

Interchain Crosslinking in a Low-Density Polyethylene/Millable Polyurethane Elastomer Blend

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Received 16 October 2003; accepted 14 April 2004

DOI 10.1002/app.20807

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Interchain crosslinking in a grafted low-density polyethylene and millable polyurethane blend is reported. The interchain crosslinking was studied by torque rheometry and IR spectra. The mechanism of interchain crosslinking was suggested based on the IR spectra. Interchain crosslinking improves thermal stability, which was measured by differential scanning calorimetry. Tensile strength increased but the swelling coefficient decreased

with increased interchain crosslinking. The degree of interchain crosslinking is higher for the glycidyl acrylate grafted sample than for the maleic anhydride grafted sample. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 130–136, 2005

Key words: interchain crosslinking; low-density polyethylene; millable polyurethane; IR spectroscopy; blends

INTRODUCTION

Interchain crosslinking is merely a chemical crosslinking between two dissimilar polymers without the use of a crosslinking agent. De and co-workers observed that mill mixed blends of rubber with appropriate functional groups can be vulcanized at high temperature in the absence of any curatives.^{1–5} Examples include blends based on epoxidized natural rubber—chlorosulfonated polyethylene, epoxidized natural rubber—carboxylated nitrile rubber, PVC—nitrile rubber, etc. Maleic anhydride grafted polypropylene reacts with amine terminated nylon to produce interchain crosslinking between polyolefin and nylon plastic.^{6,7} Phan et al.⁸ prepared interchain crosslinked blends containing α,ω -diamino polypropylene oxide and maleic anhydride grafted polypropylene. Blends prepared by melt mixing of thermoplastic material and elastomer gained considerable attention in recent years. Low-density polyethylene is a commodity thermoplastic that is widely used in packaging applications, the cable industry, etc. Millable polyurethane has applications in automotive bumpers, covers/tream, industrial rollers, shoe soles, sports goods, and various mechanical goods. In our study we grafted low-density polyethylene with glycidyl acrylate or maleic anhydride and mixed it with polyurethane elastomer to analyze the interchain crosslinking in the

blend. The presence of an appropriate functional group of the grafted low-density polyethylene makes it suitable to react with the functional group of the polyurethane elastomer to produce interchain crosslink.

EXPERIMENTAL

Materials

The mixing formulation is shown in Table I. Low-density polyethylene (LDPE MI (ASTM D 1238), 3.0 g/10 min) was supplied by Hyundai Petrochemical Co., Korea. Millable polyurethane (Urepan R 6404) was kindly obtained from Rheinm Chemie, Germany. Dicumyl peroxide (DCP) (grafting initiator), glycidyl acrylate, maleic anhydride (MA), 4,4'-diaminodiphenyl methane, and 4,4'-diaminodiphenyl sulfone were purchased from Aldrich Chemical Co.

Preparation of sample 1

LDPE was melted at 130°C inside a Haake Rheocorder. The millable polyurethane elastomer was then added and mixing was carried out for 8 min with a rotor speed of 50 rpm. The prepared sample was then removed from the Haake Rheocorder and sheeted out in a two-roll mill.

Preparation of samples 2 and 3

LDPE was melted at 130°C inside a Haake Rheocorder. Maleic anhydride and DCP were then added

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TABLE I
Mixing Formulation

Sample code	LDPE (Phr)	PU (Phr)	DCP (Phr)	Maleic anhydride (Phr)	4,4'-diaminodiphenyl methane (Phr)	4,4'-diaminodiphenyl sulfone (Phr)	Glycidyl acrylate (Phr)
Sample 1	60	40	—	—	—	—	—
Sample 2	60	40	0.2	5	2	—	—
Sample 3	60	40	0.2	5	—	2	—
Sample 4	60	40	0.2	—	—	—	5

and the temperature was increased to 175°C. After 5 min a coupling agent (4,4'-diaminodiphenyl methane for sample 2 and 4,4'-diaminodiphenyl sulfone for sample 3) was added. The mixing was continued for 5 min. Then the amine functionalized polyethylene was removed from the Haake Rheocorder. The maleic anhydride grafted and the amine functionalized polyethylene were identified by IR spectra, as shown in Figure 1. The polymer was cut into small pieces and mixed with millable polyurethane elastomer at 130°C for 5 min at 50-rpm rotor speed.

