

# Effect of Cross-Linked LLDPE/PP Blend (LLDPE-PP) as Compatibilizer on Morphology, Crystallization Behavior and Mechanical Property of LLDPE/PP Blends

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**ABSTRACT:** Moderate cross-linked blend (LLDPE-PP) of linear low-density polyethylene (LLDPE) and polypropylene (PP) with benzoyl peroxide (BPO) were prepared by the reactive melt mixing in HAAKE mixer. Effect of LLDPE-PP as compatibilizer on the morphology, crystallization behavior and mechanical properties of LLDPE/PP (87/13) blends were studied using scanning electron microscopy (SEM), polarized optical microscopy (POM), wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC) and mechanical testing machines. The results showed that LLDPE-PP not only improved the interfacial adhesion between the LLDPE and PP but also

acted as selective nucleating agent for crystal modification of PP. In the blends, the sizes of LLDPE and PP spherulites became smaller, and their melting enthalpies reduced in the presence of LLDPE-PP. Furthermore, the mechanical properties of LLDPE/PP blends were improved with the addition of LLDPE-PP, and when the concentration of LLDPE-PP was 2 phr, the ternary blend had the best mechanical properties. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 2614–2620, 2011

**Key words:** LLDPE-PP; blends; compatibilizer; morphology; crystallization behavior

## INTRODUCTION

Polyolefins (polyethylene, polypropylene) are one of the most important plastics. Linear low-density polyethylene (LLDPE), which is one class of polyethylenes with linear chains containing only short chain branching due to the insertion of  $\alpha$ -olefin units during the copolymerization of ethylene with  $\alpha$ -olefin, like 1-butene, 1-hexene, and 1-octene, is widely used in many field such as agricultural films and soft products. LLDPE has good toughness, chemical resistance, and thermal properties but is difficult to process because of narrow molecular weight distribution. Polypropylene (PP) has most remarkable comprehensive physical properties such as strength, rigidity, and heat resistance. But it shows poor impact strength due to the inherently high crystallinity and large spherulites. Blending of LLDPE with PP offers an interesting route to achieve new materials with promising property combinations by optimizing their properties.

Therefore, studies on the correlation between the morphology and properties of LLDPE/PP blends have been received great academic interests.<sup>1–5</sup>

However, the immiscibility of LLDPE and PP in the melt state leads to phase separation and bad mechanical properties of the blends, which limits their practical applications.<sup>6</sup> To our knowledge, the methods which improved compatibilization of LLDPE/PP blends can be classified into two main categories. One is chemical compatibilization,<sup>7</sup> that is, a chemical bond is formed between LLDPE and PP to enhance the interfacial adhesion between these two phases. Hogab and Lee<sup>8</sup> found that after reactive melt blending LLDPE and PP with dicumyl peroxide, the sizes of dispersed PP particles were reduced obviously. During the melt blending, the grafted or cross-linked copolymers of LLDPE and PP were generated in curative system, thus the comprehensive properties of blends were increased. Unfortunately, the chemical cross-linked blends were difficult to be recycled. The other is physical compatibilization, that is, physical melt blending LLDPE and PP with compatibilizers to improve the interfacial adhesion between two phases. Ethylene-propylene copolymers (EPR) have usually been employed to increase the compatibility of PE/PP.<sup>9</sup> Wang and Dou<sup>10</sup> discovered that poly(ethylene-co-octene) (POE) could improve the adhesion between LLDPE and PP as well. EPR and POE increased the impact strength of LLDPE/PP blends while reduced the strength (such as yield strength) and modulus.

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To expand the approach of the physical compatibilization, moderate cross-linked LLDPE/PP blend (LLDPE-PP) was prepared by chemical blending. LLDPE-PP as compatibilizer could enhance the interfacial adhesion between LLDPE and PP, so LLDPE/PP/LLDPE-PP ternary blends with favorable mechanical properties could be obtained by melt blending. To our knowledge, so far no attempts have been made to study the properties of LLDPE/PP/LLDPE-PP blends. Our previous studies had shown that the LLDPE/PP (ratio: 87/13) blends with LLDPE-PP as compatibilizer possessed good thermally stimulated shape memory effect. In this SMP blends, dispersed PP acted as fixed phase whereas continuous LLDPE phase acted as reversible or switch phase. LLDPE-PP enhanced the shape memory properties of the blends. However, the effects of the compatibilizer on the mechanical properties of LLDPE/PP (87/13) blends had not been still involved.

