Effect of Ethylene–Propylene Copolymer with Residual PE Crystallinity on Mechanical Properties and Morphology of PP/HDPE Blends

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SYNOPSIS

Morphology and mechanical properties of polypropylene (PP)/high density polyethylene (HDPE) blends modified by ethylene–propylene copolymers (EPC) with residual PE crystallinity were investigated. The EPC showed different interfacial behavior in PP/HDPE blends of different compositions. A 25/75 blend of PP/HDPE (weight ratio) showed improved tensile strength and elongation at break at low EPC content (5 wt %). For the PP/HDPE = 50/50 blend, the presence of the EPC component tended to make the PP dispersed phase structure transform into a cocontinuous one, probably caused by improved viscosity matching of the two components. Both tensile strength and elongation at break were improved at EPC content of 5 wt %. For PP/HDPE 75/25 blends, the much smaller dispersed HDPE phase and significantly improved elongation at break resulted from compatibilization by EPC copolymers. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Much attention has been paid to blends of polypropylene (PP)/high density polyethylene (HDPE)[1–7] in the wake of both scientific and commercial needs. Recycling of PP and PE in blends without necessary sorting is of substantial environmental and economic importance. Blending PP with PE or together with other polymers to get the desirable balanced properties is also important in commercial practice. Finally, relationships between structure, properties, and compatibility in connection with PP/HDPE blends is of scientific interest. To our knowledge, addition of a third polymer as a compatibilizer instead of simple blending is desirable due to poor compatibility between the two components in PP/HDPE blends.

The addition of ethylene–propylene random copolymers as a compatibilizer to the PP/HDPE blends is the most common practice,[4,6–9] although high molecular weight PE (HMWPE) has been found to be an efficient compatibilizer[10] as well. Ethylene–propylene copolymers (EPC) also exist in PP–PE sequential polymerization products (PP–PE) produced by Ziegler–Natta polymerization, surely playing an important role in the superior mechanical properties of PP-PE products of the PP/HDPE blends. This will be the subject of a following article.[11]

In this work, we attempt to examine the effects of randomly copolymerized EPC with a residual PE crystallinity on the morphology and mechanical properties of PP/HDPE blends. PP/HDPE blends of a wide composition range and modified by different amounts of this EPC copolymer were investigated.

EXPERIMENTAL

The PP used in this work is a commercial product produced by Yanshan Petrochemical Company (Beijing), melt flow index: 10 g/10 min. HDPE is a commercial product from Gaoqiao Chemical Fac-

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tory (Shanghai), melt flow index: 3 g/10 min. The EPC used as the compatibilizer was prepared in our laboratory using a Ziegler–Natta catalyst, $MgCl_2 \cdot EB \cdot TiCl_4/Et_3Al$, with ethyl benzoate (EB) as a donor and heptane as the solvent.

The composition of the EPC was determined to be of 40 mol % ethylene by infrared (IR) spectrum on a Digilab FTS-20 spectrophotometer using a calibration curve of $1380/1460/cm^{-1}$ absorption ratio.[12] Thermal behavior of EPC was measured on a Perkin–Elmer DSC-7 differential scanning calorimeter (DSC) at a scanning rate of 10°C/min. Only a weak melting peak of the PE crystallinity can be seen at about 120°C on the DSC thermogram (Fig. 1).

The PP/HDPE blends modified by the EPC were prepared by coprecipitation from a 1% (w/v) xylene solution. PP/HDPE at a required weight ratio and EPC of calculated amount were dissolved in xylene at 125°C in the presence of 2,6-di-*tert*-butyl-*p*-cresol. Then the solution was poured into an excess of ethanol. The precipitate was sufficiently dried in vacuum. Three PP/HDPE blends of weight ratio compositions 25/75, 50/50, and 75/25, together with each modified by EPC in 5, 10, and 15 wt % amounts, respectively, were prepared.

Tensile properties of the samples were tested on an Instron-1121 electronic tester at a drawing rate of 10 cm/min. The samples were heat molded at 185°C into sheets that were then cut into pieces of dimension 20 × 4 × 0.3 mm. Average values were taken from seven specimens for each sample.

The morphology of the samples were examined on a Jeol-Max-840 scanning electron microscope (SEM). The fracture surface from the tensile test was observed directly under SEM after coating with platinum.

