Structure–Property–Processing Relationships in Chemically Modified LDPE and LDPE/LLDPE Blend

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ABSTRACT: The properties of low-density polyethylene (LDPE) and its blend with linear low-density polyethylene LDPE : LLDPE (75 : 25) modified with varying concentrations of dicumyl peroxide (DCP) were compared. Chemical modification was carried out in a Brabender plasticorder under set conditions of temperature, rotor speed, and time. The results are reported in terms of the type of polyethylene used, concentration of DCP, mixing torque, temperature and time on the processing, and mechanical and physical properties of the modified samples. Interpretation of the results is given in terms of gel contents which relate to the three-dimensional network structure of polyethylene. The modified blend forms a denser network structure and, hence, better product properties relative to that of modified LDPE, indicating the influence of LLDPE in increasing the rate and extent of crosslinking on blending with LDPE. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67:** 789–797, 1998

Key words: gel content; processing; crosslinked polyethylene

INTRODUCTION

Polyethylene derives its mechanical properties from a crystalline morphology. The loss of this crystal structure with increasing temperature limits material serviceability. Crosslinking is a means of modifying the structure of the base polymer. This can be accomplished either by irradiation with high-energy electron beams or through the use of chemical crosslinking additives. Chemical crosslinking is accomplished by incorporating organic peroxides, such as dicumyl peroxide (DCP), into polyethylene and subsequently activating the peroxide which links the long-chain molecules into a three-dimensional network. This

modification is manifested by changes in the mechanical and physical properties. Many authors have studied these changes, reporting comparable or contradictory results.[1–5]

Deviations have been attributed to the variety of polyethylene types used and to the diversification of crosslinking processes (i.e., radiation or chemical technique). Polyethylenes are characterized by density (the magnitude depending directly on the crystallinity) as well as by the melt flow index (MFI), which is an indicator of the average molecular weight. These parameters are critical for the subsequent behavior and the changes caused by crosslinking. For example, a highly crystalline polyethylene sample crosslinked chemically is expected to reveal a drastic reduction of crystallinity and consequent changes in properties affected by that parameter. On the other hand, radiation-induced crosslinking does not affect the crystalline phase of the polymer,[6]

Table I   Gel Content of Modified Polyethylene Samples

| DCP (phr) | Gel Content (%) | |
	LDPE	LDPE : LLDPE (75 : 25)
0.5	10	17
1.0	24	33
1.5	36	49
2.0	70	77

Table II   Mixing Times of LDPE and LDPE : LLDPE (75 : 25) Processed at 160°C

Sample	DCP (phr)	Time (min)
LDPE	1.0	15
	1.5	14
	2.0	13
LDPE : LLDPE (75 : 25)	1.0	13
	1.5	12
	2.0	10

so that the changes in such a case should be of a different character.

Linear low-density polyethylene is a copolymer of ethylene and α-olefin, such as 1-butene, 1-hexene, and 1-octene. The presence of small amounts of α-olefin introduces short-chain branches on the polymer backbone. The mechanical properties of LLDPE films are generally influenced by the molecular structure and morphology, which are sensitive to processing conditions.[7–10] This study was undertaken in an attempt to understand the role of the structure of LLDPE on the processing characteristics of one blend system modified with varying concentrations of dicumyl peroxide.

EXPERIMENTAL

Materials

Two types of polyethylene in powder form were used: The low-density grade has a density of 0.922 g/cm³ and an MFI of 6 g/10 min; the values for the linear low-density type were 0.922 g/cm³ and 2 g/10 min, respectively. Dicumyl peroxide [DCP; Merck, bis-α,α'-dimethylbenzyl)peroxide] was used as the crosslinking agent at various concentrations of 0.5–2 phr. The two series of crosslinked samples with their gel contents are shown in Table I.

Method

Preparation of Polyethylene Powder

Polyethylene (pellets), 150 g, was dissolved in 1000 mL boiling toluene for 15 min to form a clear solution. The viscous solution was then gently poured into a threefold excess of methanol under vigorous stirring. The precipitated powder was then filtered and dried in a vacuum oven at 50°C for 24 h to yield the dry powder.

