

INVESTIGATION OF PP-EPR DIBLOCK COPOLYMER AS COMPATIBILIZER FOR PP/EPT BLEND*

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ABSTRACT

Blending isotactic polypropylene (PP) with ethylene-propylene terpolymer (EPT) is one of the simplest and most effective ways for toughening PP. In order to further improve the toughness of PP/EPT blend and to enhance the stability of the dispersed rubber phase, a diblock copolymer composed of PP and ethylene-propylene rubber blocks (PP-EPR) was added into the blend, as it is considered that "forced compatibility" of the two components will be effected through the two chemically bonded blocks, while two-phase structure still remains.

Experimental results indicate that PP-EPR is an effective compatibilizer for PP/EPT blend. It not only increases the toughness of the blend, but also decreases the loss of tensile strengths usually accompanying the toughening of plastics with an elastomer, which is very well explained by the morphological structure changes when an appropriate amount of PP-EPR was added into the blend.

Blending with rubber might be the earliest method^[1], yet it is still one of the important ways by which the toughness of a plastic may be improved^[2-4]. In order to make full use of isotactic polypropylene (PP), a plastic with many good properties, the toughening of PP has been given much attention from both the industrial and scientific point of view^[4-6]. Many work in this respect have appeared in the literature, most of which are blending PP with a rubber or thermoplastic elastomer^[7-14]. However, among the elastomers used, ethylene-propylene terpolymer (EPT) seems most effective^[14].

It is well known that in order to obtain the characteristics of a polymer blend and to achieve the purpose of modification by blending, usually it is necessary to have the two components to be compatible to some degree, but not entirely miscible, i.e. there should exist distinct two-phase structure with well mixed interface boundary^[15-17]. Accordingly, it is considered that if a diblock copolymer composed of PP and ethylene-propylene rubber blocks (PP-EPR) is added into PP/EPT blend, "forced compatibility" of the two components at the boundary will be effected through the two chemically bonded blocks, while two-phase structure remains.

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Hence further improvement of the toughness of PP/EPT blend together with enhancement of the stability of the dispersed rubber phase will be resulted. A schematic representation of the morphological structure of such binary blend containing a diblock copolymer as a compatibilizer is shown in Fig. 1. The effectiveness of PP-EPR as a compatibilizer was evaluated by the changes of the blends' physical and mechanical properties and that of the blends' morphology after the addition of PP-EPR.

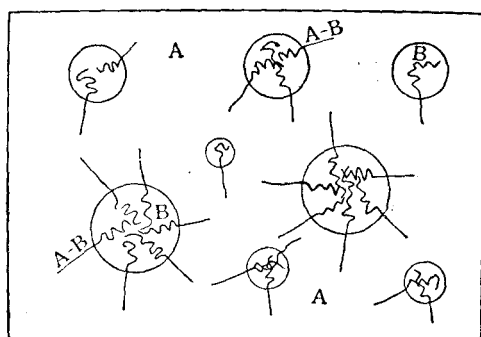


Fig. 1 Schematic diagram of diblock copolymer used as a compatibilizer in binary blend of plastic/rubber

A: Continuous phase, plastic matrix,
B: Dispersed phase, rubber particles,
A-B: Compatibilizer, diblock copolymer

EXPERIMENTAL

Material used

Powder PP was used, a commercial product of Xiangyang Chemical Plant of Yanshan Petroleum Chemical Co., Beijing, with *MI* of 0.5–2.0.

EPT was EPT-4045, a product of Mitsui Co., Japan. According to our analysis, C_3 content was 35.9%, the third monomer was ethylidene norbornene.

Laboratory prepared PP-EPR was used, two samples of which with different block lengths were provided by Group 2 of Lab 14 of the Institute. Block length was represented by the time of passing gas during polymerization, as it was very difficult to get an experimentally determined value. However, it was shown by various characterization that the block copolymers were mainly PP-EPR, although they were not clean^[18]. Some of the parameters of the two samples of PP-EPR are listed in Table 1; Nos. 1 and 2 were used for blend Group A and

Table 1 Some parameters of PP-EPR

Sample No.	Time of passing gas		$[\eta]^b$ (dl/g)	C_3 Cont. (%)
	Propylene	Ethylene/Propylene ^{a)}		
1	10	40	6.48	63.8
2	15	55	—	—

a) Ethylene/propylene ratio: 80/20,

b) Solvent: decalin; temperature: 135°C

B respectively.

