

Improved Compatibility of High-Density Polyethylene/Poly(ethylene terephthalate) Blend by the Use of Blocked Isocyanate Group

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ABSTRACT: The blocked isocyanate group (BHI) was synthesized to improve the storage stability of HI (2-hydroxyethyl methacrylate combined with isophorone diisocyanate) and characterized by Fourier transform infrared spectroscopy (FTIR). High-density polyethylene grafted with the blocked isocyanate group (HDPE-*g*-BHI) was used as a reactive compatibilizer for an immiscible high-density polyethylene/poly(ethylene terephthalate) (HDPE/PET) blend. A possible reactive compatibilization mechanism is that regenerated isocyanate groups of HDPE functionalized by BHI react with the hydroxyl and carboxyl groups of PET during melt blending. The HDPE-*g*-BHI/PET blend showed the smaller size of a dispersed phase compared to the HDPE/PET blend, indicating improved compatibility between HDPE and PET. This increased compatibility was due to the formation of an *in situ* graft copolymer, which was confirmed by dynamic mechanical analysis. Differential scanning calorimetry (DSC) analysis represented that there were few changes in the crystallinity for the continuous PET phase of the HDPE-*g*-BHI/PET blends, compared with those of the HDPE/PET blends at the same composition. Tensile strengths and elongations at the break of the HDPE-*g*-BHI/PET blends were greater than those of the HDPE/PET blends. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 1017–1024, 2000

Key words: high-density polyethylene; poly(ethylene terephthalate); blend; reactive compatibilization

INTRODUCTION

Immiscible blends are generally preferred over miscible blends because one can combine the useful properties of each blend component. However, most immiscible blends have an unstable morphology compared with their components due to unfavorable interactions at the molecular level.

This unstable morphology leads to poor mechanical properties. To overcome these problems, functionalized polymers are used as compatibilizers that can minimize interfacial tension and improve adhesion between the two phases. The results are a finely dispersed phase and improvement of the overall properties of the blends.^{1–6}

Among immiscible blends, we chose high-density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) as the blend components. HDPE is used mainly for films, pipe, blown bottles, and other consumer containers. PET is also widely used as a major synthetic fiber and in film, recording tapes, and bottles. So, these two polymers are

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significant contributors of postconsumer household waste and bring about serious waste-disposal problems.

Several studies have been reported on the reactive compatibilization of the immiscible HDPE/PET blend. Most widely used reactive functional groups for compatibilizing the HDPE/PET blend are acid anhydride and epoxy groups that can react with the hydroxyl or carboxyl end groups of PET. Traugott et al.⁷ studied the properties of HDPE/PET blends containing the polystyrene-*block*-poly(ethylene-*stat*-butylene)-*block*-polystyrene (SEBS) copolymer compatibilizer, compared with those of blends containing an ethylene-propylene-diene monomer terpolymer (EPDM) compatibilizer. Carté and Moet⁸ examined the effectiveness of various compatibilizers: SEBS, SEBS-*g*-maleic anhydride (MA), and HDPE-*g*-MA. Dagli and Kamdar,⁹ to compatibilize the HDPE/PET blends, tested four functionalized polymers: the maleated ethylene propylene copolymer, the ethylene/glycidyl methacrylate copolymer (E/GMA), SEBS-*g*-MA, and HDPE-*g*-MA. Boutevin et al.¹⁰ synthesized, as a compatibilizer, HDPE grafted with the following comonomers: methyl methacrylate, hydroxyethyl methacrylate, GMA, MA, and ethyl acrylate (EA). Pietrasanta et al.¹¹ tested the E/GMA copolymer and E/EA/GMA terpolymers with various content of reactive functional groups (1–8 wt % of GMA) to evaluate the effectiveness of compatibilization.

In this study, we synthesized the blocked isocyanate group (BHI) and suggested BHI as a new reactive functional group in the immiscible HDPE/PET blend, because isocyanate (NCO) groups can react with not only carboxyl but also with the hydroxyl end groups of PET. In our previous studies,^{12–16} isocyanate-functionalized polyolefins were prepared by grafting HI onto PE. We prepared HI by the reaction of 2-hydroxyethyl methacrylate (HEMA) with isophorone diisocyanate (IPDI) and studied the compatibilizing effect of the isocyanate group on reactive blends of PE and engineering plastics. In this article, to examine the effects of blocked NCO groups on compatibilization of the HDPE/PET blend, we blended PET and HDPE grafted with the blocked isocyanate group (HDPE-*g*-BHI) at various compositions. Also, we represented the morphological, thermal, and tensile properties of the HDPE-*g*-BHI/PET blends, compared with those of the HDPE/PET blends.

