

# Evaluation of Isocyanate Functional Groups as a Reactive Group in the Reactive Compatibilizer

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Received 24 October 2001; accepted 9 September 2002

**ABSTRACT:** Reactive compatibilization of an isocyanate (NCO) functional group as a reactive group was investigated. Five kinds of reactive polymers were prepared through solution graft polymerization of low-density polyethylene (LDPE) copolymerized with acrylic acid (AA), maleic anhydride (MAH), glycidyl methacrylate (GMA), and masked and naked NCO functional monomers and were used as compatibilizers in poly(ethylene terephthalate) (PET)/LDPE and polyamide 6 (Nylon 6)/LDPE blends. The reactivity of the NCO functional group in the reactive blend was evaluated in terms of the blend morphology, adhesive test, mechanical properties, and rheological properties. It

was found that GMA and NCO groups were the most effective compatibilizing agents in the PET/LDPE blends and MAH and NCO groups showed effective compatibilization of the Nylon 6/LDPE blends. We confirmed that the NCO functional group as a reactive group could be used as a universal reactive compatibilizer for PET/LDPE and Nylon 6/LDPE blends. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2622–2629, 2003

**Key words:** blends; compatibilization; functionalization of polymers; graft copolymers

## INTRODUCTION

The manufacturing of blends of commercial polymers is often a faster, more cost-effective means of achieving a desired set of properties than synthesizing a new polymer. But owing to the inherent thermodynamic incompatibility, most polymer blends are immiscible, giving rise to a phase-separated system which is characterized mostly by a coarse and unstable phase morphology and poor interfacial adhesion along the interphases. These problems can be alleviated by the addition of a suitable compatibilizer or interfacial active agent, which reduces the interfacial tension, suppressing the dispersed particle coalescence and improving the interfacial adhesion between immiscible polymers. Recently, to improve the compatibilizing effect, efforts have been directed toward *in situ* compatibilization of immiscible polymer blends by reactive processing.<sup>1–7</sup> Instead of synthesizing compatibilizers as a separated process,<sup>8</sup> they are created during blending through interfacial reactions between selected functional groups.

A reactive compatibilizer provides an effective and cost-efficient route in controlling properties for various immiscible blend systems. A reactive compatibilizer normally has potentially reactive groups inherent

in the backbone or at the chain ends. Compatibilizers have been functionalized with reactive groups, either through copolymerization or by chemical modification of preformed polymers. Until now, the most frequently introduced reactive monomers have been unsaturated carboxylic derivatives, such as maleic and itaconic anhydrides<sup>4,9</sup> and vinylic and acrylic substances containing an epoxy or oxazoline functionality.<sup>10–13</sup> There are a number of commercially available reactive polymers containing either acidic reactive groups such as acrylic acid (AA) and maleic anhydride (MAH) or basic reactive groups such as glycidyl methacrylate (GMA) and oxazoline.

The selection of reactive copolymers containing acid or base functional groups has been limited based on the nature of the counterpolymer in the reactive blend. Dagli et al.<sup>14</sup> and Liu et al.<sup>11</sup> reported that ethylene–GMA copolymers and polypropylene (PP)-*g*-oxazoline copolymers were effective compatibilizers in blends of high-density polyethylene with poly(ethylene terephthalate) (PET) and PP/acrylonitrile-*co*-butadiene-*co*-acrylic acid rubber (NBR) blends. Also, several researchers studied an MAH-functionalized polymer as a compatibilizer for polyamide (nylon).<sup>15,16</sup> Other than the above reactive groups, the isocyanate (NCO) group was suggested in our previous works.<sup>17–20</sup>

In this study, reactive polymers, low-density polyethylene (LDPE) copolymerized with AA, MAH, GMA, and masked and naked NCO functional monomers by solution grafting, were used as compatibilizers in PET/LDPE and Nylon 6/LDPE blends. Also, we

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Contract grant sponsor: Engineering Research Center (ERC) for Advanced Functional Polymers of Korea.

compared the compatibilization effect with the functional group through an interfacial adhesion test, rheological and mechanical properties, and morphologies in the polymer blends. So, the status of the NCO functional group as a reactive group in the compatibilizer was evaluated over the other reactive functional groups in the compatibilizers.

