

Modification of PP/HDPE Blends by PP-PE Sequential Polymerization Product

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SYNOPSIS

The morphology and mechanical properties of polypropylene/high-density polyethylene (PP/HDPE) blends in a wide range of compositions modified by a sequential Ziegler-Natta polymerization product (PP-PE) have been investigated. PP-PE contains multiple components such as PP, ethylene-propylene copolymer (EPC), and high molecular weight polyethylene (HMWPE). The effects of PP-PE on the mechanical properties and morphology of the PP/HDPE blends are the aggregative results of all its individual components. Addition of PP-PE to the blends not only improved the tensile strength of the blends, but the elongation at break increased linearly while the moduli were nearly unchanged. Morphological studies show that the adhesion between the two phases in all the blends of different compositions is enhanced and the dispersed domain sizes of the blends are reduced monotonously with the increment of the content of PP-PE. PP-PE has been demonstrated to be a more effective compatibilizer than EPC. Based on these results, it can be concluded that the tensile strength of the blends depends most on the adhesion between the two phases and the elongation at break depends most on the domain size of the dispersed component. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends involving polypropylene (PP) and polyethylene or other components, usually ethylene-propylene copolymers such as ethylene propylene rubber (EPR) or ethylene propylene diene monomer (EPDM), have received much attention¹⁻⁶ due to their scientific importance and commercial utilizations (e.g., the automobile industry).

The mechanical properties of PP/PE blends by simple blending are limited because of the high incompatibility of the two components. Addition of ethylene-propylene copolymer (EPC) to the blends as a compatibilizer can remedy the situation to some extent.^{7,8} A commercial noncrystalline EPR or EPDM can substantially improve the toughness of the blends, but at the expense of de-

teriorated moduli and tensile strengths.⁷ A high molecular weight polyethylene (HMWPE) has also been demonstrated to be an efficient compatibilizer to PP/HDPE blends,⁹ in which both the tensile strength and elongation at break of the blends were improved while the moduli were nearly unchanged. This effect on the morphology and the mechanical properties of the blends was interpreted as due to the entanglement of HMWPE (with a flexible molecular chain and low crystallinity) with both the components.

From a general viewpoint, an ideal compatibilizer for PP/HDPE blends would be a PP-*b*-PE copolymer. Sequential polymerization of propylene and ethylene with a Ziegler-Natta catalyst seems to be the only possible route to synthesize such a block copolymer. But until now, the chain structure of the product of sequential polymerization of propylene and ethylene (PP-PE) remained unclear and controversial.¹⁰⁻¹⁴ The arguments focused on whether the PP-PE product made by such a route is a PP-*b*-PE block copolymer or if it contains such a block copolymer. The claim of obtaining a complete PP-

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b-PE block copolymer had been refuted¹⁵; a view of multiple components in the PP-PE product was mostly accepted.^{12,13,16}

A possible way to probe the component and structure of the PP-PE product is to examine indirectly the effect of PP-PE on the morphology and mechanical properties of PP/HDPE blends; this is the subject of this work. To our knowledge, little work has been done along this line.^{17,18}

The effect of PP-PE on PP/HDPE blends is aggregative because of its multiple-component character. The effect of each possible component in the PP-PE product (such as HMWPE⁹ and EPC¹⁹) on the PP/HDPE blends has been investigated in our recent work.

EXPERIMENTAL

Polypropylene (PP) is a commercial product produced by the Yanshan Petrochemical Company (Beijing) and has a melt flow index of 10 g/10 min. High-density polyethylene (HDPE) is a commercial product from the Gaoqiao Chemical Plant (Shanghai) and has a melt flow index 3 g/10 min.

The PP-PE product was prepared by sequential polymerization of propylene and ethylene using a Ziegler-Natta catalyst, $\text{MgCl}_2 \cdot \text{EB}/\text{TiCl}_4$, made in our laboratory, with triethyl aluminum (Et_3Al) as a cocatalyst and ethyl benzoate (EB) as a donor. Polymerization was performed in a glass reactor at 40°C, with the pressure of the monomer at 0.05 MPa and catalyst concentration at 2×10^{-4} mol/L. Propylene was first polymerized for 1 h; then the reactor was pumped to remove the propylene gas for a short time and ethylene was fed in to 0.05 MPa. The preceding operation was repeated several times to remove the propylene gas as much as possible. Ethylene was polymerized for 1 h, and then the polymerization was terminated with ethanol. The product was washed with ethanol several times and then dried in vacuum at 60°C for 24 h.