Chemical Modification of LDPE and LDPE : LLDPE (75 : 25) Blend

The samples were dry-mixed separately with varying concentrations (0.5–2 phr) of DCP and melt-processed in a Brabender plasticorder (Model PL 3S) at a set temperature of 160°C and a rotor speed of 30 rev/min. Mixing times are given in Table II. The use of the plasticorder offers the advantage of recording the mixing torque during mixing of the molten polymer and the blend with peroxide, thus giving a first indication of the cross-linking reaction. The samples were then molded as sheets in a hydraulic press with heated platens. The molding conditions varied as seen in Table III since the thermoplastic character of the samples varied over a wide range.

Characterization

Melt flow index (MFI) measurements were made according to ASTM-D1238, and the weight of the polymer extruded in 10 min under a constant load of 2160 g at a constant temperature of 190°C was

Table III   Molding Conditions of LDPE and LDPE : LLDPE (75 : 25) Modified Samples

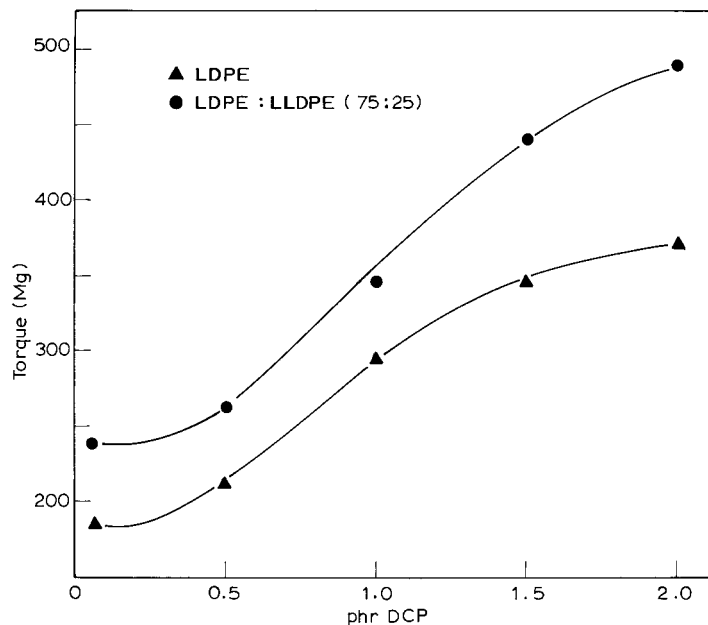| DCP (phr)	Temperature (°C)	Pressure (atm)	Time (min)
0.0	125–130	10	10
0.5	125–130	25	15
1.0	145–150	30	15
1.5	150–155	35	15
2.0	155–160	40	15

Figure 1   Torque versus DCP concentration of LDPE and LDPE : LLDPE (75 : 25) blend.

reported. Mechanical properties were examined according to ASTM D 638-84 using a Zwick tensile testing machine, Model 1445, with a crosshead speed of 50 mm/min and a gauge length of 20 mm working at room temperature.

Density measurements were performed according to ASTM D 792. Hardness was measured according to ASTM D 2240 using a Zwick durometer of the Shore D scale. The specimens were at least 3 mm thick with a surface free of scratches or other defects. For determination of wear resistance, specimens in the form of discs (50 mm diameter and about 3 mm thick) were abraded with a Zwick abrader using a no. 240 emery paper and a 0.5 kg load.

RESULTS AND DISCUSSION

Rheological Investigation

Effect of DCP Concentration on Mixing Torque

A typical trace of mixing torque as a function of DCP concentration of LDPE and the blend is shown in Figure 1. In each case, the mixing torque increases with increasing peroxide concentration.

In the case of the blend which exhibits a higher mixing torque, the rate of increase is higher compared to LDPE. This could be possibly due to the higher short-chain branches, i.e., high tertiary carbon concentration in LLDPE relative to LDPE[11] which gives rise to a higher degree of crosslinking in the blend.

Effect of Temperature on Mixing Torque

The values of mixing torque as a function of temperature and varying concentrations of DCP is shown in Figure 2(a) and for a fixed concentration of DCP in Figure 2(b). The mixing torque increases with increasing temperature, the rate of increase being relatively higher for the blend.

Effect of Time on Mixing Torque

The time of mixing for obtaining a peak value of torque for LDPE and the blend processed at 160°C is shown in Table II. A decrease in peak time with peroxide concentration can be observed for both series of samples. On a comparative scale, the blend undergoes a faster rate of reaction than does LDPE.