Blending method

Two types of mechanical blending were employed:

1. Two-step open roll blending — pre-mix of PP, EPT and PP-EPR was obtained on a two-roll open mill at room temperature. Then the pre-mix was milled on hot rolls ($170 \pm 5^\circ\text{C}$) for 8–10 min. The sheet obtained was cut into small pieces ready for preparation of specimens.

2. Open roll/extruder two-step blending — As above was obtained the pre-mix, which was further mixed with a Brabender. The extrudates were cut into small pieces for specimen preparation.

Characterization of properties and morphology

In order to show the effectiveness of PP-EPR as a compatibilizer for PP/EPT blend, some properties and morphology of the blend were characterized before and after compatibilization.

The properties measured were impact strength, tensile strength, dynamic mechanical behavior, crystallization behavior, brittle temperature and density. The specimens used were compression molded at $190 \pm 2^\circ\text{C}$, pre-heating and molding time were varied according to the thickness of the specimens.

Scanning electron microscopy (SEM), polarizing microscopy (PM), phase contrast microscopy (PCM) and small angle light scattering technique (SALS) were used for morphology characterization. Specimens used for SEM observation were fractured surfaces obtained at liquid nitrogen temperature, etched with xylene and coated with gold. Those for PM, PCM and SALS study were microtomed from molded specimens; with heat treatment at 100°C for microscopy.

RESULTS AND DISCUSSION

According to the results of our previous work^[14], composition of 85/15 and 90/10 for PP/EPT were used for two groups of specimens. For Group A (85/15), PP content was fixed at 85 wt %, while the other 15 % was the sum of EPT and PP-EPR with varying amounts of the two. For Group B, PP/EPT composition was fixed at 90/10, with additional varying amount of PP-EPR added.

Fig. 2A shows the change of impact strength of unnotched small specimens ($7 \times 2.3 \times 16\text{mm}$) with composition determined with a Dynstat Impact Tester. It may be seen from the figure that within the composition range studied, when a part of the 15 % EPT was replaced by PP-EPR, the impact strength of the specimens all increased, especially when the amount of PP-EPR added was low. For example, when PP/EPT/PP-EPR was 85/13/2, its impact strength at -20°C was 9.5 and 1.6 times of that of PP and of the corresponding PP/EPT (85/15) respectively. The impact strengths at room temperature (RT) and -40°C were also increased, although not as much as that at -20°C . However, it must be pointed out that at RT all the specimens tested were not broken, which indicates that the toughness of the specimens were enhanced. The impact strength obtained was really impact yield strength in such case. Another point is that with the increase in the amount of PP-EPR and decrease in that of EPT, the total amount of EP-rubber (both EPT and EPR blocks in PP-EPR) was decreased.

