

Improved Nylon 6/LDPE Compatibility Through Grafting of Isocyanate Functional Group

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ABSTRACT: In order to apply isocyanate (NCO) functional group to the reactive compatibilization of nylon 6/LDPE blends, low-density polyethylene grafted with 2-hydroxyethyl methacrylate-isophorone diisocyanate (LDPE-*g*-HI) was prepared. From the results of infrared spectra and Molau test, it was found that the chemical reactions of NCO and amino end group occurred during the melt blending. In view of the blend morphology, the dispersions of the nylon 6/LDPE-*g*-HI blends were very fine over the nylon 6/LDPE blends and the junctions between the phases appeared at the interface of the 50/50 nylon 6/LDPE-*g*-HI blend. For the nylon 6/LDPE-*g*-HI blends, a strong positive deviation from the mixing rule was observed in rheological measurements, as a result of the chemical reaction. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2183–2189, 1997

Key words: isocyanate group; grafted polymer; blend; reactive compatibilization

INTRODUCTION

Immiscible polymer blends are often preferred over the miscible types because they may combine some of the important characteristics of each blend component. Satisfactory performance in immiscible blends is usually attained by compatibilization that minimizes interfacial tension and improves adhesion between the two phases.^{1,2} The results are a finely dispersed phase, resistance to gross separation, and improved overall properties.³

Methods of compatibilization for immiscible blends have been introduced. According to those methods, it is well recognized that a rising of compatibility may be produced by blending suitably functionalized polymers capable of enhanced chemical reaction,^{4–16} because chemical reaction

between blend constituents may cause interfacial tension to decrease or adhesion force of interface to increase.

Several authors^{4–16} have reported that one polymer with some functional group reacted with another polymer during blend processing and this resulted in a compatible effect. Most of the functional groups were acid anhydride,^{4–8} carboxy,^{9–12} epoxy,^{13,14} and oxazoline^{15,16} reacted with the amine or carboxyl group of various thermoplastic resins.

In this study, isocyanate (NCO) group was suggested as a reactive functional group to compatibilize immiscible polymers. NCO has better potential reactivity not only with amine (or carboxy) but also with hydroxy over the above-mentioned functional groups. Furthermore, it reacts fast at the high temperature where blend processing is carried out.¹⁷

To consider compatibilization effect through the reaction of NCO on immiscible polymer blends, we blended nylon 6 and low-density polyethylene (LDPE) grafted with 2-hydroxyethyl

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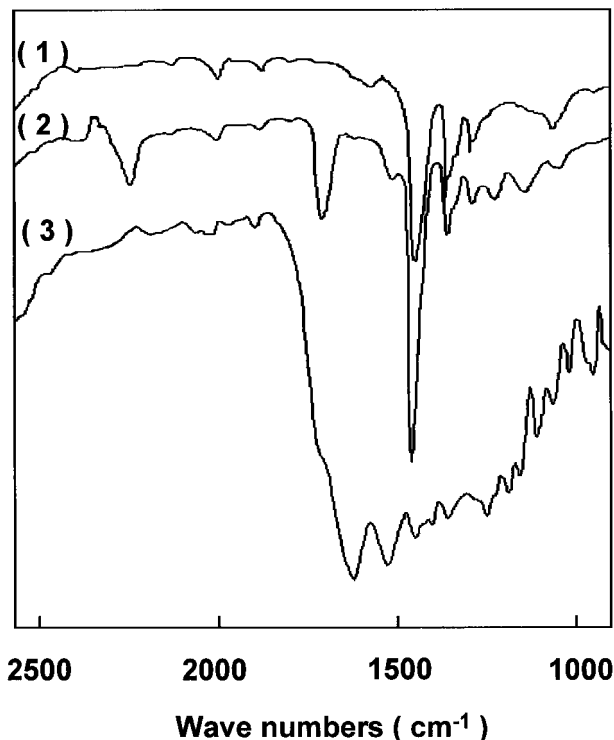


Figure 1 IR spectra: (1) LDPE, (2) LDPE-*g*-HI, and (3) 70/30 Nylon 6/LDPE-*g*-HI blend.

methacrylate-isophorone diisocyanate (HI). Also, the properties of this blend were discussed and compared with those of the nylon 6/LDPE blend.

