

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

FUNCTIONALIZED HIGH-DENSITY POLYETHYLENE WITH BLOCKED ISOCYANATE GROUP

Dong-Hyun Kim^a; Kang-Yeol Park^a; Ju-Young Kim^b; Kyoung-Do Suh^a

^a Department of Industrial Chemistry, College of Engineering, Hanyang University, Seoul, Korea ^b

Department of Materials Engineering, Samchok National University, Kangwon, Korea

Online publication date: 22 June 2000

To cite this Article Kim, Dong-Hyun , Park, Kang-Yeol , Kim, Ju-Young and Suh, Kyoung-Do(2000) 'FUNCTIONALIZED HIGH-DENSITY POLYETHYLENE WITH BLOCKED ISOCYANATE GROUP', Journal of Macromolecular Science, Part A, 37: 7, 707 – 718

To link to this Article: DOI: 10.1081/MA-100101119

URL: <http://dx.doi.org/10.1081/MA-100101119>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

FUNCTIONALIZED HIGH-DENSITY POLYETHYLENE WITH BLOCKED ISOCYANATE GROUP

Dong-Hyun Kim, Kang-Yeol Park, Ju-Young Kim,[†] and
Kyoung-Do Suh*

Department of Industrial Chemistry
College of Engineering
Hanyang University
Seoul 133-791, Korea

[†]Department of Materials Engineering
Samchok National University
Kangwon 245-711, Korea

Key Words: High-Density Polyethylene (HDPE), Grafting, Blocked Isocyanate Group, Functionalization

ABSTRACT

Blocked HI (BHI) was synthesized by the reaction of HI (2-hydroxyethyl methacrylate combined with isophorone diisocyanate) with ϵ -caprolactam (CPL). CPL was used as a blocking agent to improve storage stability of HI. From the Fourier transform infrared spectroscopy (FT-IR) and proton nuclear magnetic resonance (¹H-NMR) spectra, it was found that NH group in CPL reacted with remaining isocyanate (NCO) groups in HI at 80°C for 8 hours. Grafting of BHI onto HDPE was carried out in a xylene solution using a radical initiator. By the FT-IR spectra, we confirmed the introduction of BHI onto HDPE and measured

*Author to whom correspondence should be addressed.

the relative extent of grafting. Deblocking temperature of BHI grafted onto HDPE was determined by monitoring the regeneration of isocyanate group at 2270 cm^{-1} with FT-IR spectra. Differential scanning calorimetry (DSC) analysis was used to determine the thermal properties of HDPE and BHI functionalized HDPE. DSC results showed that there was no crosslinking reaction during the grafting reaction of BHI onto HDPE. Processability of functionalized HDPE was evaluated by its dynamic rheological behaviors. When the functional group (BHI) was introduced onto HDPE, tensile strength of BHI functionalized HDPE showed higher value than that of HDPE, while elongation at breaks *vice versa*.

INTRODUCTION

Functionalization of polymers has received considerable attention, in part due to their potential utility in polymer blend [1-2]. Functionalized polymers are ideal candidates for immiscible polymer blending, where they are present as the compatibilizers. Generally, the functional groups may be part of the polymer backbone or link to a side chain as a pendant group. Grafting reaction initiated by peroxy radicals has been increasingly being used to obtain functionalized polyolefins [3-10].

Most widely used functional groups for the functionalization of polyolefins were carboxyl [11-12], acid anhydride [13-14], epoxy [15-16], oxazoline [17-18], and isocyanate (NCO) groups that could react with hydroxyl, carboxyl or amine groups of various thermoplastic resins. Particularly, in our previous studies [19-23], 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 compatibilizing effect of the isocyanate group on reactive blends of PE and engineering plastics.

A large number of blocked NCO groups have been reported and studied during the past few decades in coatings and propellant formulations, due to the short port life and very sensitive humidity of NCO group [24-27]. A blocked NCO group is an adduct containing a comparatively weak bond formed by the reaction between an isocyanate and a compound containing an active hydrogen atom. At elevated temperatures, the deblocking reaction tends to proceed in such a way as to regenerate the NCO group and the blocking agent. The regenerated NCO group can react with a counter polymer containing the hydroxyl, carboxyl and amine functional groups.



