NOTE

Functionalization of Ethylene–Propylene Elastomer with Isocyanate Group and Its Blend with Polyamide

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INTRODUCTION

Many polymers are immiscible with each other and phase-separated due to the low entropy of the mixing of long polymer chains. These immiscible polymer blends have the advantage of maintaining the desirable properties of blend components but often have poor mechanical properties. Thus, compatibilization through a chemical reaction between the blend components, namely, reactive compatibilization, has been widely used to obtain satisfactory performance in immiscible blends.^{1–7}

Modification of polyolefins by attaching unsaturated polar groups onto their chain backbone has received considerable attention in the past decades.¹⁻⁹ An ethylene-propylene copolymer (EPM), a specialty elastomer, which possesses excellent chemical resistance and water resistance and good physical properties, was modified with various functional groups and used in polyamide/EPM blend systems.

In fact, an ethylene–propylene copolymer grafted with maleic anhydride (EPR-g-MAH) has been used in binary PA6/EPR-g-MAH or in ternary PA6/EPR/EPR-g-MAH blends^{3,10,11} and it also has been widely used as a compatibilizer in the PA6/PP blend.^{12,13} In our previous work, an isocyanate (NCO) group showed a compatibilizing effect in the PET/LDPE¹⁴ and Ny6/LDPE blends.¹⁵

In our present work, NCO, as a functional group, was introduced onto the EPM elastomer backbone. The blends of Ny6 and EPM grafted with 2-hydroxyethyl methacrylate—isophorone diisocyanate (EHI) were prepared and the compatibilizing effect of NCO on the blends was studied. Morphological and thermal analyses of these blends are discussed and compared with those of the Ny6/EPM.

EXPERIMENTAL

Materials

HI, a functional monomer, was prepared by the reaction of 2-hydroxyethyl methacrylate (2-HEMA, Aldrich Chemical Co., U.S.) and isophorone diisocyanate (IPDI, Aldrich) with a molar ratio of 0.95 to 1. The molecular structure of HI is also presented in Figure 1. The detailed synthetic method of HI followed our previous study.¹⁴

The nylon 6 (BR1031, $M_n = 25,000$) used in this study was a base-grade polymer kindly supplied by (Hyosung T&C., Korea.) It was always used after drying for at least 24 h at 80°C to remove sorbed water completely *in vacuo*. EPM elastomers (Kumho Polychem Co., Korea., KEP 020P, $M_w = 111,000$, C₂ content 69 wt %) having a Mooney viscosity of 14 at 125°C were used.

Graft Copolymerization

Grafting of HI onto EPM was carried out in xylene with dicumyl peroxide (DCP) as an initiator at 120°C. EPM (20 g) was dissolved in xylene (180 g) and heated to 120°C with agitation under a nitrogen atmosphere, followed by the addition of HI (2–6 g)/DCP (0.2 g)/ xylene (20 g) solution at once. After the complete reaction of 4 h at 120°C in N₂, the reaction mixture was cooled and precipitated by adding sufficient acetone.

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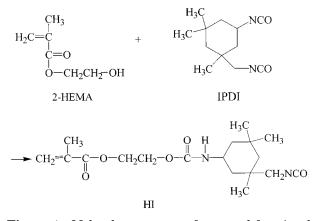


Figure 1 Molecular structure of prepared functional monomer, HI.

The product (EHI) was washed several times with acetone to remove unreacted HI and/or the residual initiator and then dried at 45°C *in vacuo*. The graft reaction was confirmed from FTIR (Nicolet, Mahgna IR-550) spectroscopy. The amount of grafted HI in EHI was determined by elemental analysis (Yanaco, MT2 CHN coder). Table I shows the experimental recipe. Here, EHI1, -2, and -3 means HI-grafted EPMs with the sequential graft ratios.

Blend Preparation

Ny6/EPM and Ny6/EHI were premixed over several composition ratios. These mixtures were then meltblended at 250°C, 90 rpm, in an internal mixer. After mixing for 8 min, the blends were quenched in water and dried in a vacuum oven for 24 h at 80°C.

Thermal analysis was carried out using a differential scanning calorimeter (Perkin–Elmer, DSC-7) to study the influence of isocyanate functional groups on the crystallinities of the Ny6/EHI3 blends. The temperature was increased from 50 to 240°C at a rate of 10°C/min and then 2 min was allowed to erase the thermal history and then it was decreased to 50°C at -10°C/min. The compositions of the Ny6/EPM and Ny6/EHI3 blends were varied over the ratios of 90/10, 70/30, 50/50, 30/70, and 10/90 by weight. To investigate the morphologies of the blends, the cryogenically fractured surfaces of the Ny6/EPM and Ny6/EHI blends were examined at a fixed elastomer content (20 wt %) using scanning electron microscopy (SEM; JEOL, JSM-6300).