EXPERIMENTAL

Materials

HDPE (J820A, melt flow index = 7.5 g/10 min, Samsung General Chemicals Co., Korea) was used as received. A bottle-grade PET (PE-BH-350, intrinsic viscosity = 0.810, Samyang Chemical Co., Korea), having carboxyl end group concentrations of 29.1 meq/kg, was used after vacuum drying at 120°C for 48 h to reduce hydrolysis. BHI was prepared by the reaction of ϵ -caprolactam (CPL, Aldrich Chemical Co.) with HEMA–isophorone diisocyanate (HI) at the molar ratio of 1.1:1. HI was synthesized by the reaction of HEMA (Junsei Chemical Co., Japan) with IPDI (Aldrich Chemical Co.) with a molar ratio 0.95:1.¹² To prepare BHI, CPL was mixed with synthesized HI. The mixtures were heated to 80°C to block the isocyanate groups of HI.^{17,18} The temperature was then maintained for another 8 h. Dicumyl peroxide (DCP, Aldrich Chemical Co.) was used as a radical initiator.

Grafting onto HDPE

Graft copolymerization was carried out in a xylene solution. HDPE (10 g) and xylene (100 g) were poured into a reaction vessel. The reaction vessel was heated in a N₂ inlet with agitation, followed by the addition of BHI (2 g) and DCP (0.1 g). The reaction continued for 3 h at 120°C. The obtained products were precipitated in excess acetone. The precipitated graft copolymer was isolated and washed several times with acetone to remove the unreacted monomer, initiator, and homopolymer of BHI which could possibly be formed during the grafting reaction. Finally, products were dried in a vacuum oven at 40°C for 24 h. The relative grafting extent of BHI onto HDPE was 0.6 wt %, which was measured by the FTIR spectrum. The peak height ratio of the C=O peak at 1730 cm⁻¹ to that for the CH₃ peak at 1340 cm⁻¹ in the FTIR spectra was used as a measure for the relative extent of grafting.^{19–21}

Blend Preparation

HDPE-*g*-BHI/PET blends at various compositions were prepared with melt mixing using an internal mixer (Hakke, Rheocorder 900). The roller speed was fixed at 90 rpm and the mixing temperature was maintained at 260°C. After HDPE-*g*-BHI and PET were mixed for 5 min, the blends were cooled slowly at room temperature. The preparation pro-

cedure of the HDPE/PET blends was identical to that of the HDPE-*g*-BHI/PET blends. The blend ratios of the HDPE-*g*-BHI/PET (or HDPE/PET) were 90/10, 70/30, 50/50, 30/70, and 10/90 by weight. The 90/10 HDPE/PET blend represents the blend that is prepared with a mixture of HDPE and PET in the weight ratio of 90/10.