EXPERIMENTAL

Materials

LDPE (940, Hanwha chemicals, melt index = 12) as received and spinning-grade nylon 6 (1011 Br, Tongyang Nylon, $\bar{M}_n = 17,500$) after drying in vacuum at 80°C for 48 hours were used. HI grafted onto LDPE was prepared by the reaction of 2-hydroxyethyl methacrylate (HEMA, Junsei Chemical) and isophorone diisocyanate (IPDI, Aldrich Chemical) with a molar ratio of 0.95 to 1 at 40°C in nitrogen (N_2) blowing for 6 hours.

Graft Copolymerization

Graft copolymerization was carried out in xylene with dicumyl peroxide (DCP). LDPE (10 g) and xylene (100 g) were put into a vessel and heated with agitation, followed by the immediate addition of HI (2 g) and DCP (0.1 g). The reaction

was continued for 4 hours at 120°C in N_2 . The reaction mixture was cooled, washed with pure xylene several times, and dried in vacuum. Evidence for grafting was obtained from Fourier transform infrared (Magna IR-550, Nicolet), and the graft ratio of 10.1% was determined from elementary analysis (MT-2 CHN coder, Yanaco).

Preparation of Blends

Nylon 6 and LDPE with a graft ratio of 10.1% (LDPE-*g*-HI) were mixed for 5 minutes in a Brabender mixing head. Additionally, the blends of nylon 6 with LDPE were prepared for comparison purposes. The temperature inside the mixing chamber was 245°C, and the speed of the rollers was 50 rpm. The preparation was carried out in a nitrogen atmosphere to prevent oxidative degradation. The blend ratios of nylon 6/LDPE-*g*-HI (or LDPE) were 10/90, 30/70, 50/50, 70/30, and 90/10 by weight.

Morphological Observation

The morphology of blend was observed by scanning electron microscopy (JSM-35CF, JEOL) from a cryogenically fractured (in liquid nitrogen) surface.

Rheological and Mechanical Measurements

The melt rheologies of the blends were measured with a rotational parallel-plate rheometer (Physica, UM/MC-100) with a 20% strain at 245°C under dry nitrogen. All of the specimens, sheets of 0.9-mm thickness, for tensile property measurement were obtained by compression

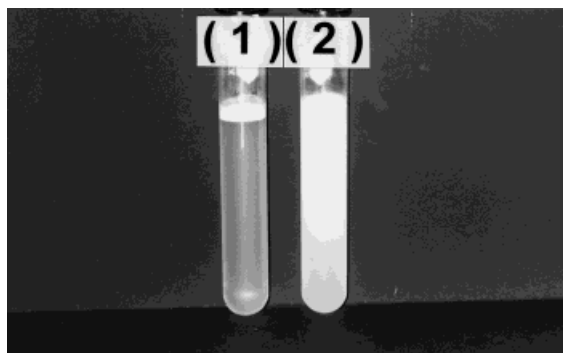


Figure 2 Molau test solutions: (1) Nylon 6/LDPE = 80/20 and (2) Nylon 6/LDPE-*g*-HI = 80/20.

molding in a heated press. Tensile strength measurements were done on an Instron machine at room temperature, following the procedure described in ASTM D638.