RESULTS AND DISCUSSION

Composition, chain structure, and crystalline behavior of EPC in general are the important factors affecting the morphology and mechanical properties of PP/PE blends. Usually noncrystalline EPC, an EPM or EPDM, is the most common polymer used to compatibilize PP/PE blends.[4,6-9] It was claimed that in the presence of noncrystalline EPC, elongation at break of PP/HDPE blends was improved, but their tensile strength and modulus deteriorated. EPC containing long sequence lengths of ethylene units that lead to imperfect PE crystals was reported to be a more efficient compatibilizer for PP/PE blends.[13] EPC containing long sequence lengths of both ethylene and propylene units with chain struc-
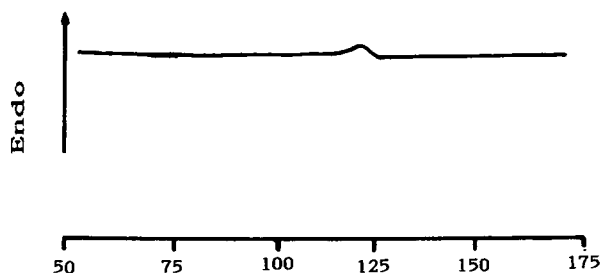

Figure 1 Melting thermogram of ethylene–propylene copolymer (EPC) used in PP/HDPE blends.

tures similar to that of the alleged PP-*b*-PE block copolymers may be supposed to be the most efficient compatibilizer for PP/HDPE blends. But, to our knowledge, no such work has been reported.

In this article, a randomly polymerized EPC containing long sequence lengths of ethylene units has been taken to be the possible compatibilizer for PP/HDPE blends. The DSC thermogram in Figure 1 shows a little residual PE crystallinity, but not quantitatively measurable in this ethylene-propylene copolymer.

