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RELATIONSHIP BETWEEN INTERFACIAL REACTION AND BULK PROPERTIES OF PET/FUNCTIONALIZED HDPE BLENDS

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RELATIONSHIP BETWEEN INTERFACIAL REACTION AND BULK PROPERTIES OF PET/FUNCTIONALIZED HDPE BLENDS

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ABSTRACT

High-density polyethylene (HDPE) grafted with blocked isocyanate group (BHI) was blended with polyethylene terephthalate (PET) to observe the relationship between interfacial chemical reaction and bulk properties of the blends. BHI was prepared by reacting ε-caprolactam (CPL) with hydroxyethyl methacrylate-isophorone diisocyanate (HI). Atomic force microscopy (AFM) analysis was used to confirm the interfacial chemical reaction of isocyanate (NCO) groups in the functionalized HDPE (HDPE-g-BHI) with carboxylic acid and hydroxyl end groups in PET after annealing. Interfacial topologies and mean roughness

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were observed. Morphological changes of the blends were observed by scanning electron microscopy (SEM) photographs. Measurements of elongation property and dynamic mechanical analysis (DMA) of the blends were also done.

INTRODUCTION

There has been an interesting way to produce improved materials through blending of commercially available polymers rather than synthesis of new polymers. Polymer blending has become an important field in polymer technologies. However, it is very difficult to obtain good phase dispersions in polymer blends due to their inherent low entropy of mixing in long chain molecules. This incompatibility often results in blends having a microscopically phase-separated structure and poor bulk properties. One of the useful methods to overcome these problems are to use compatibilizing agents, which decrease interfacial tension and increase interfacial adhesion [1-6].

There are two routes to compatibilize immiscible polymer blends: physically or chemically reactive compatibilization. In reactive compatibilization, the addition of functionalized polymer, miscible with one blend component and reactive toward the other blend component, leads to the *in situ*-formed graft copolymer [7-10]. Although reactive compatibilization has attracted great attention recently because of its effectiveness and cost efficiency, there has been limited study of the relationship between interfacial chemical reaction and bulk properties when functionalized polymers appear in immiscible polymer blends [11-13]. Recently, several studies related to polymer interfaces and interfacial topology have been reported [14-16].

Most widely used functional groups for the functionalization of polyolefins were carboxylic acid [17, 18], acid anhydride [19, 20], epoxy [21, 22], oxazoline [23, 24], and isocyanate (NCO) groups that could react with hydroxyl, carboxyl or amine groups of various thermoplastic resins. Particularly, in our previous studies [25-29], isocyanate functionalized polyolefins were prepared by grafting HI onto PE. In this study, we synthesized BHI by the reaction of HI with CPL. As a reactive polymer, the BHI functionalized HDPE (HDPE-g-BHI) was prepared with varying amounts of relative degree of grafting. We blended HDPE-g-BHI (or HDPE) with polyethylene terephthalate (PET) [30, 31]. Atomic force microscopy (AFM) was used to examine interfacial chemical reaction between PET and HDPE-g-BHI films, which results in the formation of *in* *situ* graft copolymer (HDPE-g-PET). Bulk properties of the blends were discussed using morphological, elongation, and dynamic mechanical properties to confirm the influence of *in situ* copolymer on the interface between two polymers.

EXPERIMENTAL

Materials

HDPE (Samsung J820A, melt flow index = 7.5 g/10 min) was used as received. PET (a bottle grade having end group concentrations of 42.5 mol/1000 kg OH and 29.2 mol/1000 kg COOH), supplied by SK Chemicals, was used after drying in vacuum at 120°C for 48 hours. Dicumyl peroxide (DCP, Aldrich Chemical) as a radical initiator was of reagent grade and was used without further purification. BHI was prepared by a continuous two-step reaction in N_2 inlet. HI was first synthesized by the reaction of 2-hydroxyethyl methacrylate (HEMA, Junsei Chemical) and isophorone diisocyanate (IPDI, Aldrich Chemical) at the molar ratio of 0.95:1 [25]. Secondly, synthesized HI and ε-caprolactam (CPL, Aldrich Chemical) were mixed with a molar ratio of 0.95:1. After the addition of hydroquinone (Kanto Chemical Co.), the mixtures were heated to 80°C to block remaining isocyanate groups of HI. The reaction continued for 8 hours.