RESULTS AND DISCUSSION

Preparation of LDPE-g-HI

Ono et al.¹⁸ reported on the relative reactivities of the two isocyanate groups of IPDI. According to them, the secondary NCO group is most reac-

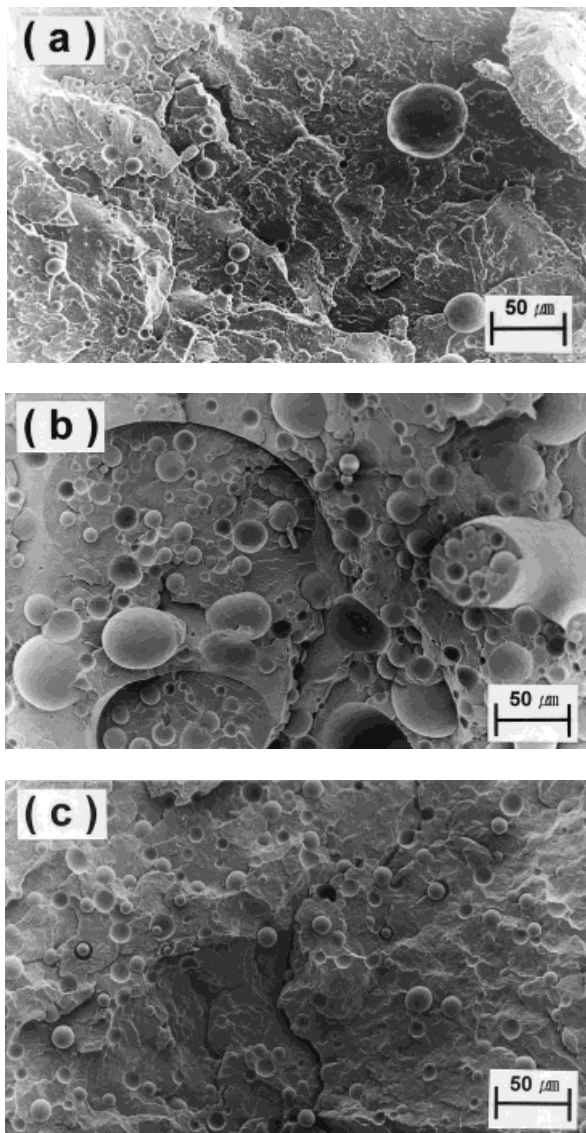


Figure 3 SEM micrographs of the cryogenically fractured surfaces of the nylon 6/LDPE blends: (a) 10/90, (b) 50/50, and (c) 90/10.