Figure 2 shows SEM micrographs of the fracture surfaces of the PP/HDPE blend specimens in weight ratio of 25/75 modified by an EPC with a little PE crystalline residual in amounts of 0, 5, 10, 15 wt %, respectively. In the case of blend without EPC, the PP component presented as a spherical dispersed phase with domain size of 5–10 μm [Fig. 2(A)]. Both the PP particles and the surfaces of the holes where PP particles had been are smooth and clear, indicating poor interfacial adhesion of the two phases. In the blend with 5 wt % EPC, the domain size of the PP dispersed phase did not change much [Fig. 2(B)]. But one may notice that there exist some inclusions on the dispersed particles of PP that may belong to the EPC with long sequence lengths of ethylene units, and that the surfaces of the holes become rough, depicting an enhanced interfacial adhesion between the two phases. From the inclusions in the PP fracture phase, one may infer that the majority of EPC component presented in both the PP phase and the interface of the two phases. That the domain size of the PP dispersed phase did not change much may mean that such an amount of EPC as a compatibilizer is not efficient enough to lower the surface tension to a level so as to hamper the agglomeration of the PP particles; but on the other hand, due to the fact that the majority of EPC presented in the PP phase, the PP phase was enlarged somewhat, which would offset the tendency to decrease the PP domain size caused by the compatibility of EPC. In the sample with 10
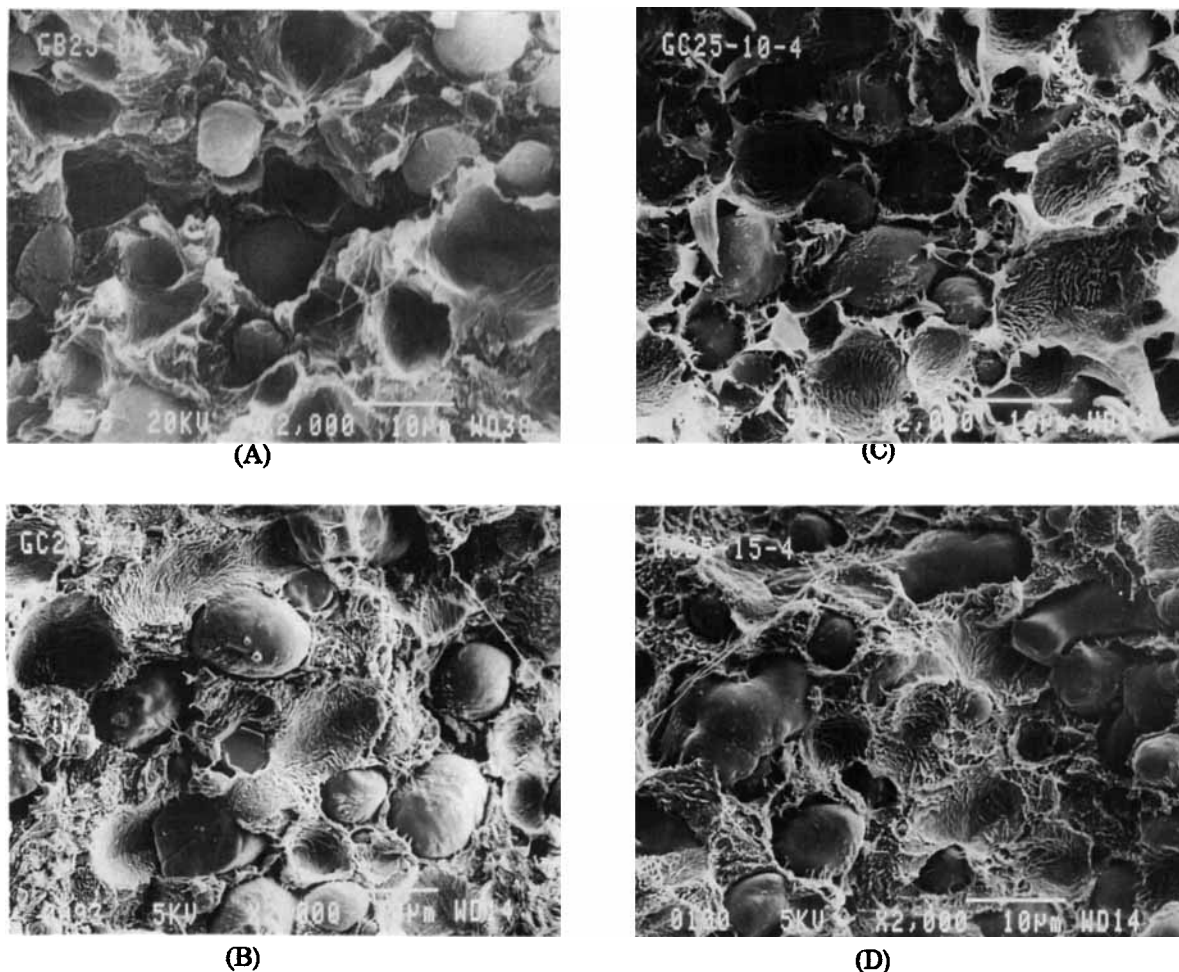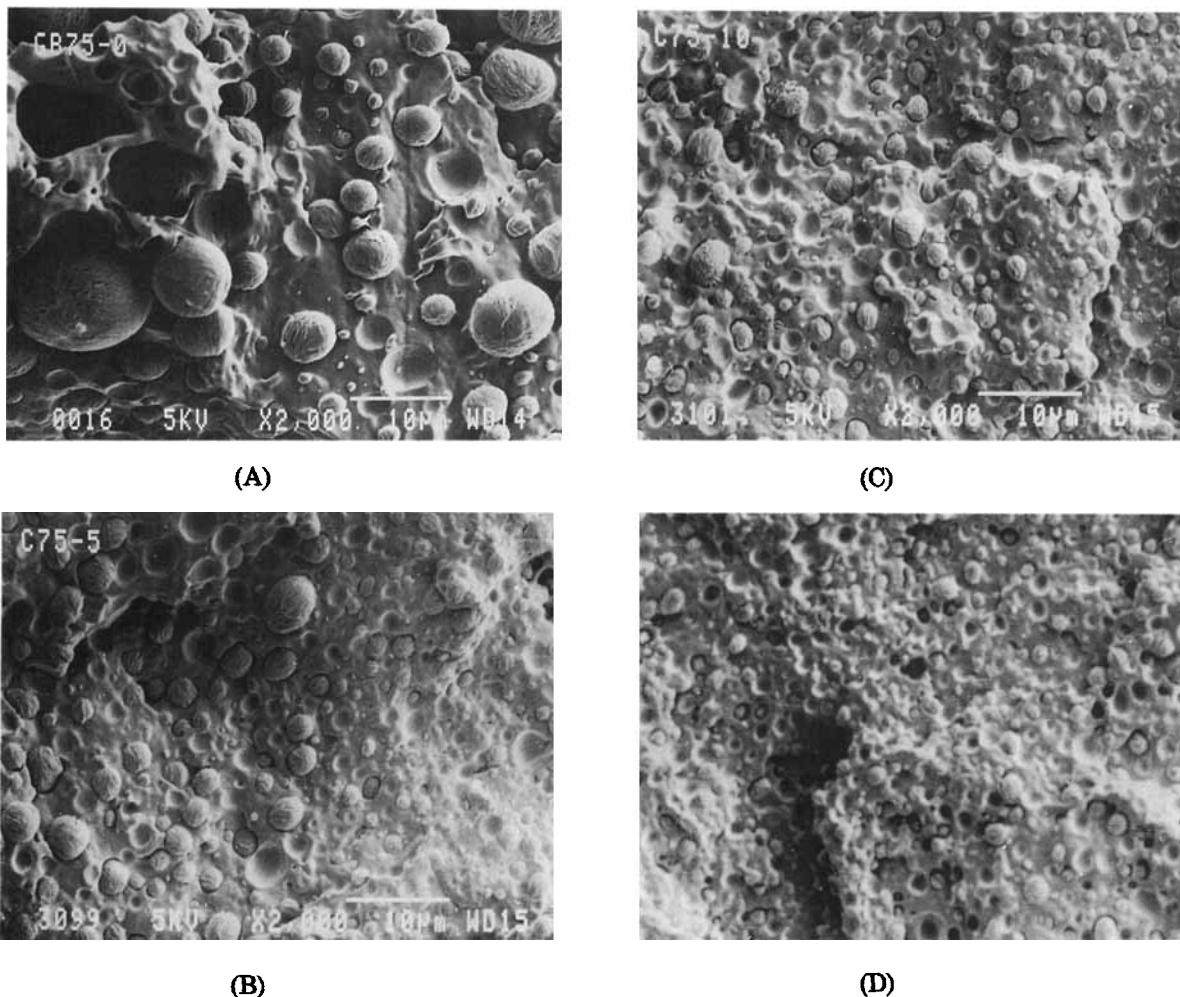
Figure 2 SEM micrographs of PP/HDPE blends in weight ratio of 25/75 modified by different amounts of EPC. (A) 0 wt %; (B) 5 wt %; (C) 10 wt %; (D) 15 wt %.

