

Crosslinking of Low-Density Polyethylene by Diisocyanates for Superior Barrier Properties

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ABSTRACT: The chemical modification of low-density polyethylene (LDPE) resins with hexamethylene diisocyanate and toluene diisocyanate was achieved. The reaction of LDPE with diisocyanate was monitored by Fourier transform infrared spectroscopy, wherein the appearance of new peaks at 3326, 1620, and 1572 cm^{-1} corresponding to —N—H stretching, —(C=O)—NH_2 stretching, and —N—H bending in an amide moiety, respectively, was observed. Modified films of excellent clarity and uniform thickness were obtained by the solution casting of crosslinked polyethylene. The oxygen transmission rate (OTR), water vapor transmission rate (WVTR), grease resistance, and thermal

properties of the modified films were studied. The results clearly indicate that the OTR was improved by 35% and that grease resistance was improved by 90–125% in the crosslinked LDPE films with little change in their strengths. The heat seal characteristics, however, showed that relatively higher temperatures were needed to achieve efficient sealing in these films. Differential scanning calorimetry showed a decrease in the melting temperature from 104°C for LDPE to 101°C for both of the crosslinked LDPE films. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1193–1199, 2005

Key words: polyethylene (PE); crosslinking; FT-IR

INTRODUCTION

In food packaging, polyethylene, especially low-density polyethylene (LDPE), is the most widely used polymer because of several advantages. However, the use of pure LDPE is restricted because of some of its inherent properties, including a high oxygen transmission rate (OTR), poor grease resistance, and limited adhesion to other substances. Hence, it is mostly used in combination with other films that possess superior barrier properties as laminated films, which invariably require the use of adhesives,¹ or as co-extruded films for better packaging applications. Alternatively, the desirable properties could be achieved by the suitable modification of polyethylene films. The intrinsic properties of polyethylene mainly arise from its totally nonpolar nature. The structural modification of LDPE may be helpful in improving some of its properties and, thereby, enhancing its utility by decreasing the need for its lamination with expensive materials such as polyester and nylon. Structural modification may

also help to bring down the production and packaging costs.

The useful properties of many polymers can be attributed to their unique structural features, such as the presence or absence of intermolecular attractions or rigidity in their molecules. Hence, these determine the physicochemical properties and the ultimate utility of the polymer. The structure–property relationship, therefore, is a powerful tool for designing polymers for special applications. As mentioned earlier, the chemical modification of readily available polymers offers an attractive route to the improvement of some of the polymers' inherent characteristics or the creation of new ones. The aim of this study was to chemically modify LDPE to decrease its OTR and to improve its grease resistance without adversely affecting its excellent mechanical and moisture resistance properties.

Although there are a few reports on the modification of polyethylene,^{2–5} with regard to the improvement of adhesion, there is scant information available on modification aimed at the improvement of barrier properties. There are some reports on the modification of polyethylene with maleic anhydride and *n*-phenyl maleimide.⁶ Also, there have been attempts to modify the surface of LDPE films by treatment with chromic acid⁷ and SO_3 .⁸ LDPE resins have been modified by