The composition of the composite sequential polymerization product, PP-PE, was measured by infrared (IR) spectroscopy on a Perkin-Elmer 580B IR spectrometer at 150°C to exclude complications from the crystallinity of the sample. The samples were pressed at 185°C. The ethylene content of PP-PE was found from a calibration curve²⁰ (absorption ratio of $1460 \text{ cm}^{-1}/1378 \text{ cm}^{-1}$ measured at 150°C) to be 60 wt %. The intrinsic viscosity of the PP part was measured independently to be $[\eta]_{\text{decalin}}^{135^\circ\text{C}} = 41.2 \text{ dL/g}$. The melting behavior of PP-PE was mea-

sured using a Perkin-Elmer DSC-7 calorimeter at a scanning rate of 10°C/min.

PP/HDPE blends modified by different amounts of PP-PE were prepared by coprecipitation from a 1% (w/v) xylene solution. PP and HDPE at a required ratio and PP-PE in a calculated amount were dissolved in xylene at 120°C in the presence of 2,6-di-*tert*-butyl-*p*-cresol and the solution was poured into an excess of ethanol. The precipitate was sufficiently dried in vacuum. Three PP/HDPE blends of compositions 25/75, 50/50, and 75/25 in weight ratio, together with each modified by PP-PE in amounts of 5, 10, and 15 wt %, respectively, were prepared.

Tensile properties of samples were tested on an Instron 1211 electronic tester at a drawing speed of 10 mm/min. Samples were heat molded into sheets at 185°C. The sheets were naturally cooled to room temperature under 10 MPa and then cut into pieces of $20 \times 4 \times 0.3 \text{ mm}$. The morphology of samples was examined by scanning electron microscopy (SEM) on JEOL-MAX-840 SEM equipment. SEM observation were on the fracture surface of samples directly from the tensile test after coating with platinum.

RESULTS AND DISCUSSION

Figure 1 shows the thermograph of the collective sequential polymerization product PP-PE. The melting temperature (T_m) of the PP component appeared at 157°C, and that of the PE component split into two at 123.0°C and 131.6°C. The melting peak at 123.0°C is related to the imperfect crystallization of the highly branched PE component (or EPC with long sequence lengths of ethylene units) due to the incorporation of propylene that is not thoroughly exhausted, and probably to the contribution of some kind of block copolymer. The peak at 131.6°C was the contribution of the well-crystallized PE component of high molecular weight. This is evidence

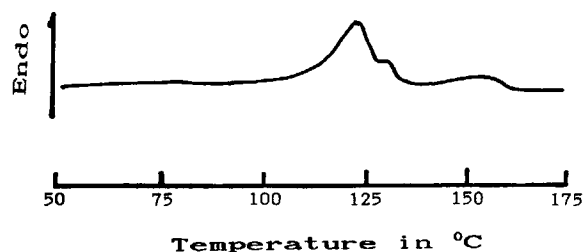


Figure 1 Melting thermogram of PP-PE product in ethylene content of 60 wt %.

of the multiple-component character of the PP-PE product. The effect of PP-PE on the morphology and mechanical properties of PP/HDPE blends is the contribution of all its composing components.

Figure 2 shows the micrographs of PP/HDPE = 25/75 (weight ratio) modified by PP-PE in amounts of 5, 10, 15 wt %, respectively. In the absence of PP-PE [Fig. 2(A)], PP is in large spherical domains (ca. 10 μm) dispersed in the HDPE matrix. Although the HDPE matrix showed signs of yielding and draw-necking, the large PP particles remained smooth and intact, indicating the poor tensile transmission from phase to phase caused by the poor adhesion between the two phases. With addition of 5 wt % of PP-PE, the dispersed PP particles became much smaller (ca. 5 μm), and their rough surface indicates the greatly enhanced adhesion between the two phases. With further increments of PP-PE to 10 wt % and 15 wt %, the PP dispersed domain size

was reduced further [Figs. 2(C) and 2(D)]. This is different from the compatibilization of PP/HDPE blends at this composition by EPC with residual PE crystallinity, whereby the size of PP dispersed domains did not vary much¹⁹ although adhesion between the two phases was improved.