Graft Copolymerization

20 g of HDPE were dissolved in xylene solution (160 g) at 120°C in a reaction vessel equipped with a N_2 inlet and agitation. When HDPE completely dissolved, varying amounts of BHI (2, 4, 6, 8, or 10 g) were added to the reaction vessel together with solution prepared by dissolving 0.2 g of DCP in 40 g of xylene. After 3 hours, the reaction was stopped and the mixtures were cooled, precipitated in acetone, repeatedly washed with acetone, and dried in a vacuum oven for 48 hours at 40°C.

Characterization

Reaction procedures of HI and CPL were confirmed by Fourier-transform infrared spectroscopy (FT-IR, Nicolet, model Mahgna IR-550). The graft copolymerizaton of BHI onto HDPE was characterized by nuclear magnetic resonance (NMR, Varian, model Unity Inova NMR300) analysis. Relative grafting

TABLE 1. The Standard Recipe and Relative Degree of Grafting Ratio for HDPE-g-BHI

HB	HDPE	Xylene (*g*)	BHI (*g*)	Dicumyl Peroxide (*g*)	Relative Degree of Grafting (%)
HB-0	20	0	0	0	0
HB-1	20	200	2	0.2	0.4
HB-2	20	200	4	0.2	0.63
HB-3	20	200	6	0.2	1.57
HB-4	20	200	8	0.2	2.43
HB-5	20	200	10	0.2	2.78

extents of BHI onto HDPE were measured by FT-IR spectra. The peak height ratios of the C=O peak at 1730 cm^{-1} to that for the CH_3 peak at 1340 cm^{-1} were used to obtain a relative degree of graft copolymerizaion [32-34]. All recipes and relative grafting extents of BHI onto HDPE were summarized in Table 1.

Atomic Force Microscopy

Surface topologies and mean roughness were examined with AFM (PSI, Autoprobe CP). AFM specimens were consisted of two layered films, i.e., PET and HB series films. To begin with, the PET film was cast from a cosolvent consisting of phenol and tetrachloroethane (50/50 v/v). HB series films were cast from toluene solvent at 120°C. After placing the HB series film on the top of PET film, these two layered films were annealed at 200°C under vacuum for 15 minutes, then immersed in xylene at 120°C to dissolve unreacted HDPE-g-BHI. The surfaces of these samples were imaged by AFM in contact mode with the tip (diameter, 10 nm). In contact with the sample surface, a short repulsive force was probed. In addition, the cantilever had 0.4 nm of spring constant oscillated at its proper frequency (45kHz).

Melt Blending

All blends were prepared on an internal mixer (Haake, Rheocorder 900) with a rotational speed of 90 rpm. After PET was mixed with HB series at 270°C for 5 minutes, the blends cooled slowly at room temperature. The weight ratio of PET/HB series is 70/30.

Scanning Electron Microscopy

Morphologies of the blends were observed by scanning electron microscopy (SEM, JEOL JSM-35CF). SEM micrographs were taken from cryogenically fractured (in liquid nitrogen) surfaces of the blends that were coated with gold before viewing.

Elongation Property

Tensile stress-strain properties were obtained at room temperature with a Instron machine (Ueshima, TS 201) following the procedures described in ASTM D638. All the specimens for testing were prepared at 270°C with a mold temperature of 80°C, using a Mini Max molder (SC-183, MMX, Custom Scientific Instruments, Inc.).