Determination of Gel Content

The gel content of each sample modified with DCP was determined by extraction in boiling toluene for 12 h in a Soxhlet extractor in order to correlate the mechanical properties with the degree of crosslinking. Figure 3 shows the gel contents of LDPE and the blend as a function of DCP concen-
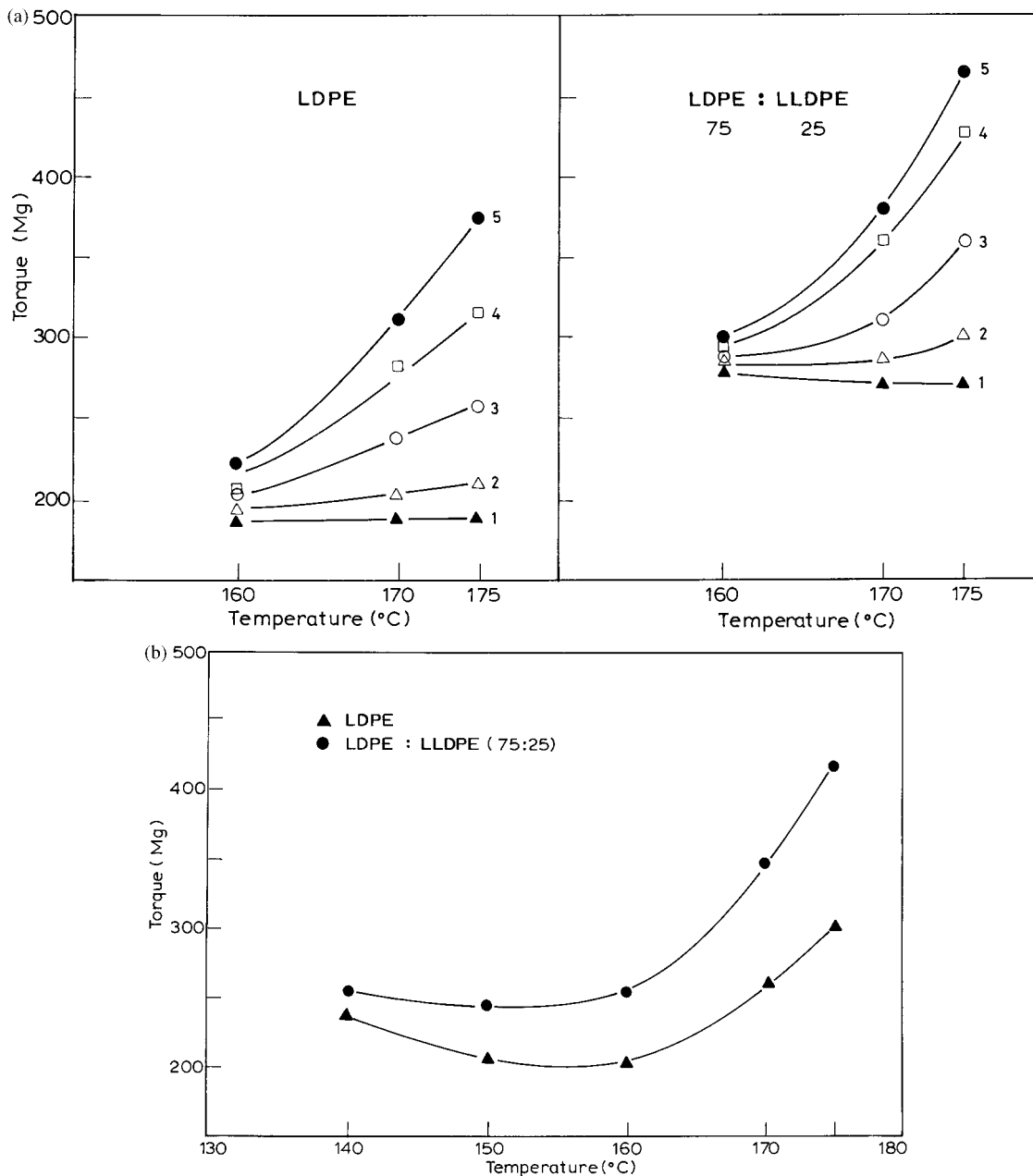
Figure 2 (a) Torque versus temperature of LDPE and LDPE : LLDPE (75 : 25) blend for varying concentrations of DCP (phr): (1) 0; (2) 0.5; (3) 1.0; (4) 1.5; (5) 2.0. (b) Torque versus temperature of LDPE and LDPE/LLDPE (75 : 25) blend for a fixed concentration of DCP of 1 phr.

tration, where there is a continuous increase in gel content with increase in DCP concentration.