Figure 3 shows the micrographs of PP/HDPE blends in a weight ratio of 50/50. High incompatibility in the absence of PP-PE is seen in Figure 3(A), where PP in very large spherical particles is dispersed in HDPE matrix. On addition of 5 wt % PP-PE [Fig. 3(B)], the morphology changed from PP in dispersion to a co-continuous structure. A lamellar phase structure with lamellar thickness of about 10 μm can be seen in Figure 3(B). The phenomenon is similar to that of compatibilization of 5 wt % EPC to PP/HDPE blends at this composition,¹⁹ but the lamellae of the latter are much thicker than that of former. This also demonstrates

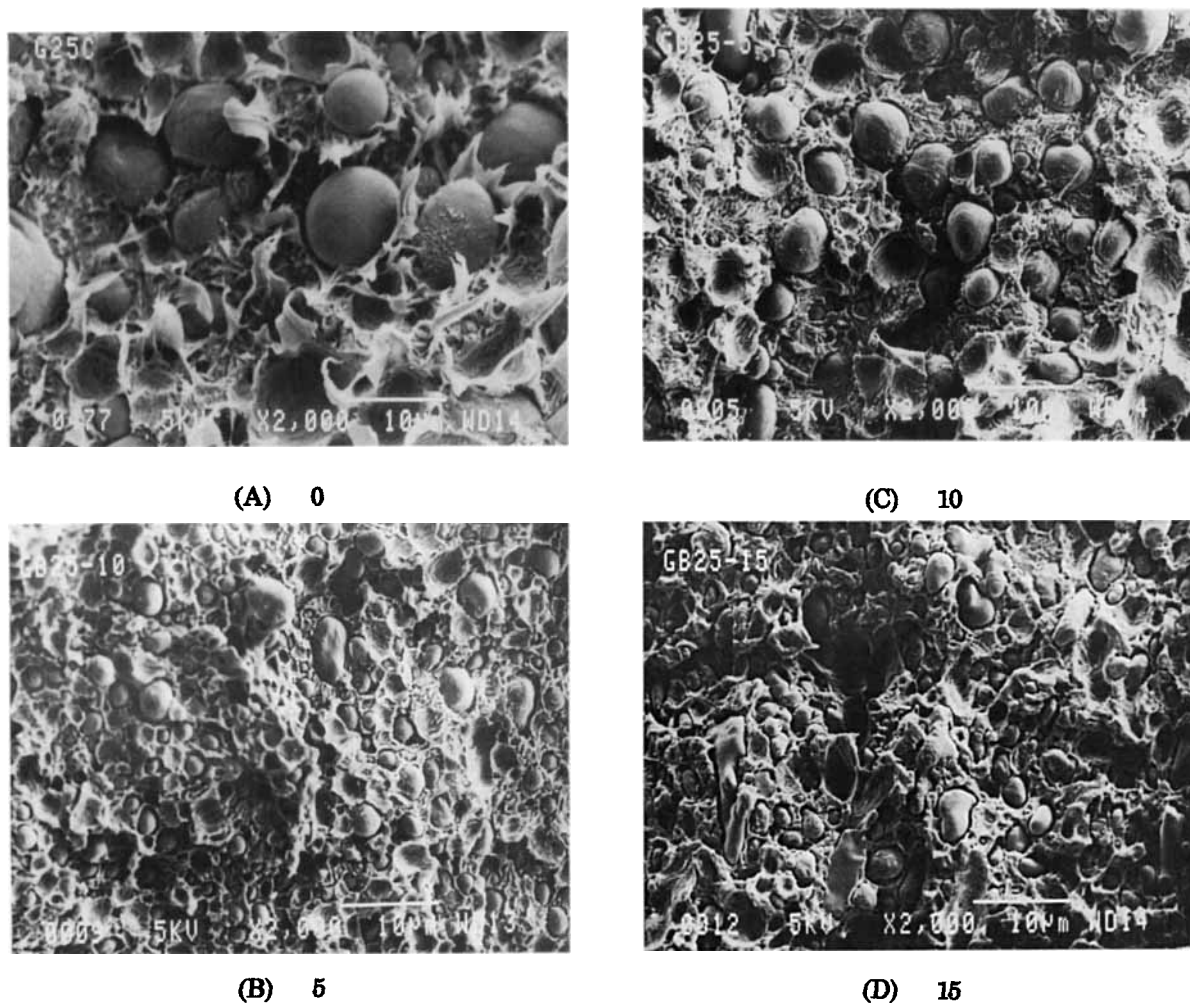


Figure 2 SEM micrographs of PP/HDPE blends in weight ratio of 25/75 modified by PP-PE of varying amounts.