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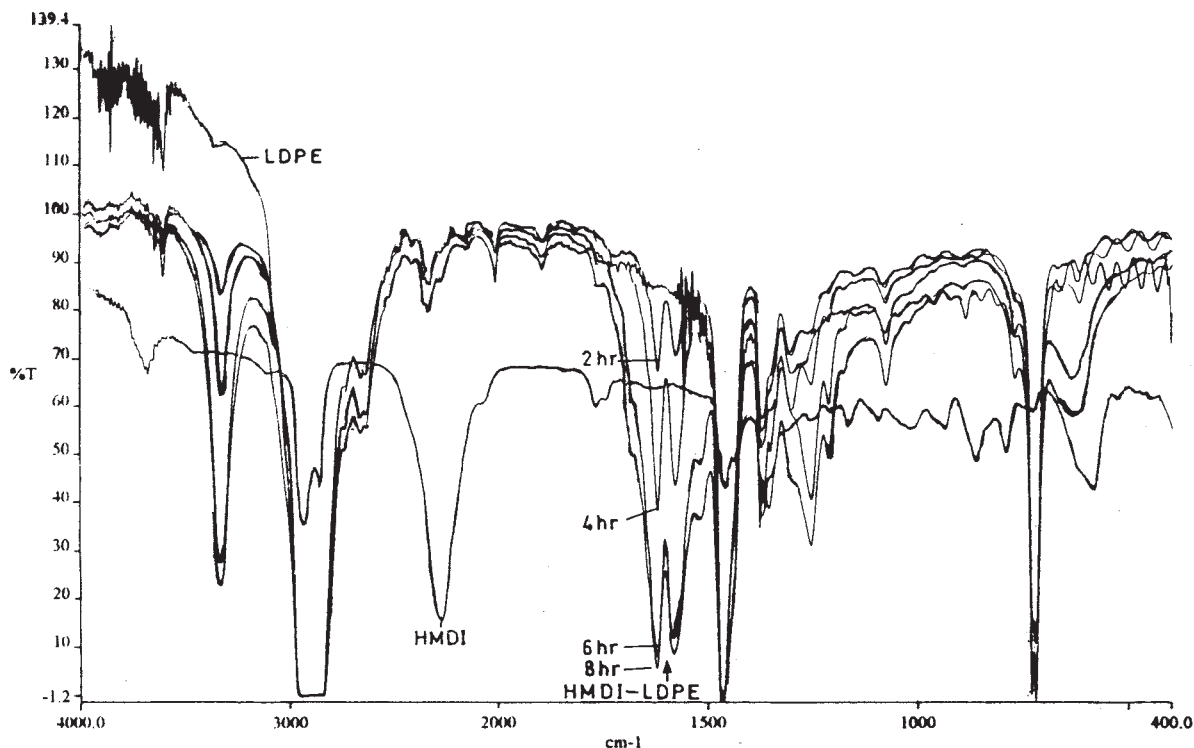


Figure 1 IR spectrum of the reaction product of LDPE with HMDI in the presence of BPO at different time intervals.

reactions with carbonyl-functional unsaturated compounds.²⁻⁴ The treatment of LDPE films with oleum and SO_3^8 has been carried out to decrease the OTR. Most of the studies on LDPE resins, however, have been mostly concerned with the improvement of its impact strength⁹⁻¹¹ and adhesion properties.²⁻⁵ The results of the chemical modification of LDPE resins with hexamethylene diisocyanate (HMDI) and toluene diisocyanate (TDI) with respect to improvement in OTR, water vapor transmission rate (WVTR), and grease resistance properties are reported in this article.

EXPERIMENTAL

Materials

All solvents used were distilled before use. We purified LDPE by dissolving it in toluene and reprecipitating it with acetone, followed by Soxhlet extraction for 16 h with acetone. Benzoyl peroxide (BPO), HMDI, and TDI were procured from Aldrich Chemical Co. (Milwaukee, WI) and were used without further purification.

Methods

Reaction of LDPE with HMDI or TDI

LDPE was dissolved in CCl_4 (10% w/v solution) by refluxing in a two-necked, 1-L, round-bottom flask

fitted with a condenser and a mechanical stirrer. After complete dissolution, HMDI or TDI along with a catalytic amount of BPO were added and refluxed with constant stirring. The progress of the reaction was monitored by IR spectra (Fig. 1) after 2, 4, 6, and 8 h. At the end of the reaction, the contents were transferred to a beaker and allowed to cool to room temperature to precipitate out the modified LDPE. Acetone was slowly added with stirring, and the contents were allowed to settle. The polymer was collected by filtration and washed with fresh acetone (150 mL \times 3). The product was reprecipitated from a CCl_4 solution with acetone. The product was further purified by Soxhlet extraction for 8 h with acetone and dried *in vacuo* to a fine powder.