Preparation of sample 4

LDPE was melted at 130°C inside a Haake Rheocorder. Glycidyl acrylate was then added dropwise,

followed by DCP, and the temperature was increased to 175°C. The rotor speed was 50 rpm. After 5 min, the polymer was removed from the Haake Rheocorder. The modified polymer was cut into small pieces and melted inside a Haake Rheocorder at 130°C temperature with 50-rpm rotor speed. The structure of the glycidyl acrylate grafted polyethylene was identified by the IR spectrum, as shown in Figure 1c. The millable polyurethane was then added and mixing was continued for 5 min. The polymer was then removed from the Haake Rheocorder and sheeted out in a two-roll mill.

The prepared samples were crosslinked in a compression mold for half an hour at 150°C and 2800 psi. Interchain crosslinking was studied using a Monsanto Rheometer (R-100) at 150°C at 2800 psi pressure.

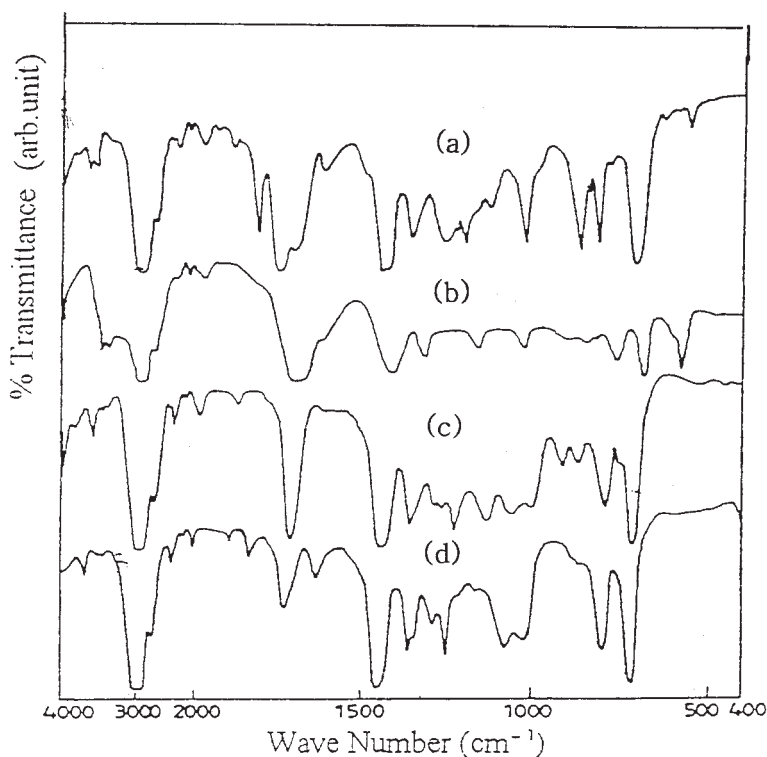


Figure 1 IR spectra of grafted low-density polyethylene. (a) Amine functionalized low-density polyethylene (corresponding to 4,4'-diaminodiphenyl methane); (b) amine functionalized low-density polyethylene (corresponding to 4,4'-diaminodiphenyl sulfone); (c) glycidyl acrylate grafted low-density polyethylene; (d) maleic anhydride grafted low-density polyethylene.