## EXPERIMENTAL

### Materials

The LDPE ( $M_n$  23,800) used in this study was obtained from the Hanhwha Co. (Korea), and Nylon 6 ( $M_n$  17,500) and PET ( $M_n$  28,000), from the Hyosung T&C Co. (Korea). The naked NCO functional monomer (HI) was prepared by the reaction of 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co.) with isophorone diisocyanate (IPDI, Aldrich) and the masked NCO functional monomer (MAC) was synthesized from the reaction of methacryl amide (MAA, Aldrich) with ethyl chloroformate (ECF, Junsei Chemical Co., Japan) as described in the previous literature<sup>17,18</sup> GMA, AA, and MAH were purchased from Junsei.

### Graft copolymerization

The solution grafting of monomers with various functional groups onto the LDPE homopolymer was carried out at 120°C (boiling xylene) using dicumyl peroxide (DCP, Aldrich) as a radical initiator under a nitrogen gas stream. The DCP (1 phr) and functional monomer (30 phr) were added to this homogenized solution and the reaction was continued for 4 h. After the reaction was finished, the reaction mixture was cooled to 80°C and washed with pure xylene several times, precipitated in a large amount of acetone at

room temperature during 12 h to eliminate xylene and unreacted functional monomers and initiator, and, finally, dried in a vacuum.

### Blends

Blends of PET/LDPE and Nylon 6/LDPE containing functionalized LDPE copolymers were prepared at 80/10/10 (wt/wt/wt %). The blending was carried out using an internal mixer (Haake, Rheomix 900) at 260°C, 50 rpm for 5 min. The homopolymer mixtures were vacuum-dried for 48 h at 70°C and the functionalized LDPEs were dried for 1 week at 40°C under a vacuum.

### Blend morphologies

To compare the morphologies of each blend, the surfaces were cryogenically fractured under liquid nitrogen and analyzed using scanning electron microscopy (SEM, JSM-35CF, JEOL). Before scanning, all samples were coated with gold-palladium to reduce any charge buildup on the fracture surface.

### Measurement of adhesive strengths

LDPE, Nylon 6, and PET were molded into film of 0.1-mm thickness using a hot press at 180, 250, and 260°C. The functionalized LDPE films of 10- $\mu$ m thickness were prepared using a hot press at 180°C and then inserted between LDPE and PET or the Nylon 6 film. The assembly was heated at 260°C for 60 s under light pressure. To measure the adhesive strength, a 180°-peel test was performed on an Instron machine at room temperature according to ASTM D903-93. Adhesive strengths were calculated as follows:

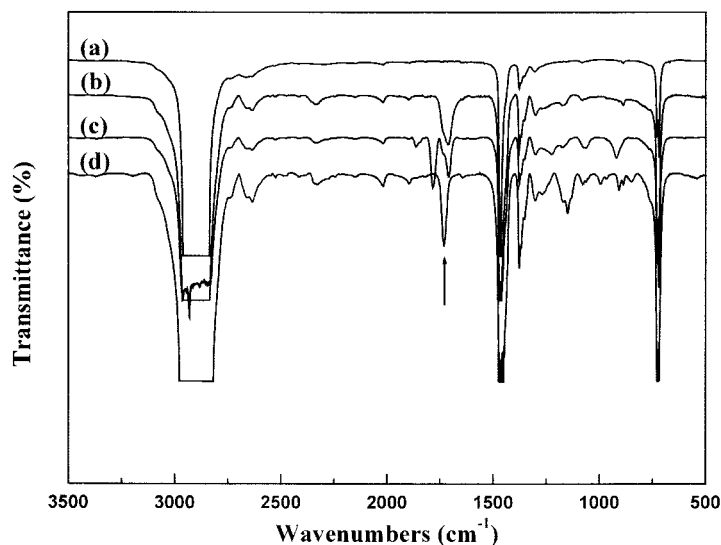


Figure 1 FTIR spectra of (a) virgin LDPE, (b) AA-grafted LDPE, (c) MAH-grafted LDPE, and (d) GMA-grafted LDPE.