wt % EPC [Fig. 2(C)], the interfacial adhesion was further enhanced although the domain size of the dispersed PP phase still did not change much. More EPC can be seen on the dispersed particles of PP, and the surfaces of the holes left by PP particles show the sign of being drawn. The apparent yielding of the HDPE matrix indicates the enhanced penetration of EPC into the HDPE phase. With further increase in EPC content (15 wt %), the deformed dispersed PP particles [Fig. 2(D)] demonstrate that transfering of stress from the HDPE matrix to the PP dispersed phase occurred due to the much enhanced interfacial adhesion.

The micrographs of PP/HDPE blends of 75/25 weight ratio containing different amounts of EPC are shown in Figure 3. For the sample without EPC [Fig. 3(A)], the HDPE particles are nonuniform in size, 10 μm, and also nonuniformly dispersed. With addition of EPC, the HDPE particles disintegrated

and their size became much smaller [Fig. 3(B)]. And it is clearly seen that the size of HDPE domains decreased continuously with the increase in EPC content [Fig. 3(B–D)]. This is evidence of good compatibilization of EPC in the 75/25 PP/HDPE blends. In other words, EPC with a little PE crystalline residual may be a more efficient compatibilizer for PP/HDPE blends at the composition of 75/25 than that for the blends of 25/75 weight ratio.

