

Interfacial Adhesion Enhancement of Polyethylene–Polypropylene Mixtures by Adding Synthesized Diisocyanate Compatibilizers

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ABSTRACT: Immiscible and incompatible binary blends of commercial polypropylene (PP)/polyethylene (PE) display poor mechanical properties. The addition of compatibilizer to reinforce and enhance an adhesion at the interfaces between PE–PP mixtures has been conducted. The compatibilizer chosen was in the group of Ziegler–Natta's PE–PP block copolymer with diisocyanate linkage. The effects of adding the compatibilizers were assessed by morphology studies, thermal analysis, and mechanical test-

ing. DSC curves of crystallization and FTIR provided evidences to support the formation of PP/PE block copolymer. Significant improvements in the mechanical properties of 50/50 PE/PP blends containing compatibilizer have been noted. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3766–3773, 2007

Key words: PE/PP blend; polyethylene–polypropylene block copolymer; compatibilizer

INTRODUCTION

Polyethylene (PE) and polypropylene (PP) are among the most common plastic wastes, because they are among the most frequently used commercial plastics in our daily lives as well as in industries.¹ It is impossible and not appropriate to identify and totally separate the waste mixtures of these two polymers. Usually, their waste mixture can recycle as mixed waste plastics in the form of blends. This reuse approach is attractive, because it avoids the difficult task of separation. As a consequence, academic and industrial interest in virgin and recycled polymer blends is rapidly expanding.

Unfortunately, the incompatibility between PE and PP has already been reported by various authors.² The strong phase separation leading to a coarse-phase structure and the low interfacial adhesion between the phases is responsible for a decrease in mechanical properties especially related to its morphology, including impact strength, strain at break, and ductile to brittle transition. According to Shanks,³ the immiscibility between the phases makes the rule of mixtures ineffective in predicting some properties of interest.

To overcome this difficulty, the usages of various coupling agents have been reported. Incorporating a compatibilizer into a multiphase system generally leads to a fine phase structure and results in the enhanced interfacial adhesion. Among others,^{4–6} Yang⁷ showed that the addition of a commercial ethylene/propylene block copolymer improved the ductility of LDPE/PP blends, particularly for PP-rich blends. Bertin and Robin⁸ studied and characterized virgin and recycled LDPE/PP blends and the usage of compatibilizing agents, such as ethylene–propylene–diene monomer (EPDM) copolymer or PE-g (2-methyl-1,3-butadiene) graft copolymer, to enhance their impact strength and elongation at break. Claudia and Agnes showed the partial compatibility of the PP/HDPE reflected in the improvement of tensile strength and elongation by the addition of extracted recycled PP.⁹ Although this may solve the compatibility problem, the use of compatibilizers adds cost to the recycled product, usually resulting in loss of interest from the recycling sector.

In this work, we try to synthesize the cost-effective compatibilizer in simple system that can improve the mechanical properties of PE/PP mixtures. Thus, we applied the rapid reaction between a polyfunctional isocyanate and a hydroxyl-terminated oligomer leads to urethane linkage. Consequently, the addition of Ziegler–Natta PE/PP-block copolymer synthesized by diisocyanate has the ability to reinforce the PE–PP mixtures as it is expected. Thermodynamically, the PP-*b*-PE will sit at the interface between the two components. In this work, the morphology, thermal

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properties, and tensile properties of PP/PE blends were evaluated.

EXPERIMENTAL

Chemicals

Commercially graded PP and PE were donated from Thai Polyplastic Industry. Polymerization-grade propylene and ethylene were donated from National Petrochemical, Thailand. The AlEt₃ (TEA) and MDI were donated from Bangkok Polyethylene, Thailand. The TiCl₄ were purchased from Merck. Anhydrous MgCl₂ was supplied from Sigma-Aldrich, phthalic anhydride, diethylphthalate (DEP, used as an internal donor), and *n*-decane were purchased from Fluka Chemie A.G., Switzerland. Hexane was donated from Exxon Chemical, Thailand. It was purified by refluxing over sodium/benzophenone under argon atmosphere prior to use. Ultra high purity (UHP) argon (99.999%) and oxygen (UHP) was obtained from Thai Industrial Gas and was further purified by passing through molecular sieves 3Å, BASF catalyst R3-11G, NaOH, and phosphorus pentoxide (P₂O₅) to remove traces of oxygen and moisture.

