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# Low density polyethylene with an isocyanate functional group

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In order to introduce an isocyanate (NCO) functional group into low density polyethylene (LDPE), grafting of 2-hydroxyethyl methacrylate (HEMA) combined with isophorone diisocyanate (IPDI) on to LDPE was carried out in solution using a radical initiator. The spectra of infrared (i.r.) and proton nuclear magnetic resonance for HEMA combined with IPDI showed that the hydroxyl group of HEMA and the NCO group of IPDI were reacted to form urethane, and the secondary NCO group preferentially reacted over the primary NCO group. From the i.r. spectra of the grafted LDPE, it was found that NCO groups were introduced into LDPE. Thermal stability of the grafted LDPE was investigated by differential scanning calorimeter analysis, and rheological values were observed to evaluate processability. © *1998 Kluwer Academic Publishers*

## 1. Introduction

Functionalized polymers, especially polyolefins with functional groups, have been extensively used for the improvement of adhesion, dyeability, or other properties of parent polymers, and the compatibilization of immiscible polymer blends as well as interfacial adhesion in polymeric composites [1–3].

The functionalization of polyolefins has been successfully achieved by grafting of unsaturated functional monomers. Grafting is usually performed in the presence of a radical initiator in solution or in the polyolefin melt phase [4–7]. Until quite recently, most of the functional groups used for the functionalization of polyolefins were carboxy, acid anhydride and epoxy that have potential reactivities [8–11].

Because almost no research work for the introduction of isocyanate (NCO) as a functional group to polyolefins has been published, we have carried out a study looking at the possibility of grafting a monomer with a NCO group on to polyolefins. Also, the compatibilizing effect of the NCO group on blends of engineering resins and low density polyethylene (LDPE) has been shown in previous work [12, 13].

In this study, the preparation of a functional monomer with a NCO group and the grafting of the monomer on to LDPE are discussed in detail. In addition, the thermal and rheological properties of LDPE functionalized by grafting are investigated, compared with LDPE base resin.

## 2. Experimental procedure

### 2.1. Materials

LDPE (Hanwha, melt flow index = 12) was used as-received. A functional monomer with a NCO group was prepared by reaction of 2-hydroxyethyl methacrylate (HEMA, Junsei) and isophorone diisocyanate (IPDI, Aldrich), with a molar ratio of 0.95 : 1. IPDI was put into a vessel at 40 °C under nitrogen ($N_2$) stream, followed by dropping of HEMA, and then the reaction was maintained for 6 h. HEMA combined with IPDI (HI) by the above reaction was used as a monomer to be grafted on to LDPE. Dicumyl peroxide (DCP), obtained from Akzo Novel, was used as a radical initiator. This organic peroxide is characterized by having a half-life of 408 min at 120 °C.

### 2.2. Grafting

The grafting reaction was carried out using xylene as a solvent medium. LDPE and xylene were put into a vessel and heated with agitation, followed by the immediate addition of 20 parts HI per 100 parts LDPE and 1 part DCP per 100 parts LDPE. The reaction was continued for 4 h at 120 °C in $N_2$. After the reaction was finished, the reaction mixture was cooled to 40 °C and isolated by precipitation. The precipitate was washed with pure xylene and acetone several times to eliminate unreacted monomers, initiators and homopolymers of HI.

### 2.3. Measurement

The HI was characterized by Fourier-transform infrared (FTIR, Nicolet, model Mahgna IR-550) and nuclear magnetic resonance (NMR, Varian, model Unity Inova NMR 300), and the evidence for grafting was obtained from FTIR analysis. A grafting efficiency of 10.1% and a grafting extent of 1.92% were determined from elementary analysis (Yanaco, MT-2 CHN coder).

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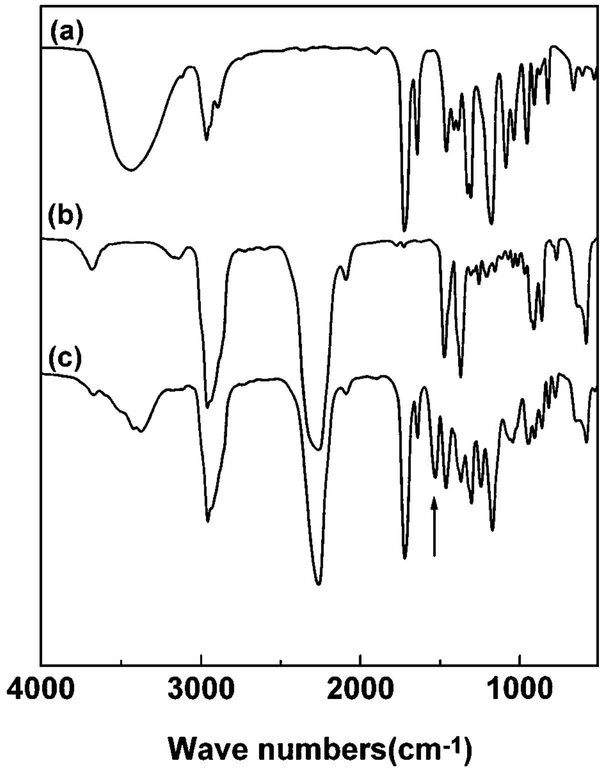

*Figure 1* I.r. spectra for (a) HEMA, (b) IPDI, and (c) HI.