Casting of films

Simple glass molds (17 \times 17 cm) were designed and fabricated for the film casting. For this purpose, glass strips 17 cm long, 1 cm wide, and 2 mm thick were fixed with an adhesive on all four sides of a flat, defect-free, clean glass plate to give an effective working area of 15 \times 15 cm. For making films, a hot toluene solution of the crosslinked LDPE (1% w/v) was poured into the preheated (115–120°C) glass mold in an oven and covered with a plate to control the rate of solvent evaporation. After complete evaporation of the solvent (ca. 2–3 h), the mold was cooled to ambient

temperature. Crosslinked polyethylene films of excellent clarity and uniform thickness were obtained and characterized for spectroscopic, physicochemical (barrier), and thermal properties.

Spectral studies

These prepared films were characterized for the crosslinking reaction by IR spectra with a PerkinElmer Spectrum 2000 gas chromatograph–Fourier transform infrared (FTIR) spectrometer (Norwalk, CT). All of the measurements were carried out at 20°C in anhydrous conditions and with air as the background. For each sample, 32 scans at a 2-cm⁻¹ resolution were collected in the range of 4000–400 cm⁻¹. The spectra were then analyzed with a curve-resolving technique based on a linear least squares analysis to fit a combination of Lorentzian and Gaussian curve shapes.

Physicomechanical studies

Physicomechanical properties, such as tensile strength and percentage elongation at break, for the crosslinked films and heat seal strength were measured as per ASTM D-882 with an Instron universal testing machine (model 4302) (Canton, MA) at an ambient temperature of 20 ± 2°C. For each property, six measurements were made, and the average value is reported.

Barrier properties, such as WVTR, OTR, and grease resistance, were conducted. WVTR was gravimetrically measured as per ASTM E 96-95, and the results are expressed as grams of moisture vapor permeated through the film per square meter per day at a 90% relative humidity (RH) gradient at 38°C; the OTR of films was measured as per ASTM D 1434-66, and the results were expressed as milliliters per square meter per day at atmospheric pressure.

Differential scanning calorimetry (DSC) studies on various melt and crystallization parameters were determined with a differential scanning calorimeter (Rheometric Scientific, Surrey, UK). About 3–5 mg of the sample, weighed accurately and encapsulated in an aluminum crucible, was first heated to 150°C and cooled to room temperature to terminate any previous history of melt characterization. DSC runs were carried against an encapsulated empty crucible. The temperature of onset, crystallization melting temperature (T_p), and temperature of completion of the endotherm during melting, exotherm during crystallization, and heat of enthalpy (ΔH) were obtained on thermograms with Thermal Analysis Software V 5.45 (Surrey, UK).

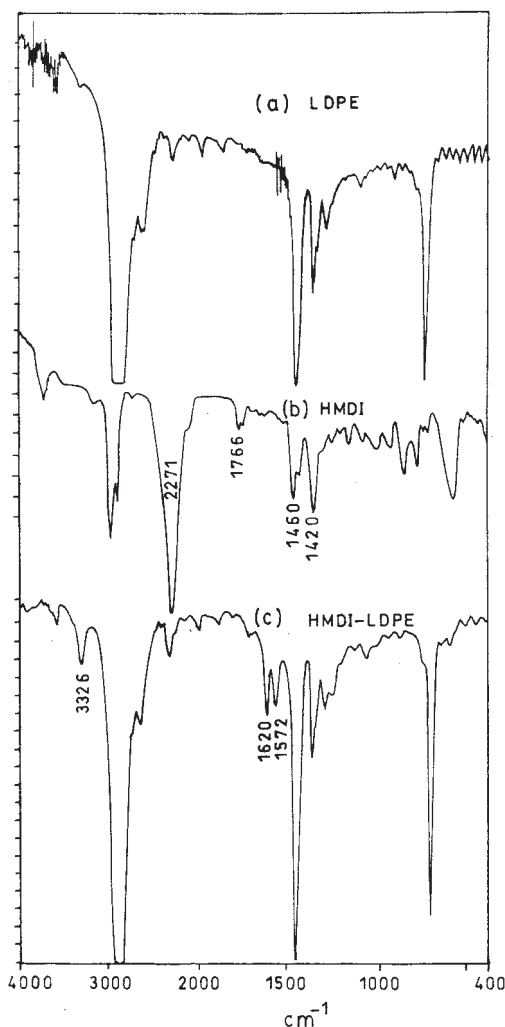


Figure 2 IR spectra of (a) LDPE, (b) HMDI, and (c) crosslinked LDPE with HMDI.