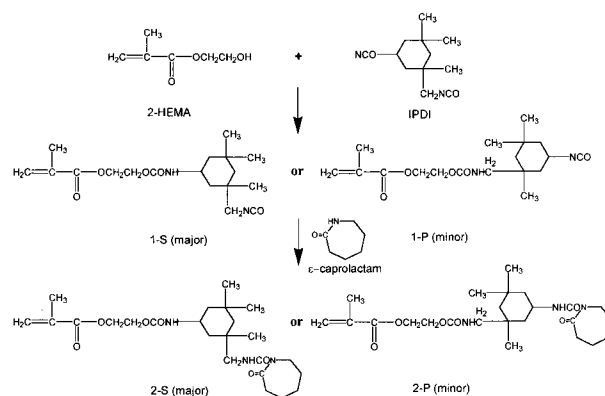
Measurements

The procedure of BHI preparation was characterized using FTIR (Nicolet, Magna IR-550). For FTIR analysis, films were prepared by a hot press (Masada Seisakusho Co., Ltd., MH-7). The evidence and relative extent of the grafting reaction onto HDPE were also characterized by their FTIR spectra. Also, the deblocking temperature of BHI in HDPE-*g*-BHI was determined by FTIR spectra at various temperatures. By using regeneration of the NCO peak at 2270 cm^{-1} , we can find that the deblocking reaction of BHI in the functionalized HDPE occurs from 200°C .²² To study the morphology of the blends, the cryogenically fractured surfaces in a liquid nitrogen atmosphere were examined by scanning electron microscopy (SEM, JSM-35CF, JEOL). Measurement of the storage modulus (G') as a function of the temperature was made by a dynamic mechanical thermal analyzer (Rheometric Scientific, ARES) in the single cantilever bending mode at a strain of 10% with a temperature increase of $2^\circ\text{C}/\text{min}$. DSC (Perkin-Elmer, DSC-7) was used to check whether the crystallinity of the continuous PET phase in the HDPE/PET (or HDPE-*g*-BHI/PET) blends changes at the same composition. The heating scan up to 280°C was followed by a cooling scan down to 50°C at $10^\circ\text{C}/\text{min}$ scanning rates. Two minutes were allowed between the heating and cooling scans. All the specimens for tensile testing and dynamic mechanical analysis were prepared by injection molding (Toshiba, IS-60B) at 260°C with a mold temperature of 80°C . Tensile properties (Ushima, TS 201) were measured following the procedures described in ASTM D638.

RESULTS AND DISCUSSION

Preparation and Characterization of BHI

Scheme 1 represents probable reaction procedure and molecular structure of BHI. HI has monourethane linkage because the OH group of HEMA reacts with either of the two NCO groups in IPDI. Since the secondary NCO group of IPDI has a



Scheme 1 Reaction procedure and molecular structure of BHI.

higher reactivity than that of the primary NCO group of IPDI,¹⁹ HI has one major form (1-S) and another minor form (1-P). After one of the two NCO groups in IPDI, mainly secondary, reacts with the OH group in HEMA, the remaining NCO group in IPDI will react with NH group in CPL at a higher temperature (80°C) because of very low reactivity stemming from a very mild activating effect of the urethane group.²³ Consequently, BHI comprises two types of molecules, that is, major (2-S) and minor (2-P) types.

Figure 1 shows three FTIR spectra of HI reacting with CPL as a function of reaction times. The absorption peak at 2270 cm^{-1} (NCO) disappeared in 8 h, indicating that the remaining NCO groups of HI were completely blocked by CPL [Fig. 1(c)]. Absorption spectra showed that most of the remaining NCO groups in HI are blocked in the first 4 h [Fig. 1(b)].

Grafting Reaction

FTIR spectra of HDPE and HDPE-*g*-BHI are shown in Figure 2. HDPE-*g*-BHI exhibits three peaks that are not found in pure HDPE. These new absorption peaks are attributed to the grafting of BHI onto HDPE. The absorption peak at 1730 cm^{-1} corresponds to the carbonyl stretching of the methacrylic ester of HEMA, while the absorption peak at 1650 cm^{-1} is due to that of the amide group, resulting from the reaction of HI with CPL. On the other hand, the absorption peak at 3400 cm^{-1} corresponds to the NH stretching vibration of the urethane or amide bond in BHI grafted onto HDPE.

Blend Morphology

HDPE/PET blend produces two-phase materials because of their chemical incompatibility. We ex-

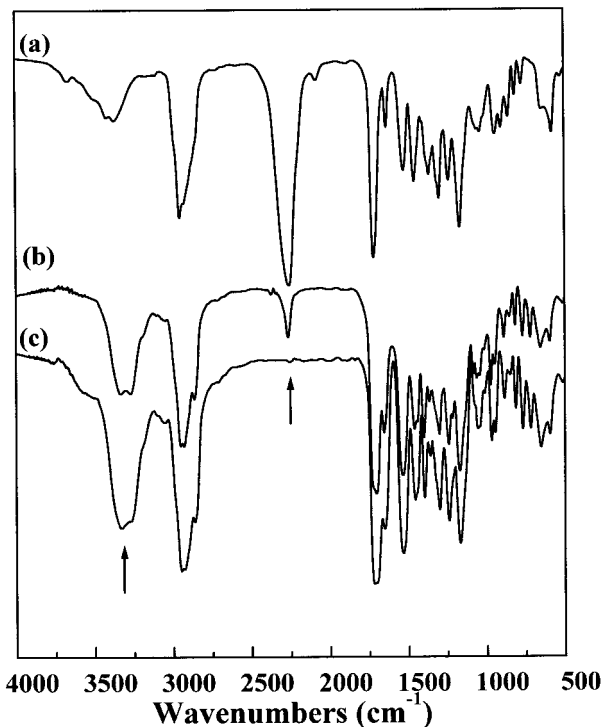


Figure 1 FTIR spectra of HI reacting with CPL as a function of reaction times: (a) 0 h; (b) 4 h; (c) 8 h.