All operations were carried out under an inert atmosphere of argon using a vacuum atmosphere glove box and/or standard Schlenk techniques.

Catalyst preparation

A catalyst of type TiCl₄/DEP/MgCl₂ was synthesized in the following manner. About 0.476 g of anhydrous MgCl₂ was added to 2.5 mL of *n*-decane. This suspension was treated with 2.34 mL of 2-ethylhexanol and 0.1089 g of phthalic anhydride at 130°C. It was stirred until the MgCl₂ was dissolved. TiCl₄ (20 mL) was added dropwise at -20°C, with subsequent treatment of the solution in the presence of 0.26 mL of DEP at 110°C for 2 h. The resulting solid product was separated by filtration and the addition of 20 mL of TiCl₄ was repeated at room temperature. After keeping the solution at 120°C for 2 h, this slurry was siphoned-off and washed twice with 10 mL of *n*-decane and thrice with 10 mL of hexane, respectively. The catalyst was dried under vacuum for 30 min at 40°C and contained 3% Ti.

Polymerization reaction

PE and PP terminal hydroxyl group

The propylene polymerization and ethylene polymerization reactions were carried out in a 100-mL semi-batch stainless steel reactor equipped with magnetic stirrer. About 26.55-mL hexane, 0.01 g catalyst (Al/Ti molar ratio = 167), and 3.45-mL TEA were introduced into the reactor and stirred for 5 min at room temper-

ature in the atmospheric glove boxes. Followed by that, the reactor was put in liquid nitrogen immediately to stop the reaction between the catalyst and cocatalyst. After the solution was frozen for 15 min, the reactor was evacuated for 3 min to remove argon. The reactions were conducted at 60°C and the polymerization was started by continuous feeding of ethylene (propylene) at constant pressure of 50 psi for 1 h. Then the polymerization was stopped by directly bringing into contact with oxygen gas at room temperature followed by precipitation in hydrochloric acid solution in methanol and dried at room temperature.

PE block PP copolymerization

Copolymerization was carried out in a glass reactor equipped with magnetic stirrer. PE and PP-containing hydroxyl group 50/50 wt % were added and dissolved in *o*-dichlorobenzene at 120°C. Followed by that excess MDI was dropped in the solution that remained stir for 1 h. The solution was washed with excess methanol and polymer was filtered and dried.

Blend and molding preparation

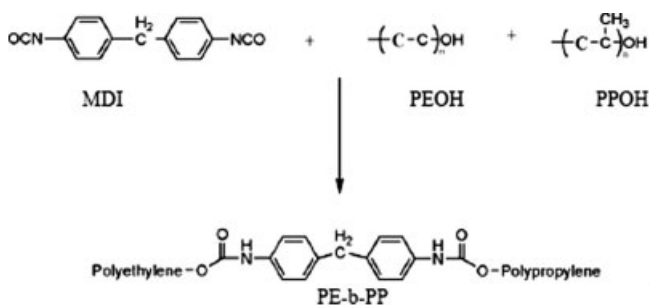
The melt mixing method was performed in digital hot plate stirrer at 220°C, further kept for 5 min at 300°C, and annealed at 200°C for 20 min before the experiments¹⁰ to allow the equilibrium and ensure the migration of the PE-*b*-PP to the interfaces. All blends were prepared with 50 wt % of commercial grade PE and 50 wt % of commercial grade PP (PE/PP), because PE/PP will become the easiest phase-separated and large amount of interfaces obtained. When the block copolymer was used, 3 wt % of the block copolymer was added base on the total weight of the 50/50 blend. And then, the block copolymer was added in PE/PP blend for 3, 6, 12, and 20 wt %. All polymer blends were molded with the LAB TECH hydraulic hot press LP-50M/C 9701.