RESULTS AND DISCUSSION

Chemical characterization by FTIR spectroscopy

The IR spectra of LDPE, HMDI, and crosslinked LDPE with HMDI are depicted in Figure 2(a–c). The IR spectra of HMDI [Fig. 2(b)] showed a strong band at 2271 cm⁻¹ due to the asymmetric stretching of —N=C— in the isocyanate group, which is reported in the range 2240–2290 cm⁻¹ for alkyl isocyanates. A less intense absorption peak was expected for the symmetric stretching of the same group in the 1240–1450-cm⁻¹ range. Two peaks were, in fact, observed at 1420 and 1460 cm⁻¹, which were attributed to the isocyanate groups. In addition to this peak, an absorption peak at 1766 cm⁻¹, corresponding to —C=O stretching, was also observed. As shown in Figure 2(c), in the IR spectra of HMDI-LDPE, these absorption characteristics of the isocyanate group were totally absent. Interestingly, new peaks were seen at 3326, 1620, and

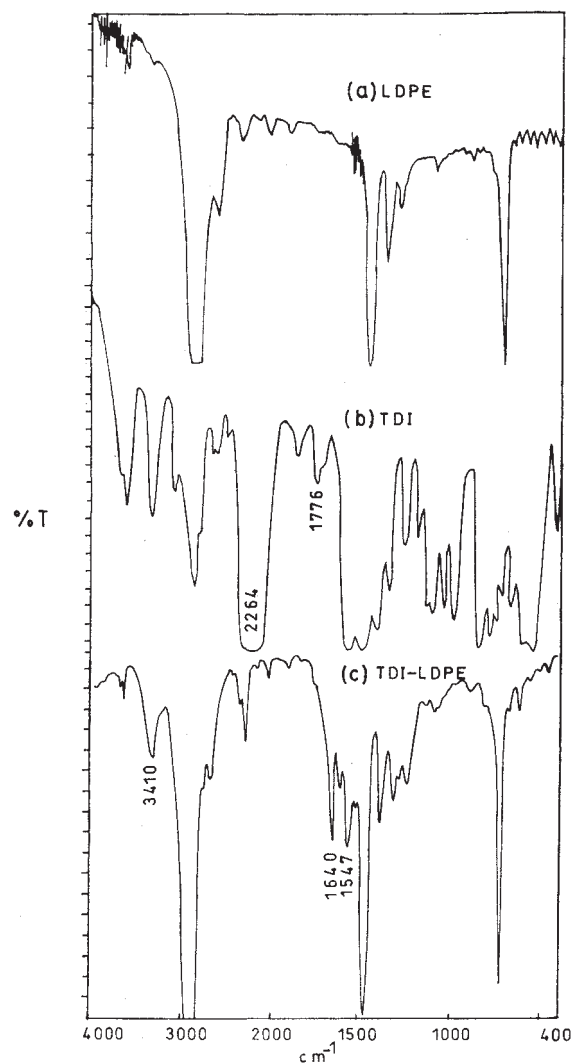


Figure 3 IR spectra of (a) LDPE, (b) TDI, and (c) crosslinked LDPE with TDI. %T = transmittance.