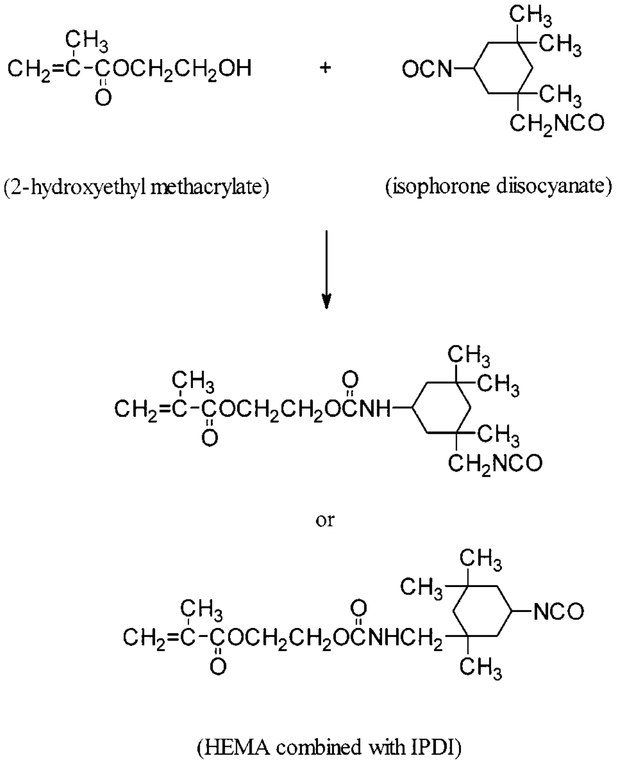

*Figure 2* Scheme to show the formation of HEMA combined with IPDI.

A differential scanning calorimeter (DSC-7, Perkin-Elmer) was used for thermal analysis. The heating scan up to 180 °C was followed by cooling down to 50 °C at a 10 °C min$^{-1}$ scanning rate. Two minutes were allowed between the heating and cooling scan. Rheological properties were measured by a rotational rheometer (Rheometric Scientific, ARES), with a 20% strain at 230 °C under dry nitrogen. Parallel plates, 25 mm in diameter and a gap of 2 mm, were used for the frequency sweep.

## 3. Results and discussion

### 3.1. Reaction of HEMA with IPDI

HEMA was reacted with IPDI to prepare HI, a functional monomer with a NCO group, for grafting. The hydroxyl group (OH) of HEMA and the NCO group of IPDI were combined to form urethane. The infrared (i.r.) spectrum for HI is shown in Fig. 1c. The new peak at 1530 cm$^{-1}$, absent in HEMA and IPDI, is assigned to the NH bending vibration of urethane produced by reaction of the NCO and OH groups.

The kinetics of diisocyanate reactions has been studied with great interest [14]. The initial reactivity of a diisocyanate is similar to that of monoisocyanate substituted by an activating group, in this case the second NCO group. As soon as one NCO group has reacted with an alcohol, the remaining NCO group has reactivity similar to that of monoisocyanate substituted by a urethane group. Because the urethane group has only a very mild activating effect (much less than the NCO group), the reactivity of the remaining NCO group should decrease significantly once one NCO group has reacted.

Expected adducts from the reactions of HEMA with IPDI are monourethanes formed by reaction of the OH group with either of the two NCO groups, and diurethane formed by the reaction of OH with both NCO groups. With the OH : NCO molar ratio of 0.95 : 2.0 used in the present reaction, it would be difficult to form diurethane as above mentioned, and then to enable the formation of monourethanes alone, as represented in Fig. 2. Actually, the absence of diurethane was confirmed from gas chromatography.