In this study, we prepared BHI to improve storage stability of HI, using CPL that has been widely reported in the literature [26-27] as an effective blocking agent for NCO group. The grafting evidence and relative grafting extent of BHI onto HDPE were described. In addition, we presented the thermal, rheological and tensile properties of modified HDPE, compared with those of HDPE.

EXPERIMENTAL

Materials

HDPE (Samsung J820A, melt flow index = 7.5 g/10min) was used as received. BHI was prepared by the reaction of CPL (Aldrich Chemical Co.) with HI at the molar ratio of 1.1:1. HI was synthesized by the reaction of 2-hydroxyethyl methacrylate (HEMA, Junsei Chemical Co.) with isophorone diisocyanate (IPDI, Aldrich Chemical Co.) with a molar ratio at 0.95:1 [19], and in addition, synthesized HI and CPL were mixed and heated to 80°C to block isocyanate group of HI. The temperature was then maintained for another 8 hours. Dicum-yl peroxide (DCP, Aldrich Chemical Co.) was used as a radical initiator.

Grafting onto HDPE

Graft copolymerization was carried out in xylene solution with DCP. HDPE (10 g) and xylene (100 g) were poured into a reaction vessel and heated in N₂ with agitation followed by the addition of BHI and DCP (0.1g). The reaction continued at 120°C for 3 hours. The obtained products were precipitated in excess acetone. The precipitated graft copolymer was isolated and washed several times with acetone to remove unreacted monomer, initiator, and homopolymer of BHI that could possibly be formed during the grafting reaction. Finally, products were dried in a vacuum oven at 40°C for 24 hours.

Measurements

Prepared BHI was characterized using FT-IR (Nicolet, Magna IR-550) and ¹H-NMR (Varian, model Unity Inova NMR 300). For FT-IR analysis, films were prepared by hot press (Masada Seisakusho Co., LTD, MH-7). The evidence and extent of the grafting reaction onto HDPE were also characterized by their FT-IR spectra. Also, the deblocking temperature of BHI was determined by FT-IR spectra of BHI functionalized HDPE at various temperatures. DSC (Perkin-Elmer, DSC-7) was used for measuring the thermal properties of HDPE and



modified HDPE. The heating run up to 200°C was followed by a cooling run down to 50°C at 10°C/min scanning rates. Two minutes were allowed between the heating and cooling run. Rheological properties of HDPE and modified HDPE were measured by a rotational rheometer (Rheometric Scientific, ARES). Parallel Plates mode, 25 mm in diameter and a gap height of 1 mm, was used for the frequency sweep test under N₂ atmosphere. The frequency range and strain of frequency sweep test used were 0.1 to 100 rad/s and 10%, respectively, and were confirmed to be within linear viscoelastic region. All the specimens for tensile testing were prepared by injection molding (Toshiba, IS-60B) at 150°C with a mold temperature of 50°C. Tensile properties (Ushima, TS 201) were measured following the procedures described in ASTM D638.