Measurements and characterization of block copolymers and blends

Infrared survey spectra were recorded with FTIR (IFS28). The scanning ranged from 400 to 4000 cm⁻¹ on the pallet sample of KBr powder (to hold the powder samples as a blank) with scanning 12 times.

The molecular weight and its distribution were determined by using GPC Model: Waters 2000 Column: Styragel HT6E with 1,2,4-trichlorobenzene as a solvent at 135°C.

The melting temperatures of the block copolymer-added polymer blends were determined with a PerkinElmer DSC-Pyris Diamond over the range -60 to



200°C of scanning rate 40°C/min under nitrogen atmosphere.

Tensile properties were characterized using an Instron universal testing machine with a test speed of 12.5 mm/min. The tests were conducted according to ASTM D 882-02.

The morphologies of all block copolymers were investigated by JSM-5410LV Scanning Microscope. The samples for SEM analysis were coated with gold particles by ion-sputtering device to provide electrical contact to the specimens.

RESULTS AND DISCUSSION

Chain structure of PE/PP block copolymer diisocyanate linkage

On the basis of this result, a plausible products of the block copolymerization are proposed as shown in Scheme 1.

In addition, besides PE-*b*-PP, there have others: two byproducts of the reaction, which are PE-*b*-PE and PP-*b*-PP. Moreover, there are other two products that end chain with hydrogen (not hydroxyl and OH) are

PE, PP, and the small amount of remaining reactant, that is, PEOH and PPOH. The fractions of these byproducts are hardly to be quantified and it cannot be completely fractionated by solvent extraction. Thus, unidentified fraction distribution of the block copolymers will be along with what is identified as PE-*b*-PP throughout this study. However, the mixture identify as PE-*b*-PP had good phase binding with the melted blend of PP/PE that can be seen in SEM photo (Figs. 2 and 3). Consequently, the mixture of PE-*b*-PP copolymer in this study (PE-*b*-PP, and various sizes of PP and PE) comprised the phases that will dissolve in the melted blend of PP/PE without any difficulty.

Characterization of PE-*b*-PP and their blends

From GPC results, the PE-*b*-PP has a wide molecular weight distribution resulted from the reaction of wide MWD of PPOH and PEOH with diisocyanate. To confirm the reaction that contribute to the block copolymer of PE-*b*-PP in this system, the IR spectrum of block copolymer obtained at 25°C is illustrated in Figure 1. The peak of isocyanate (NCO) transmittance is 1530 cm⁻¹, ν_{C=O} MDI = 1711 cm⁻¹, ν_{NH} = 3404, 1599, and 814 cm⁻¹. Thus, IR spectrum has identified the diisocyanate linkage in PE-*b*-PP copolymer structure. Moreover, the binding properties of PE-*b*-PP can be confirmed in SEM photo (Figs. 2 and 3) to ensure the abilities of our compatibilizer.

As shown in Table I, the effects of adding isocyanate compatibilizer can be clearly assured by their blends properties. The PEOH has larger molecular weight compared to PPOH. Consequently, the molecular weights of PE-*b*-PP are higher than PPOH and change according to the isocyanate reaction. The Δ*H* of the melted blend of pure PE/PP is lower than all of