In this article, we selected the component ratio of 87/13 LLDPE/PP blends as basic samples. The effects of LLDPE-PP content on the morphology, crystallization behavior and mechanical properties of LLDPE/PP blends were investigated and the relationship between phase morphology and mechanical properties were discussed.

## EXPERIMENTAL

### Materials

LLDPE (DGM-1820) with a density of 0.92 g/cm<sup>3</sup> and a melt flow rate (MFR) of 0.51 g/10 min (ASTM D1238, 190°C, 2.16 kg) produced by Petro-Chemical Corp. Tianjin, China. PP (T30s) with a density of 0.9 g/cm<sup>3</sup> and a MFR of 3.6 g/10 min (230°C, 2.16 kg) produced by Petro-Chemical Corp. Tianjin, China. Benzoyl peroxide (BPO, the initiator) was analyze-grade and produced by Tianlian Fine Chemical Corp. Shanghai, China.

### Sample preparation

Preparation of LLDPE-PP used as compatibilizers

The cross-linked blend of LLDPE/PP (LLDPE/PP ratio: 70/30) was carried out in a Haake mixer (PolylabRC.300P, Thermal Electron, Karlsruhe, Germany) using 0.4 wt % BPO in the blend. Before the reactive melt blending, BPO was dissolved in acetone, then mixed with LLDPE and PP granules. After volatilizing the acetone, BPO adhered onto the granules homogeneously. The temperature of mixing chamber was 180°C, the rotation speed was 60 rpm, and the selected mixing time was 3.5 min. After cooling, the LLDPE-PP melt was broken into granules and dried (12 h, 60°C) in a vacuum oven. The MFR of LLDPE-PP was 0.2 g/10 min (230°C, 2.16 kg). According to

**TABLE I**  
Compositions of LLDPE/PP/LLDPE-PP Blends

Sample	LLDPE (phr)	PP (phr)	LLDPE-PP (phr)
LLDPE	100	0	0
PP	0	100	0
LP-0	87	13	0
LP-2	87	13	2
LP-6	87	13	6
LP-10	87	13	10

ASTM D2765, the gel content of LLDPE-PP was 3.75%.

### Preparation of LLDPE/PP/LLDPE-PP ternary blends

LLDPE/PP blends with and without the LLDPE-PP were prepared by melt extrusion, which was carried out in a single-screw extruder (PLE330 Brabender OHG, Duisburg, Germany) with a diameter of 19 mm and a length-to-diameter ratio (L/D) of 25. LLDPE, PP, and LLDPE-PP in a given ratio were introduced into the hopper of the extruder at a screw speed of 35 rpm and barrel temperatures (from the feeding zone to the die) of 160, 180, 200, and 190°C. The extrudate was cooled in air, cut into pellets, and dried for 12 h at 60°C.

The test specimens for the measurement of mechanical properties were made through an injection molding machine (JPH50, ONLY, Guangdong, China) with screw diameter of 28 mm, length-to-diameter ratio (L/D) of 21, temperatures (from hopper to nozzle) of 180, 195, 210, and 200°C, temperature of 25°C at mold, and injection pressure of 45 MPa. The period of time for cooling was 25 s. The compositions of the samples are shown in Table I.

### Characterizations and measurements

#### Scanning electron microscopy (SEM)

Injection-molded sample were used to investigate the phase structure of these blends. The specimens were cryogenically fractured in liquid nitrogen and sputter coated with Au. All of the SEM images were observed on a scanning electron microscopy (SEM; JSM-6380, JEOL, Tokyo, Japan).

#### Polarized optical microscope (POM)

The crystal morphology of LLDPE, PP, and their blends were investigated with a polarized optical microscope (PM-10AD, Olympus, Japan). About 3 mg of sample was heated between two microscope glass slides in the hot oven to 200°C for 5 min, then squeezed on the slides by a certain weight, and rapidly moved to another oven heating to the

isothermal crystallization temperature (110°C for LLDPE, 118°C for PP and the blends). After a time long enough to crystallize completely (about 3 h), the glass slides were taken out of the hot oven, cooled in air to room temperature and observed.