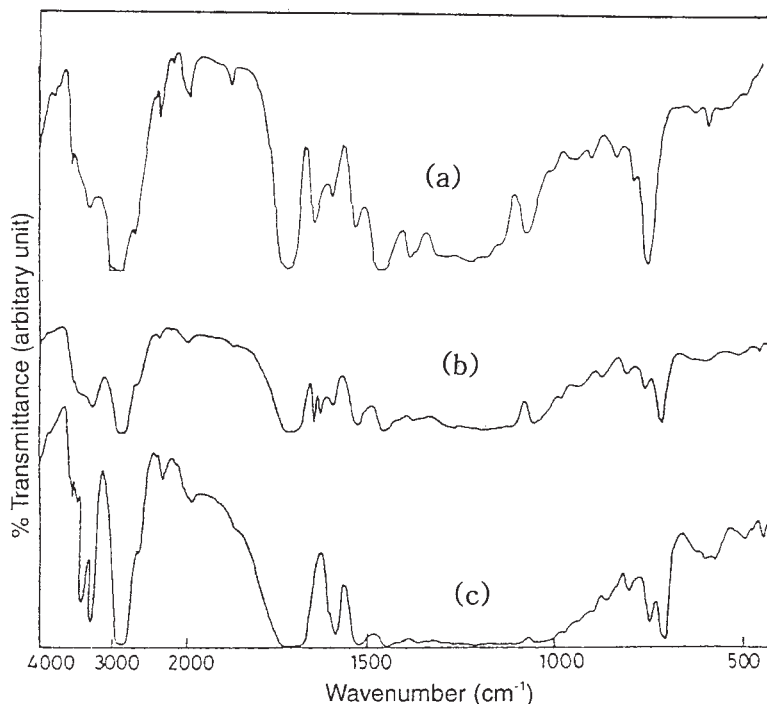


Figure 2 IR spectra of samples. (a) Sample 2 (LDPE/PU/DCP/4,4'-diaminodiphenyl methane); (b) sample 3 (LDPE/PU/DCP/4,4'-diaminodiphenyl sulfone); (c) sample 4 (LDPE/PU/DCP/glycidyl acrylate).

A swelling experiment was performed in dimethyl formamide to dissolve the rubbery phase (millable polyurethane). The swelling coefficient was determined using the formula⁹

$$Q = \frac{m - m_0}{m_0} \frac{1}{\rho'}$$

where Q = swelling coefficient; m = weight of the swollen sample; m_0 = original weight of the sample; ρ = density of the solvent.

Infrared (IR) spectroscopy was carried out with a Shimadzu IR-470 IR spectrophotometer using pressed films. The thickness of the film was 0.03 mm.

The tensile properties of the samples were measured using a Universal tester (H.T.E, H 25 km and 500 Lm extensometer) at a strain rate of 100 mm/min. At least five dogbone-shape replicas of each sample were used.

Differential scanning calorimetry studies were carried out using a Stanton Redcroft STA-625 thermal analyzer in the temperature range of 25–625°C at a heating rate 10°C min⁻¹ in air.

RESULTS AND DISCUSSION

IR spectroscopy

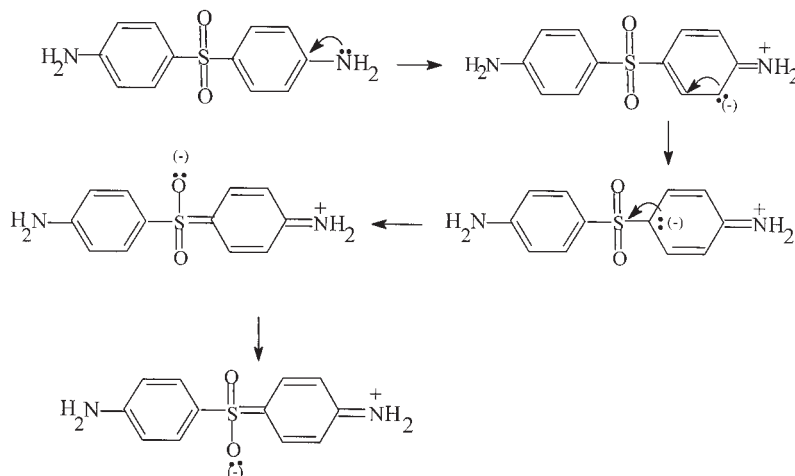
The mechanism of interchain crosslinking reaction is given by IR spectroscopy.

Sample 2

The IR spectrum of sample 2 is shown in Figure 2a. In the first step of the reaction maleic anhydride is grafted with low-density polyethylene.^{10–14} Then maleic anhydride grafted low-density polyethylene reacts with 4,4'-diaminodiphenyl methane, which results in the formation of an amine functional group in the low-density polyethylene.¹⁵ The spectrum of this amine functionalized polyethylene (corresponding to the 4,4'-diaminodiphenyl methane) is shown in Figure 1a. The symmetric and asymmetric stretching frequencies of the primary amine functional group appear as a doublet at 3355 and 3220 cm⁻¹.¹⁶ This doublet is not observed in the IR spectrum of sample 2. Thus, the primary amine group of the grafted low-density polyethylene is considered to have taken part in the interchain crosslinking reaction. Again, a peak appearing at 1650 cm⁻¹ in the IR spectrum of sample 2 (Figure 2a) is attributed to the C=N stretching frequency. This confirms the fact that a reaction has taken place through the amine group of grafted low-density polyethylene and the carbonyl moiety of polyurethane. The reactions are shown in Scheme 1.

