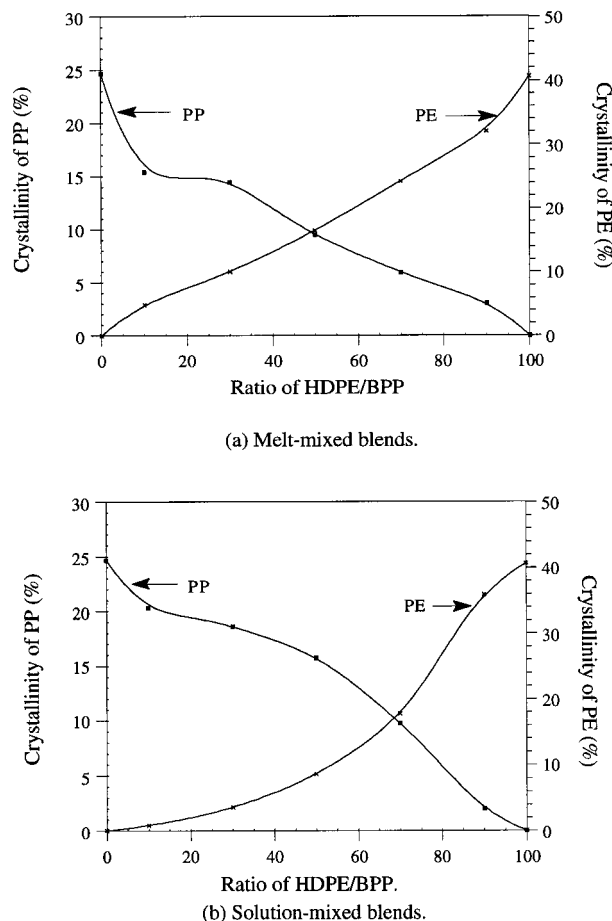

(b) Solution-mixed blends.

Figure 4 Variation of crystallinity of each component with composition of blend.

between 0 and 1, $\Phi = 0$ implies that $T_m = T_m^0$ for all T_c, whereas $\Phi = 1$ implies that $T_m = T_c$. Therefore, the crystals are more stable at $\Phi = 0$ and inherently unstable at $\Phi = 1$. Usually, plots of T_m versus T_c are linear with a constant slope independent of the blend composition, that is, constant Φ If the T_m depression is due mainly to morphological effects, then Φ, which is, in fact, a morphological parameter, would not be independent of composition, and the plots of T_m versus T_c would have different slopes extrapolating to a single equilibrium melting point. In this work, it was found that Φ depended on the blend composition. This suggested that the T_m is depressed by an amount proportional to concentration of the impurity, that is, EPR presented in the PP phase. However, for both the melt- and solution-mixed blends, they have no single equilibrium melting point (Table III). From the values of Φ, it can be seen that PP crystals are comparatively unstable in the HDPE-rich blends.

Morphology of BPP/HDPE Blend

The growth of the spherulitic texture of the blends was observed with an optical polarized light microscope (PLM) using a video camera and a colored TV monitor. Specimens were prepared from thin micron slices of the sample, placed between coverglasses, and inserted into the hot plate at 200°C. Figure 5 shows the optical micrographs of i-PP and a blend with HDPE/BPP at 30/70 which were isothermally crystallized at 130°C for 30 min after melting samples at 240°C for 5 min. The i-PP sample exhibited α-form spherulites, while all the blends showed α-PP spherulites of a similar size to that of i-PP. At this temperature, the HDPE and EPR components exist in the form of droplets within the spherulites.

These droplets obviously consisted of molten EPR and PE at 130°C. The droplets were enclosed within the growing spherulite. During crystallization, the PP spherulites form with the droplets still in the molten state. Upon lowering the temperature, the droplets crystallize at the lower crystallization temperature of PE.

The blend morphology of the HDPE in the BPP/HDPE blends were viewed with an SEM after nitric acid etching. The samples were etched with fuming nitric acid at 108°C for 2.5 h. The surface skin layer of the etched sample was stripped off in 10 min after dipping into acetone.
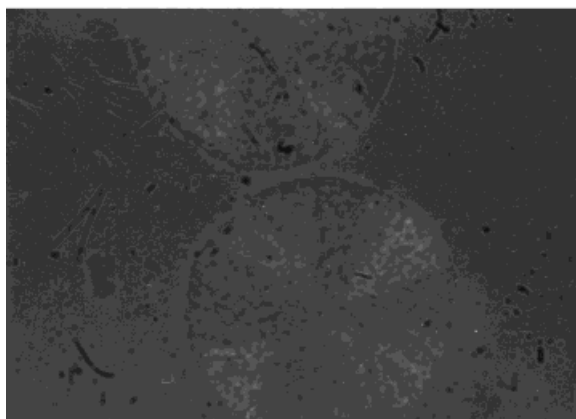
Figures 6 are micrographs of an etched BPP/HDPE blend (HDPE/BPP = 30/70). It is apparent