#### Wide-angle X-ray diffraction (WAXD)

Sample prepared similarly to those used in POM were used to determine the crystal structure. WAXD measurements were made with an X-ray diffractometer (D8 Discover, Bruker Corp., Germany) with a Cu K $\alpha$  source. The equipment was operated at 40 KV and 40 mA under ambient temperature, and the scan range was between 5 and 35°.

#### Differential scanning calorimetry (DSC)

DSC measurements were performed on a differential scanning calorimeter (DSC141, Setaram, Caluire, France). This apparatus was calibrated with standard indium before measurement. For each measurement, about 5 mg of extruded pellet was sealed in an aluminum pan, then heated from 50 to 200°C at a rate of 10°C/min, held at 200°C for 5 min to erase all the thermal memory, then cooled to 50°C at a constant cooling rate of 10°C/min, held for 3 min, and then heated to 200°C at a rate of 10°C/min. The heat flow versus temperature was recorded. The analysis of the melting behavior of these blends was carried out for the second run data.  $T_m$  was considered to be the maximum of the endothermic melting peak from the heating scans and  $T_c$  that of the exothermic peak of the crystallization from the cooling scans. The heat of fusion ( $\Delta H_m$ ) and crystallization enthalpy ( $\Delta H_c$ ) were determined from the areas of melting peaks and crystallization peaks.

#### Mechanical testing measurements

The tensile and flexural properties of these blends were measured at room temperature using a universal testing machine (CMT4503 SANS Testing Machine, Shenzhen, China). Tensile testing was carried out according to ASTM D638, with tensile speed of 50 mm/min. Flexural strength measurements was carried out according to ISO178:1993, with the flexural rate of 2 mm/min. The impact specimens were notched, and Izod impact strength testing was carried out on an impact tester (XJU-22, Chengde Testing Machine Co., Chengde, China) according to ASTM D256 at 23°C, and the impact rate was 3.5 m/s. All samples were conditioned at 23°C with 50%RH for 24 h before testing. Six measurements were performed for each sample, from which the standard deviation of the values was calculated.