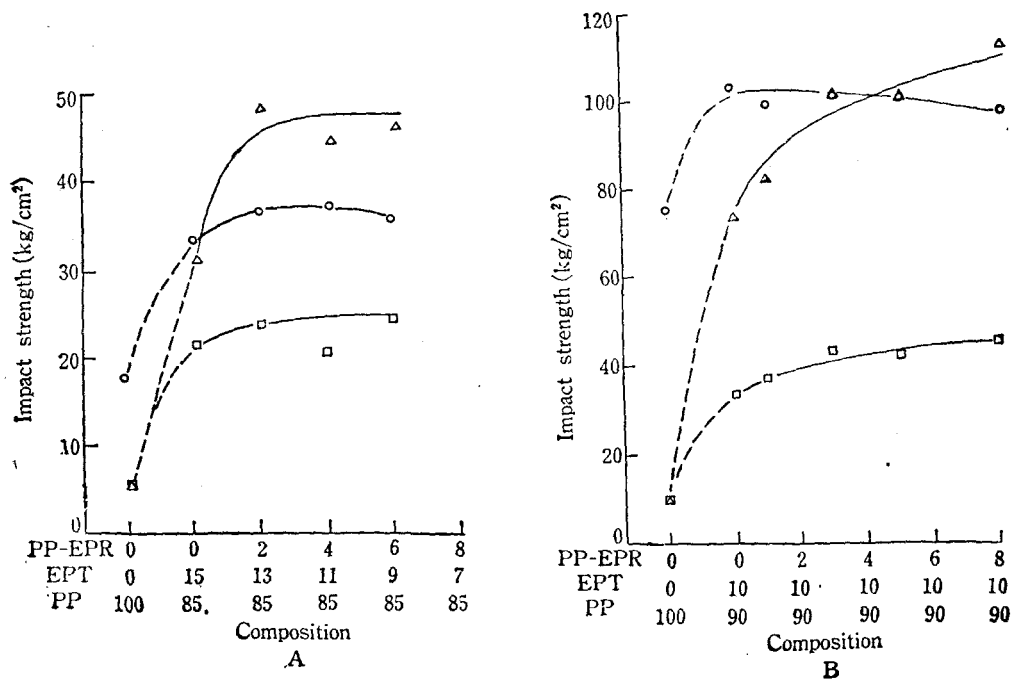


Fig. 2 Impact/strength of PP and its blends
○ RT; △ -20°C; □ -40°C

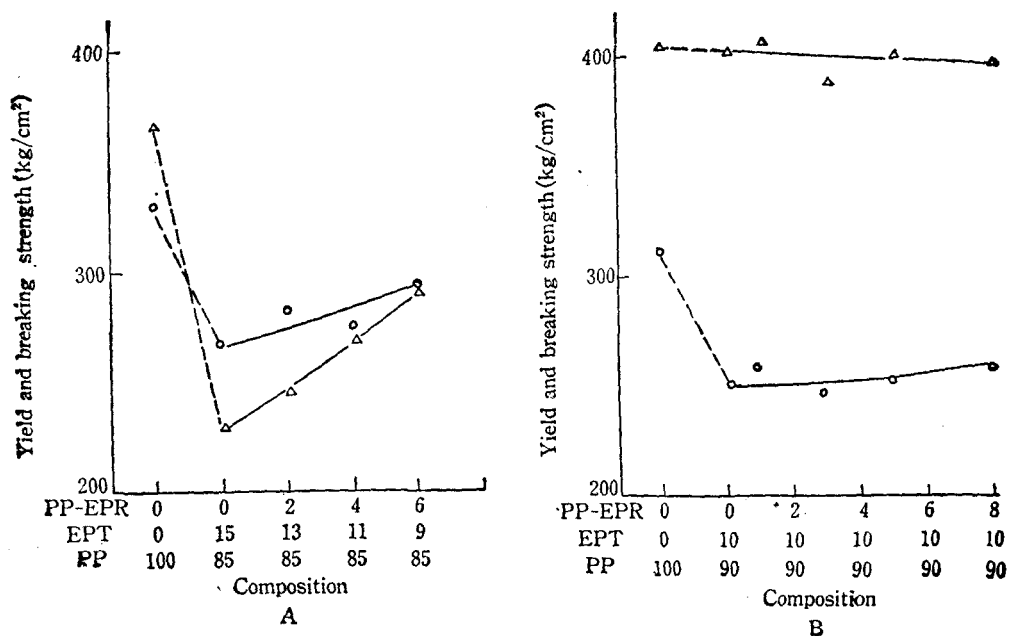


Fig. 3 Tensile strength of PP and its blends
○ Yield strength; △ Breaking strength

but the toughness of the blend increased. This fact does strongly demonstrate that "forced compatibility" was effected between PP and EPT through PP-EPR. In Fig. 2B are plots of impact strength vs. composition of Group B specimens at different temperatures. Although it does not show any increase in impact strength at RT, the fact that none of the specimens was broken during test again showed that the toughness of the blend was enhanced. The toughening effectiveness was more evident at -20°C and -40°C , as the impact strength of the PP/EPT (90/10) with PP-EPR added were 1.5 and 1.4 times of that of PP/EPT, and 12 and 15 times of that of PP respectively.