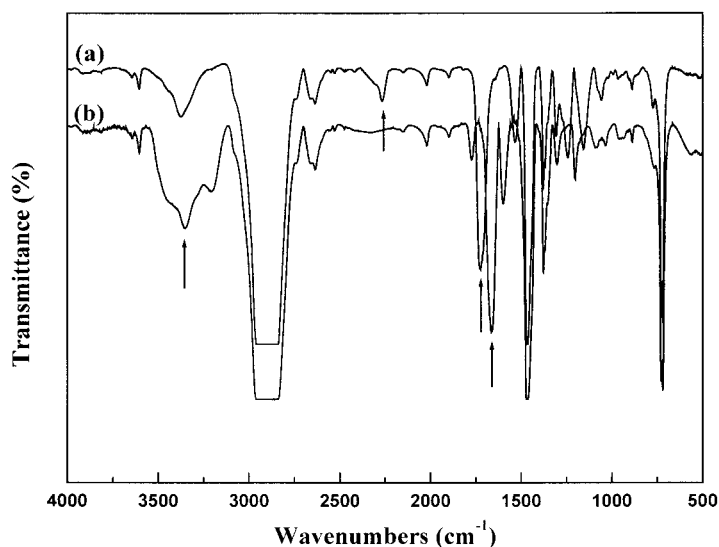


Figure 2 FTIR spectra of (a) HI-grafted LDPE and (b) MAC-grafted LDPE.

$$G_a = \frac{2F}{w} \quad (1)$$

where  $G_a$  is the adhesive strength;  $F$  the peeling force; and  $w$ , the width of the sample. All the measurements were carried out at room temperature and at a 50-mm/min rate.

### Rheological properties

Dynamic rheological properties including the complex viscosity ( $\eta^*$ ) of the reaction products were measured using a rotational rheometer (Rheometric Scientific, ARES), with a 10% strain at 260°C under dry nitrogen. Parallel plates, 25 mm in diameter and a gap of 1 mm, were used for the frequency sweep.

### Mechanical properties

All the specimens for tensile testing were prepared using a Mini Max molder (SC-183 MMX, Custom Scientific Instruments, Inc.) at 265°C with a mold temperature of 120°C. Tensile properties were measured on an Instron machine at room temperature following the procedures described in ASTM D638.

## RESULTS AND DISCUSSION

### Functionalization of LDPE

Figures 1 and 2 show spectra of the virgin LDPE and AA-, MAH-, GMA-, HI-, and MAC-grafted LDPEs measured by Fourier transform infrared spectroscopy (FTIR, Nicolet Model Magna IR-550). The FTIR spectra obtained for AA, MAH, and GMA of the purified grafted LDPEs showed a carbonyl peak at 1730  $\text{cm}^{-1}$ , confirming that the grafting processes were successful

(see Fig. 1). The carbonyl peaks of HI- and MAC-grafted LDPEs also showed carbonyl peaks (1730 and 1680  $\text{cm}^{-1}$ ; see Fig. 2) and were identified as being due to the N=C=O absorption band of the isocyanate group of HI around 2270  $\text{cm}^{-1}$  and the N—H stretching band of HI and MAC around 3300  $\text{cm}^{-1}$ , respectively.

The grafting extent of the reactive monomer was characterized by FTIR spectroscopy analysis. Quantitative analysis of the extent of grafting was performed by our previous method.<sup>18,19</sup> For equivalent functionality blending, each functionalized LDPE was blended with virgin LDPE. All the used functional monomers and the extent of the grafting for the functionalized LDPEs are listed in Table I.