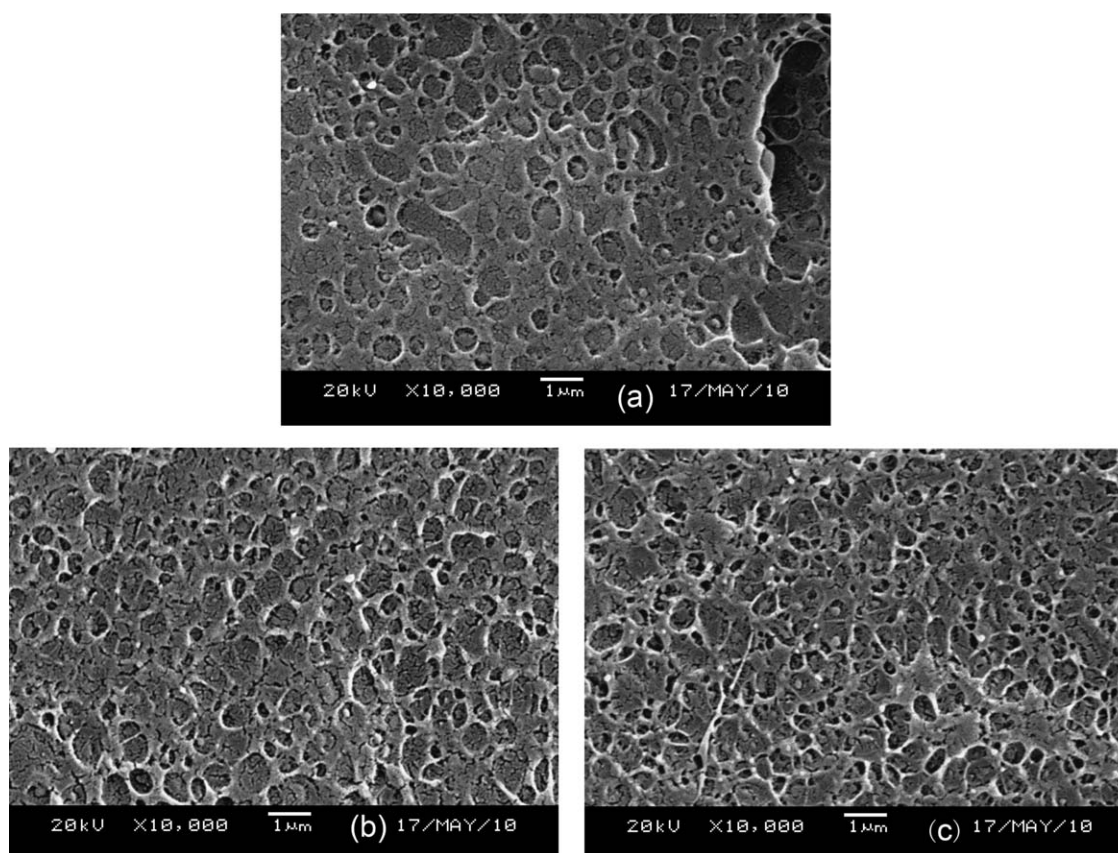
## RESULTS AND DISCUSSION

### Phase structure

SEM micrographs of the cryogenic fracture surfaces of the various LLDPE/PP/LLDPE-PP blends were shown in Figure 1. For LLDPE/PP blend, the droplets of PP dispersed in the continuous matrix of LLDPE [Fig. 1(a)], the size of the dispersed particles was about 0.5–1  $\mu\text{m}$ . The binary blend showed a typical morphology of phase segregation and poor interfacial adhesion with the appearance of a discrete interface between the two phases. The similar structure was reported elsewhere.<sup>11</sup> With the introduction of LLDPE-PP, the PP particle size decreased, the interface of LLDPE and PP became blurry and adherence between the two phases was promoted, as shown in Figure 1(b, c). In LLDPE-PP systems, grafted or cross-linked copolymers of LLDPE and PP were generated *in situ* through covalent bonding (chemical reaction) during the reactive melt blending.<sup>12</sup> Hence, the compatibility of LLDPE/PP blends was obviously improved with the addition of LLDPE-PP.

### Crystal morphology

Figure 2 shows the POM images of LLDPE, PP, and LLDPE/PP/LLDPE-PP blends. It was clearly shown that the pure PP presented the typical spherulites with the Maltese cross pattern [Fig. 2(b)], compared with the pure LLDPE [Fig. 2(a)]. For LLDPE/PP (87/13) binary blends, PP spherulites which dispersed in continuous LLDPE matrix were not as sharp or as well defined as that in the blank PP, however they could still be easily distinguished [Fig. 2(c)]. The spherulites became misshapen, appeared to be open armed. A similar result was reported by Li et al.<sup>13</sup> During crystallization, the PP tended to crystallize on its own, rejecting foreign components.<sup>14</sup> The spherulite structure was irregular because the concentration of PP in the matrix was significantly diluted by LLDPE and so the supply of PP was diminished. With the addition of LLDPE-PP, the sizes of PP and LLDPE spherulites in ternary blends was smaller than that in LLDPE/PP binary blends [Fig. 2(d)], and the bright spherulites probably revealed that some small amounts of  $\beta$ -PP crystal form occurred in the blends. This might be mainly related to the following factors. First, SEM images showed that LLDPE-PP could improve the interfacial adhesion between LLDPE and PP. The LLDPE and PP chain segments were difficult to arrange in an ordered manner due to the increasing interaction between these two phases. Therefore, the growths of spherulites were prohibited in a certain extent. Second, the LLDPE-PP might act as selective nucleating agent for crystal modification of PP, so



**Figure 1** SEM photographs of fracture surface of LLDPE/PP/LLDPE-PP blends: (a) LP-0; (b) LP-2; and (c) LP-6.

that some small amounts of  $\alpha$  crystal form of PP was transformed to  $\beta$  crystal form.