pect that the reactive compatibilized HDPE-*g*-BHI/PET blend shows a reduction in interfacial tension between the two phases, resulting in finer particle sizes of the dispersed phase.²⁴ The cryogenically fractured surfaces of the HDPE/PET and HDPE-*g*-BHI/PET blends at various compositions are represented in Figures 3 and 4, respectively. It is generally known that, in an HDPE-rich blend (by volume), PET forms the dispersed phase in the continuous HDPE phase and vice versa. In other words, the volume fraction of each polymer in the blend appears to play an important role in determining which of the two components forms the continuous phase or the dispersed phase. When the weight ratios of the HDPE/PET blends are 90/10 and 50/50, the dispersed phase is PET and the matrix is HDPE [Fig. 3(a, b)]. The reverse is true for the HDPE/PET blends prepared in the weight ratio of 30/70 and 10/90 [Fig. 3(c, d)]. For the HDPE/PET blends (see Fig. 3), the presence of holes on the matrix formed by the pullout of particles indicates that there is little adhesion between the continuous and the dispersed phases. On the other hand, the HDPE-*g*-BHI/PET blends have little holes, indicating increase in the adhesion between two phases (see Fig. 4). Also, the HDPE-*g*-BHI/PET

blends show that sizes of the dispersed phase are noticeably reduced, and the morphology is relatively homogeneous at all blend compositions, compared to the HDPE/PET blends. The sizes of the dispersed phases of HDPE/PET blends range from 3.5 to 60 μm in diameter depending upon the blend compositions, while those of the HDPE-*g*-BHI/PET blends are below 17 μm . During the melt blending, the deblocking reaction of BHI grafted onto HDPE occurs and regenerates the isocyanate groups and the blocking agents (CPL). The regenerated isocyanate groups can react with the carboxyl and hydroxyl end groups of PET. These reactions make up the chemical linkage between HDPE-*g*-BHI and PET, resulting in graft copolymers that act as *in situ* compatibilizers during the melt blending. These *in situ*-formed compatibilizers locate at the interfaces and decrease the interfacial tension between the incompatible phases. The lowering of interfacial tension reduces the sizes of dispersed phases in HDPE-*g*-BHI/PET blends.

Thermal Analysis

To examine the crystallinity of the continuous PET phase in HDPE/PET and HDPE-*g*-BHI/PET

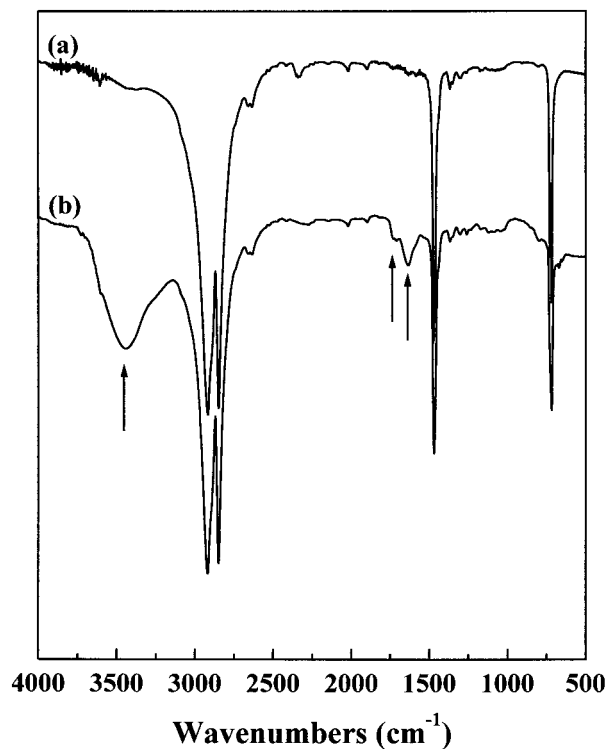


Figure 2 FTIR spectra of (a) HDPE and (b) HDPE-*g*-BHI.