### Blend morphologies

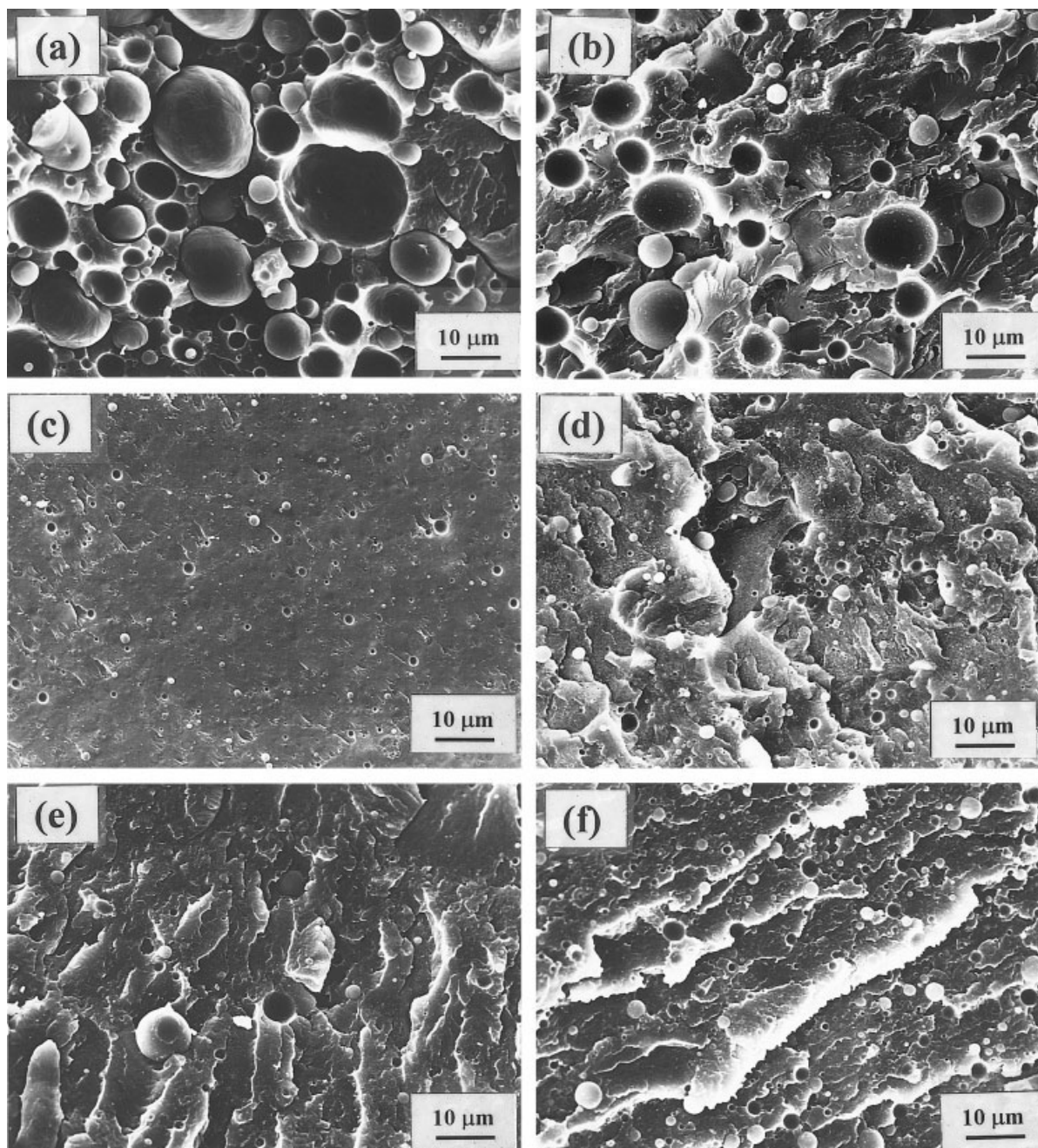
The effect of the different functionalized LDPEs in the PET/LDPE and Nylon 6/LDPE blends was first observed in SEM surface morphologies. Figure 3 shows SEM micrographs of PET/LDPE blends with function-

TABLE I  
Extent of Grafting of Each Monomer onto LDPE

Reactive monomers (phr) <sup>a</sup>	Initiator concentration (phr) <sup>a</sup>	Grafting extent (wt %)	Adjustment of grafting ratio (wt %) <sup>b</sup>
AA (30)	1.0	1.12	1.12
MAH (30)	1.0	3.07	1.09
GMA (30)	1.0	1.83	1.11
HI (30)	1.0	1.25	1.10
MAC (30)	1.0	2.84	1.08

<sup>a</sup> phr: parts per hundred parts of resin.

<sup>b</sup> The equivalent grafting extent of functionalized LDPEs was obtained by blend of functionalized-LDPE with virgin LDPE.