Dynamic Mechanical Properties

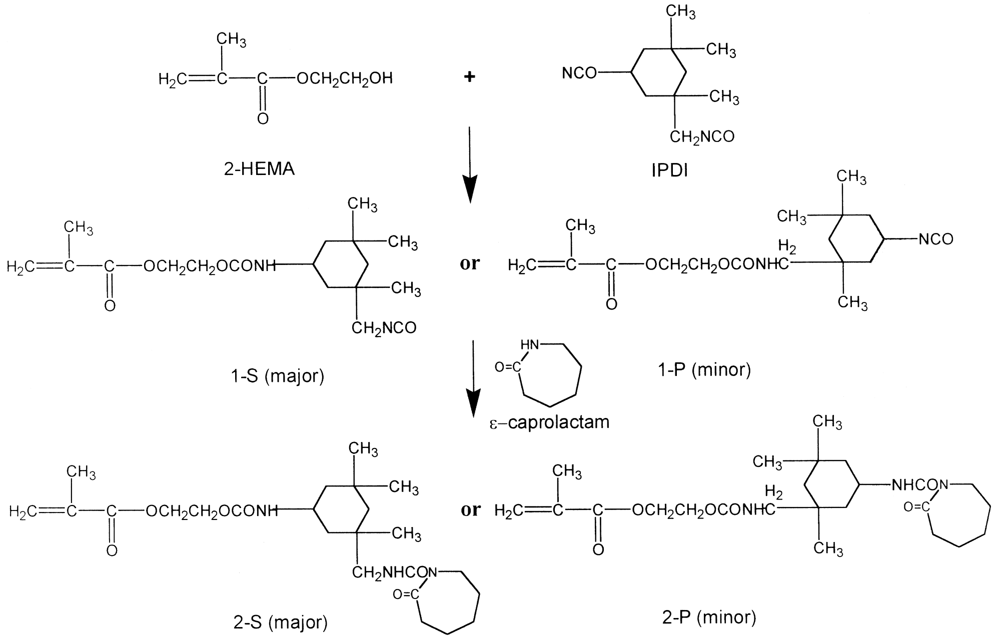
Measurements of dynamic loss and dynamic storage moduli were performed by a Dynamic Mechanical Thermal Analyzer (model MK-II, Polymer Laboratories, UK) in shear mode. The temperature ranges were from 30 to 180°C. Dynamic mechanical properties were measured at every 5°C with increasing temperature.

RESULTS AND DISCUSSION

Preparation and Characterization of BHI

Scheme 1 represents reaction procedures and schematic 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 does have higher reactivity than the primary NCO group of IPDI [35, 36], HI has one major form (1-S) and the other minor form (1-P). After one of two NCO groups in IPDI, mainly secondary, reacts with the OH group in HEMA, the remaining NCO group in IPDI will react with the NH group in CPL at higher temperature (80°C) because of very low reactivity which stemmed from a very mild activating effect of the urethane group [37]. Consequently, BHI is comprised of two types of molecules, that is, major (2-S) and minor (2-P) types.

Figure 1 shows three FT-IR spectra of HI reacting with CPL as a function of reaction times. The absorption peak at 2270 cm^{-1} (NCO) disappeared in 8



Scheme 1. The reaction procedures and molecular structure of BHI.

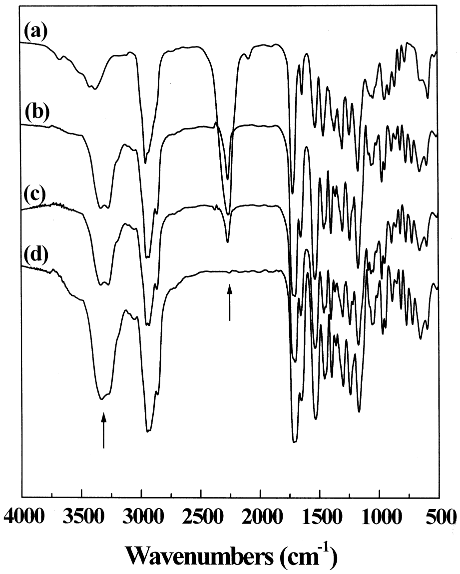


Figure 1. FT-IR spectra of HI reacting with CPL as a function of reaction times: (a) 0 hours, (b) 2 hours, (c) 4 hours and (d) 8 hours.

hours, indicating the remaining NCO groups of HI are completely blocked by CPL (Figure 1 (d)). Absorption spectra show that most of the remaining NCO groups in HI are blocked in the first 4 hours (Figure 1 (c)).

Graft Copolymerization

^{1}H-NMR spectroscopy of HB-2 in toluene-d_8 solution is used to confirm graft copolymerization of BHI onto HDPE as shown in Figure 2. Arrows indicate the peaks that are not observed in the corresponding spectrum of the unfunctionalized HDPE. The resonance of two protons on carbon attached to the oxygen of BHI appears at 4.2-4.3 ppm (a). The resonance of NH produces absorbencies at 5.9-6.05 ppm (b). The ^{1}H-NMR spectrum of BHI also shows resonance at 2.8 ppm (c) and 2.4 ppm (d) assigned to two protons on carbon attached to the nitrogen and two protons on carbon attached to the carbonyl group, respectively.