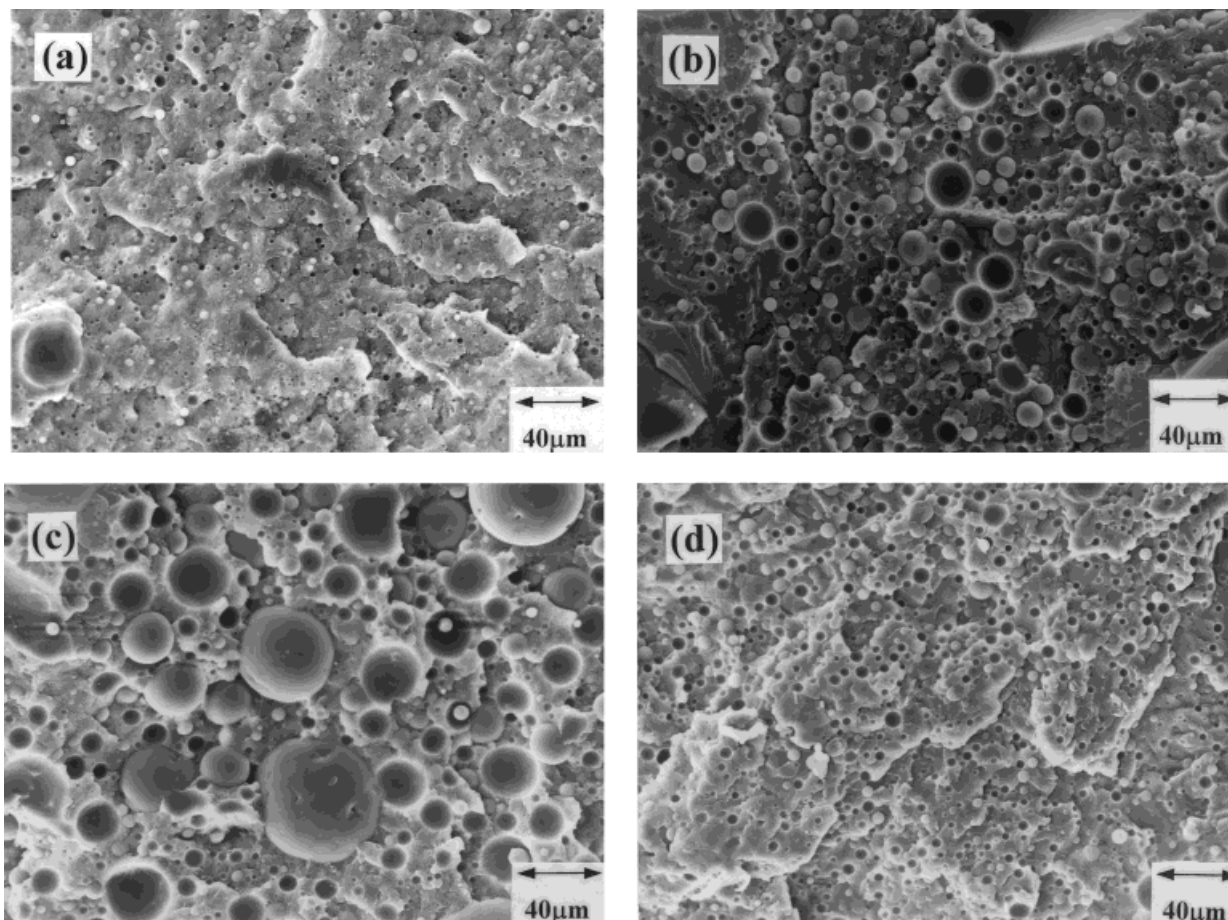


Figure 3 SEM micrographs of the (a) 90/10, (b) 50/50, (c) 30/70, and (d) 10/90 HDPE/PET blends.

blends, Table I gives the DSC thermogram results for the 30/70 and 10/90 blend compositions in the heating and cooling runs. There appears to be little difference in the endothermic heat by PET melting and the exothermic heat by PET crystallization at the same composition. These results indicate that the crystallinity of the continuous PET phase in the HDPE/PET blends remains unchanged regardless of the reactive compatibilization of the blocked isocyanate group grafted onto HDPE.