In Fig. 3 are plots of tensile strength vs. composition of the blends. For Group A (Fig. 3A), the curves show that both the tensile yield strength and breaking strength were lower than that of PP; this is in agreement with the usual result of toughening plastics with rubber. However, both the yield and breaking strengths increased with the increase in the amount of PP-EPR replacing EPT. This change of tensile behavior of compatibilized PP/EPT may be due to two reasons. One is that the replacement of EPT with PP-EPR reduced the amount of EPT and also the total amount of EP-rubber but increased the amount of PP. The other is that covalent bonds were introduced between the PP and EPT phases through the addition of PP-EPR (Fig. 1). The curves in Fig. 3B tells another story, that the addition of PP-EPR to the PP/EPT blend of 90/10 had little effect on their tensile strengths. This might be due to the fact that EPT content was rather low in this blend and PP-EPR was not a replacement of EPT but was an extra addition. Therefore the total amount of EP-rubber was increased with the addition of PP-EPR. Another factor, which should not be neglected, is that the ratio of EPR length to PP length of PP-EPR sample No. 2 is greater than that of No. 1 (Table 1). Thus the increase in the amount of EP-rubber may overbalance the effect of the covalent bonds introduced by PP-EPR.

It is obvious from the above results that the addition of an appropriate amount of PP-EPR into PP/EPT not only further increases the blend's toughness, especially the impact strength at -20°C , but also reduces the loss of tensile yield and breaking strengths usually accompanying the toughening of plastics with rubber, and that by regulating the ratio of PP, EPT and PP-EPR, blends with different mechanical properties may be obtained for different uses.

For Group A, the addition of PP-EPR did not affect the sample's brittle temperature (T_B) much, being around -50°C for all the specimens. However, as the total amount of EP-rubber in the blend exceeded 15 wt%, T_B went down further, e.g., the T_B of the blend with composition of 85/15/2 (PP/EPT/PP-EPR) is -57°C , which is in good agreement with our previous result^[14].

The increase in density of Group A samples (Fig. 4) is evidently due to the difference between densities of PP-EPR (0.882g/cm^3) and of EPT (0.875g/cm^3) and the increase in crystallinity of the compatibilized PP-EPT (Table 2).

In Fig. 5 are DSC curves of blends of Group A and of the components. It may be seen from the curves that the thermal behavior of the three components were entirely different as expected. PP is a typical crystalline polymer exhibiting only a single endothermic and a single exothermic peaks (Fig. 5, curve 1). As known, the EPT used in this work was a noncrystalline ternary elastomer, the DSC curve of which shows only a glass transition

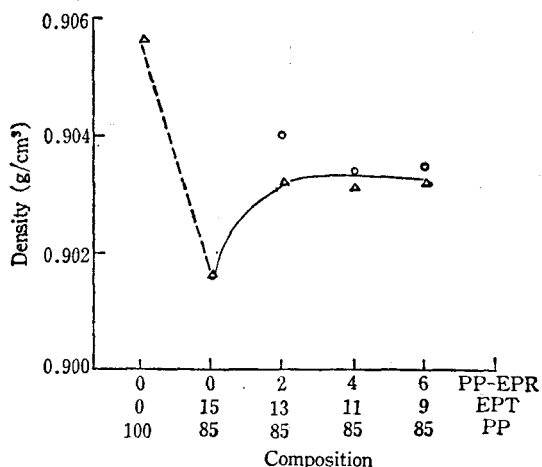


Fig. 4 Density of PP and its blends of Group A
 ○ Solution blended; △ Mechanical blended