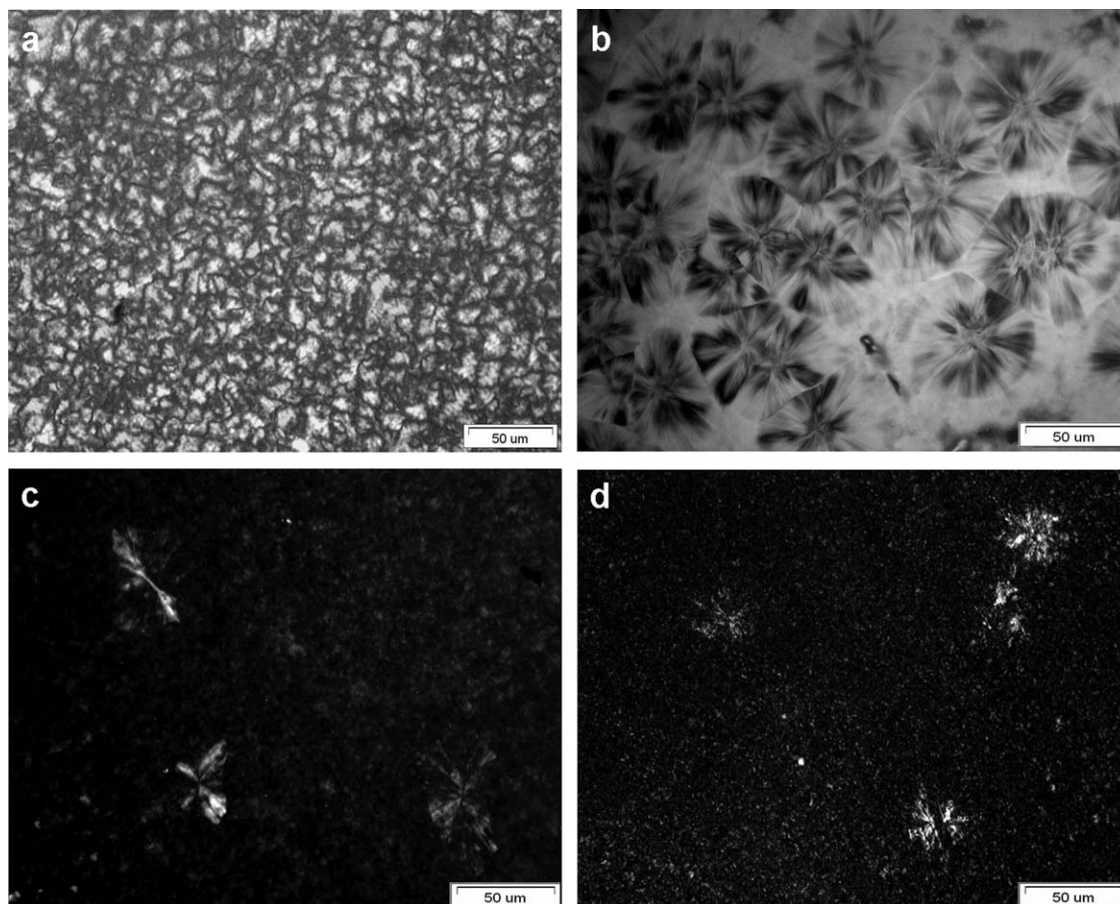
### Crystal structure

The WAXD patterns of LLDPE, PP, and their blends are shown in Figure 3. For the blank LLDPE, only the orthorhombic form presented because of the 110 and 200 reflections at  $2\theta$  equal to  $21.4^\circ$  and  $23.6^\circ$ , respectively.<sup>15</sup> For the blank PP, only the monoclinic  $\alpha$  phase was presented because of the characteristic reflections at  $2\theta$  equal to  $13.9^\circ$ ,  $16.8^\circ$ ,  $18.4^\circ$ ,  $21.2^\circ$ , and  $21.7^\circ$ , corresponding to the respective crystalline planes: (110), (040), (130), (111), and (041) of the  $\alpha$ -PP.<sup>16</sup> The diffraction patterns of LLDPE/PP binary blend was a simple addition of that of LLDPE and PP; no reflection or any measurable shift of the diffraction peaks were observed. However, in the patterns of LLDPE/PP/LLDPE-PP ternary blend, an extra very small peak was observed at  $2\theta$  equal to  $16.0^\circ$ , which was peculiar to the hexagonal  $\beta$  phase,<sup>17</sup> indicating that some small amounts of  $\beta$ -PP crystal in the blends were formed by adding LLDPE-PP, it was well consistent with the results of POM.