RESULTS AND DISCUSSION

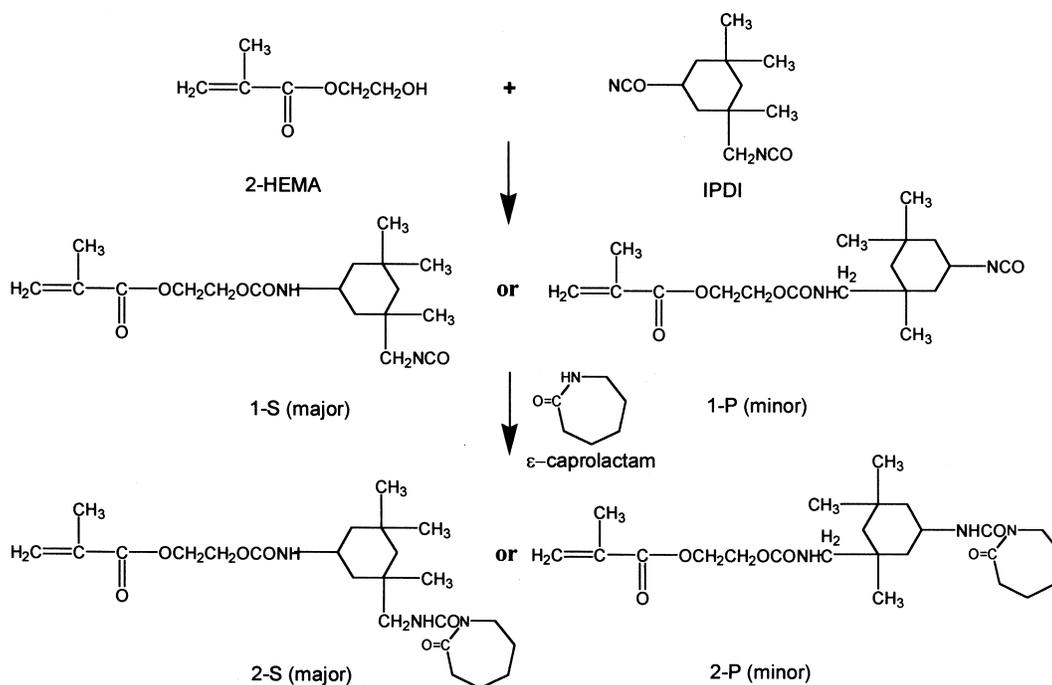
Preparation and Characterization of BHI

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 higher reactivity than the primary NCO group of IPDI [28], 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) due to very low reactivity stemming from a very mild activating effect of urethane group [24]. Consequently, BHI is comprised of two types of molecules, that is, major (2-S) and minor (2-P) types.

Figure 1 shows four 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 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)).

Figure 2 shows ¹H-NMR spectra of (a) CPL, (b) HI, and (c) BHI. The spectrum of (a) shows the unreacted NH peak of CPL at 6.7 p.p.m.. When the reaction of HI with CPL is completed, cycloamide hydrogen peak of CPL almost disappears. As shown in spectrum of (c), CH₂NCO singlet of IPDI at 3.0 p.p.m. and CHNCO singlet of IPDI at 3.8 ppm. almost disappear by the blocking reaction with CPL [29]. The formation of NH produces absorbencies at 4.7 (5.2 ppm.





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

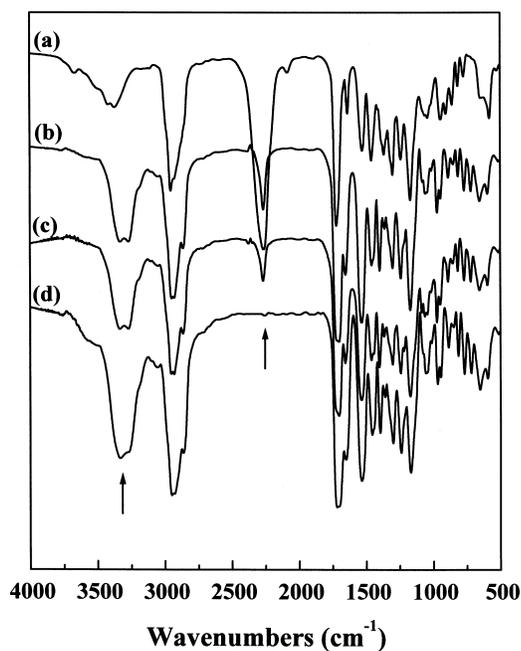


Figure 1. FT-IR spectra of HI reacting with CPL as a function of reaction times: (a) 0 hours, (b) 2 hours, (c) 4 hours, and (d) 8 hours.