Mechanical Properties

The tensile behavior of LDPE and its blend correlated with the gel content is shown in Figure 4.

The values of the tensile strength are given in Table IV. As the curves indicate, for low values of the gel (up to 30%), the tensile strength increases linearly in either case, the blend exhibiting higher values compared to LDPE. At higher values of the gel (50% and above), the tensile strength seems to level off in the case of LDPE and increases in
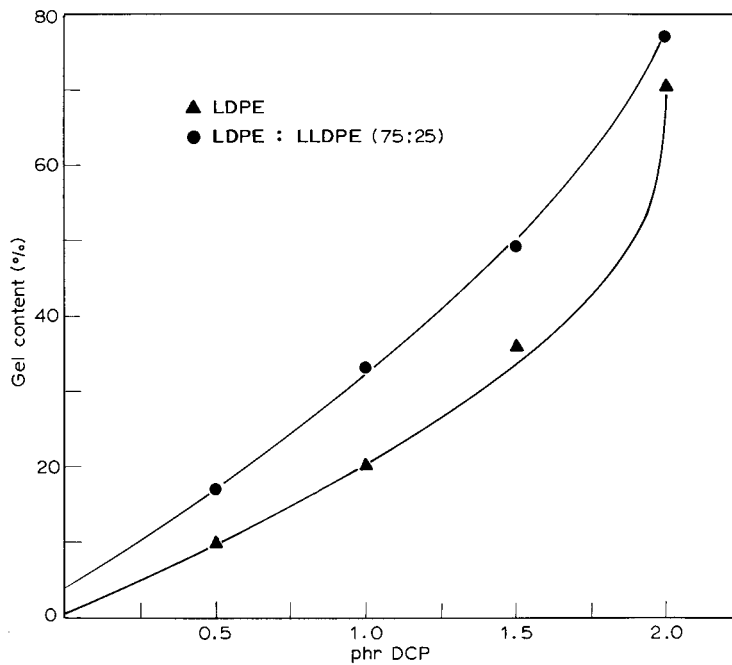
Figure 3 Gel content versus DCP concentration of LDPE and LDPE : LLDPE (75 : 25) blend.
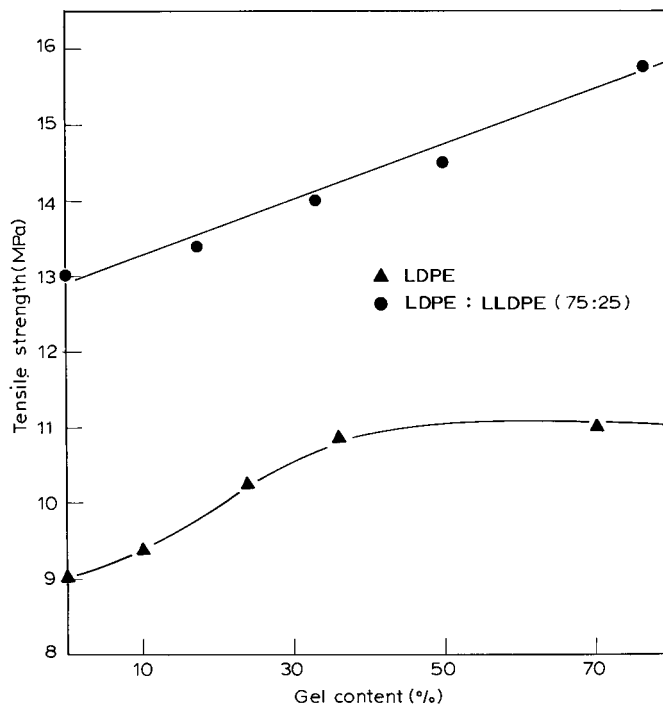

Figure 4 Correlation of tensile strength with gel content of LDPE and LDPE : LLDPE (75 : 25) blend.