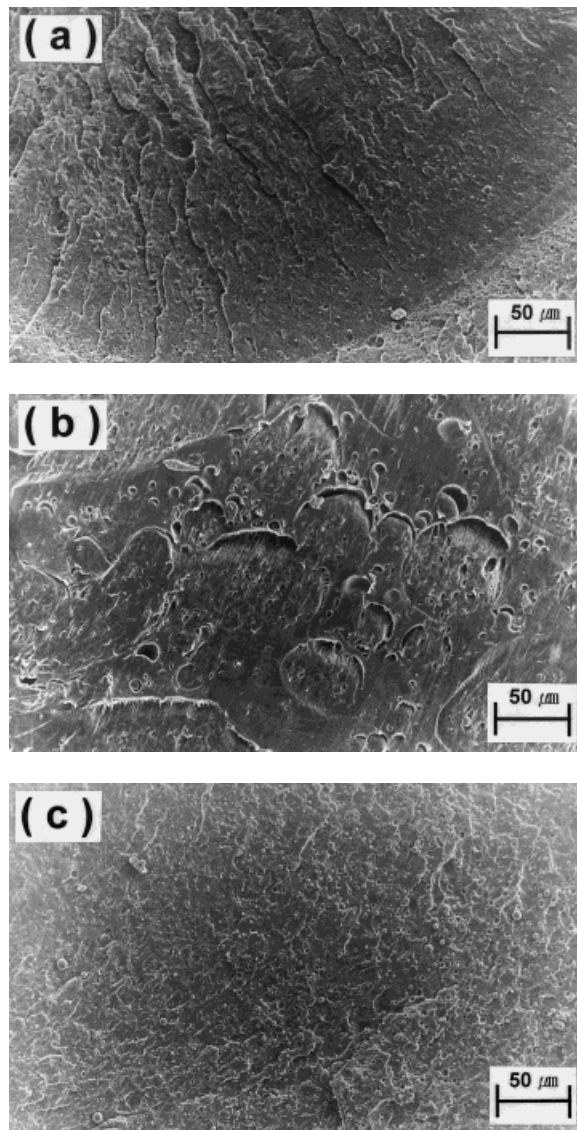


Figure 4 SEM micrographs of the cryogenically fractured surfaces of the nylon 6/LDPE-g-HI blends: (a) 10/90, (b) 50/50, and (c) 90/10.

tive in the absence of catalyst when IPDI reacts with alcohol. Viewed in this light, it can be thought that OH of HEMA reacted mostly with the secondary NCO of IPDI under our mild condition, at the OH/NCO ratio of 0.95/2 (our reaction ratio). That is, most of the primary NCO groups remained naturally, having a potential reactivity with other functional groups.

The infrared (IR) spectra of LDPE grafted with HI was represented at Figure 1 (2). Grafting was confirmed by the C=O peak (about 1730 cm^{-1}) of HEMA. In addition, an NCO group was observed at about 2270 cm^{-1} for C=N.

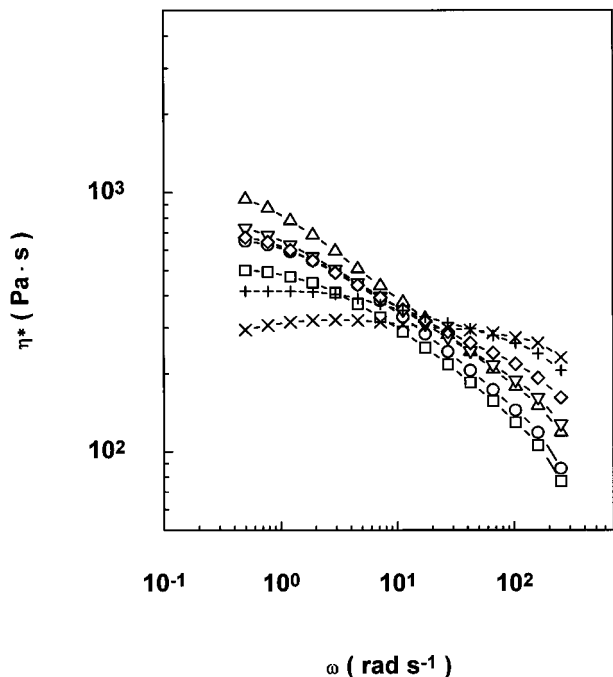


Figure 5 η^* versus ω for the nylon 6/LDPE blends: (□) 0/100, (○) 10/90, (△) 30/70, (▽) 50/50, (◇) 70/30, (+) 90/10, and (×) 100/0.

Reaction of Nylon 6 and LDPE-*g*-HI

In order to investigate the reactions of NCO groups and amino end groups (of nylon 6) in the melt blending, we confirmed the IR spectra of the nylon 6/LDPE-*g*-HI blend. The peak (about 2270 cm^{-1}) for C=N of NCO disappeared in the spectra of the nylon 6/LDPE-*g*-HI blend with 70/30 composition [Fig. 1 (3)]. This is considered to be the result from reactions that occurred during the melt blending.

In our investigation, we also performed the Molau^{19,20} test by mixing about 1 g of the 80/20 nylon 6/LDPE-*g*-HI blend with 50 mL of formic acid. The mixture was first shaken thoroughly in a beaker and then left in a test tube for 12 hours. The same procedure with the blend of nylon 6/LDPE was repeated. Figure 2 shows the results of the Molau test. A phase separation in the nylon 6/LDPE blend was observed in Figure 2 (1), whereas turbidity persisted in the solution containing the nylon 6/LDPE-*g*-HI blend [Fig. 2 (2)]. For the nylon 6/LDPE blend, the lower part and the upper part represent a solution of formic acid dissolving nylon 6 and a suspension of LDPE particles, respectively. Note in Figure 2 (2) that, for the blend of nylon 6/LDPE-*g*-HI, the lower part

represents a suspension of LDPE-*g*-HI particles reacted with nylon 6 during the melt blending.