1572 cm^{-1} , which corresponded to —N—H stretching, —(C=O)—NH_2 stretching, and —N—H bending in an amide moiety, showing the crosslinking of HMDI with LDPE. Pure LDPE [Fig. 2(a)] did not show any such peak. The IR spectra of LDPE, TDI, and

crosslinked LDPE with TDI are shown in Figure 3(a–c). As shown in Figure 3(b), the IR spectra of TDI showed a very strong absorption band at 2264 cm^{-1} , corresponding to —N=C— symmetrical stretching. It also contained absorptions at 1445.59 cm^{-1} arising from —N=C— asymmetric stretching and also at 1776 cm^{-1} from —C=O groups. In TDI–LDPE [Fig. 3(c)], these absorption bands were absent, indicating a reaction occurring at the cyanate group. The absorptions at 3410, 1640, and 1547 cm^{-1} , corresponding to —N—H stretching, —(C=O)NH_2 stretching, and —N—H bending in an amide moiety, were observed in this product, too, showing the crosslinking of TDI with LDPE. Table I summarizes the characteristic peaks of the reactant and the products.

Reaction mechanism

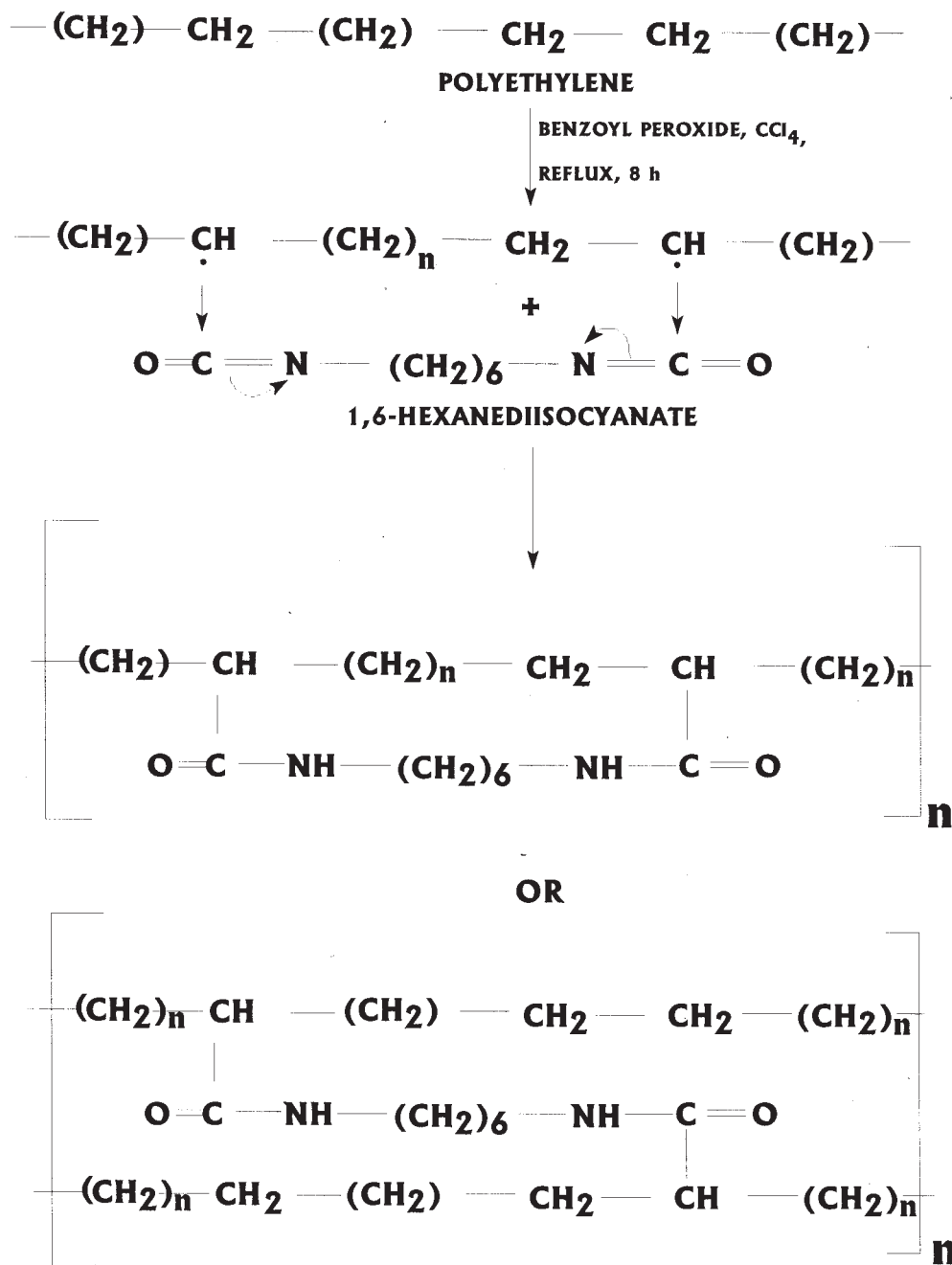
The reaction of HMDI–LDPE is shown in Scheme 1. The BPO (initiator) used in the reaction produced the benzoyl radicals. The latter abstracted hydrogen from the aliphatic carbon in the LDPE molecule. The carbon radical thus generated attacked the nucleophilic carbonyl center in the isocyanate group in both HMDI. The subsequent abstraction of a hydrogen by the molecule resulted in the formation of an amide functional group. This reaction of LDPE with HMDI or TDI, therefore, resulted in the chemical functionalization of the aliphatic side chain with the isocyanate group, which led to the crosslinking of the polymer, which then carried amide functionalities.