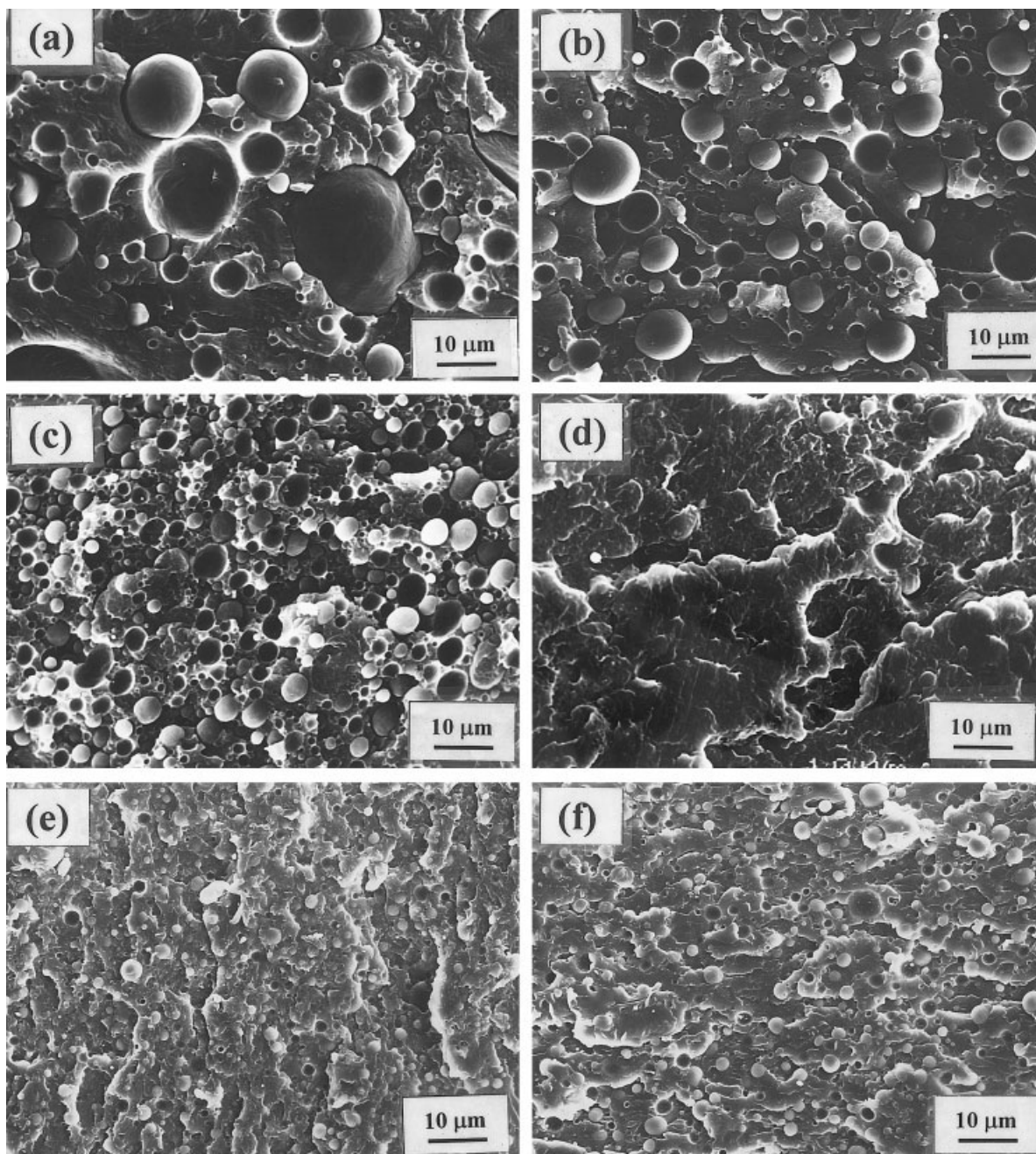


**Figure 3** SEM micrographs obtained for PET/LDPE blends with different functionalized LDPEs: (a) virgin LDPE; (b) AA-grafted LDPE; (c) GMA-grafted LDPE; (d) MAH-grafted LDPE; (e) HI-grafted LDPE; (f) MAC-grafted LDPE.

alized LDPEs in the blend phase. Clearly, a significant reduction of the particle size and the uniform size distribution in the blend morphologies were observed when the functionalized LDPEs were added into the blend phase [Fig. 3(b–f)]. However, the blend morphologies have shown inequality according to the species of functionalized LDPE. The order of the reactive compatibilization of the PET/LDPE blends with the functional group is as follows: GMA > HI  $\cong$  MAC > MAH > AA, indicating that the most effective chemical reactions between the epoxy group of LDPE

and PET occurred during the blending process of the PET/LDPE interface.