Fig. 3 shows proton H-NMR spectra recorded in chloroform solution for the HI prepared by reaction of HEMA and IPDI. These spectra provide clear evidence for the formation of a urethane bond. The singlet at 3.44 p.p.m. assigned to OH of HEMA almost disappeared from the HI spectrum due to reaction of OH with the NCO of IPDI. Also, the extents of absorbencies at 4.2 p.p.m. (corresponding to $—CH_2—O—$) were increased by the decrease of extents of absorbencies at 3.8 p.p.m. (corresponding to $—CH_2—OH$). Concurrently, new

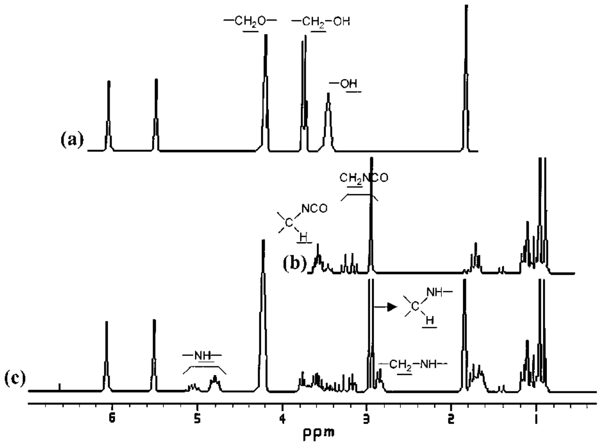

*Figure 3* NMR spectra for (a) HEMA, (b) IPDI, and (c) HI.

absorptions at 2.8–2.9 p.p.m. and a singlet at 2.96 p.p.m. appeared. A new singlet at 2.96 p.p.m., clearly separated from the $CH_2NCO$ singlet of IPDI, represents CH adjacent to NH formed from secondary NCO, whereas the 2.8–2.9 p.p.m. region is assigned to $CH_2$ near NH formed from primary NCO. The formation of NH also produced absorbencies at 4.7–5.1 p.p.m. These results demonstrate that the early-appearing NH signal centred at 4.8 p.p.m. is coupled to the CH group arising from reaction of secondary NCO, whereas the later-appearing NH signal centred at 5.05 p.p.m. is coupled to the $CH_2$ group arising from reaction of primary NCO. From the absorption areas in the H-NMR spectra, it was seen that 95% conversion of HEMA to HI was attained.

One *et al.* [15] reported on the relative reactivities of the two NCO groups of IPDI. According to them, the secondary NCO group is more reactive than the primary NCO group in the absence of a catalyst when IPDI reacts with alcohol. In our experiment, as determined in the H-NMR spectra of HI, secondary NCO reacted with the OH of HEMA was twice as reactive as the primary NCO. This also led us to conclude that the secondary NCO group preferentially reacted, instead of the primary NCO group, under our mild reaction conditions.

## 3.2. Grafting reaction

Grafting of HI on to LDPE was confirmed by i.r. spectroscopy. Fig. 4b shows the i.r. spectra for LDPE incorporated with the HI monomer. It is possible to observe the carbonyl absorption band of HEMA at 1730 $cm^{-1}$. Additionally, the peak due to the NCO group is present at 2270 $cm^{-1}$. The figure gives clear evidence for the presence of a NCO functional group in LDPE.

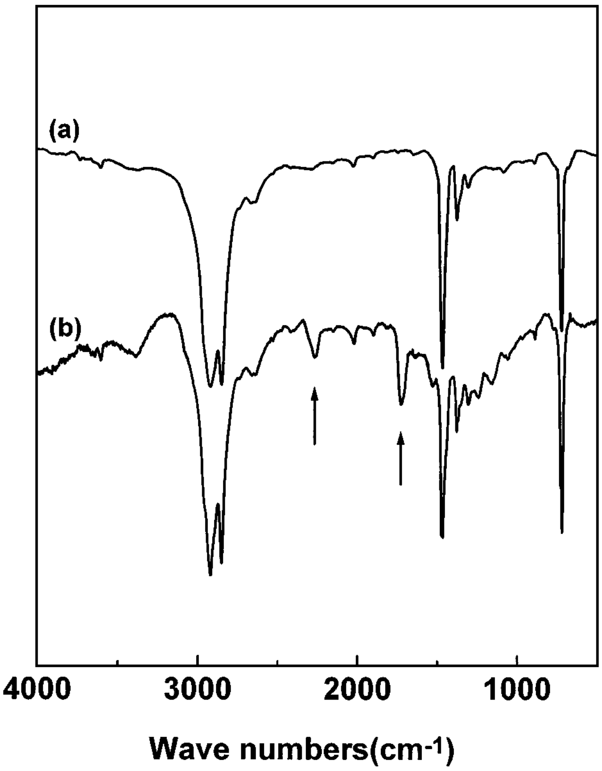

*Figure 4* I.r. spectra for (a) LDPE and (b) LDPE grafted with HI.