RESULTS AND DISCUSSION

Preparation of EPM-g-HI

HI, a functional monomer, was prepared for the functionalization of the EPM elastomer. The FTIR spectra show that the reaction between 2-HEMA and IPDI successfully occurred [Fig. 2(1)]. Compared with each spectrum of (a) 2-HEMA and (b) IPDI, the spectrum of (c) HI presents a new peak at 1530 cm^{-1} , which is due to the -NH- produced by the reaction between -NCO and -OH.

Figure 2(2) shows the FTIR spectra of EPM and EHIs. The peak at 1730 cm⁻¹, characteristic peak of the C=O bond in 2-HEMA, revealed evidence of grafting. In addition, the characteristic peak of -NCO(about 2270 cm⁻¹) from IPDI is also present. The magnitudes of these two peaks increased with an increasing amount of HI in the graft reaction. The degree of grafting of HI onto EPM is also listed in Table I. The graft ratios of HI increased with increasing HI concentration in the reaction. This result is in accordance with that of the FTIR spectra in Figure 2(2).

Thermal Analysis

A DSC study of each blend supported the effect of isocyanate functional groups on the Ny6/EPM and Ny6/ EHI blends. DSC cooling thermograms of the Ny6/EPM and Ny6/EHI3 blends at a cooling rate of -10°C/min are shown in Figure 3. Each thermogram of the Ny6/ EPM and Nv6/EHI3 blends shows one exothermic peak at about 182-189°C, which is the characteristic crystallization peak of Ny6. Blended EPM, an amorphous polymer, shows no peak in the DSC cooling curves. At a given blend composition, the heat of crystallization (ΔH_c) of Ny6 in the Ny6/EHI3 blend was decreased compared with that in the Nv6/EPM blend. As the content of EHI3 in the Ny6/EHI3 blends increased, the crystallization of Ny6 decreased more distinctly. Moreover, the crystallization peak of Ny6 disappeared in the Ny6/EHI3 (10/90) blend. It is supposed that the crystallization behavior of Ny6 is restricted by the in situformed Nv6-g-EPM copolymers. It seems that the grafted Ny6 copolymer constrained the crystallization at the melt-crystallization temperature of Ny6, which,

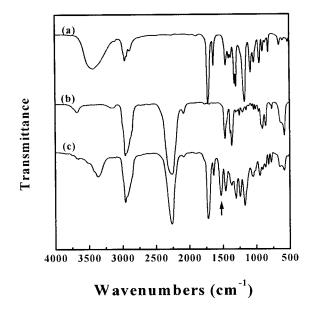
Table IVariation of HI Concentration in EPMGraft Reaction

	Ingredient			
Sample	HI (phr)	DCP (phr) ^a	Reaction Time ^b (min)	Graft Ratio (wt %)
EHI1 EHI2 EHI3	10 20 30	1.0 1.0 1.0	240 240 240	$1.48 \\ 3.51 \\ 5.75$

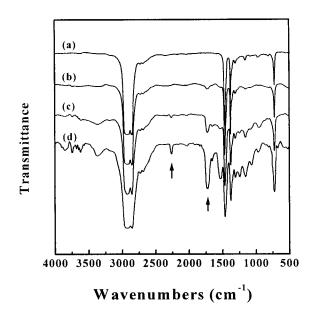
All graft reactions were carried out in xylene at 120°C.

 $^{\rm a}$ DCP concentration was fixed at 1.0 phr in all graft reactions.

^b Reaction time was fixed at 240 min in all graft reactions.



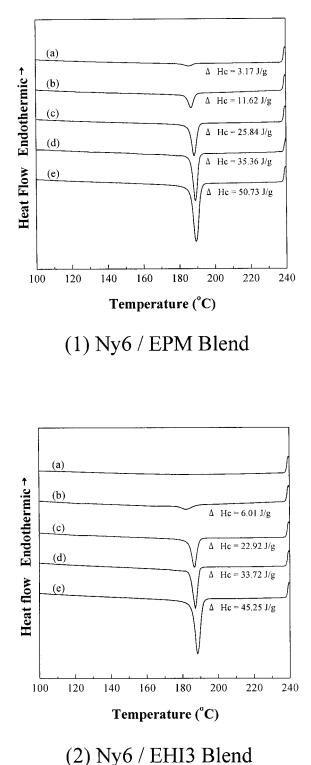
(1) Prepared functional monomer, HI



(2) Graft reaction products of EHI

Figure 2 FTIR spectra for (1) prepared functional monomer, HI: (a) 2-HEMA; (b) IPDI; (c) HI, and (2) graft reaction products of EHI with 1.0 phr of DCP: (a) EPM; (b) EHI1; (c) EHI2; (d) EHI3.

consequently, resulted in a decrease in the peak magnitude and a slight shift of the peak to lower temperature. From this result, it is confirmed that the reaction between —NCO in grafted EPM and —NH₂ (or —COOH) in Ny6 occurred.