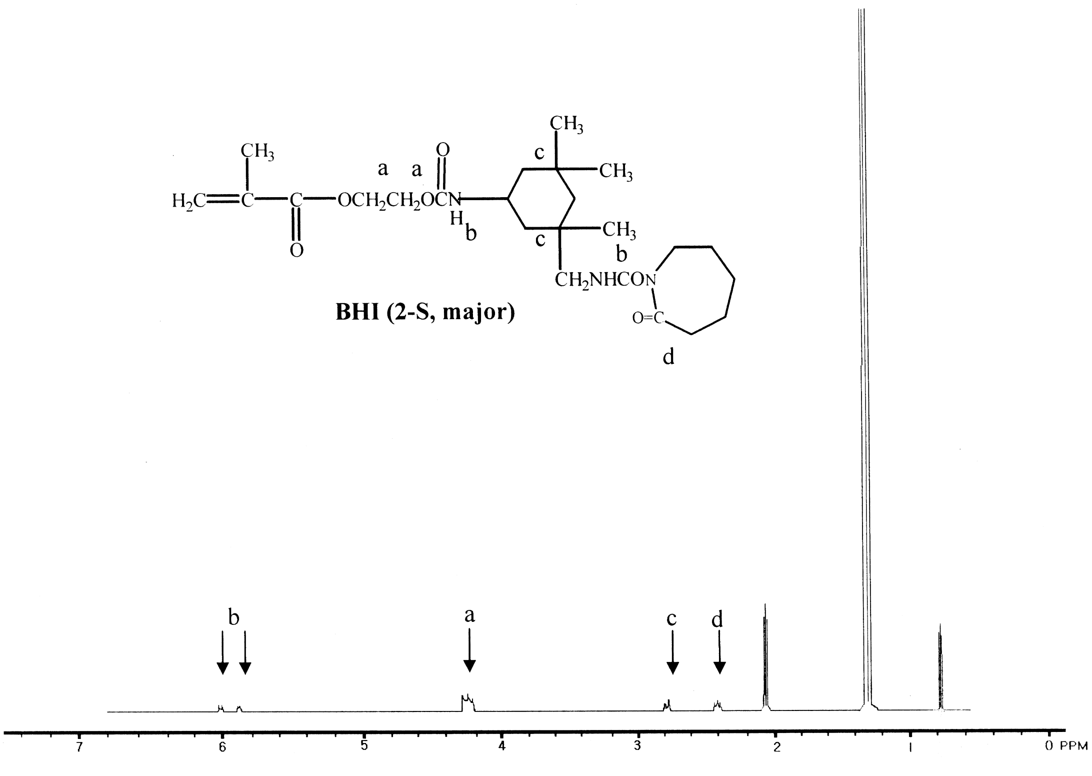
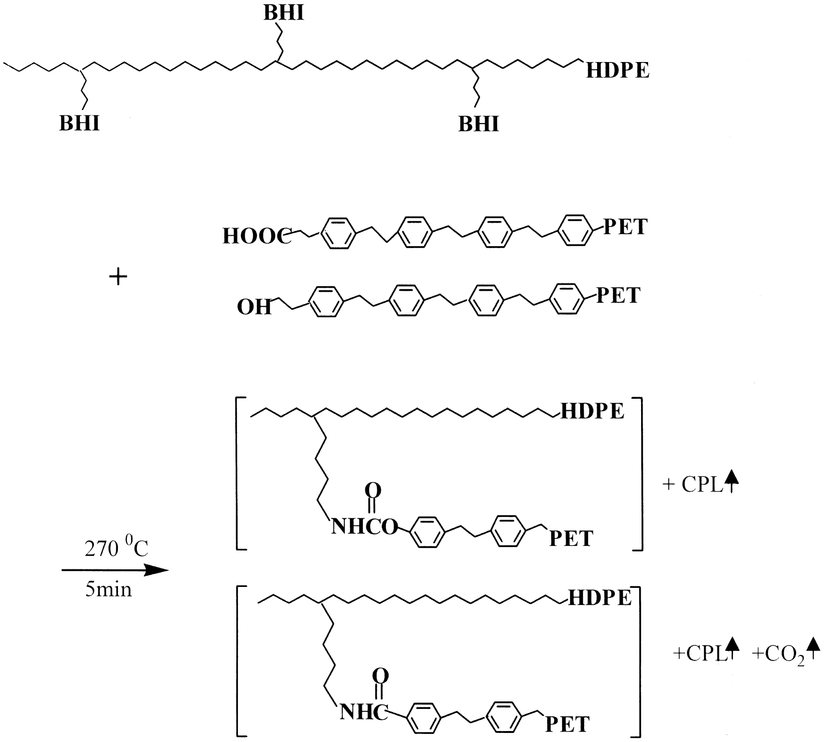


Figure 2. ^{1}H-NMR spectrum of HB-2.