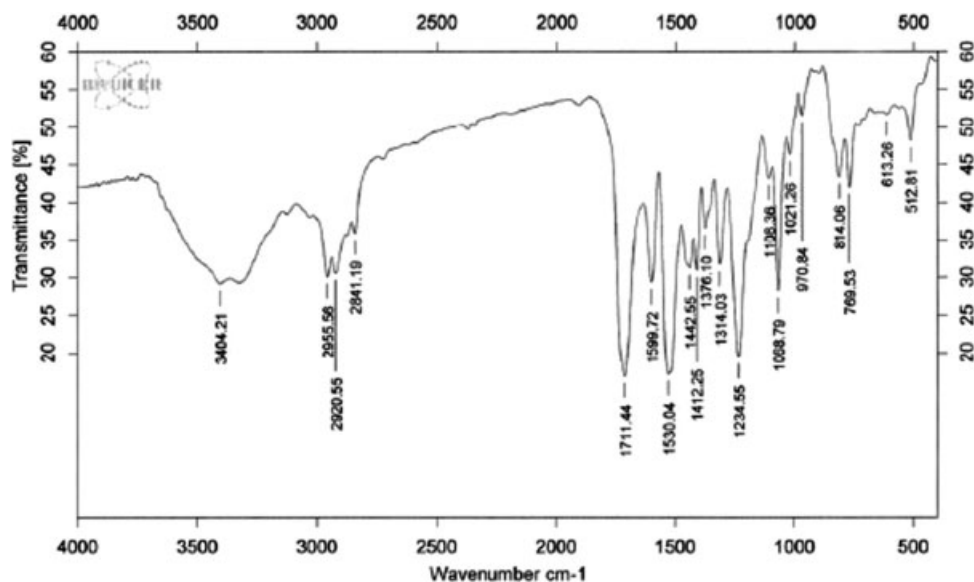


Figure 1 IR spectra of PE-*b*-PP at 25°C.