### Melting and crystallization behavior

Figure 4 shows DSC melting (a) and crystallization (b) curves of pure polymers and their blends. The melting temperature, melting enthalpy, crystallization temperature, and crystallization enthalpy of LLDPE and PP in these samples, which were analyzed from these DSC curves, are listed in Table II. The blends displayed two single melting peaks at the temperatures corresponding to the pure polymers, indicating separate melting in all blends [Fig. 4(a)]. The melting temperatures of LLDPE and PP were  $121.3^\circ\text{C}$  and  $163^\circ\text{C}$ , respectively [Table II]. Table II displayed that while the content of LLDPE-PP was increasing, melting temperatures of LLDPE ( $T_{m,LLDPE}$ ,  $122.9$ – $122.2^\circ\text{C}$ ) and PP ( $T_{m,PP}$ ,  $160.9$ – $161.9^\circ\text{C}$ ) were not changed significantly, but melting enthalpy values of LLDPE ( $\Delta H_{m,LLDPE}$ ,  $47.19$ – $42.57$  J/g) and PP ( $\Delta H_{m,PP}$ ,  $10.73$ – $9.14$  J/g) slightly decreased, indicating that the crystallinities of LLDPE and PP were decreased.

The LLDPE/PP (87/13) blend showed only a single peak between the crystallization temperatures of LLDPE and PP [Fig. 4(b)]. It was explained that in a normal cooling regime, the main crystallization temperature of LLDPE ( $109.8^\circ\text{C}$ ) is close to that of PP



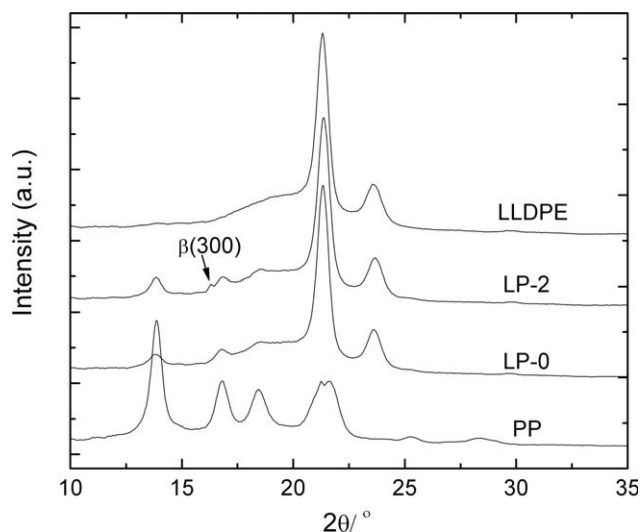
**Figure 2** POM images of the samples: (a) LLDPE; (b) PP; (c) LP-0; and (d) LP-2.

(118.8°C) so that the two peaks overlapped. The similar result was reported by Long et al.<sup>18</sup> With the addition of LLDPE-PP, the crystallization temperature ( $T_c$ , 112.3–112.6°C) of the blends was not changed while the crystallization enthalpy ( $\Delta H_c$ , 53.4–48.6 J/g) decreased [Table II], indicating that the crystallization capacities of LLDPE/PP/LLDPE-PP blends were declined. The slight reduction of the melt and crystallization enthalpies of LLDPE and PP components in LLDPE/PP/LLDPE-PP blends was attributed to enhance the interaction between LLDPE and PP phases due to LLDPE-PP as compatibilizer, and hence disturbed their crystallization.