Earlier, Molau^{19,20} and Illing²¹ conducted similar experiments, using the solutions prepared with nylon/polyolefin blends. Our Molau test indicates that the chemical reactions took place between NCO groups and amino end groups during the melt blending.

Morphology

The SEM photomicrographs for cryogenically fractured surfaces of nylon 6/LDPE blends show the typical morphology of an incompatible blend (see Fig. 3). At the 10/90 nylon 6/LDPE blend, the dispersed phase is nylon 6 and LDPE is the matrix phase. The reverse is true at the blend with the composition of 90/10. At the intermediate composition (50/50), there are the composite droplets involving matrix phase in the nylon droplet. Similarly, the blends of nylon 6/LDPE-*g*-HI appeared to be incompatible (see Fig. 4). However, the dispersions of the nylon 6/LDPE-*g*-HI blends were much finer than those of the nylon 6/LDPE blends [See Fig. 4 (a) and (c)]; also note the fine dispersions compared with the large ones

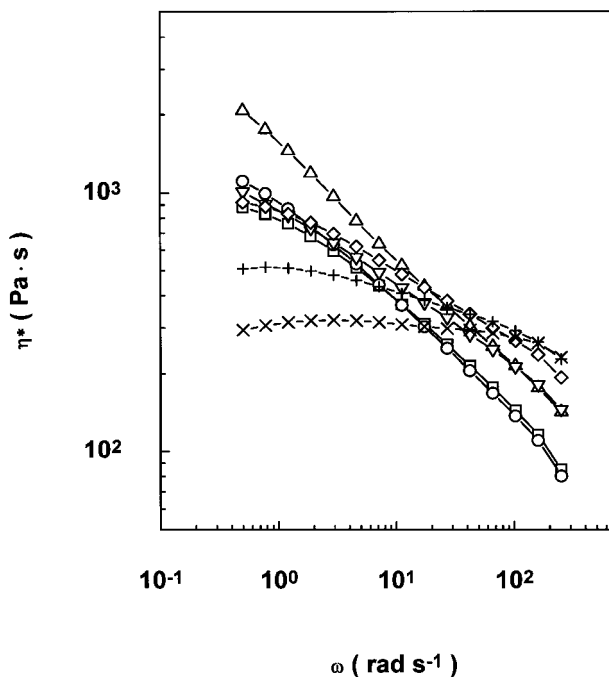


Figure 6 η^* versus ω for the nylon 6/LDPE-*g*-HI blends: (□) 0/100, (○) 10/90, (△) 30/70, (▽) 50/50, (◇) 70/30, (+) 90/10, and (×) 100/0.