Also, the effect of LDPE having a different functionality and morphology from the Nylon 6/LDPE blend was observed in the SEM micrographs. Figure 4 shows the cryogenically fractured surface of the Nylon 6/LDPE blends with the functionalized LDPEs. As can be seen in Figure 4(a), the binary Nylon 6/LDPE blend exhibits very big spherical-shaped domains with a broad distribution of the diameter, which is usually attributed to weak adhe-



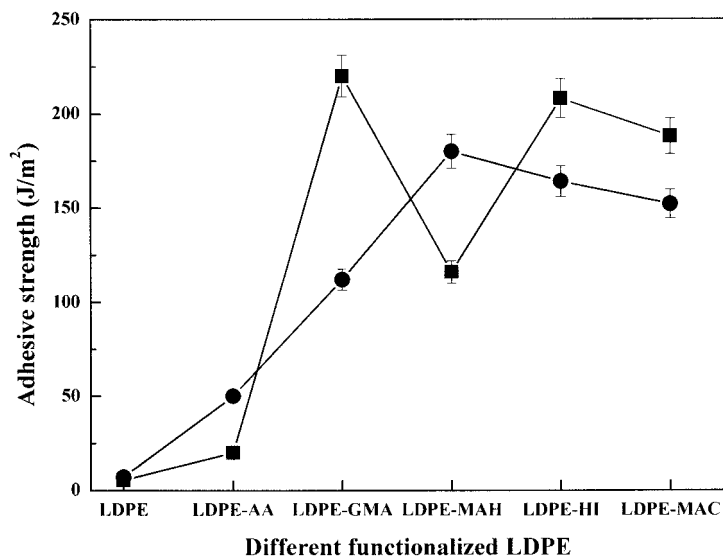
**Figure 4** SEM micrographs obtained for Nylon 6/LDPE blends with different functionalized LDPEs: (a) virgin LDPE; (b) AA-grafted LDPE; (c) GMA-grafted LDPE; (d) MAH-grafted LDPE; (e) HI-grafted LDPE; (f) MAC-grafted LDPE.

sion and high interfacial tension. However, in Figure 4(b–f), we can see that the domain size was significantly decreased with addition of each functionalized LDPE. The order of the reactive compatibilization of Nylon 6/LDPE blends with the reactive group is as follows: MAH > HI  $\cong$  MAC > GMA > AA. From the above results, we confirmed that the GMA-functionalized LDPE was the most effective reactive polymer in the PET/LDPE blend and MAH-functionalized LDPE was the most effective reactive polymer in the Nylon 6/LDPE blend. How-

ever, masked and naked NCO groups have shown suitable compatibilization effects on both PET/LDPE and Nylon 6/LDPE.

#### Adhesive strengths

Interfacial adhesion was estimated by measuring the adhesive strength using the 180°-peel test. Figure 5 represents the adhesive-strength results of the PET/LDPE blend and the Nylon 6/LDPE blend plotted with different functionalized LDPEs. The maximum



**Figure 5** Plots of the interfacial adhesive strength versus different functionalized LDPEs: (■) PET/LDPE; (●) Nylon 6/LDPE.