Table III Melting Parameter of HDPE/BPP Blends

| Type of Mixing	HDPE/BPP Ratio	PP	
		T_m^0 (K)	Φ
	BPP	438.88	0.09
Melt-mixed	10/90	442.91	0.14
	30/70	448.73	0.25
	50/50	451.78	0.27
	70/30	451.65	0.28
	90/10	457.08	0.40
Solution-mixed	10/90	440.19	0.18
	30/70	440.91	0.24
	50/50	444.59	0.27
	70/30	449.64	0.33
	90/10	453.61	0.39
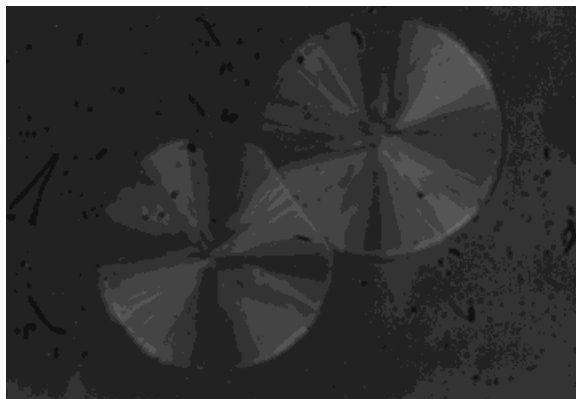
(a) i-PP

(b) HDPE/ BPP blend (30/70)

Figure 5 PLM pictures of i-PP and HDPE blend spherulites.

that the particles are HDPE dispersed in a PP matrix. In the ternary PP/EPR/PE blend system, the PE phase can form a core in the dispersed EPR particles.[10,11] For the tertiary blend system, it is reasonable that the HDPE phase and the EPR phase will form a core–shell structure in the PP matrix from thermodynamic consideration. The surface tension of PP, amorphous EPR having an E content of 80 mol %, and PE are 22.6, 26.4, and 27.3 dyn cm^{-1} at 150°C, respectively.[12] The difference between the surface tensions remain the same at higher temperatures, since the surface tension decreases in proportion to the increasing in the temperature according to the following equation:

$$\gamma = E^s - S^s T \tag{4}$$

where γ is the surface tension; E^s, the surface energy; S^s, the surface entropy; and T, the absolute temperature. S^s is about 0.06 erg cm^{-2} deg^{-1} for PE. When PP, EPR, and PE are blended under the melting condition, the blend system will form a morphology which reduces the interfacial area and the interfacial surface tension.

From the SEM micrographs, the surface of the HDPE particle is not smooth but contains many ridges. The amorphous EPR shell may penetrate
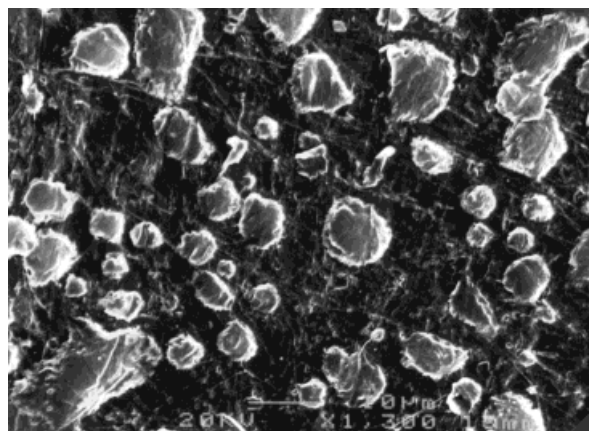
(a)
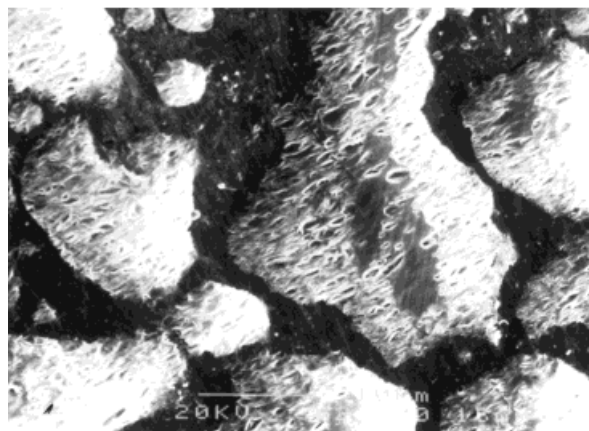
(b)

Figure 6 SEM pictures of HDPE/BPP (30/70) blend surface etched by fume nitric acid.

into the melt core of PE to form the transition layer. These results suggests that the blends have an interpenetrating EPR–HDPE layer as suggested by Stehling and coworkers,[13] which they called a transition layer.

CONCLUSIONS

The crystallization, melting behavior, and morphology of the BPP/HDPE blend were studied. The experimental results showed that the presence of EPR has more influence on the crystallization of HDPE than on that of PP. This leads to the decreasing of the melting temperature of the PE component in the blends. It is suggested that the EPR component in BPP shifts to the PE component during the blending process. The crystallinity of the HDPE phase in the blends decreased with increasing BPP content. The morphology of these blends was studied by PLM and SEM. For a BPP-rich blend, it was observed that the PE phase formed particles dispersed in the PP matrix. The amorphous EPR chains may penetrate into PE particles to form a transition layer.

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