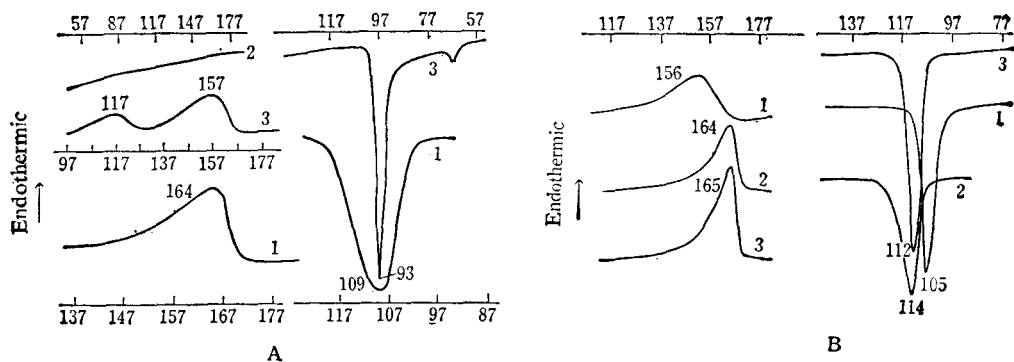


Fig. 5 DSC curves of blends of Group A and the components
 A: DSC curves of the components
 1 pure PP, 2 EPT, 3 PP-EPR
 B: DSC curves of three blends of different compositions
 1 85/15/0, 2 85/13/2, 3 85/9/6

(T_g) within the range of -150 to 150°C (Fig. 5, curve 2). However two for PP-EPR peaks appeared on both the curves of increasing and decreasing temperature (Fig. 5, curve 3), being the peaks of crystallization of PP and of the crystallizable part in EPR blocks respectively. It was proved that the latter peak was due to the crystallization of the long-sequence PE contained in the EPR blocks of PP-EPR used in this work^[18]. It is noticed that only one peak corresponding to crystallization of PP appeared on the curves of PP/EPT blends with PP-EPR added, similar to the DSC result of blends of PP with PP-EPR only^[18]. In our case, EPT formed the rubber phase together with the EPR blocks of PP-EPR, therefore the long PE sequences had little chances to aggregate to form PE crystallites. So the disappearance of the PE crystallization peak very well demonstrates the compatibilizing effect of PP-EPR in PP/EPT as expected. Moreover, the fact that the shape of the blends' curves are similar

Table 2 Crystallization parameters and transition temperatures of PP and its blends^{a)}

Sample No.	Composition PP/EPT/PP-EPR	T_m (°C)	T_c (°C)	Crystallinity ^{b)} (%)	Transition temperature (°C)				
PP	100/0/0	164	109	69	—	(-80)—(-100) ^{c)}	—	0—10 ^{c)}	60—100 ^{c)}
EPT	0/100/0	—	—	—	—	—	-52	—	—
PP-EPR	0/0/100	157	97	16.8	—	—	—	—	—
		117	69						
A-1	85/15/0	156	103	64.6	—	-80	-52(P)	13	50—60
A-2	85/13/2	164	114	68.5	-120	-100	-51(S)	5	50—60
A-3	85/11/4	165	113	68.9	-123	-92	-52(S)	6	50—60
A-4	85/9/6	165	112	74.5	-119	-80	-45(S)	2	50—60

a) Crystallization parameters and transition temperatures were obtained from DSC thermograms and dynamic mechanical loss-temperature curves respectively.

b) Calculated from area under the exothermic peak.

c) Data from literature [9].

d) P=peak, S="shoulder"

to that of PP (Fig. 5A, curve 1 and Fig. 5B), and the blends' recrystallization temperatures are all higher than that of PP (Table 2) suggests that PP-EPR acted also as a nucleation agent in PP/EPT, which was well supported by the morphological structure obtained in this work. The increase in crystallinity of PP/EPT/PP-EPR blends by 5—10% (Table 2) is in accordance with the density data.