Surface Property

Scheme 2 illustrates the probable graft copolymerization of the HB series with PET and the formation of *in situ* graft copolymers. Since blocked isocyanate groups of HB series can regenerate reactive isocyanate groups above 200°C [30], NCO groups of HDPE-g-BHI will react with the hydroxyl and carboxyl end groups of PET during melt blending. Such a reaction leads to the formation of *in situ* copolymers.

The formation of *in situ* graft copolymers has been mainly characterized by FT-IR analysis and a molau test [38, 39]. In this work, AFM analysis is used to confirm the chemical reaction of COOH and OH end groups of PET with NCO groups of HB series after annealing. In Figures 3 and 4, 3-Dimensional AFM images show the changes of topologies and roughness between two polymer films. As seen in Figure 3 (a), PET/HB-0 film, where there is no interfacial chemical reaction, has a relatively smooth surface. On the other hand, the topolo-



Scheme 2. Schematic representation of *in situ* graft copolymerization between NCO groups of HDPE-g-BHI and end groups of PET.

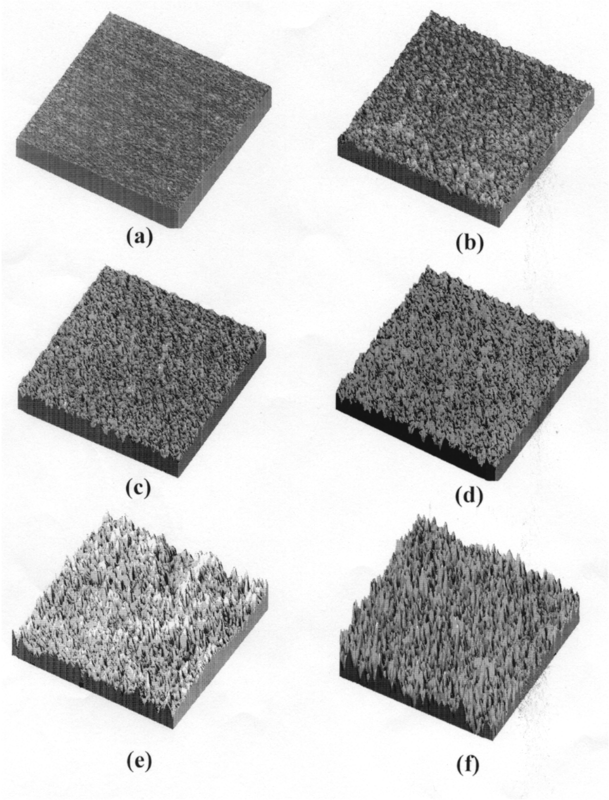


Figure 3. Interfacial topographies between PET and HB series films: (a) HB-0; (b) HB-1; (c) HB-2; (d) HB-3; (e) HB-4; (f) HB-5.

gies of the other samples show rougher interface than that of PET/HB-0 film. Lyu *et al.* observed interfacial roughening in a system of amine terminated PS and anhydride terminated polymethyl methacrylate. They suggested that interfacial curvature induced by thermal fluctuations stimulated the formation of block copolymer, eventually forming a rough interface [16]. From this point of view, results of AFM images can be explained in terms of chemical reaction between PET and HB series during annealing and formation of *in si*tu graft copolymers.

Figure 4 shows the mean roughness of interface of PET/HB series films. As the contents of BHI grafts increase, the mean roughness at interface also increase. This result may be due to the increase of reactive site between two polymers. The increase of the reactive site results in sufficient formation of *in situ* copolymers and rough surface.