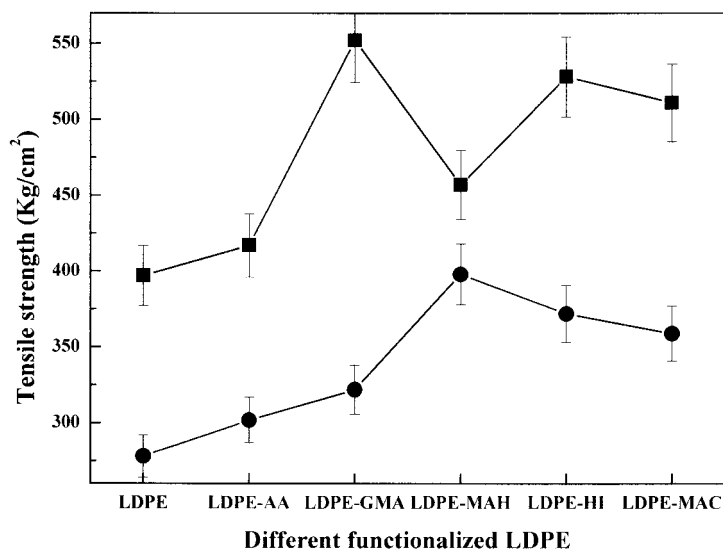
adhesive strength between PET and LDPE was achieved by the GMA-functionalized LDPE. Also, the adhesive strength between Nylon 6 and LDPE shows superlative values when the MAH-functionalized LDPE film was inserted. The adhesion strengths of the masked and naked NCO groups are not susceptible to the alteration of the counterpolymers, indicating that the NCO reactive groups give sufficient adhesion strengths at the PET/LDPE interface as well as at the Nylon 6/LDPE interface.

Norton et al.<sup>21</sup> and other workers reported that interfacial adhesion increased with an increasing number of the interlinking chains or density of an *in situ* copolymer at the interface. Therefore, it is considered that the chemical reactions of the GMA- and NCO-

functionalized polymers in the PET/LDPE blends or MAH- and NCO-functionalized polymers in the Nylon 6/LDPE blends at the interface result in formation of a greater amount of *in situ* copolymers (PET-g-LDPE or Nylon 6-g-LDPE, respectively), leading to greater interfacial adhesion at the interface of PET/LDPE and Nylon 6/LDPE.

#### Tensile properties

Figure 6 shows the effect of reactive groups in the LDPE on the tensile strength of PET/LDPE and Nylon 6/LDPE blends. By using GMA- or MAH-functionalized LDPE, the tensile strength was maximized and then leveled off with the other functional groups. It is