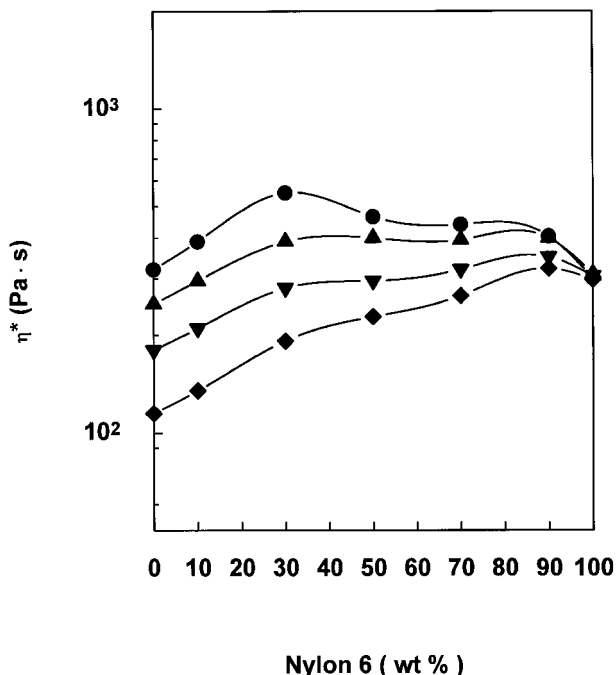


Figure 7 The dependence of η^* on blend composition in the nylon 6/LDPE blends, at four different shear stresses (Pa): (●) 500, (▲) 1000, (▼) 2000, and (◆) 4000.

of the nylon 6/LDPE blends. In addition, there was a difference in the morphologies of the two blends at the 50/50 composition [Fig. 3 (b), Fig. 4 (b)]. It seems that the partial junctions between the phases at the interface exist, not in the nylon 6/LDPE, but in the nylon 6/LDPE-*g*-HI blend.

Undoubtedly, the chemical reactions between the dispersed and the matrix phases in immiscible polymer blends can cause the interfacial tension to be reduced or the adhesion of interface to improve. That is to say, an improvement of compatibility is produced. This results in the fine dispersions or the attachments of the two phases. In our experiment, we could observe the fine dispersions and the junctions between the phases in nylon 6/LDPE-*g*-HI blends. This also leads us to expect that the compatibility of nylon 6/LDPE blends can be improved by the modification of LDPE with HI, of which NCO groups react with amino end groups of nylon 6.

Rheological Properties

Figure 5 gives the plots of complex viscosity (η^*) versus angular frequency (ω) for the nylon 6/LDPE blend system. The dependence of η^* on ω

for the nylon/LDPE-*g*-HI blend system is represented in Figure 6.

The rheological behavior of polymer blends differs from that of pure polymer because of the generally incompatible nature of polymers. Several researchers^{22,23} have done experimental studies on the rheological properties of homopolymer and copolymer blends. Those investigators have considered the effects of the blending ratio on the viscosity and elasticity of blends and their variation with processing variables (that is, shear rate and melt temperature). Because the viscosity of a polymer melt exhibits a large shear dependence, the respective dependencies can be evaluated either at constant stress or at constant shear rate.² It has been suggested²⁴ that the use of shear stress instead of shear rate is more appropriate for correlating the viscoelastic properties of two-phase polymer melts because of the discontinuity of the shear rate at the phase interfaces in the flow.

The η^* value of nylon 6/LDPE blends versus the blend composition at constant shear stress is given in Figure 7. Figure 8 shows the effect of the blend composition on η^* , for the nylon 6/LDPE-*g*-HI blends. It is seen that η^* of the nylon 6/

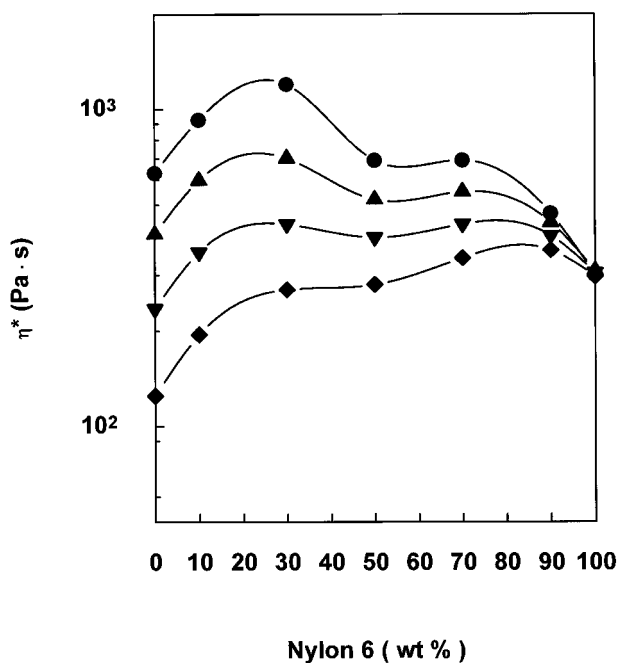


Figure 8 The dependence of η^* on blend composition in the nylon 6/LDPE-*g*-HI blends, at four different shear stresses (Pa): (●) 500, (▲) 1000, (▼) 2000, and (◆) 4000.