For the blends of 50/50 PP/HDPE weight ratio (Fig. 4) in the absence of EPC, PP appeared as very smooth and large domains dispersed in the HDPE matrix [Fig. 4(A)], indicating the poor adhesion between the two phases. High incompatibility of the two components made the mechanical properties of the blend the worst among the blends of the three different compositions. Addition of EPC into the blend made the phase structure of the blend cocontinuous due to the decrease in surface tension and

Figure 3   SEM micrographs of PP/HDPE blends in weight ratio of 75/25 modified by different amounts of EPC. (A) 0 wt %; (B) 5 wt %; (C) 10 wt %; (D) 15 wt %.

partly improved viscosity matching of the two components. It was noticed that in the PP phase there are very small particles, which may be the EPC with long sequence lengths of ethylene units, indicating that the EPC were mostly present in the PP phase similar to the case of the 25/75 blends series (Fig. 2). This is further demonstrated in a blend containing 15 wt % EPC [Fig. 4(D)], where obviously yielded PP phase can be seen.

From the morphological studies, it may be seen that the interfacial behavior of EPC in the three blend compositions are different, which indicates the composition dependency of emulsifying behavior of EPC in the blends of PP/HDPE. This should give rise to different mechanical properties.

Shown in Figure 5 are plots of mechanical properties vs. EPC content of the three different PP/HDPE blends. It is obvious that the blends of the 75/25 series have the best mechanical properties and

the 50/50 series the lowest, in order of 75/25 > 25/75 > 50/50. PP/HDPE blends are highly incompatible and show the negative synergic effect in tensile strength and elongation at break, and this may be the reason for such a sequence of the three blend series.

Addition of 5 wt % of EPC into the PP/HDPE blends of 25/75 weight ratio and the substantial increase in both tensile strength and elongation at break [Fig. 5(A–B)] may be attributed to the improved interfacial adhesion and stress transfer, although the domain size of the PP phase did not change much (Fig. 2). The tensile strength of the blend decreased remarkably and the elongation at break increased rather slowly with 10 wt % EPC. Apparently 5 wt % EPC is enough to saturate the interface and for the surface tension to reach its minimum. A further increase in EPC would be detrimental to the mechanical properties of the blends.
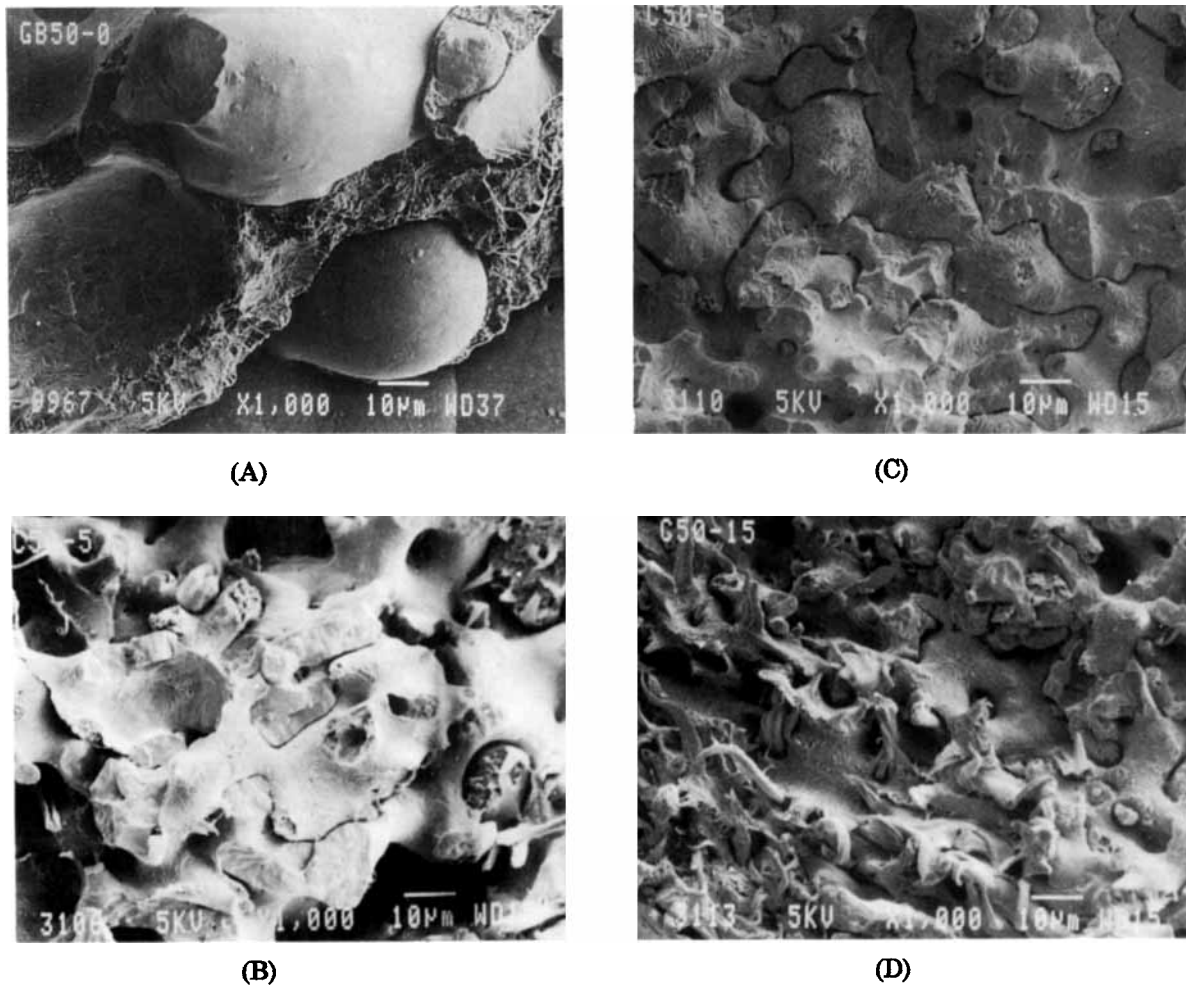
Figure 4 SEM micrographs of PP/HDPE blends in weight ratio of 50/50 modified by different amounts of EPC. (A) 0 wt %; (B) 5 wt %; (C) 10 wt %; (D) 15 wt %.