TABLE I DSC results for LDPE and LDPE grafted with HI

| | LDPE | LDPE grafted with HI |
|---|---|---|
| Crystallinity, % | | |
| Heating run | 44 | 64 |
| Cooling run | 38 | 38 |
| Melting point, °C | | |
| Heating run | 105 | 104 |
| Cooling run | 89 | 90 |

It has been known that the grafting of vinyl monomer or acrylic substances on to polyethylene is accompanied with crosslinking of polyethylene macroradicals. In this experiment, the reaction mixture in solution remained homogeneous and transparent at 120 °C during the grafting reaction. There was no evidence for extensive crosslinking of LDPE and formation of a HI homopolymer under our reaction procedure, because crosslinks of LDPE and homopolymer of HI were obviously insoluble in hot xylene. It is considered that the absence of HI homopolymer is attributable to the lower reactivities of DCP, the radical initiator used in this grafting reaction, for monomer initiation.

## 3.3. Properties of grafted LDPE

The thermal stability of the grafted material was a major concern. If grafting resulted in a less stable material, it would not be an acceptable way of producing functionalized polyethylene. Pure LDPE was processed and reprecipitated in the same way as a charge containing DCP and HI, and thermal analysis was carried out as described above. The observed crystallinities and melting points in the heating and cooling run are given in Table I.

There appears to be a difference in crystalline content of the samples in the heating run. However, this property is known to be very sensitive to thermal history, and it is not clear at this time whether the differences observed are genuine or whether they reflected differences in drying times, rates of precipitation, or some other type of pretreatment. As expected, the difference in crystalline content of the samples in the cooling run was not shown. The melting points of LDPE and the grafted material are nearly the same. Presumably if thermal stability was decreased by reaction, like extensive crosslinking, the melting point of the grafted LDPE would be much lower than that of LDPE.

The rheological properties of the grafted material are also important for polymer processing. Fig. 5 shows dependencies of loss, $G''$, and storage modulus, $G'$, for LDPE and grafted LDPE on the frequency. $G'$ of the grafted LDPE shifted to values higher than that of the LDPE base resin, indicating that there may be some high molecular weight material present. The presence of a high molecular weight material is believed to arise from crosslinking of LDPE radicals. However, the grafted LDPE did not exhibit any transition in which $G'$ and $G''$ crossed over at the low frequencies tested, as in the case of LDPE. At low frequencies, deformation is generally more viscous than elastic for most thermoplastics, hence $G''$ is greater than $G'$, the reverse is true

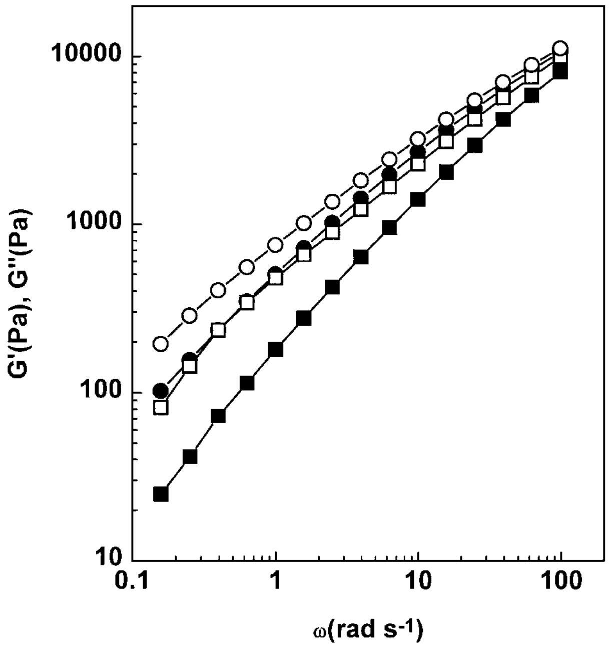

*Figure 5* Loss (●) and storage modulus (■) versus angular frequency, *ω*, for (●) LDPE and (O) LDPE grafted with HI.

for elastomeric or crosslinked materials [16]. In the observation of rheological values, lower $G'$ than $G''$ over the frequency range tested indicates that the grafted LDPE is not highly, but partially crosslinked. It is not considered that the processability of the grafted LDPE is affected by such partial crosslinking.

## 4. Conclusions

In order to introduce a NCO functional group into LDPE, grafting of HEMA combined with IPDI on to LDPE was carried out in solution using a radical initiator. The spectra of i.r. and H-NMR for HI showed that the OH group of HEMA and the NCO group of IPDI reacted to form urethane, and the secondary NCO group preferentially reacted over the primary NCO group. From the i.r. spectra of the grafted LDPE, it was found that NCO groups were introduced into LDPE. There was no evidence for extensive crosslinking of LDPE and the formation of HI homopolymer under the reaction procedure used. Thermal stability of the grafted LDPE was established by DSC analysis, and the rheological values indicated that the grafted material was not highly, but partially crosslinked. Because the NCO group has better reactivity compared with other functional groups, LDPE grafted with a monomer with a NCO group can be applied to the reactive compatibilization of incompatible polymer blends.

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