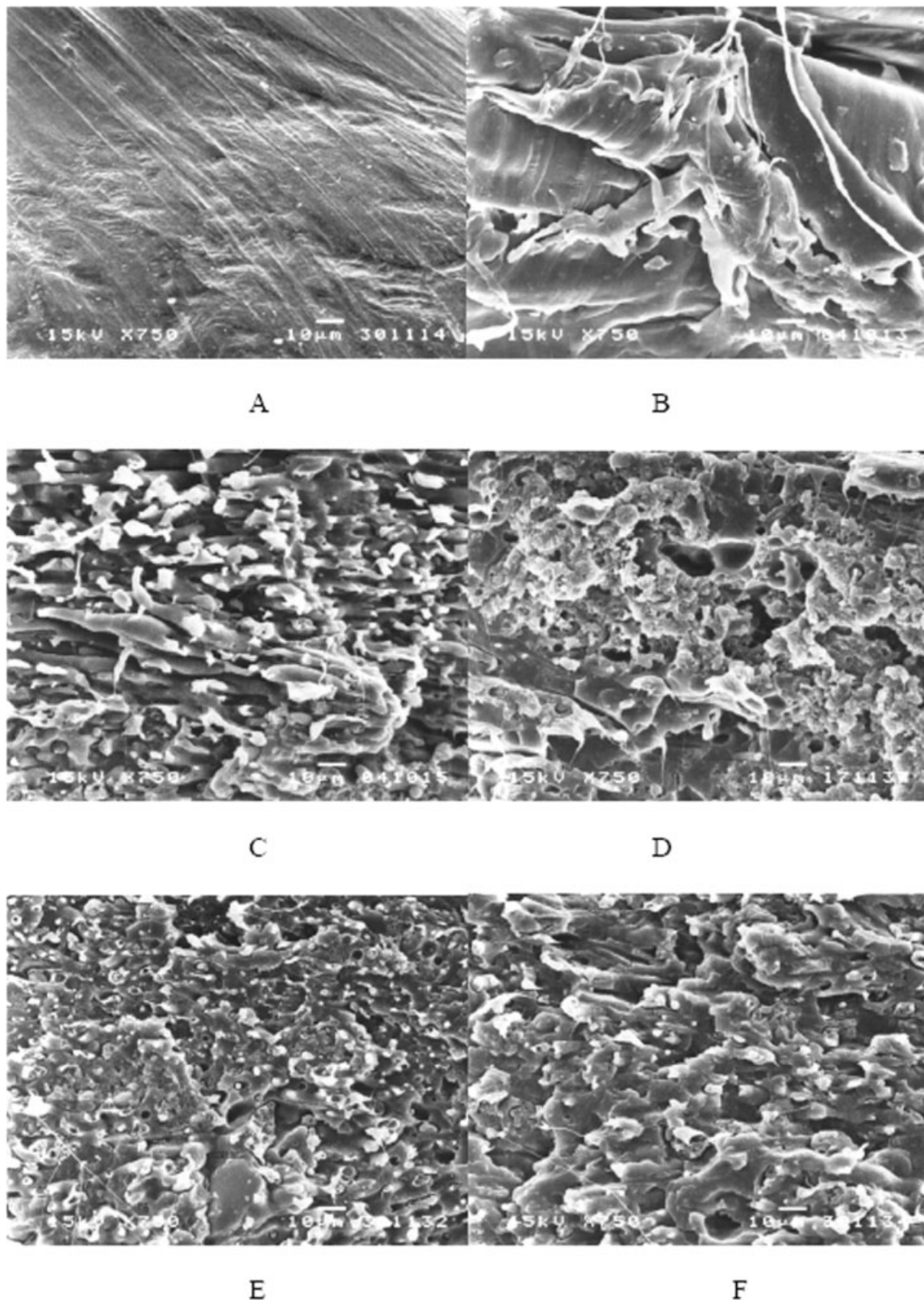


Figure 2 SEM of tensile fracture surface of (a) PP, (b) PE/PP blend, (c) PE/PP+ PEbPP3%, (d) PE/PP+ PEbPP6%, (e) PE/PP+ PEbPP12%, and (f) PE/PP+ PEbPP20%.

the PE-*b*-PP addition samples, and this implied that the crystallinity of melted blend of pure PE/PP is increased when added with PE-*b*-PP. In other words,

the copolymer enhanced the crystallization of both PE and PP in the melted blend of PE/PP. From the highest ΔH , the largest percent of crystallinity is at 6% PE-