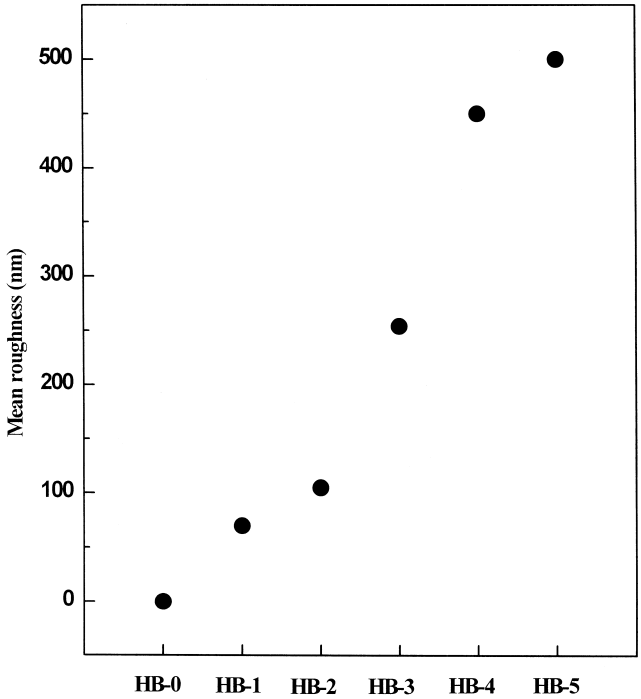


Figure 4. The changes of mean roughness between PET and HB series films after annealing.

Morphology

Morphologies of cryofractured PET/HB series blends were examined in Figure 5. Since the blend volume determines which of the two components forms the dispersed phases and which the matrix phase, in PET-rich blends HB series is the dispersed phase. The blend of PET/HB-0 is comprised of a PET matrix where spherical HDPE particles are embedded (Figure 5 (a)). The surface hole resulting from the fracture appears to be very smooth, indicating low interfacial adhesion in the incompatibilized PET/HB-0 blend and small contact areas with the matrix. From SEM micrographs of the other blends, it is clear that HDPE-g-BHI has been finely dispersed and anchored onto the matrix PET phase. Moreover, it is difficult to find any phase separation between the two polymers (Figure 5 (a) and (b)).

Elongation Property

Generally, elongations are properties that reflect toughness and effectiveness of the compatibilizer [40]. Table 2 shows elongation properties of

PET/HB series blends, when the weight ratio of PET/HB series is 70/30. Elongations of the blends increase with the increase of BHI grafts in HB series, indicating that adhesion between two polymers increases by the formation of *in situ* graft copolymer. And then, elongations level off above critical concentration. Fredrickson *et al.* showed that an increase of *in situ* copolymer coverage with reaction time which resulted in an increase of an energy barrier to the diffusion of homopolymer through interface [41]. From this viewpoint, when the relative degree of grafting ratio of HDPE-g-BHI is too high, *in situ* copolymer having very large molecular weight or even crosslinked copolymer can be formed. The excessively grafted *in situ* copolymers tend to restrain the diffusion of polymers, which result in limited compatibilizing effects of HDPE-g-BHI in the blends.

Dynamic Mechanical Property

The dynamic mechanical behaviors are shown in Figures 6 and 7 to study the interactions between PET and HB series. The loss modulus (G”) versus temperature from the DMA of the PET/HB series blends illustrated in Figure 7. G” of PET and HDPE homopolymer is also measured to compare with the other blends. G” curves of the blends exhibit combined transition peaks. The combined peaks are so broad that we cannot determine their shift with PET/HB series. However, an increase of BHI contents in HB series leads to the broadening of combined peaks.

The storage modulus (G′) vs. temperature is given in Figure 7. The PET/HB-0 blend shows the characteristic hump above 100°C due to cold crystallization of PET. At the blends of PET and HB series having high relative degree of grafting of BHI onto HDPE there is a reduction in the crystallization

TABLE 2. Elongation Properties of PET/HB Series Blends

PET/HB Series Blends (70/30)	Elongation at Break (%)
PET/HB-0	1.2
PET/HB-1	3.1
PET/HB-2	4
PET/HB-3	11.7
PET/HB-4	17.5
PET/HB-5	17.9