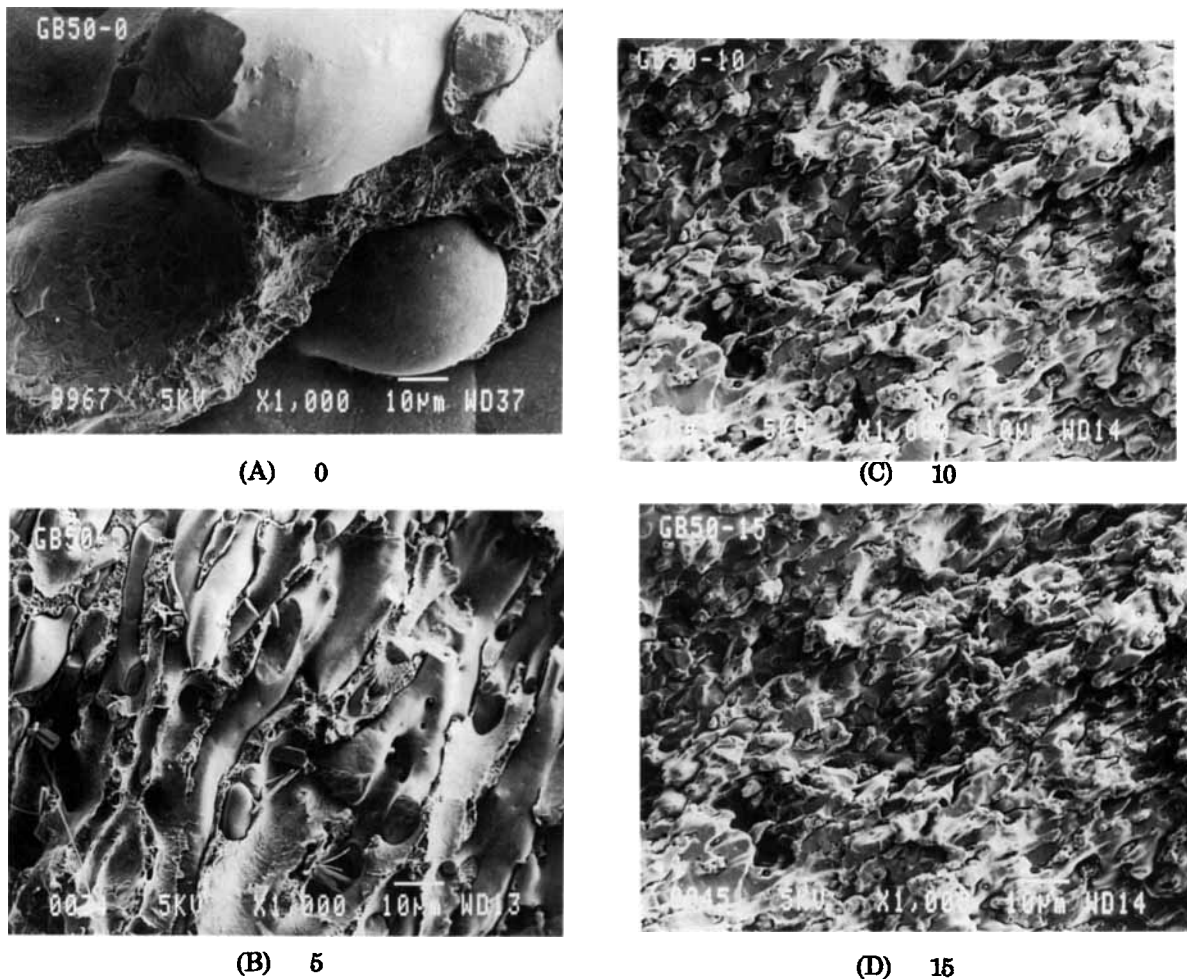


Figure 3 SEM micrographs of PP/HDPE blends in weight ratio of 50/50 modified by PP-PE of varying amounts.

that PP-PE is a more effective compatibilizer than EPC. The thickness of the co-continuous phase size of the blends reduced dramatically with further increments of PP-PE [Figs. 3(C) and 3(D)]. The PP phase seems to become more co-continuous than that of HDPE.

Micrographs of PP/HDPE blends in weight ratio of 75/25 show the morphology of the best compatibility of the three blends of different compositions (Fig. 4). In the absence of PP-PE [Fig. 4(A)], the size of the dispersed spherical domains of HDPE is about 5 μm , which is the smallest dispersed domain size of the three blends [see Figs. 2(A) and 3(A)]. After addition of 5 wt % PP-PE [Fig. 4(B)], the dispersed HDPE domain size was reduced to 1–2 μm . When the PP-PE content reached 10 wt % [Fig. 4(C)], the dispersed HDPE domains were no longer spherical but deformed probably by good tensile transmission from phase to phase under much enhanced adhesion of the two phases. The tendency

became clearer when the content of PP-PE reached 15 wt % [Fig. 4(D)], at which point the dispersed HDPE domains were hardly recognized due to the diffused phase boundary. This demonstrated the strong compatibilization action of PP-PE on the blends at this composition.

Figure 5 shows the mechanical properties of the three PP/HDPE blends of different compositions, each modified by varying amounts of PP-PE. Here the blends of 75/25 (weight ratio) show the best mechanical properties and that of 50/50 the lowest, consistent with the results of morphology studies.

Addition of 5 wt % of PP-PE made the tensile strength of all three blends increase [Fig. 5(A)]. The increase in tensile strength was the largest for the 50/50 blend because of its high susceptibility to compatibilization of PP-PE based on the original incompatibility between the two components. With further increments of increase in the content of PP-PE, the tensile strength of the blends either was