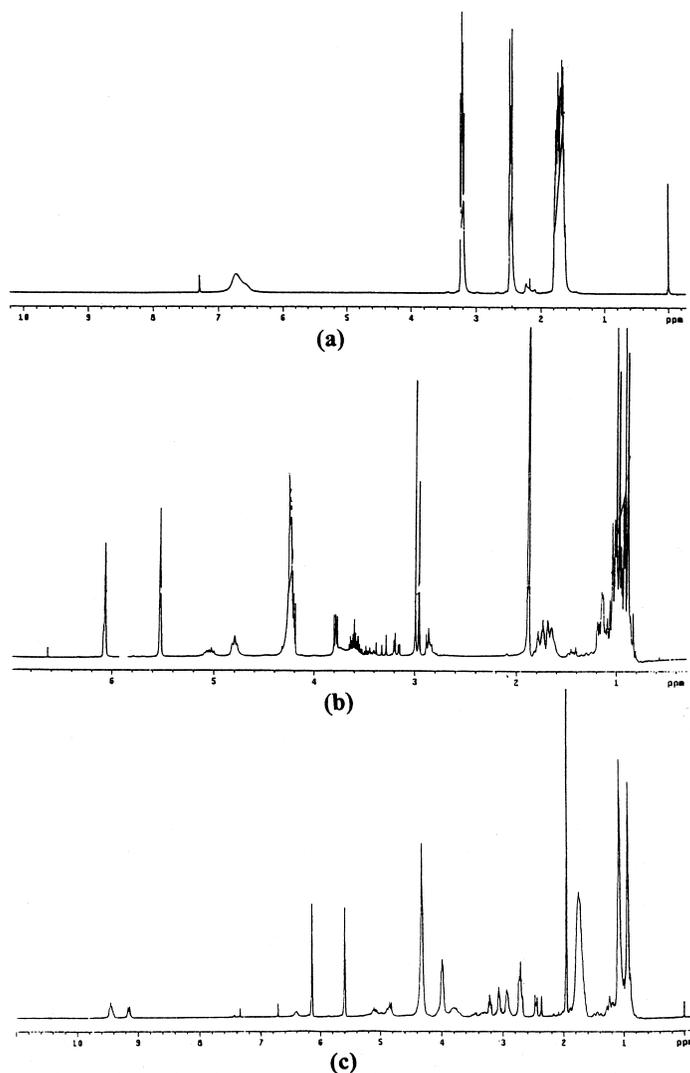


Figure 2. NMR spectra for (a) CPL, (b) HI, and (c) BHI.

in spectra (b) and (c). The early-appearing NH signal centered at 4.8 ppm. is coupled to the CH group arising from the reaction of secondary NCO, whereas the later-appearing NH signal centered at 5.05–5.1 ppm. is coupled to the CH₂ group arising from the reaction of primary NCO [19]. These spectra provide the evidence for the reaction of HI with CPL.



Grafting and Deblocking Reaction

FT-IR spectra of HDPE and modified HDPE are shown in Figure 3. Modified HDPE exhibited 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 methacrylic ester of HEMA, while the absorption peak at 3400 cm^{-1} due to the NH stretching vibration of urethane or amide bond in BHI. The peak height ratio of the C=O peak at 1730 cm^{-1} to that for the CH_3 peak at 1340 cm^{-1} is used as a measure for the relative extent of grafting in the FT-IR spectra [4, 5, 10]. The relative grafting extents of BHI onto HDPE are 0.6 and 1.5 wt%. BHI concentrations to HDPE are 20 and 30 phr, respectively, in the solution grafting reaction.

Figure 4 presents the FT-IR spectra of BHI functionalized HDPE at various temperatures. For BHI grafted onto HDPE, the bond between the carbonyl carbon atom of HI and CPL is thermally labile at certain temperature. Using regeneration of NCO peak at 2270 cm^{-1} , we can confirm the temperature of deblocking reaction of BHI in modified HDPE. When grafting reaction of BHI onto HDPE is carried out at 120°C , there is no NCO peak in the FT-IR spectra

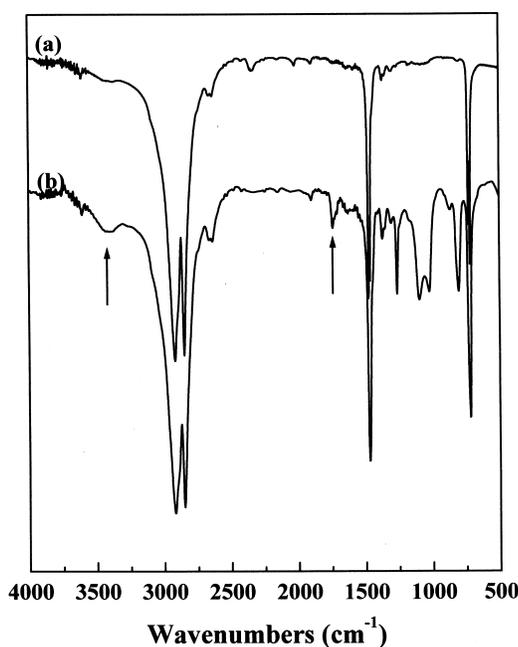


Figure 3. FT-IR spectra of (a) HDPE and (b) BHI functionalized HDPE.