This saturation behavior is also demonstrated by the further decrease in tensile strength and almost no longer increase in elongation at break when the EPC content was increased to 15 wt % in the blend.

For PP/HDPE blends of the 75/25 series, there appeared to be no maximum but instead a slow decrease in tensile strength with the addition of the EPC copolymer [Fig. 5(A)]. Meanwhile, the significant increase in elongation at break of the 75/25 series [Fig. 5(B)] is associated with the decrease in domain size of the dispersed HDPE (Fig. 3), resulting probably from the decreased surface tension of the HDPE phase. According to Wu,[14,15] the toughness of pseudoductile polymers modified by flexible polymers would shear when the ligament of the matrix is thinner than a critical value. The tremendous increase in elongation at break of the blend implicates the achievement of a thin enough ligament of the PP matrix to the fine dispersed HDPE domains

resulting from the decreased surface tension from the presence of EPC copolymer.

In the 50/50 series blends, the tensile strength improved remarkably and reached its maximum on addition of 5 wt % EPC [Fig. 5(A)]. On further increase in EPC content, much improved stress transfer and enhanced toughness of both phases, especially the PP phase where yielding is obvious as shown in Figure 4(D), by EPC are responsible for the linear increment in elongation at break at this composition.

The moduli of the three series PP/HDPE blends modified with different amount of EPC are shown in Figure 5(C). With an increase in EPC, the moduli of the blends of the 25/75 series decreased most rapidly and reached its minimum at 10 wt % EPC. A weak synergistic effect seems to appear in the moduli of the 75/25 series blends with the addition of 5 wt % EPC, where the compatibilization of EPC is ap-
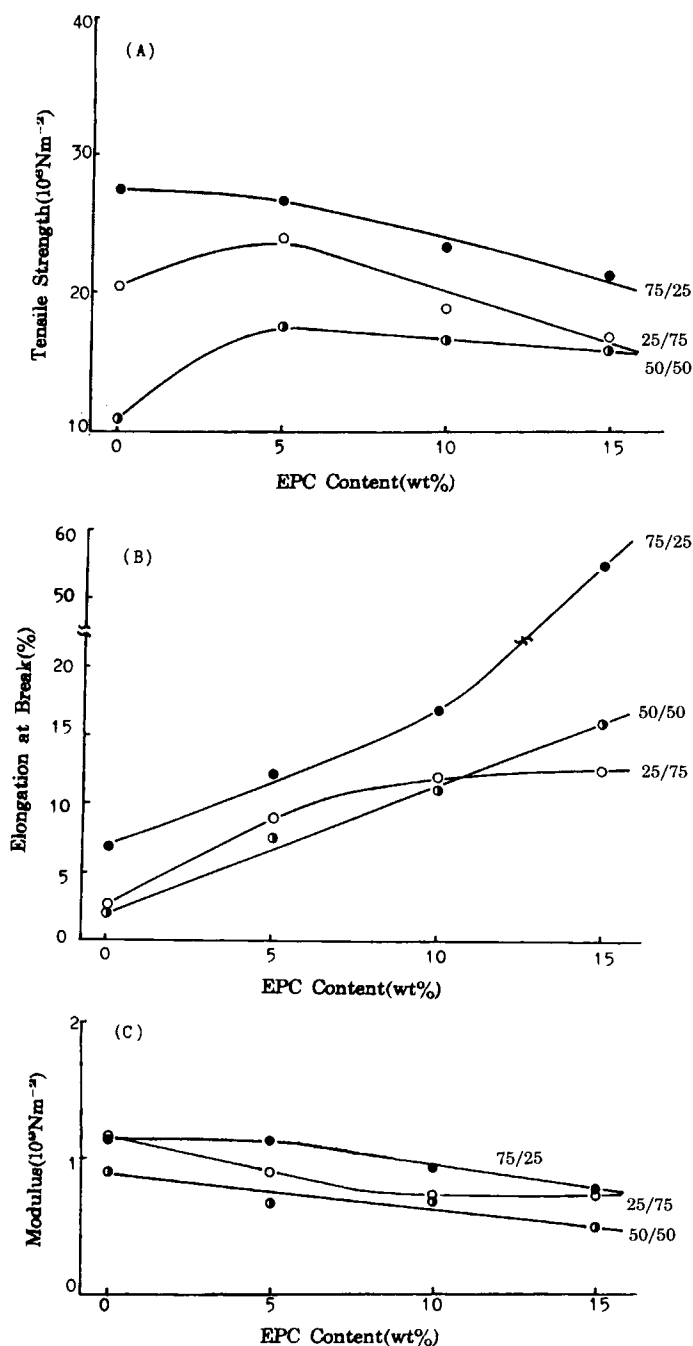
Figure 5 Mechanical properties of PP/HDPE blends in weight ratio of (O) 25/75, (◐) 50/50, and (●) 75/25 modified by different amount of EPC. (A) Tensile strength; (B) elongation at break; (C) modulus.

parently most effective. The slow decrease of moduli afterward may mean that EPC exists mostly in the PP matrix in addition to existing in between the interface. Moduli of the 50/50 series decreased linearly with the increase in EPC. The enhanced toughness of both the PP and HDPE phases by EPC

(Fig. 4) was probably the main factor as discussed above.

Considering that the crystallinity of PP component is much lower than that of HDPE, PP would admit more EPC copolymer than HDPE. From this we conjecture that the penetration of EPC into the HDPE phase is the dominating factor controlling the morphology and mechanical properties of the PP/HDPE blends. EPC with a little PE crystal residual that could cocrystallize with HDPE would penetrate more into the HDPE phase than a noncrystalline EPC. This has been demonstrated by the improved mechanical properties, both tensile strength and elongation at break, at low EPC content. This is quite different from the compatibilization of a noncrystalline EPC in PP/HDPE blends, where both tensile strength and moduli of the blends decreased, although the elongation at break was improved.[4] From this information, it is reasonable to assume that the EPC with both long sequence lengths of ethylene and propylene units would not be as efficient a compatibilizer for PP/HDPE blends as the EPC with only a little PE crystalline residuals. This is to be demonstrated in a following study.

CONCLUSION

PP/HDPE blends are highly incompatible. The compatibility in PP/HDPE blends is a function of composition. The three series of PP/HDPE blends with and without EPC show that both their tensile strength and elongation at break have the order 75/25 > 25/75 > 50/50.

The interfacial behavior of EPC with long sequence lengths of ethylene varies with composition of PP/HDPE blends. The compatibilization of EPC in blends with PP as the dispersed phase (25/75 series) is mainly due to an improvement in interfacial adhesion. A more effective compatibilization by EPC is found in the blends with HDPE as the minor component (75/25 series).

The addition of a small amount of EPC, around 5 wt %, could improve the mechanical properties of PP/HDPE blends both in tensile strength and elongation at break. This indicates that EPC with a little PE crystalline residual is more effective than amorphous EPC.

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