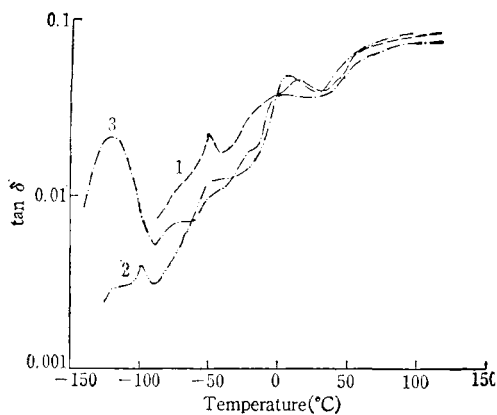


Fig. 6 Plots of $\tan \delta$ vs. temperature of blends of PP with EPT and/or PP-EPR
1 PP/EPT; 2 PP/EPT/PP-EPR; 3 PP/PP-EPR

Dynamic mechanical loss vs. temperature curve is often used to judge the compatibility of polymer blends. Fig. 6 shows the $\tan \delta$ -temperature curves of the blends of PP/EPT (85/15) and PP/EPT/PP-EPR (85/13/2). It is very clear that within the temperature range studied, there are five transitions appeared (Table 2). With the exception of the transition around -150°C, the rest three transitions of PP all appeared on the curves, especially PP's T_g peak

is very clear. The peak around -50°C is the glass transition of EPT, which is also very prominent as shown on curve 1. This means that there existed EPT phase in the blend of PP/EPT. However, after addition of PP-EPR, the -50°C peak changed into a "shoulder" (Fig. 6, curve 2). It is considered that the presence of PP-EPR made the dispersed EPT phase and the PP continuous phase be joined by covalent bonds. Hence the movement of the EPT segments was hindered by PP phase. In PP/PP-EPR blend, the -50°C peak is even weaker (Fig. 6, curve 3), which indicates that when EPR phase and PP phase are connected mainly by covalent bonds, such hinderance is much stronger. The fact that the appearance of both the glass transition peaks of PP and EPT, and the change of EPT's T_g peak to a shoulder with the addition of PP-EPR proves that these blends are of two-phase structure and that PP-EPR did act as a compatibilizer in the blends. It should be pointed out that for both PP/EPT/PP-EPR and PP/PP-EPR (Fig. 6, curve 3), there existed a transition around -120°C , which might be the γ -transition of PE due to the long PE sequences presenting in PP-EPR, as already shown by DSC data.

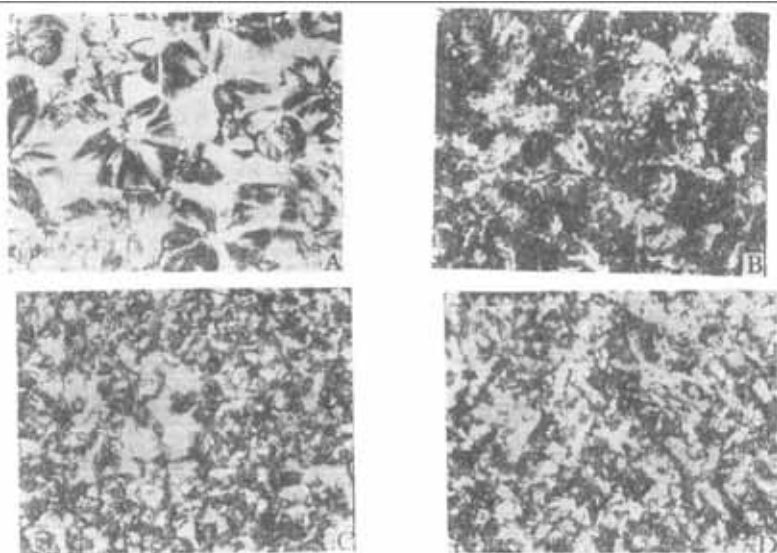


Fig. 7 PM micrographs of PP and its blends of different compositions
A: pure PP, B: 85/15/0, C: 85/11/4, D: 85/13/2