Figure 5 shows the results of dynamic mechanical analysis for the 30/70 and 10/90 HDPE (or HDPE-*g*-BHI)/PET blends in the temperature range from 35 to 170°C. The HDPE-*g*-BHI/PET blends show a greater storage modulus (G') than that of the HDPE/PET blends at the same composition. This result can be interpreted as due to the *in situ* graft copolymer formed by a chemical reaction between regenerated isocyanate groups in HDPE-*g*-BHI and carboxyl (and hydroxyl) end

groups in PET.²⁴ It is noteworthy that this increase in G' for the HDPE-*g*-BHI/PET blends is not due to a change in crystallinity of the continuous PET phase (cf. Table I).

Tensile Properties

For an immiscible polymer blend, its resulting morphology induces low mechanical properties compared to either of the pure components. Immiscible HDPE/PET blends also have poor mechanical properties, particularly near the inversion of the phases. Compatibilization of these blends is therefore necessary to improve their mechanical properties. Figure 6 shows the tensile strengths of HDPE/PET and HDPE-*g*-BHI/PET blends plotted as a function of the weight ratio of PET. In the HDPE-rich blend, the tensile strength of the HDPE/PET blends decreases with increase of the weight ratio of PET due to little or no adhesion between the continuous phase

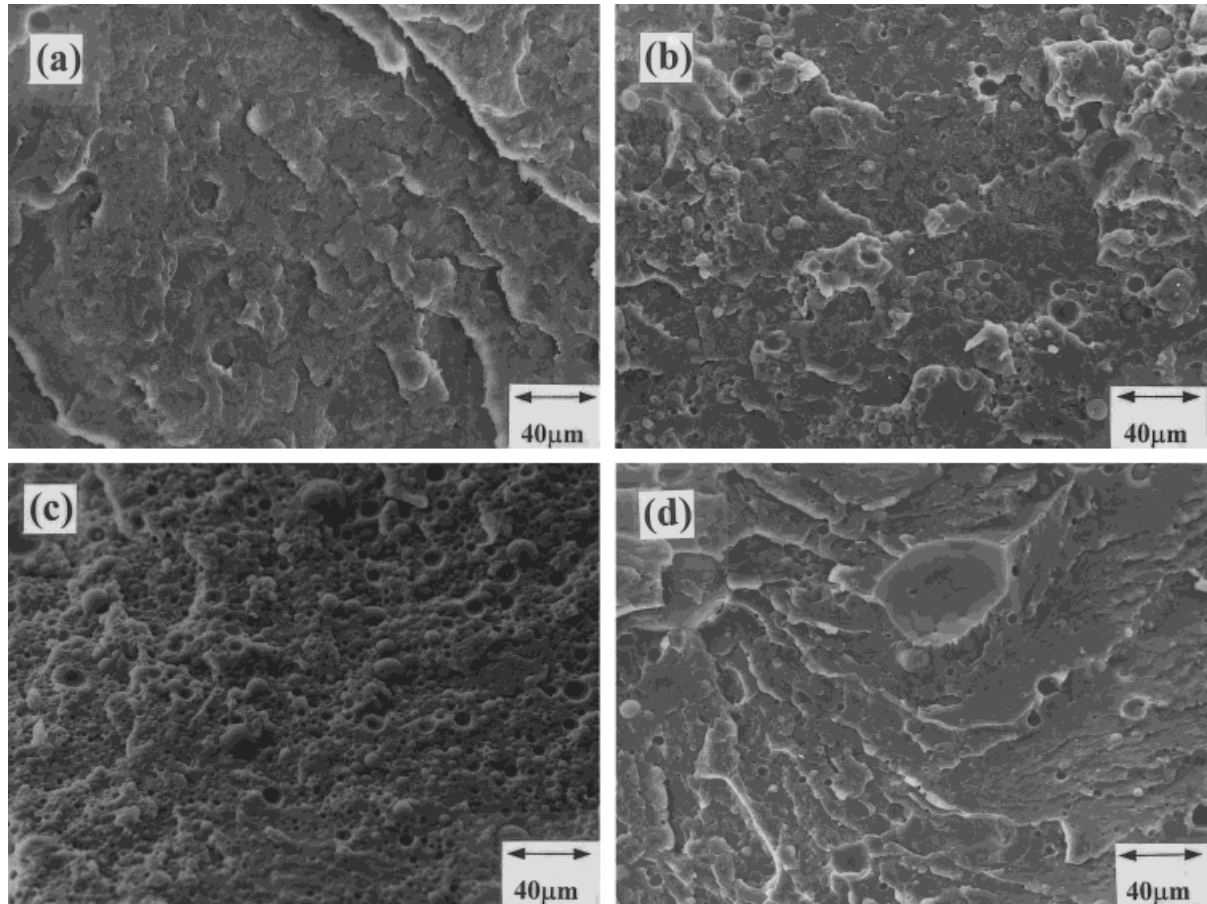


Figure 4 SEM micrographs of the (a) 90/10, (b) 50/50, (c) 30/70, and (d) 10/90 HDPE-*g*-BHI/PET blends.

(HDPE) and the dispersed phase (PET). In case of the HDPE-*g*-BHI/PET blend, however, the tensile strength slightly increases with increase of the weight ratio of PET, indicating that adhesion between the two phases increases by the formation of an *in situ* graft copolymer. Although HDPE/