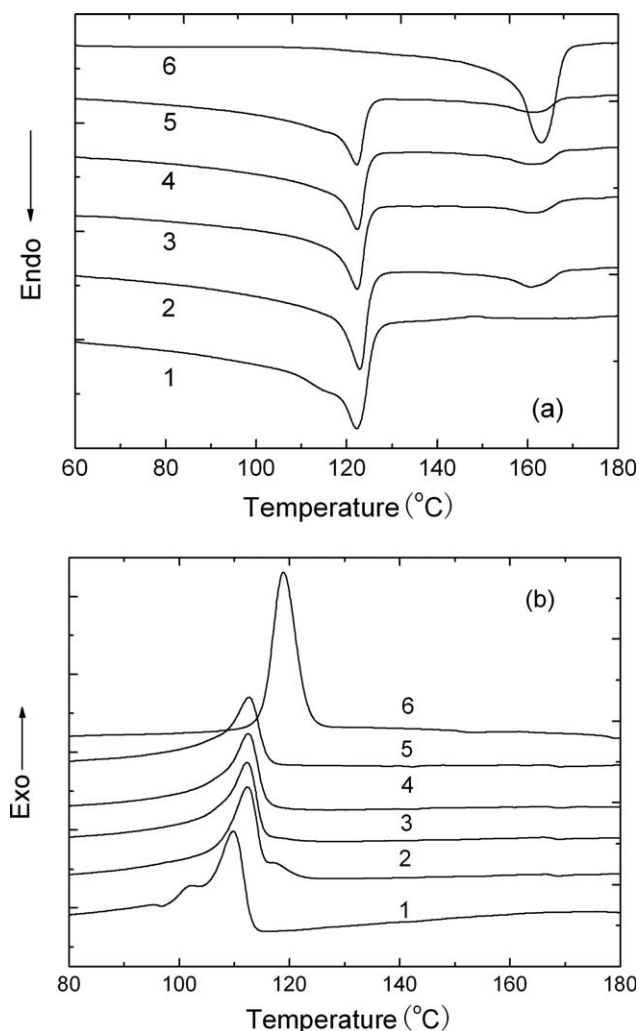
### Mechanical property

The effects of LLDPE-PP on the tensile, flexural, and impact properties of LLDPE/PP blends were shown in Figures 5 and 6, respectively. As shown in Figure 5, the addition of 2 phr LLDPE-PP increased the tensile strength of LLDPE/PP/LLDPE-PP ternary blends. However, the tensile strength decreased with further increase of LLDPE-PP content, and leveled off when the concentration of LLDPE-PP exceeded 6

phr. The values of the elongation at break steady increased with increasing LLDPE-PP content. An interesting observation from Figure 6 was that the flexural strength of the blends had the similar trend to the tensile strength. Izod notched impact strength

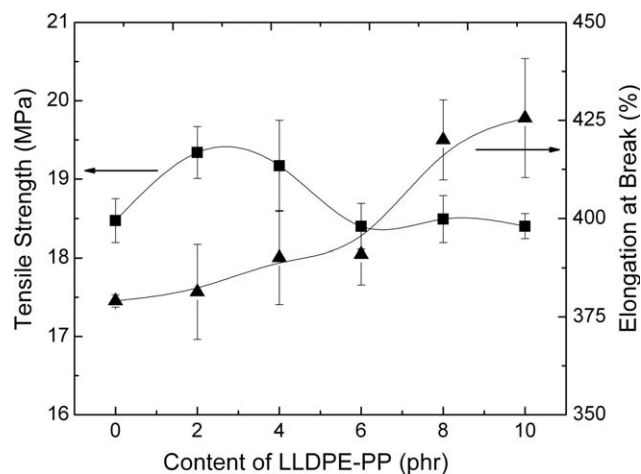


**Figure 3** WAXRD patterns of various LLDPE/PP/LLDPE-PP blends.



**Figure 4** DSC melting (a) and crystallization (b) curves of pure polymers and their blends: (1) LLDPE; (2) LP-0; (3) LP-2; (4) LP-6; (5) LP-10; and (6) PP.

of LLDPE/PP/LLDPE-PP blends were initially increased significantly with increasing LLDPE-PP content from 0 to 2 phr, and then leveled off with further increase in LLDPE-PP content (>2 phr). (Fig. 6). Consequently, the LLDPE/PP/LLDPE-PP