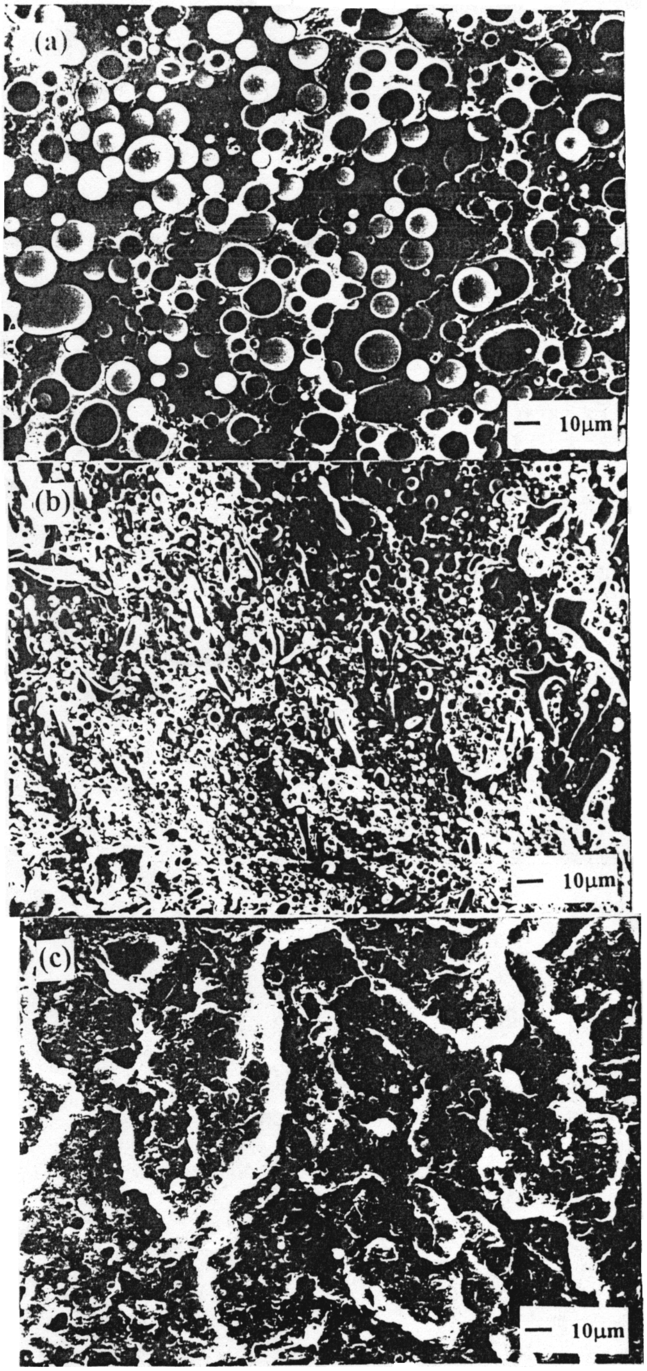


Figure 5. SEM micrographs of the cryofractured PET and HB series blends: (a) HB-0; (b) HB-1; (c) HB-2; (d) HB-3; (e) HB-4; (f) HB-5.