PET and HDPE-*g*-BHI/PET blends show a lower tensile strength than that of pure PET and the HDPE sample, HDPE-*g*-BHI/PET blends exhibit greater tensile strengths than those of the HDPE/PET blends at all compositions. When the weight ratio of HDPE/PET and HDPE-*g*-BHI/PET is 30/70, the difference of tensile strength between these two blends is greater than that of any other compositions. This greatest difference of tensile strength can be explained in terms of the improved compatibility of HDPE-*g*-BHI/PET, owing to the *in situ* compatibilization.

Elongation at break is very sensitive to the adhesion strength of the blend components and generally used to evaluate the degree of compatibilization in a polymer alloy. The elongation at break is represented in Figure 7 as a function of blend compositions. HDPE/PET and HDPE-*g*-BHI/PET blends show lower elongation at break than that of pure HDPE and PET samples at all blend compositions. However, elongations of

Table I DSC Results for the HDPE/PET and HDPE-*g*-BHI/PET Blends

	30/70	10/90
Crystalline melting endotherms (J/g) (heating run)		
HDPE/PET	29.80	39.54
HDPE- <i>g</i> -BHI/PET	30.26	39.00
Crystallization exotherms (J/g) (cooling run)		
HDPE/PET	26.56	37.20
HDPE- <i>g</i> -BHI/PET	25.85	38.09

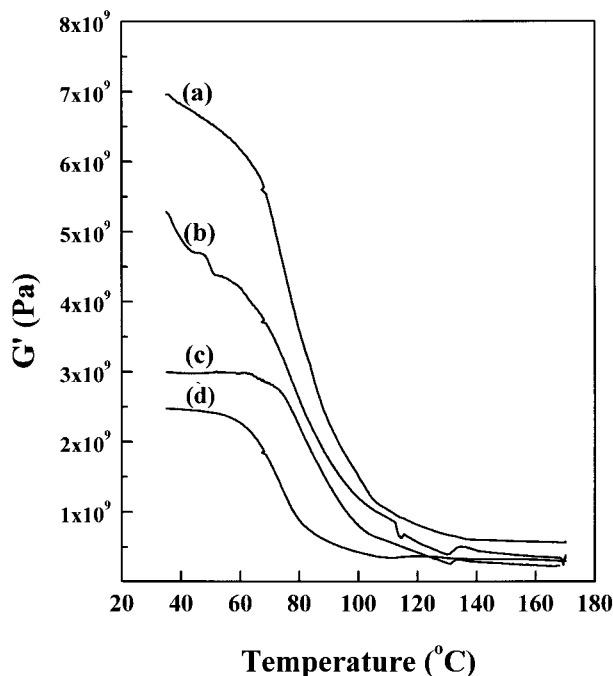


Figure 5 Temperature dependence of storage modulus (G'): (a) 10/90 HDPE-*g*-BHI/PET; (b) 10/90 HDPE/PET; (c) 30/70 HDPE-*g*-BHI/PET; (d) 30/70 HDPE/PET blend.