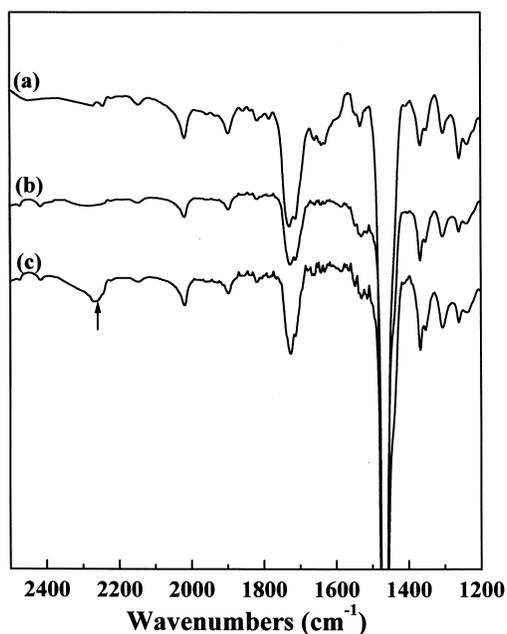


Figure 4. FT-IR spectra of BHI functionalized HDPE (1.5 wt%) at different temperatures: (a) 120, (b) 150, and (c) 200°C.

of modified HDPE, indicating deblocking reaction do not occur. However, at 200°C, we can observe the presence of NCO peak at 2270 cm^{-1} . These results show that deblocking reaction of BHI in modified HDPE occurs from 200°C.

Thermal, Rheological, and Tensile Properties

Generally, crosslinking is dominant side reaction in functionalization of PE with the peroxide-initiated. Hence, a major concern is the effect of side reaction on the structure and rheological properties of functionalized HDPE. Figure 5 shows the DSC results for HDPE and modified HDPE in the heating and cooling run. The melting points of HDPE and BHI modified HDPE are almost the same, indicating extensive crosslinking do not occur in the course of grafting reaction of BHI onto HDPE. If extensive crosslinking takes place during the grafting reaction, melting points of BHI modified HDPE samples will be lower than that of HDPE, due to the decrease of crystallinity. The difference of crystallinity between HDPE and functionalized HDPE is shown in the heating run (Figure 5 (a) and (b)), using heat of fusion. Because this property is very sensi-



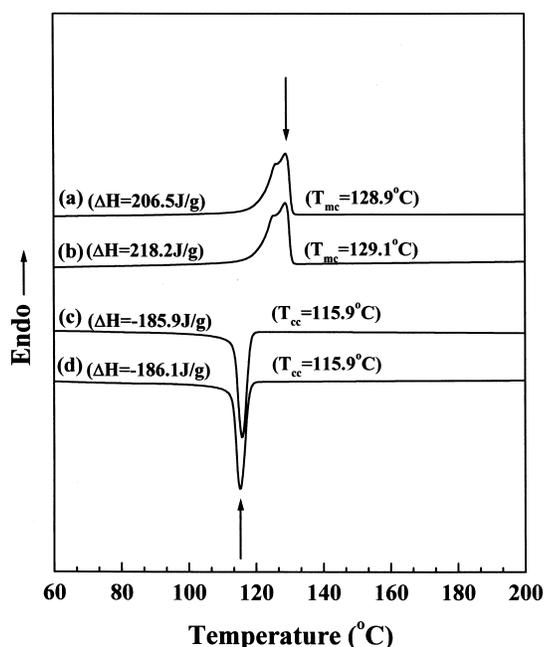


Figure 5. The DSC results for HDPE (a and c) and functionalized HDPE (1.5 wt%) (b and d) in the heating (a and b) and cooling (c and d) run.

tive to thermal history such as drying times, precipitation rates, it is not clear that at this point whether differences observed are genuine or whether they reflect different thermal history. As expected, the difference in crystallinity of the samples is not shown in the cooling run, when the different thermal history is excluded (Figure 5 (c) and (d)).

Figure 6 shows storage (G') and loss (G'') modulus plotted as a function of angular frequency (ω) for HDPE and BHI functionalized HDPE samples at 190°C . At low frequencies, deformation is generally more viscous than elastic for most thermoplastics, hence G'' is greater than G' ; the reverse is true for elastomeric materials. BHI modified HDPE samples exhibit greater G'' than G' at low frequency range and there is no transition where G'' and G' cross over.