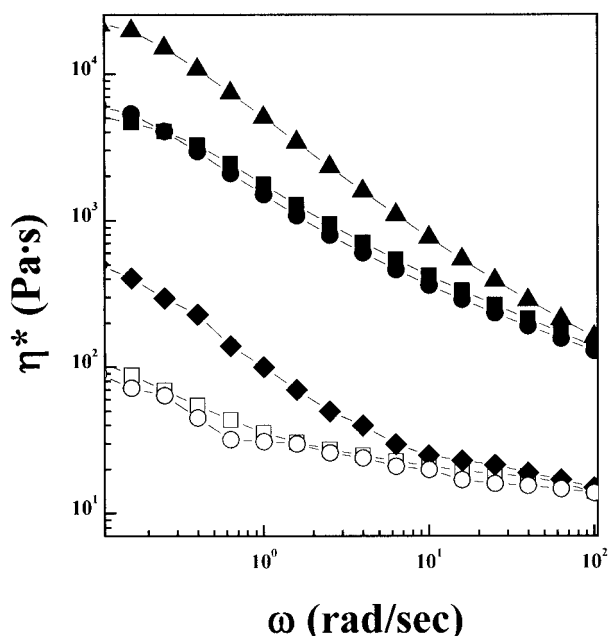


**Figure 6** Plots of tensile strength versus different functionalized LDPEs: (■) PET/LDPE; (●) Nylon 6/LDPE.

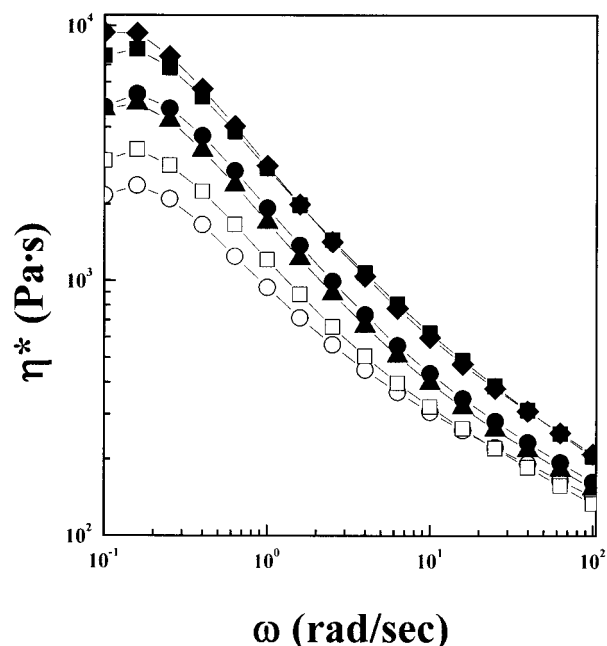
known that there is a close relation between the tensile property of the blend and the interfacial adhesion. In our experiment, the result of the tensile strength is well consistent with that of the adhesive strength. This result also supports our assumption that NCO-functionalized LDPE acts as an effective reactive polymer in the PET/LDPE and Nylon 6/LDPE blends.

### Rheological properties

Figure 7 gives plots of the complex viscosity ( $\eta^*$ ) versus the angular frequency ( $\omega$ ) for the PET/LDPE blends. The dependence of  $\eta^*$  on  $\omega$  for the Nylon 6/LDPE blends is represented in Figure 8. It is known that an increase in the complex viscosity of a blend generally results from a specific interaction between the phases<sup>22,23</sup> or a chemical reaction between the blend components.<sup>24</sup> Such a chemical reaction will produce *in situ* copolymers, causing a strong interaction between the phases. As a consequence, the matrix will be more resistant to flow, resulting in higher viscosity. When there is no interaction or chemical reaction between the phases, however, low viscosity will be found because the dispersed phase can be detached easily in the matrix. So, the higher complex viscosity of the PET/LDPE blend prepared with GMA- and NCO-functionalized LDPE can be interpreted in terms of the formation of a larger amount of the *in situ* copolymer at the interface in the course of melt blending. Also, similar results were observed for



**Figure 7** Complex viscosity versus frequency for PET/LDPE blends with different functionalized LDPEs: ( $\Delta$ ) GMA-grafted LDPE; ( $\blacksquare$ ) HI-grafted LDPE; ( $\bullet$ ) MAC-grafted LDPE; ( $\blacklozenge$ ) MAH-grafted LDPE; ( $\square$ ) AA-grafted LDPE; ( $\circ$ ) virgin LDPE.



**Figure 8** Complex viscosity versus frequency for Nylon 6/LDPE blends with different functionalized LDPEs: ( $\Delta$ ) GMA-grafted LDPE; ( $\blacksquare$ ) HI-grafted LDPE; ( $\bullet$ ) MAC-grafted LDPE; ( $\blacklozenge$ ) MAH-grafted LDPE; ( $\square$ ) AA-grafted LDPE; ( $\circ$ ) virgin LDPE.

the Nylon 6/LDPE blends prepared with MAH- and NCO-functionalized LDPE, indicating formation of a larger amount of the *in situ* copolymer due to the reactions between MAH and Nylon 6 and between NCO and Nylon 6.

### CONCLUSIONS

The morphologies of PET/(GMA-g-LDPE) or (NCO-g-LDPE)/LDPE and Nylon 6/(MAH-g-LDPE) or (NCO-g-LDPE)/LDPE blends were significantly affected by the PET/LDPE and Nylon 6/LDPE blends. The NCO reactive groups give sufficient adhesion strength at the interface. The reduction of the dispersed phase size and interfacial adhesion strength are maximized in the PET/LDPE and Nylon 6/LDPE blends prepared with GMA- and MAH-functionalized LDPE, respectively, whereas the reactivity of the GMA- and MAH-functional groups in LDPE was altered with the counterpolymer. The morphologies and adhesion strengths of the masked and naked NCO groups were not susceptible to the alteration of the counterpolymers. These results are well reflected in the tensile strength and complex viscosity of the PET/LDPE and Nylon 6/LDPE blends. The NCO-functionalized LDPE could be evaluated as a universal reactive compatibilizer for PET/LDPE and Nylon 6/LDPE blends.

This work was supported by the Engineering Research Center (ERC) for Advanced Functional Polymers of Korea.

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