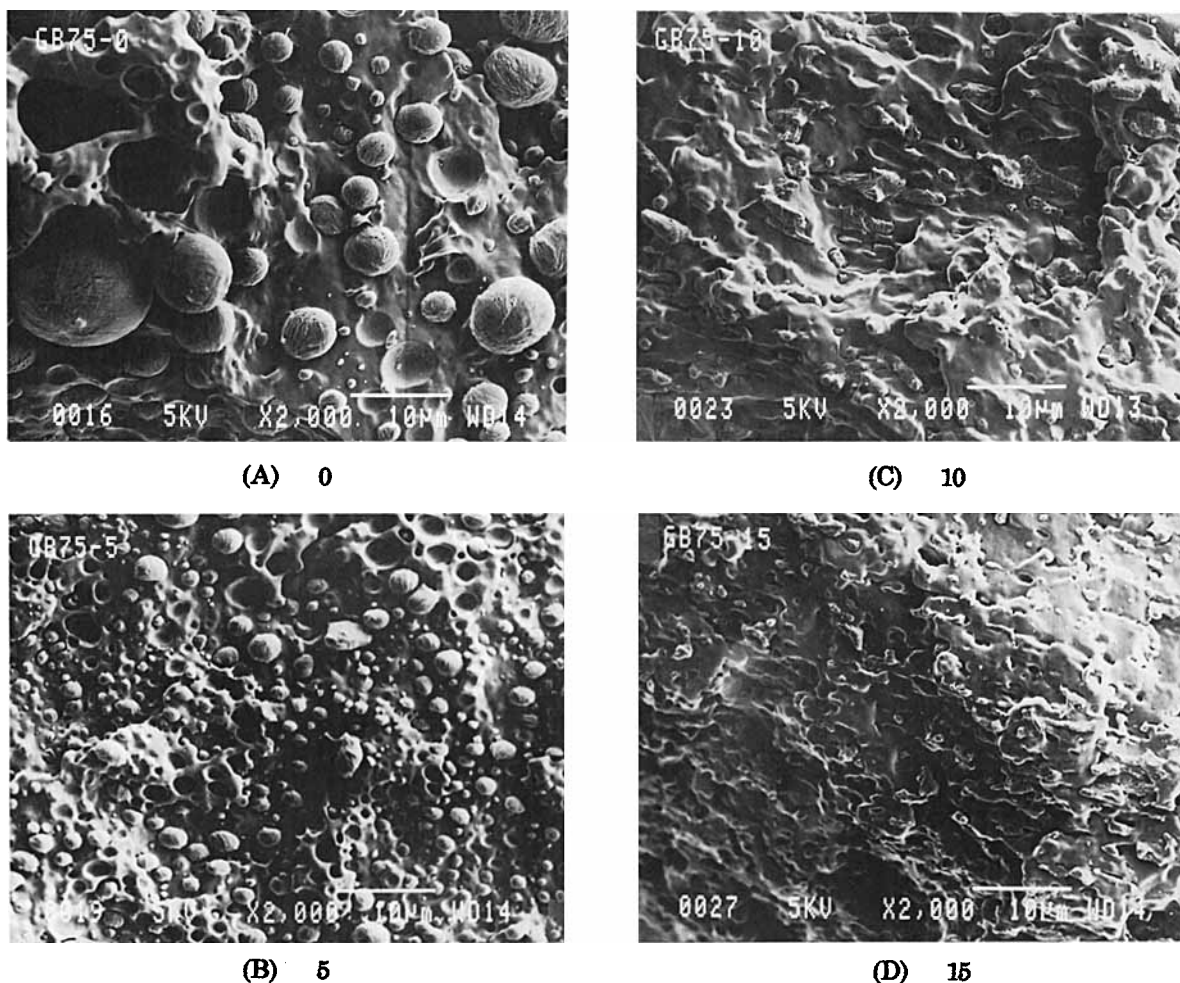


Figure 4 SEM micrographs of PP/HDPE blends in weight ratio of 75/25 modified by PP-PE of varying amounts.

nearly unchanged (25/75 and 75/25 weight ratio) or increased only slowly (50/50 weight ratio). This probably means that the tensile strength of blends depends mainly on adhesion of the two phases; 5 wt % PP-PE nearly reached its maximum in improving the adhesion between the two phases.

The moduli of the three blends of different compositions did not vary much with the addition of PP-PE, as shown in Figure 5(B).

Elongation at break of all three blends increased almost linearly with increments of PP-PE [Fig. 5(C)]. From morphological studies, the size of the dispersed domains (PP in 25/75 and HDPE in 75/25 blends) and both phase sizes in 50/50 blends reduced monotonously with increments in PP-PE content. The thinner matrix ligament on size reduction in the dispersed domains would lead to the greatly enhanced toughness of the blends and the greatly improved elongation at break.²¹⁻²³

The tensile properties of incompatible and partly compatible blends depend on two interrelated factors: the adhesion between the two phases and the domain size of the dispersed component, both controlled mainly by the interfacial tension.²⁴ Based on our results, it seems wise to conclude that the tensile strength of the blends is mainly related to the adhesion between the two phases, and the elongation at break depends mostly on the domain size of the dispersed component. This will be discussed further in a future article.