HDPE-*g*-BHI/PET blends are greater than those of HDPE/PET blends at all compositions, indicating that interfacial adhesion is increased by *in*

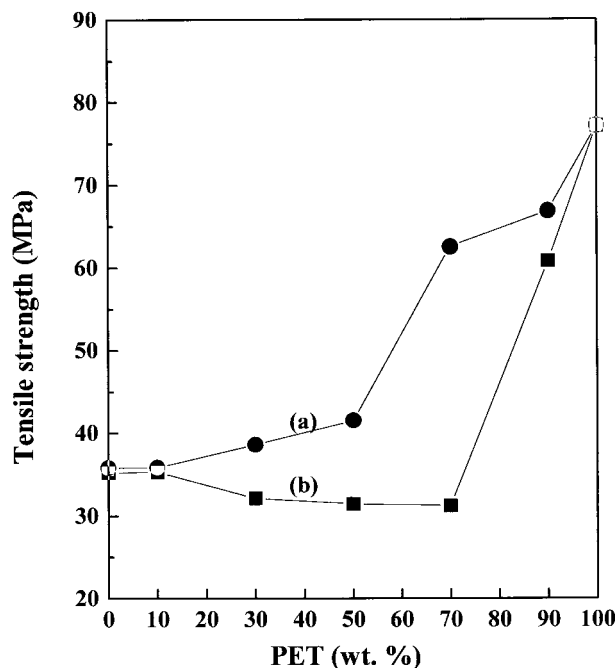


Figure 6 Tensile strengths of (a) HDPE-*g*-BHI/PET and (b) HDPE/PET blends.

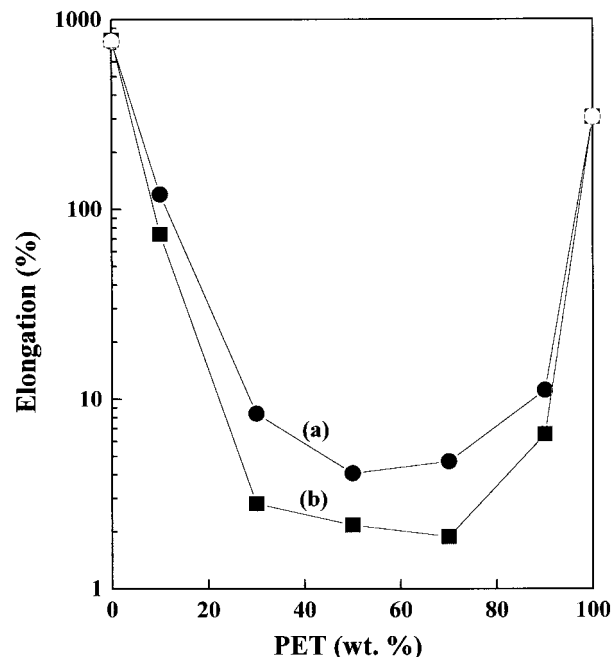


Figure 7 Elongations at break of (a) HDPE-*g*-BHI/PET and (b) HDPE/PET blends.

situ-formed graft copolymers, which prevent coalescence of the dispersed phase and enhance interfacial adhesion between the two phases.^{25,26} The HDPE (or HDPE-*g*-BHI)/PET blends show some toughness at the 90/10 blend composition due to a dominant ductile HDPE or HDPE-*g*-BHI continuous phase.

CONCLUSIONS

This work showed the possibility to compatibilize an immiscible HDPE/PET blend by introducing blocked isocyanate groups onto HDPE. During the melt blending, the chemical reaction between the regenerated isocyanate group and carboxyl (and hydroxyl) end groups of PET occurred. An *in situ*-formed graft copolymer reduced interfacial tension and increased interfacial adhesion between the two phases. SEM micrographs of cryogenically fractured surfaces in HDPE-*g*-BHI/PET blends exhibited that HDPE-*g*-BHI/PET blends had a much finer dispersion of the dispersed phase than that of HDPE/PET due to decrease of the interfacial tension between the continuous and dispersed phases. The storage modulus of compatibilized blends where PET was the matrix was greater than that of immiscible HDPE/PET blends due to the formation of an *in situ* graft

copolymer. The tensile properties of reactive compatibilized blends showed higher values than those of incompatibilized blends due to increase in the interfacial adhesion.

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