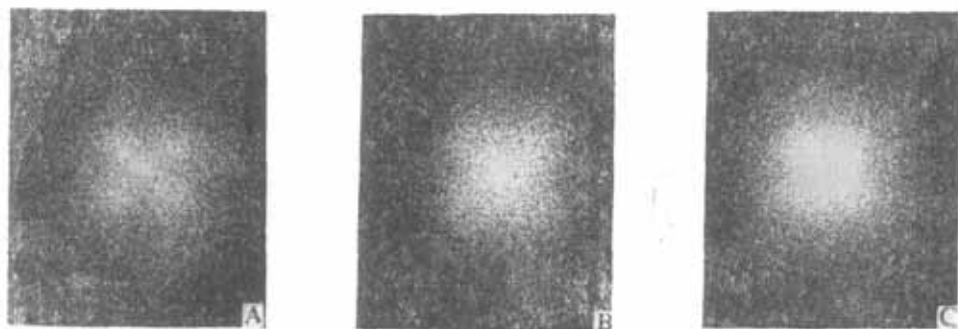


Fig. 8 H_v patterns of SALS of PP and its blends
A: pure PP; B: PP/EPT; C: PP/EPT/PP-EPR

Fig. 7 gives the PM micrographs of PP, PP/EPT and PP/EPT/PP-EPR, from which it is seen that EPT made the PP spherulites imperfect and that with the addition of PP-EPR the PP spherulites got even more imperfect and smaller in agreement with the results obtained by SALS characterization (Fig. 8).

Observation of the fractured surfaces of the blends by SEM showed that beside the decreasing in spherulite size and perfectness, the addition of PP-EPR made the EPT particles smaller and more evenly dispersed in PP matrix (Fig. 9), in agreement with the observation by PCM (Fig. 10).



Fig. 9 SEM micrographs of PP and its blends
A: pure PP; B: PP/EPT; C: PP/EPT/PP-EPR



Fig. 10 PCM micrographs of PP and its blends
A: pure PP; B: PP/EPT; C: PP/EPT/PP-EPR

The change of morphological structure of the blends suggests that in PP/EPT blends PP-EPR behave as a nucleation agent and also as an emulsifying agent, both are beneficial to further increase in impact strength and decreasing the loss of tensile strengths due to toughening plastics with rubber.

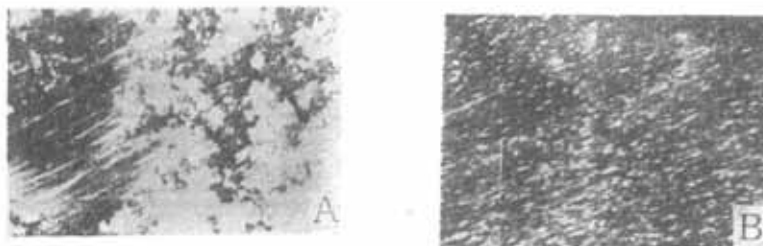


Fig. 11 SEM micrographs of the "neck" part of tensile specimens of PP/EPT and PP/EPT/PP-EPR

Observation of the "neck" part of the tensile specimen with SEM has revealed that cracks and voids were developed during stretching the PP/EPT specimens, while in the "neck" of PP/EPT / PP-EPR specimens very well oriented morphological structure along the direction of stretching was developed but no defects appeared, as shown in Fig. 11. The difference between the changes of morphology of these two blends during tensile testing again and directly proved the effectiveness of PP-EPR as a compatibilizer in PP-EPT, and also explained why tensile yield and breaking strengths of PP/EPT had increased after it was compatibilized with PP-EPR.

CONCLUSION

1. When an appropriate amount of PP-EPR diblock copolymer was added into PP/EPT blend, the blend's toughness was further increased, as shown by the further increase in its impact strength and decrease in brittle temperature. The increase in impact strength varied with the blend's composition and temperature.

2. Another advantage of addition of PP-EPR into PP/EPT was the increase in its tensile yield and breaking strengths, thus reducing the decrease in tensile strength usually accompanying the toughening of plastics with elastomers.

3. Dynamic mechanical analysis, DSC data, observation of morphology changes with SEM and light microscopes all showed that PP/EPT/PP-EPR was of two phase morphology and that in PP/EPT blend PP-EPR did behave as a compatibilizer, and also as a nucleation agent as well as an emulsifying agent. These are all beneficial to the further increase in toughness and tensile strengths of the blend.

4. Observation with SEM of the "neck" part, formed during tensile testing, of the specimens again and directly proved the effectiveness of PP-EPR as a compatibilizer and explained the cause of the increase in tensile strengths from the point of view of morphology.

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