In conclusion, the addition of PP-PE improved both the tensile strength and the elongation at break of all three PP/HDPE blends, while their moduli were unchanged. Like typical block copolymers, the PP-PE product made by sequential polymerization of propylene and ethylene using a Ziegler-Natta catalyst showed good behavior in compatibilizing PP/HDPE blends, in spite of its multiple compo-

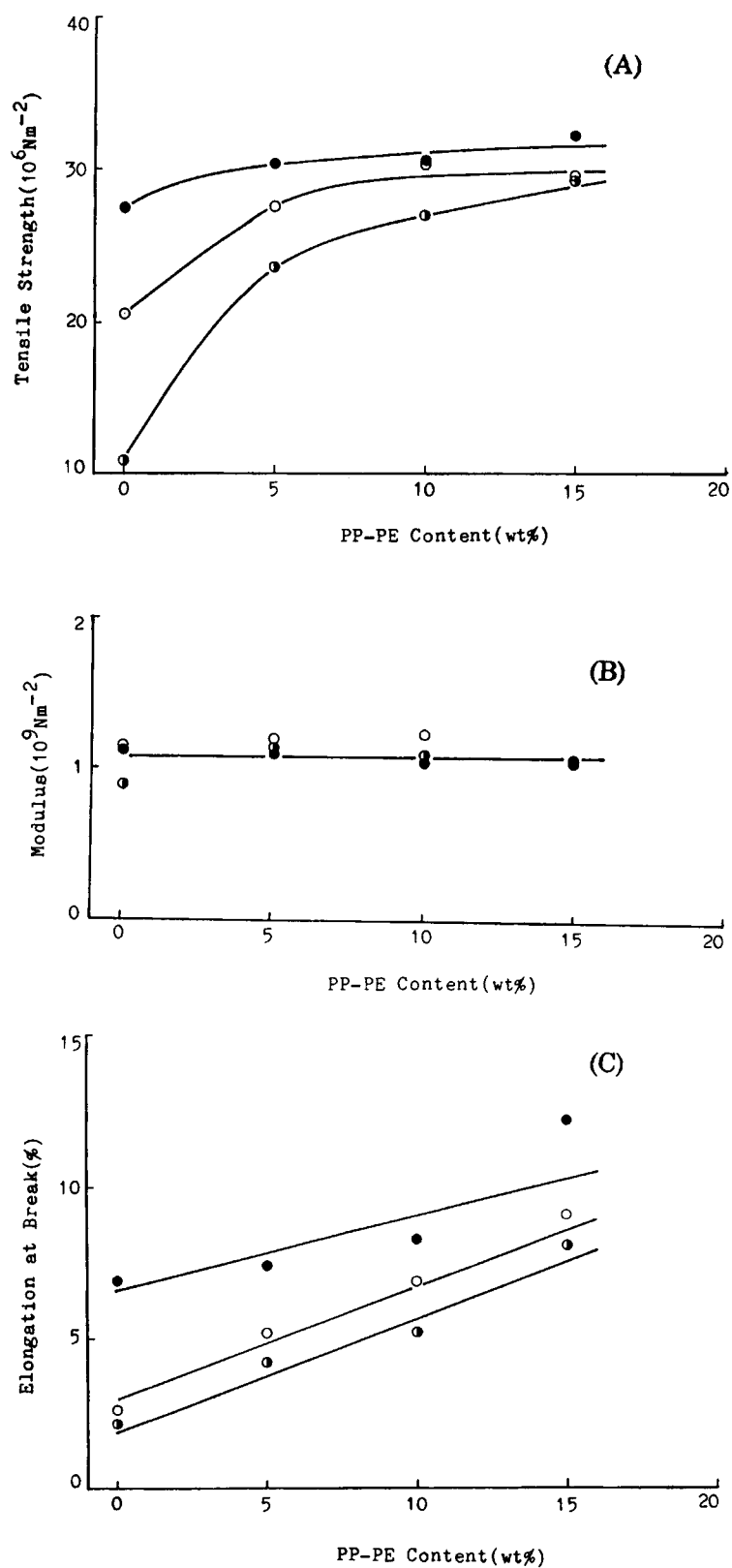


Figure 5 Mechanical properties—(a) Tensile strength, (b) modulus, and (c) elongation at break—of PP/HDPE blends of compositions of (○) 25/75, (◐) 50/50, and (●) 75/25 (weight ratio) modified by PP-PE of varying amounts.

nents. More work is needed to clarify whether the compatibilization was caused by the PP-*b*-PE block structure in PP-PE, another component, or the collective effect of all the individual components.

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