S DSC cooling thermograms of (1) Ny6

Figure 3 DSC cooling thermograms of (1) Ny6/EPM and (2) NY6/EHI3 blends: (a) 10/90, (b) 30/70, (c) 50/50, (d) 70/30, and (e) 90/10 by wt %, respectively.

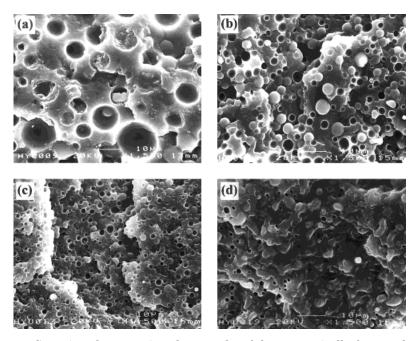


Figure 4 Scanning electron microphotographs of the cryogenically fractured surface of the blends in the same composition by wt % (80/20): (a) Ny6/EPM; (b) Ny6/EHI1; (c) Ny6/EHI2; (d) Ny6/EHI3.

Blend Morphology

In this study, the reaction between the -- NCO group in for improving the compatibility of the blends. In compatibilized blends, we expected that the formation of the graft copolymer by the chemical reaction at the interface should result in a decrease of the rubber domain size by lowering the interfacial tension and in an increase of the interfacial adhesion between the blend components. Figure 4 shows scanning electron microphotographs of the blends at a fixed elastomer content (20 wt %). The blend of Ny6/EPM shows the typical morphology of an incompatible blend [Fig. 4 (a)], that is, a large particle size and poor interfacial adhesion between the matrix and dispersed phase. On the contrary, it was found that when HI-grafted EPMs (EHI1 and EHI2) were blended, the average size of the dispersed phase was decreased, compared with that of the uncompatibilized blend [Fig. 3 (b,c)], indicating that the presence of in situ-formed Ny6-co-EPM reduced the interfacial tension between the EPM dispersed phase and the Ny6 matrix. Especially, the particle size became smaller when the grafting ratio of HI increased. Moreover, at the highest extent of HI in EHI3, the interfacial adhesion was strongly increased [Fig. 3(d)]. From these results, it is obvious that the grafted HI and the graft ratios of HI had a significant effect on the particle size and interfacial adhesion.

From the above results, we concluded that the reaction between the —NCO groups and amine and/or the carboxyl groups of Ny6 formed *in situ* Ny6-co-EPM copolymers which could act as a compatibilizer in the Ny6/EPM blend and that these copolymers improved the compatibility of Ny6/EPM. Furthermore, from the reduced particle size and improved interfacial adhesion, we expected that the EPM elastomer functionalized with isocyanate groups (EHI) could serve as a toughening agent of polyamide and polyester that have amine (or carboxyl) and hydroxyl end groups.

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REFERENCES

- Baldwin , E. P.; Strate, V. Rubb Chem Technol 1972, 45, 834.
- Minoura, Y.; Veda, M.; Minozuma, S.; Oba, M. J Appl Polym Sci 1969, 13, 1625.
- Cimmino, S.; D'Orazio, L.; Greco, R.; Malinconico, M.; Mancarella, C.; Martuscelli, E.; Palumbo, R.; Ragosta, G. Polym Eng Sci 1984, 24, 48.
- Cimmino, S.; D'Orazio, L.; Greco, R.; Malinconico, M.; Mancarella, C.; Martuscelli, E.; Palumbo, R.; Ragosta, G. Polym Eng Sci 1985, 25, 193.
- Greco, R.; Maglio, G.; Musto, P. V. J Appl Polym Sci 1987, 33, 2513.

- Zhang, X.; Whang, D.; Yin, Z.; Yin, J. J Appl Polym Sci 1996, 62, 67.
- De Vitio, G.; Lanzetta, N.; Maglio, G.; Malinconico, M.; Musto, P;. Palumbo, R. J Polym Sci Polym Chem Ed 1984, 22, 1335.
- Gaylord, N. G.; Mehta, M.; Mehta, R. J Appl Polym Sci 1987, 33, 2549.
- 9. Wu, C. H.; Su, A. C. Polym Eng Sci 1991, 31, 1629.
- Borggreve, R. J. M.; Gaymans, R. J. Polymer 1989, 30, 63.
- Borggreve, R. J. M.; Gaymans, R. J.; Eichenwald, H. M. Polymer 1989, 30, 78.
- González-Montiel, A.; Keskkula, H. Paul, D. R. Polymer 1995, 36, 4587.
- González-Montiel, A.; Keskkula, H. Paul, D. R. Polymer 1995, 36, 4605.
- Park, S. H.; Park, K. Y.; Suh, K. D. J Polym Sci Part B Polym Phys 1998, 36, 447.
- Park, K. Y.; Park, S. H.; Suh, K. D. J Appl Polym Sci 1997, 66, 2183.