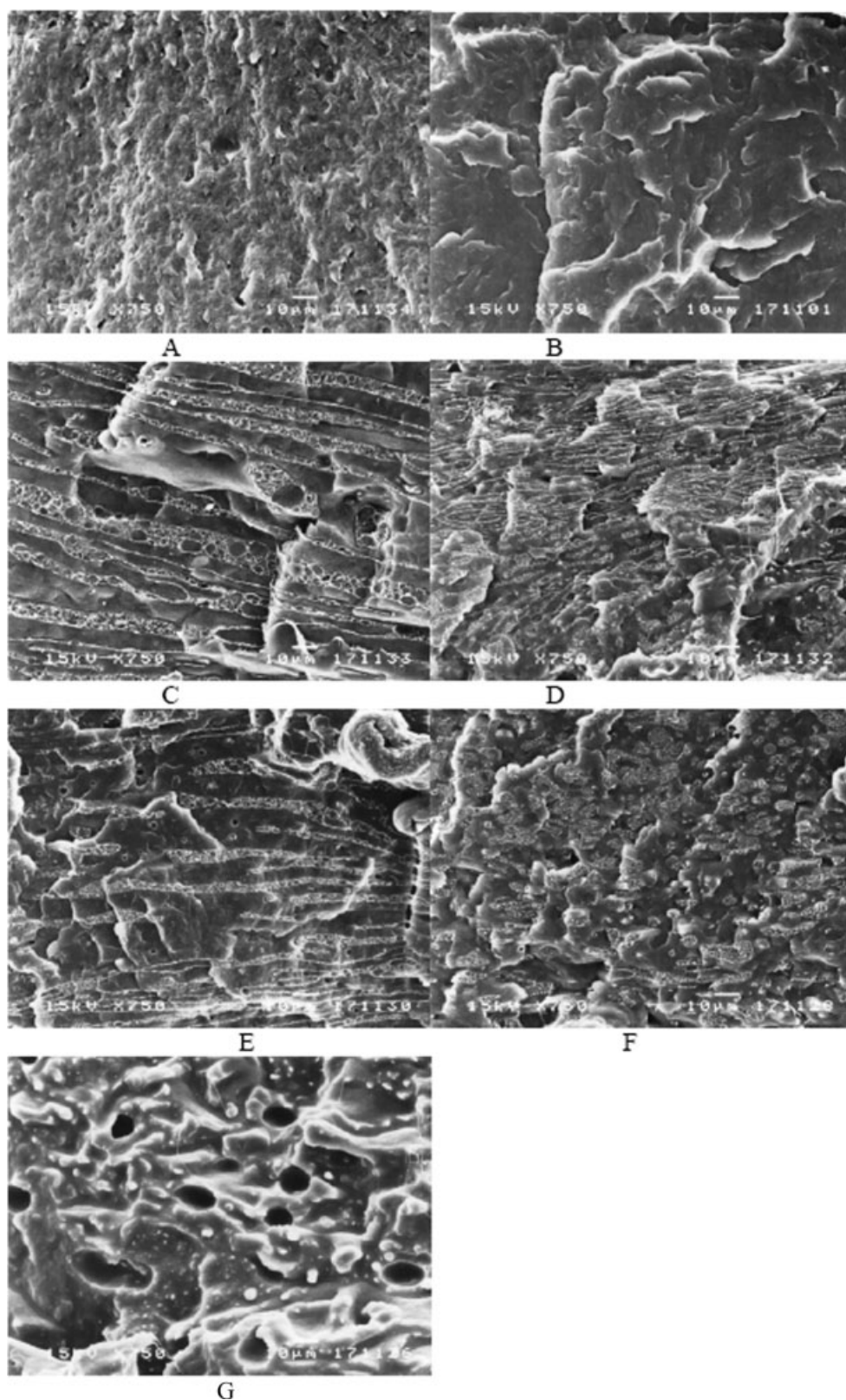


Figure 3 SEM of cryogenic fracture surface of (a) PE, (b) PP, (c) PE/PP blend, (d) PE/PP+ PEbPP3%, (e) PE/PP+ PEbPP6%, (f) PE/PP+ PEbPP12%, and (g) PE/PP+ PEbPP20%.

b-PP in PE/PP. This may result in the best mechanical properties because of the formed crystal and contribute to the highest tensile strength. In addition, portion

of T_m that represented the PP crystal in PE/PP were increased from pure PE/PP in all the composition of added PE-*b*-PP (usually, T_m described the quality of

TABLE I
Characterization of Polymer

| Polymer | Mw ^a ($\times 10^{-4}$) | MWD ^a | Heating 1 ($^{\circ}\text{C}$) ^b | | | | Cooling ($^{\circ}\text{C}$) ^b | | | Heating 2 ($^{\circ}\text{C}$) ^b | | | |
|------------------|--------------------------------------|------------------|---|----------|-------|--------------|---|----------|--------------|---|----------|-------|--------------|
| | | | T_{m1} | T_{m2} | T_g | ΔH_1 | T_{c1} | T_{c2} | ΔH_2 | T_{m1} | T_{m2} | T_g | ΔH_3 |
| PEOH | 117.3 | 7.5 | 145 | Nd | Nd | 181.4 | 110 | Nd | 123.6 | 137 | Nd | Nd | 118.9 |
| PPOH | 39.5 | 8.7 | Nd | 156 | -5 | 40.7 | 100 | Nd | 58.8 | Nd | 154 | -5 | 51.4 |
| PE- <i>b</i> -PE | Na | Na | 135 | Nd | Nd | 255.4 | 108 | Nd | 83.2 | 132 | Nd | Nd | 84.1 |
| PP- <i>b</i> -PP | Na | Na | 93 | 158 | -7 | 32.5 | 102 | Nd | 28.7 | Nd | 153 | -8 | 29.7 |
| PE- <i>b</i> -PP | 58.3 | 12.5 | 130 | 153 | -6 | 71.7 | 113 | 120 | 96.7 | 129 | 152 | -7 | 59.3 |
| PE/PP | 32.4 | 6.1 | 135 | 151 | -6 | 68.3 | 98 | 110 | 67.1 | 135 | 151 | -6 | 64.7 |
| 3%PEbPP | Na | Na | 136 | 163 | Nd | 131.6 | 111 | Nd | 133.7 | 134 | 164 | Nd | 137.3 |
| 6%PEbPP | Na | Na | 138 | 166 | Nd | 137.9 | 109 | Nd | 134.7 | 138 | 164 | Nd | 137.8 |
| 12%PEbPP | Na | Na | 138 | 165 | Nd | 122.9 | 109 | Nd | 122.3 | 136 | 163 | Nd | 122.3 |
| 20%PEbPP | Na | Na | 137 | 164 | Nd | 119.9 | 109 | Nd | 120.9 | 136 | 164 | Nd | 113.9 |

Na, not available.