Physicochemical properties

The physicochemical properties, WVTR, OTR, and grease resistance, were measured for both of the crosslinked materials (HMDI–LDPE and TDI–LDPE) along with their mechanical properties, including tensile strength and percentage elongation at break. All of these properties were compared with those of the LDPE film, as shown in Table II.

TABLE I
Characteristic IR Peaks of the Reactants and Products

Basic functional groups	Peaks of characteristic functional groups (cm^{-1})			
	HMDI	TDI	HMDI–LDPE	TDI–LDPE
—NH stretch	—	—	3326	3410
—N=C asymmetric stretch	2271 s	2264 s	—	—
—C=O stretch	1766	1776	—	—
—(C=O) NH stretch	—	—	1620	1640
—NH bending in the —CONH moiety	—	—	1572	1547
—N=C— symmetric stretch	1420	1445	—	—
	1460			



Scheme 1 Mechanism of the reaction of LDPE with HMDI.

Clearly, the tensile strength and percentage elongation at break for HMDI-LDPE and TDI-LDPE were not affected by crosslinking and were comparable with those of the LDPE film. The WVTR values were also not significantly different from that of the plain LDPE film. The results show that the polarity change in the crosslinked LDPE did not affect these properties of LDPE adversely. However, the effect of crosslinking was significant in decreasing the OTR and increasing the grease resistance. Also, there was some improvement in the oxygen barrier properties in the

crosslinked LDPE films by 35%. The OTR values decreased from approximately 14,000 to 9000 cc m⁻² day⁻¹. The grease resistance for HMDI-LDPE was 22 days and that for TDI-LDPE was 18 days, compared to 9 days for the LDPE films at 40°C, with a significant improvement in the grease resistance properties of the crosslinked LDPE films. Usually, polymeric materials such as polyethylene, because of their nonpolar nature, are good barriers to water vapor transmission but poor barriers to gases. However, materials such as polyester, nylon, and poly(vinyl chloride), because of

TABLE II
Physicomechanical Properties of the Crosslinked LDPE Films

Material (film)	Tensile strength (MPa)	Elongation at break (%)	WVTR ^a	OTR ^b	Grease resistance (days)
LDPE	7.4	>500	18	14,000	7
HMDI-LDPE (crosslinked)	8.2	>500	20	9,600	22
TDI-LDPE (crosslinked)	7.8	>500	19	8,550	18

^a g/m²/days at 90% RH gradient and 38°C.