Sample 3

The IR spectrum of the sample is shown in Figure 2b. In the first step of the reaction maleic anhydride is grafted with low-density polyethylene. The maleic an-



Scheme 4

reactive than 4,4'-diaminodiphenyl methane. As a result, the obtained degree of crosslinking is higher in sample 2 than in sample 3.

In the glycidyl acrylate grafted sample, the reaction occurs in a single step. The lone pair of electron of nitrogen of the polyurethane elastomer attacks directly the less hindered carbon atom of the epoxy group, followed by the reaction of the SN2 pathway. In the maleic anhydride grafted sample, however, a coupling agent was used for the interchain crosslinking reaction. The interchain crosslinking reaction, therefore, occurs in two steps, which is not as easy as for sample 4. It is observed from Schemes 1 and 2 that the amine group of the coupling agent attacks the anhydride group of the maleic anhydride grafted LDPE. The reaction is slow because the carbon atom is not sufficiently polar as it withdraws the electron of the neighboring oxygen atom. Again, in the second step the amine group of the amine functional polyethylene reacts with the carbonyl group of the PU elastomer. This carbonyl carbon is not sufficiently positive because it withdraws the electron from the neighboring carbon atom through resonance; thus, the rate is not high. Because these reactions are heterogeneous, the mixing of the coupling agent at that temperature is also important. An easy single-step reaction produces

more interchain crosslinks in the glycidyl acrylate grafted sample compared to the maleic anhydride grafted sample where reaction occurs in two steps. In this way, the degree of interchain crosslinking reaction in the glycidyl acrylate grafted sample is higher than that of the maleic anhydride grafted sample.

Mechanical properties

The tensile strength and the elongation at break of the samples are shown in Table II.

Tensile strength increases with increased degree of interchain crosslinking. The tensile strength of the

TABLE II
Mechanical Properties and Swelling
Coefficients of the Samples

Sample code	Tensile strength (kgf/cm ²)	Elongation at break (%)	Swelling coefficient
Sample 1	51	140	2.1
Sample 2	74	119	1.15
Sample 3	62	126	1.6
Sample 4	81	114	0.8

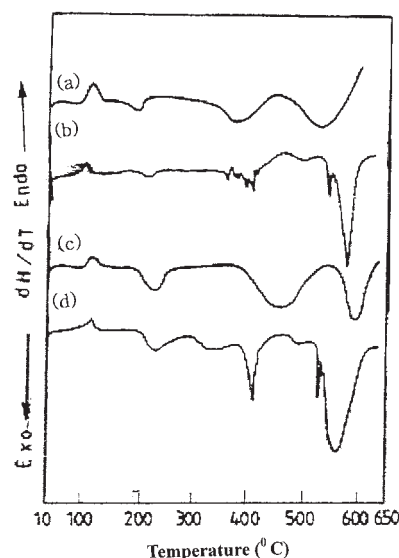


Figure 4 DSC plots of four different blend samples. (a) Sample 1 (LDPE/PU); (b) sample 2 ((LDPE/PU/DCP/4,4'-diaminodiphenyl methane); (c) sample 3 (LDPE/PU/DCP/4,4'-diaminodiphenyl sulfone); (d) sample 4 (LDPE/PU/DCP/glycidyl acrylate).

TABLE III
DSC Parameters

Sample code	First onset temp of degradation (°C)	Second onset temp of degradation (°C)	Initial heat of degradation (J/g)
Sample 1	170	355	36
Sample 2	188	375	39.7
Sample 3	182	369	35
Sample 4	194	394	135.8

sample 1 is the lowest and that of sample 4 is the highest. The tensile strength of sample 4 is 1.58 times higher than that of sample 1. This may be due to the fact that interchain crosslinking enhances the compatibility of the blend.