Nd, not detected.

^a Determined by gel permeation chromatography, PS standard.

^b Determined by DSC, $\Delta H = (\text{J/g})$.

crystallinity in polymer blend). This can be concluded that the addition of our PE-*b*-PP alter both the quality and quantity of the crystallinity of PE/PP.

The chain structure of polymer blend and block copolymer was studied by DSC analysis of crystalline-segregated samples. After stepwise annealing of the samples at different temperatures, the long PP and PE segments can form crystalline lamellae of different thickness according to their sequential lengths, and these lamellae will melt at different temperatures.¹¹ By recording the endothermic curves of the polymer blend and block copolymer in a DSC scan, we are able to identify the sequential contribution of PE/PP blend and effects of the synthesized PE-*b*-PP in crystallinity of PE/PP.

The T_g of the block copolymer should exhibit the glass transition of each of the respective homopolymer component as same as polymer blends.^{12,13} According to Table I, the T_g of PP¹⁴ around -5°C indicate the cooperation of PP in the compatibilizer. Unfortunately, because of the low T_g of PE at -110°C ,¹⁵ it cannot be detected in these DSC experiments. However, the crystalline melting characteristic of PE-*b*-PP shows the combination characteristics of both PE and PP. The melting peak at about $130\text{--}140^{\circ}\text{C}$ corresponds to the melting temperature of PE crystal and the peak above 140°C corresponds to the melting temperature originate from PP crystal. The appearance of the curves of PE/PP blend and PE-*b*-PP is similar. In the cases of adding PE-*b*-PP to PE/PP blend, the melting temperatures of PP in PE/PP increase about 10°C (as shown in Table I). This may confirm the appearance of the synthesized PE-*b*-PP and the consequence of the addition of block copolymer.

Morphology

According to SEM picture, it clearly shows the differences of the rough surface particles and the bridge

formation with PP matrix of PE/PP blend, which continuously changed according to the concentration of PE-*b*-PP. The addition of PE-*b*-PP to PE/PP blend vividly shows the smaller phase particles size as increased concentrations. Many studies¹⁶⁻¹⁹ on polymer alloys have shown that for multiphase polymer systems, the toughening effect is determined by two factors. First, the smaller the particles and the narrower the particles size distributions are, the better impact the strength is. Second, the stronger the adhesion between particle and the matrix, the better is the impact properties.

The SEM micrographs of compatibilized PE/PP blends (3, 6, 12, and 20% PE-*b*-PP) are shown in Figures 2 and 3. Figure 2 shows the tensile fracture of PE/PP and compatibilized PE/PP, while indicated that the interfacial adhesions, and therefore the compatibility of the PE and PP phases is better than the uncompatibilized PE/PP. In room temperature fracture experiments, the PE is in the form of tough rubbery polymer compared to PP. These might be shown as the stretch rubbery structure in the blends. The cryogenic fracture of the similar blends in Figure 3 will result in the clear domain size because at the cryogenic temperature both PE/PP are in the glassy states and the fractures cut directly to the cross sections of the segregation size in the blends.

In Figure 3, the cryogenic fracture of PE/PP and compatibilized PE/PP indicated clearly decrease in domain sizes (dispersion of PE in PP) and finer particle size distributions when adding more PE-*b*-PP in the blends. As might be confirmed by the SEM, the phase segregation decrease deliberately but the clear second dots of PE/PP are captured in the 12% and 20 wt % PE-*b*-PP, which might be the reason for the weaker interfacial ability than the 6 wt % PE-*b*-PP. Those samples have lower tensile properties than the 6 wt % PE-*b*-PP. These phenomena can confirm mechanical properties results.