^b cc/m²/days at standard temperature and pressure.

their polar nature, are good barriers to oxygen but poor barriers to water vapor. In this study, although the polarity difference caused by the degree of amide group crosslinking achieved appeared to be adequate to cause an appreciable reduction in OTR and an increase in grease resistance properties, the change in the basic nonpolar nature of the original LDPE appar-

ently was not enough to cause corresponding changes in the WVTR.

Both HMDI-LDPE and TDI-LDPE needed relatively higher temperatures for heat sealing (450°F for 2 s at 30 psi) compared to that of virgin PE (350° F for 0.5 s at 20 psi). This increase could have been due to partial rigidity in the polymer conferred by the change in polarity.

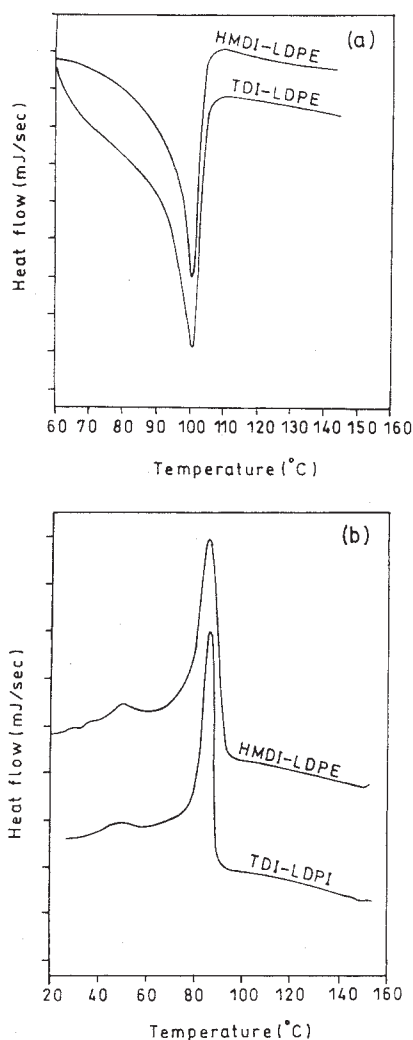


Figure 4 DSC thermograms of crosslinked LDPE films: (a) heating curves and (b) cooling curves.

Dsc studies

The effect of crosslinking LDPE with HMDI and TDI was studied by DSC. Typical DSC thermograms for the heating and cooling curves of the crosslinked LDPE systems are shown in Figure 4(a,b). T_p , the area under the DSC curve (ΔH), and the melt range values are given in Table III for both the crosslinked LDPE (HMDI-LDPE and TDI-LDPE) and the LDPE film. T_p decreased from 104°C for LDPE to 101°C for both of the crosslinked LDPE systems, which may have been due to the change in chemical structure after crosslinking. The decrease in T_p , which showed the degree of crosslinking, might have been very low. Similarly, there was a marginal reduction in the melt range area under the melt curves from 47 in LDPE to 42 in the crosslinked LDPE (HMDI-LDPE and TDI-LDPE). The cooling curves (crystallization behavior) of the crosslinked LDPE were also analyzed. As shown in Table III, similar changes in crystallization melt were observed in the T_p of crosslinked LDPE. However, there was a marginal increase in crystallization range in the crosslinked LDPE systems, but a reduction in the enthalpy of crystallization was observed. This may have been due to the increase in crystalline nature in the crosslinked LDPE.

CONCLUSIONS

LDPE was effectively modified by crosslinking with HMDI or TDI. Even substitution at a low level was sufficient to bring about a significant reduction in OTR and an appreciable improvement in grease resistance. At such a level of substitution, however, the other

TABLE III
Thermal Properties of Crosslinked LDPE Films by DSC

Sample	Heating curve			Cooling curve		
	T_p (°C)	Melt range	ΔH (mJ/mg)	T_p (°C)	Crystalline range	ΔH (mJ/mg)
LDPE	104	47	120	88	22	111
HMDI-LDPE	101	44	96	85	26	86
TDI-LDPE	101	42	111	83	24	90

essential characteristics of LDPE were not affected appreciably.

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