Swelling coefficient

The swelling coefficient of the samples is given in Table II. The swelling coefficient decreases as the degree of interchain crosslinking increases. Sample 4 has the lowest swelling coefficient and sample 1 has the highest. It is well known that the swelling coefficient increases as the degree of interchain crosslinking decreases. The substantial amount of interchain crosslinking of sample-4 is responsible for its low swelling coefficient. The results show good agreement with the torque rheometry results.

Thermal analysis

The DSC plots of the samples are shown in Figure 4. The various thermal degradation parameters such as onset temperature of degradation and heat of degradation are summarized in Table III. The DSC plots show that the melting point of the sample appears within the range of 113–115°C. The melting point of LDPE is 116.5°C.¹⁹ The slight depression of melting point is due to the presence of an amorphous rubbery phase inside the sample, which is known as the dilution effect.²⁰ The onset temperature of sample 4 is the highest and that of the sample 1 is the lowest. The onset temperature of sample 2 is higher than that of the sample 3. This is due to the interchain crosslinking, which is highest in sample 4 and lowest in sample 1.

Interchain crosslinking increases the rigidity of the system. Thermal stability increases with increased rigidity of the system. Thus, interchain crosslinking improves the thermal stability of the sample.²¹

CONCLUSIONS

Interchain crosslinking in a grafted low-density polyethylene and millable polyurethane elastomer blend was studied thoroughly. The plausible mechanism of interchain crosslinking reaction was suggested based on the IR spectra. The degree of interchain crosslinking is determined by torque rheometry. The degree of interchain crosslinking depended on the reactivity of the coupling agent used (4,4'-diaminodiphenyl methane or 4,4'-diaminodiphenyl sulfone). Tensile strength increases with the increased degree of interchain crosslinking. However, this trend is reverse for the swelling coefficient. The degree of interchain crosslinking is higher when glycidyl acrylate is used for grafting compared to the maleic anhydride grafted samples. Interchain crosslinking in the blend also improved thermal stability.

This work was supported by the National Research Laboratory Program, the Center for Integrated Molecular Systems, POSTECH, Korea, and the Brain Korea 21 Project.

References

- Mukhopadhyaya, S.; De, S. K. *J Appl Polym Sci* 1991, 43, 2773.
- Ramesh, P.; De, S. K. *J Mater Sci* 1991, 26, 2846.
- Manoj, N. R.; De, P. P.; De, S. K. *J Appl Polym Sci* 1993, 49, 133.
- Alex, R.; De, P. P.; De, S. K. *Kutsch Gumi Kunsts* 1991, 44, 333.
- Alex, P.; De, P. P.; De, S. K. *Polym Commun*, 1990, 31, 118.
- Ide, F.; Hasegawa, A. *J Appl Polym Sci* 1974, 18, 947.
- Sedan, M.; Grebling, D.; Lamba, M. *Polym Networks and Blends* 1993, 3, 115.
- Phan, T. T. M.; Denicola, A. J. I.; Schadler, L. S. *J Appl Polym Sci* 1998, 68, 1451.
- Tanner, R. T. *J Polym Sci*, 1970, A-28, 2076.
- Schnukler, S.; Machonis, J.; M Shida, U.S. Patent No. 4 419 408 (1983).
- Schnulker, S.; Machonis, J.; M Shida, U.S. Patent No. 4 477 532 (1987).
- Wong, C. S. U.S. Patent No. 4 857 254, 1989.
- Gaylord, N. G.; Mehta, M. *J Polym Sci, Polym* 1982, 20, 481.
- Gaylord, N. G. U.S. Patent No. 4 506 056 (1985).
- Nagano, R. U.S. Patent No. 4 632 954 (1986).
- Silverstein, R. M.; Basseler, G. C. *Spectrophotometric Identification of Organic Compounds*; Wiley: New York, 1976; Chapter 3.
- Galluch, R. R.; Going, R. C. *J Appl Polym Sci* 1982, 27, 425.
- Socrates, G. *Infrared Characteristics Group Frequency*; Wiley Interscience: New York, 1980.
- Mishra, J. K.; Roychowdhury, S.; Das C. K. *Polym Adv Tech* 2002, 13, 112.
- Defrew, G.; Groencis, G.; Reyners, I. *Polymer* 1989, 30, 595.
- Allen, N. S. *Degradation and Stabilization of Polyolefins*; Allied Science: New York, 1983; Chapter 3.