Table 1 gives the tensile strengths and elongations at break of HDPE and BHI functionalized HDPE with a relative grafting ratio of 0.6 and 1.5 wt %. The tensile strengths of modified HDPE samples are greater than that of a pure HDPE sample, while elongations at break *vice versa*. Generally, crystallinity has an effect on the mechanical properties of a crystalline polymer. However, DSC

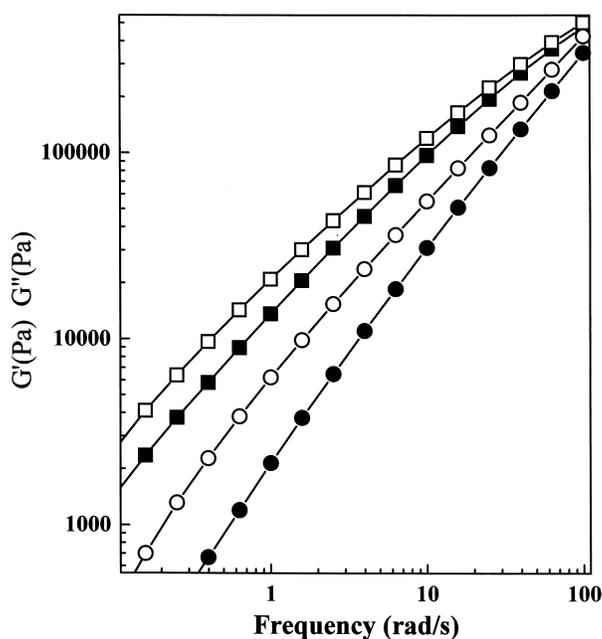


Figure 6. Loss (■) and storage (●) modulus versus angular frequency. Open symbols for functionalized HDPE (1.5 wt%) and closed symbols for pure HDPE sample.

thermograms indicate that there is little or no difference in crystallinity between HDPE and BHI modified HDPE samples. Hence, greater tensile strengths and smaller elongations at break of functionalized HDPE than pure HDPE can be ascribed to the effect of interaction between polar BHI groups grafted onto HDPE.

TABLE 1. Tensile Properties of the HDPE and BHI Functionalized HDPE Sample

	Tensile strength (Mpa)	Elongation at break (%)
HDPE	35.22	780.2
Functionalized HDPE (0.6 wt%)	35.84	767.2
Functionalized HDPE (1.5 wt%)	37.04	747.4



CONCLUSION

In order to improve storage stability of HI, BHI was prepared and characterized by FT-IR and $^1\text{H-NMR}$ spectra. Grafting of BHI onto HDPE and deblocking temperature of BHI were confirmed by the spectra of FT-IR for functionalized HDPE. The onset temperature of deblocking reaction was 200°C . There was little difference in the melting temperature of HDPE and functionalized HDPE, indicating modified HDPE was thermally stable. G' and G'' of HDPE and modified HDPE showed that there was no transition where G' and G'' crossed over. The tensile strengths of modified HDPE samples were greater than that of a pure HDPE sample. However, elongations at break of functionalized HDPE samples were smaller than that of a HDPE sample. These results indicated that there was interaction between polar BHI groups grafted onto HDPE. Since blocked isocyanate group of modified HDPE can regenerate reactive isocyanate group at elevated temperature, BHI modified HDPE has a potential application in the reactive compatibilization of immiscible blend.

ACKNOWLEDGEMENT

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

REFERENCES

- [1] D. R. Paul and S. Newman, *Polymer Blends*, Academic Press, New York, 35, 1978.
- [2] M. Xanthos, *Polym. Eng. Sci.*, 28, 1392 (1988).
- [3] P. Ghosh, B. Chattopadhyay, and A. K. Sen, *Polymer*, 39, 193 (1998).
- [4] J. B. Wong Shing, W. E. Baker, and K. E. Russel, *J. Polym. Sci., Polym. Chem.*, 33, 633 (1995).
- [5] Z. Song and W. E. Baker, *Polymer*, 33, 3266 (1992).
- [6] Y. J. Sun, G. H. Hu, and M. Lambla, *Angew. Makromol. Chem.*, 229, 1 (1995).
- [7] K. E. Oliphant, K. E. Russel, and W. E. Baker, *Polymer*, 36, 1597 (1995).
- [8] G. Samay, T. Nagy, and J. L. White, *J. Appl. Polym. Sci.*, 56, 1423 (1995).