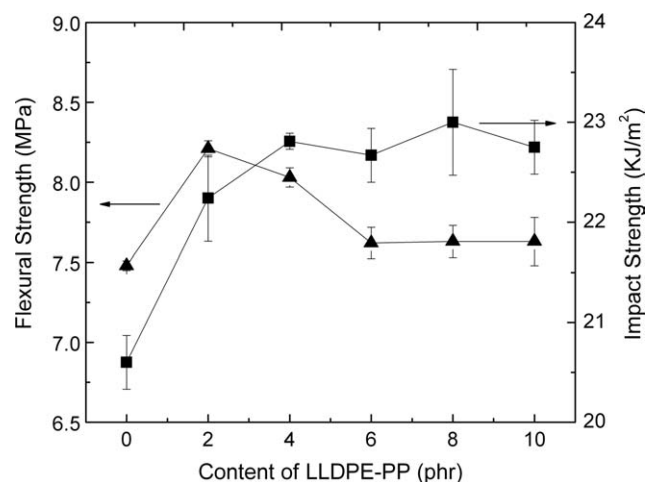
**Figure 5** Tensile properties of LLDPE/PP/LLDPE-PP blends as a function of LLDPE-PP content.

blend with 2 phr LLDPE-PP possessed the best mechanical properties.

The higher impact strength of LLDPE/PP/LLDPE-PP blends can be explained by two reasons. First, the dispersed PP particles of LLDPE/PP/LLDPE-PP blends, which uniformly distributed in the continuous phase, were much smaller than those in binary blends [seen Fig. 1(c)] and were able to absorb high impact energy. Second, some amounts of  $\beta$ -PP crystal form were formed in the ternary blends [seen Fig. 2(d)], which would be beneficial to the improvement of the impact strength of the blends.<sup>19</sup> On the other hand, LLDPE-PP as compatibilizer improved the compatibility of LLDPE/PP blends and enhanced the interaction between these two phases [Fig. 1(c)], thus the tensile and flexural strengths of LLDPE/PP blends were enhanced by adding proper amount of LLDPE-PP. But when the content of LLDPE-PP was excessive, the strengths were decreased due to the reduction of the crystallinities of LLDPE and PP, and the low tensile (18.72 MPa) and flexural strengths (7.50 MPa) of LLDPE-PP itself.

**TABLE II**  
The DSC Results of LLDPE, PP, and LLDPE/PP/LLDPE-PP Blends

Sample	Melting				Crystallization	
	$T_{m,LLDPE}$ (°C)	$\Delta H_{m,LLDPE}$ (J/g)	$T_{m,PP}$ (°C)	$\Delta H_{m,PP}$ (J/g)	$T_c$ (°C)	$\Delta T_c$ (J/g)
LLDPE	121.3	51.57	–	–	109.8	–47.3
LP-0	122.9	47.29	160.9	10.73	112.4	–53.4
LP-2	122.6	43.67	161.9	9.63	112.3	–48.8
LP-6	122.4	43.02	161.1	9.16	112.5	–49.5
LP-10	122.2	42.57	161.6	9.14	112.6	–48.6
PP	–	–	163.1	86.84	118.8	–91.7



**Figure 6** Flexural and impact strengths of LLDPE/PP/LLDPE-PP blends as a function of LLDPE-PP content.

### CONCLUSIONS

In this study, cross-linked LLDPE/PP blends (LLDPE-PP), which used as compatibilizer of LLDPE/PP blends, were prepared by reactive melt blending. And the morphology, crystallization behavior, and mechanical properties of LLDPE/PP/LLDPE-PP ternary blends were investigated. The following conclusions were obtained:

1. SEM photos showed that LLDPE and PP were incompatible, two phases morphology were observed in LLDPE/PP blends. LLDPE-PP enhanced the interfacial adhesion between LLDPE and PP and improved the compatibility of LLDPE/PP blends.
2. With the addition of LLDPE-PP, the sizes of PP and LLDPE spherulites in ternary blends

became smaller and some amounts of  $\alpha$  crystal form of PP was transformed to  $\beta$  crystal form.

3. The addition of LLDPE-PP had little influence on the melt and crystallization temperatures of LLDPE and PP in the blends but declined the blends' crystallization capacity. The melt enthalpies of LLDPE and PP were decreased with increasing the content of LLDPE-PP.
4. LLDPE-PP improved the mechanical properties of LLDPE/PP blends, and when the concentration of LLDPE-PP was 2 phr, the ternary blend had the best mechanical properties.

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