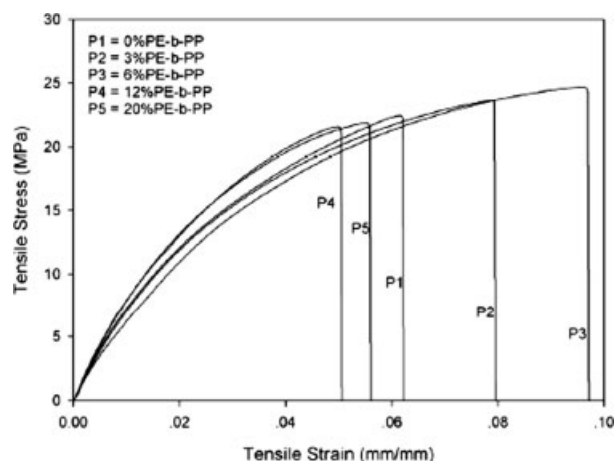


Figure 4 Additive effect of PE-*b*-PP to PE/PP blend on stress-strain behavior at 25°C.

Mechanical properties

The results of tensile stress tests are shown in Figure 4 and Table II. As the concentration of PE-*b*-PP in melted blend of pure PE/PP increased, both the tensile strength and the elongation at break increased. These show that the addition of PE-*b*-PP to PE/PP can improve the reinforcement of polymer by increasing the interfacial adhesion between PE and PP. At 6% PE-*b*-PP in PE/PP, the highest tensile stress of the blend occurred, which resulted from more stiffness and toughness of the samples. Thus, the tensile properties of PE-*b*-PP in PE/PP were in agreement with DSC results as we discussed earlier that the 6 wt % PE-*b*-PP has the most reinforcement characteristics. The reasons of decreasing tensile strength and elongation at break at 12 and 20% PE-*b*-PP contents might be because of the lower percent crystal in the samples together with the increase of PE, PP pure from PE-*b*-PP that have the higher molecular weight than the commercial PE/PP. The amount of high molecular weight might result in the more incompatible of PE/PP. As usual, the portion of high molecular weight in the blend will result in phase separation of the high molecular weight species easier than the low molecular weight portions.²⁰ The SEM results supported what

TABLE II
Summary of Mechanical Properties

| Sample | Modulus (MPa) | Tensile strength (MPa) | Elongation (%) |
|---------------------|---------------|------------------------|----------------|
| PE/PP | 879.89 | 22.46 | 6.2 |
| 3%PE- <i>b</i> -PP | 782.19 | 23.63 | 8.0 |
| 6%PE- <i>b</i> -PP | 763.14 | 24.67 | 9.7 |
| 12%PE- <i>b</i> -PP | 927.01 | 21.59 | 5.1 |
| 20%PE- <i>b</i> -PP | 854.27 | 21.88 | 5.6 |

can be found in tensile testing. As the consequence, this can be concluded that the addition of our PE-*b*-PP will have the optimum at 6 wt % PE-*b*-PP.

CONCLUSIONS

A new synthesis method of PE-*b*-PP copolymer by converting the H-terminated chain ends to hydroxyl-terminated ones and blocking with diisocyanate is performed by the effective compatibilizer for immiscible blend of PE/PP. The diisocyanate linkages of PE-*b*-PP copolymers were confirmed by IR, which indicated that PE-*b*-PP copolymers occurred in the blocking reaction. The effects of PE-*b*-PP copolymers on the morphology of PE/PP blends were investigated by SEM with image analysis. The presence of the block copolymer dramatically reduced the phase size. Furthermore, the mechanical properties, such as tensile strength, elongation at break, and crystallinity, have been improved because of PE-*b*-PP copolymers. The phase-binding phenomena happened because the PE-*b*-PP contained PE and PP segments, which attached and bound the PE/PP segregate phase blend, leading to superior properties via changing morphology than the normal mixing blend without PE-*b*-PP. As confirmed by DSC, the compatibilized blends showed the increase of crystallinity percentage. The optimum content of compatibilizer is 6 wt % PE-*b*-PP, which shows the best optimal values from DSC, tensile tests, and SEM results.

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