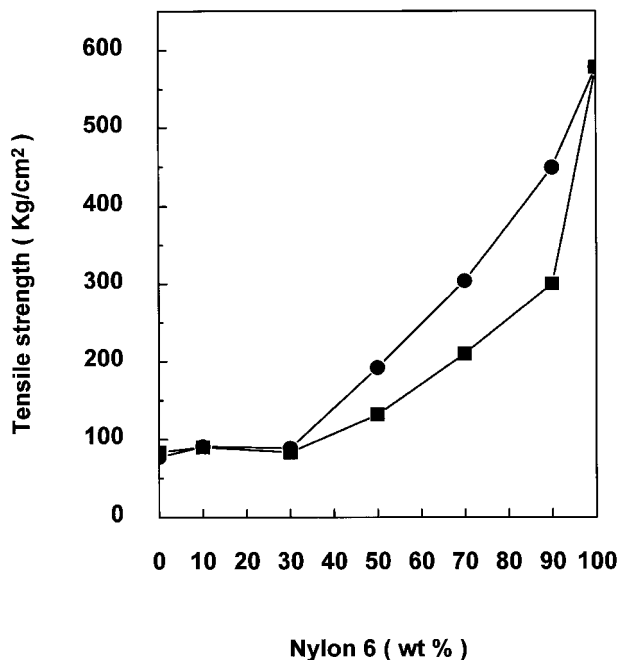


Figure 9 The dependence of tensile strength on blend composition: (■) in the nylon 6/LDPE blends and (●) in the nylon 6/LDPE-*g*-HI blends.

LDPE-*g*-HI blends shows a strong positive deviation from the mixing rule. A positive deviation from the mixing rule generally occurs when there are strong interactions between the phases of blend.²⁵ We believe that a strong positive deviation in the nylon 6/LDPE-*g*-HI blends resulted from the chemical bonding occurred in the melt blending.

Tensile Property

Figure 9 shows the tensile strengths of the blend systems investigated. It was seen that in the nylon-lean blends having nylon 6 as the dispersed phase, the tensile strengths stayed almost constant as the amount of nylon 6 is increased. However, in the nylon-rich blends having nylon 6 as the matrix phase, the tensile strengths decreased as the amount of nylon 6 in a blend decreased. Also, the tensile strengths of the nylon 6/LDPE-*g*-HI blends decreased monotonically, while those of the nylon 6/LDPE blends decreased dramatically as the amount of nylon 6 decreased in the nylon-rich blends.

As Kunori and Geil²⁶ and Nielsen²⁷ pointed out, the tensile failure of a blend is attributable to the failure of the adhesion between the dispersed

phase and the matrix phase, through crazing or a dewetting effect. In our study, the dramatic decrease is also thought to be due to the failure of the adhesion between nylon 6 and LDPE.

CONCLUSION

LDPE grafted with HI was prepared and blended with nylon 6 to compare with the blends of nylon 6 and LDPE. From the results of IR spectra and the Molau test, it was found that the chemical reactions of NCO and amino end group occurred during the melt blending. In view of the blend morphology, the dispersions of the nylon 6/LDPE-*g*-HI blends were very fine over the nylon 6/LDPE blends and the junctions between the phases at the interface appeared in the 50/50 nylon 6/LDPE-*g*-HI blend. For the nylon 6/LDPE-*g*-HI blends, a positive deviation from the mixing rule was observed in rheological measurements, due to the chemical reaction. With the above-mentioned results, it could be concluded that the compatibility of the nylon 6/LDPE blends was improved by the modification of LDPE with HI.

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