- [9] K. J. Ganzeveld and L. P. B. M. Janssen, *Polym. Eng. Sci.*, **32**, 467 (1992).
- [10] A. Simmons and W. E. Baker, *Ibid*, **29**, 1117 (1989).
- [11] G. Fairley and R. E. Prud'homme, *Ibid*, **27**, 1495 (1987).
- [12] P. M. Subramonian and V. Mehra, *Ibid*, **27**, 663 (1987).
- [13] Y. Minoura, M. Ueda, S. Mizunuma, and M. Oba, *J. Appl. Polym. Sci.*, **13**, 1625 (1969).
- [14] F. Ide and A. Hasegawa, *Ibid*, **18**, 963 (1974).
- [15] M. K. Akkapeddi and B. Vanbuskirk, *Polym. Mater. Sci. Eng.*, **67**, 317 (1992).
- [16] T. C. Maa and F. C. Chang, *J. Appl. Polym. Sci.*, **49**, 913 (1994).
- [17] W. E. Baker and M. Saleem, *Polym. Eng. Sci.*, **27**, 1634 (1987).
- [18] S. Gotoh, M. Fuji, and S. Kitakawa, *S. P. E. ANTEC*, **32**, 54 (1986).
- [19] S. H. Park, J. S. Lee, and K. D. Suh, *J. Mater. Sci.*, **33**, 5145 (1998).
- [20] K. Y. Park, S. H. Park, and K. D. Suh, *J. Appl. Polym. Sci.*, **66**, 2183 (1997).
- [21] S. H. Park, K. Y. Park, and K. D. Suh, *J. Polym. Sci., Polym. Phys.*, **36**, 447 (1998).
- [22] S. H. Park, G. J. Lee, S. S. Im, and K. D. Suh, *Polym. Eng. Sci.*, **38**, 1420 (1998).
- [23] S. H. Park, T. Y. Bae, and K. D. Suh, *Journ. Mac. Sci.—Pure & Appl. Chem.*, **A35**, 1763 (1998).
- [24] H. Kothandaraman and R. Thangavel, *J. Appl. Polym. Sci.*, **47**, 1791 (1993).
- [25] H. Kothandaraman and A. Sultan Nasar, *Polymer*, **34**, 610 (1993).
- [26] K. Schmitt, J. Disteldorf, F. Schmitt, and W. Eickel, *US Patent* 4,212,962, Jul. 15, 1980.
- [27] Chin-Hsing Chen and Chen-Chi M. MA, *Journ. Appl. Polym. Sci.*, **46**, 937 (1992).
- [28] O. Lorenz, H. Decker, and G. Rose, *Angew. Makromol. Chem.*, **122**, 83 (1984).
- [29] H. K. Ono, F. N. Jones, and S. Pappas, *J. Polym. Sci., Polym. Lett. Ed.*, **23**, 509 (1985).

Received October 25, 1999

Revision received February 14, 2000



Request Permission or Order Reprints Instantly!

Interested in copying and sharing this article? In most cases, U.S. Copyright Law requires that you get permission from the article's rightsholder before using copyrighted content.

All information and materials found in this article, including but not limited to text, trademarks, patents, logos, graphics and images (the "Materials"), are the copyrighted works and other forms of intellectual property of Marcel Dekker, Inc., or its licensors. All rights not expressly granted are reserved.

Get permission to lawfully reproduce and distribute the Materials or order reprints quickly and painlessly. Simply click on the "Request Permission/Reprints Here" link below and follow the instructions. Visit the [U.S. Copyright Office](#) for information on Fair Use limitations of U.S. copyright law. Please refer to The Association of American Publishers' (AAP) website for guidelines on [Fair Use in the Classroom](#).

The Materials are for your personal use only and cannot be reformatted, reposted, resold or distributed by electronic means or otherwise without permission from Marcel Dekker, Inc. Marcel Dekker, Inc. grants you the limited right to display the Materials only on your personal computer or personal wireless device, and to copy and download single copies of such Materials provided that any copyright, trademark or other notice appearing on such Materials is also retained by, displayed, copied or downloaded as part of the Materials and is not removed or obscured, and provided you do not edit, modify, alter or enhance the Materials. Please refer to our [Website User Agreement](#) for more details.

[Order now!](#)

Reprints of this article can also be ordered at

<http://www.dekker.com/servlet/product/DOI/101081MA100101119>