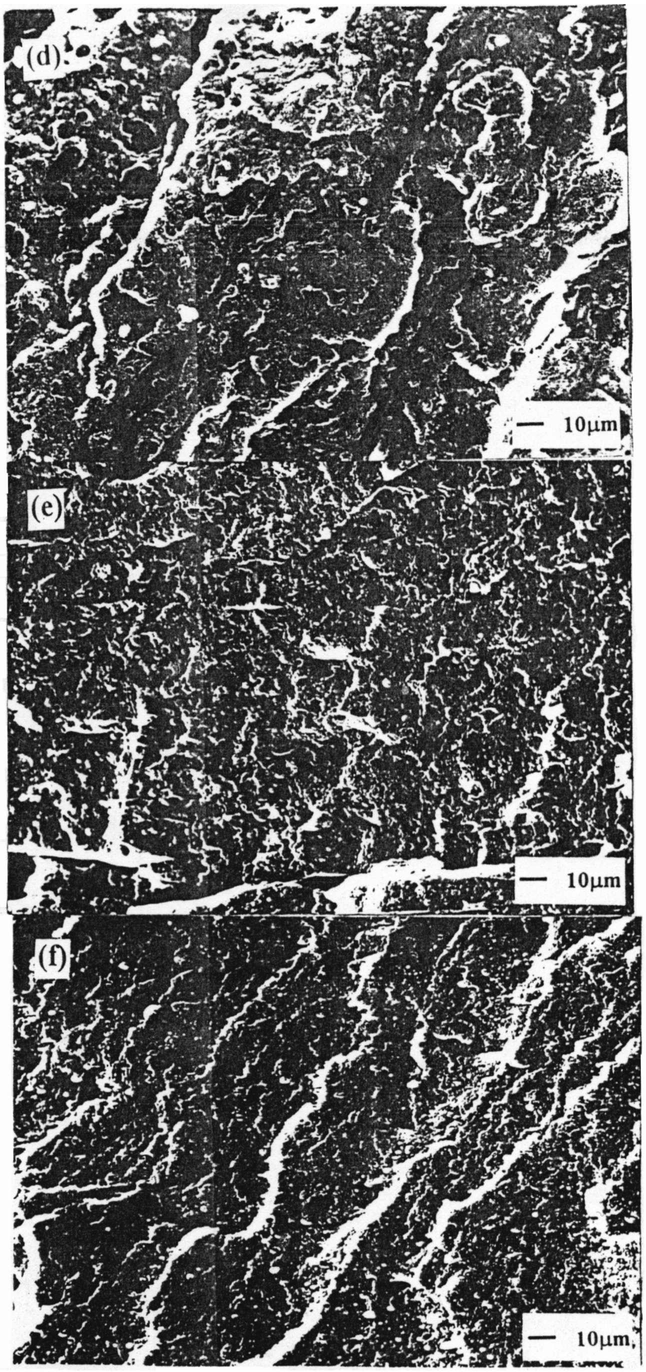


Figure 5. Continued.

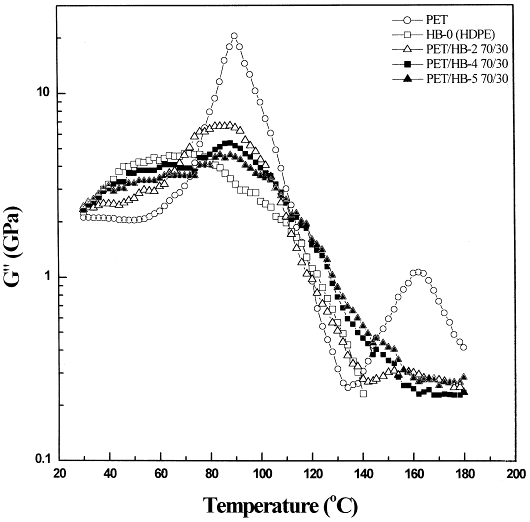


Figure 6. Temperature dependencies of loss modulus (G”) of (a) PET, (b) HB-0, (c) PET/HB-2 blend, (d) PET/HB-4 blend, and (e) PET/HB-5 blend.

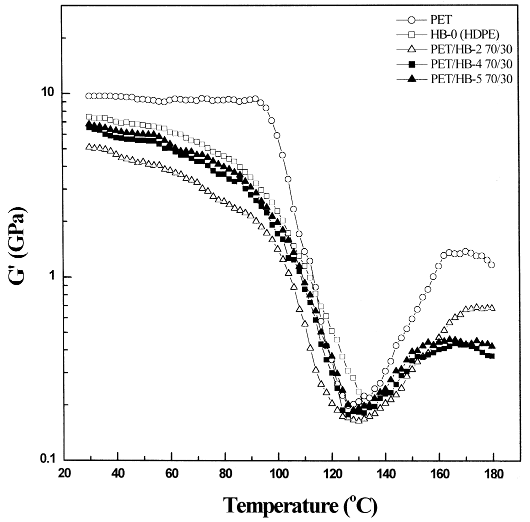


Figure 7. Temperature dependencies of storage modulus (G′) of (a) PET, (b) HB-0, (c) PET/HB-2 blend, (d) PET/HB-4 blend, and (e) PET/HB-5 blend.

hump. The reduction of hump indicates the low level of cold crystallization due to the presence of a chemical reaction between two polymers. The PET/functionalized HDPE blends show a higher value of storage modulus than PET/HB-0 blend. This can be also ascribed to the chemical interaction between the components. Especially, G′ curves of PET/HB-4 and PET/HB-5 blends exhibit almost a similar trend. This result also confirms the results of elongation measurements, which can be explained in terms of the reciprocal relationship between excessive formation of *in situ* copolymer and diffusion rate of polymers to interface.

CONCLUSION

In order to study the role of interfacial chemical reaction in reactive blend system, HDPE-g-BHI having various relative degree of grafting ratio was prepared. HB series were blended with PET. AFM analysis showed interfacial chemical reaction between the reactive group in functionalized HDPE and end groups of PET, observing surface topologies and mean roughness between two films after annealing. With increasing contents of BHI grafts in HDPE, the topologies of PET/functionalized HDPE films show a rougher surface than that of PET/unfunctionalized HDPE film. Also, mean roughness linearly increases due to surface reaction between PET and functionalized HDPE films. Through measurements of elongation and DMA analysis, we can obtain the facts that there are optimum relative degrees of grafting ratios in compatibilizing effect of HDPE-g-BHI. Below optimum ratio, interfacial reaction between two polymers produces *in situ* copolymer that acts as an emulsifying agent in immiscible polymer components. However, over optimum ratio, excessive formation of *in situ* copolymers suppresses the diffusion of polymers through interface.

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