Table IV   Effect of Gel Content on the Mechanical Properties of LDPE and LDPE : LLDPE (75 : 25) Modified Samples

Sample	Gel Content (%)	TS (MPa)	Eb (%)	Modulus (MPa)
LDPE	0	9.0	100	51
	10	9.4	185	46
	24	10.2	225	41
	36	10.8	197	35
	70	11.0	130	31
LDPE : LLDPE				
(75 : 25)	0	13.0	350	57
	17	13.2	350	52
	33	13.6	260	42
	49	14.2	260	42
	77	15.6	230	36

TS, tensile strength; Eb, elongation at break.

the case of the blend. This indicates the role of short-chain branches in LLDPE which serve to induce interlamellar linking of the crystalline domains via tie molecules.[12-14] Since the concentration of short-chain branches is higher in LLDPE than in LDPE, the results are as expected.

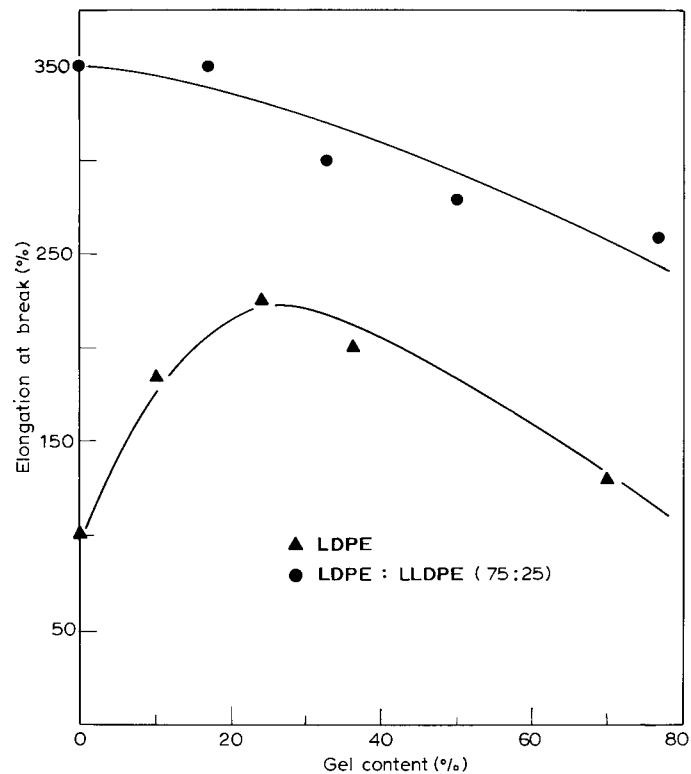The elongation at break of LDPE and its blend of varying gel contents is shown in Figure 5 and

Figure 5   Elongation at break versus gel content of LDPE and LDPE : LLDPE (75 : 25) blend.
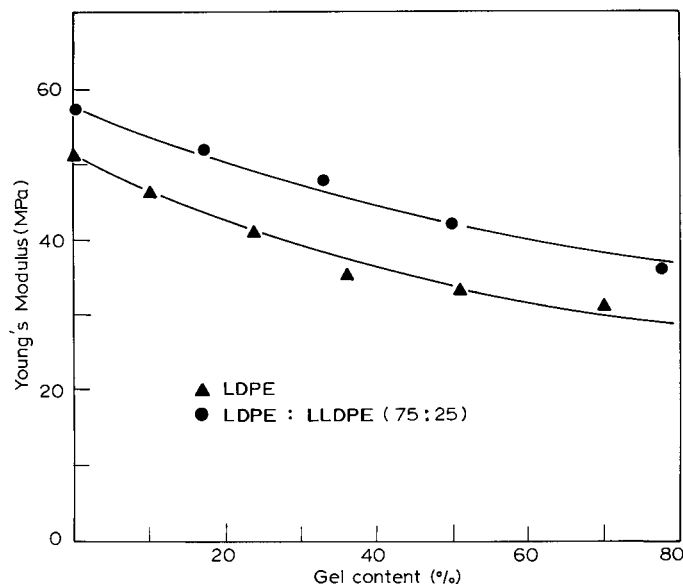
Figure 6 Correlation of modulus of elasticity with gel content of LDPE and LDPE : LLDPE (75 : 25) blend.

Table IV. As the curves indicate, within the limits of experimental conditions followed, there is a linear decrease in the elongation with the gel content for the blend. On the other hand, for modified LDPE, the elongation at break increases at low values of gel content (20%) and thereafter de-
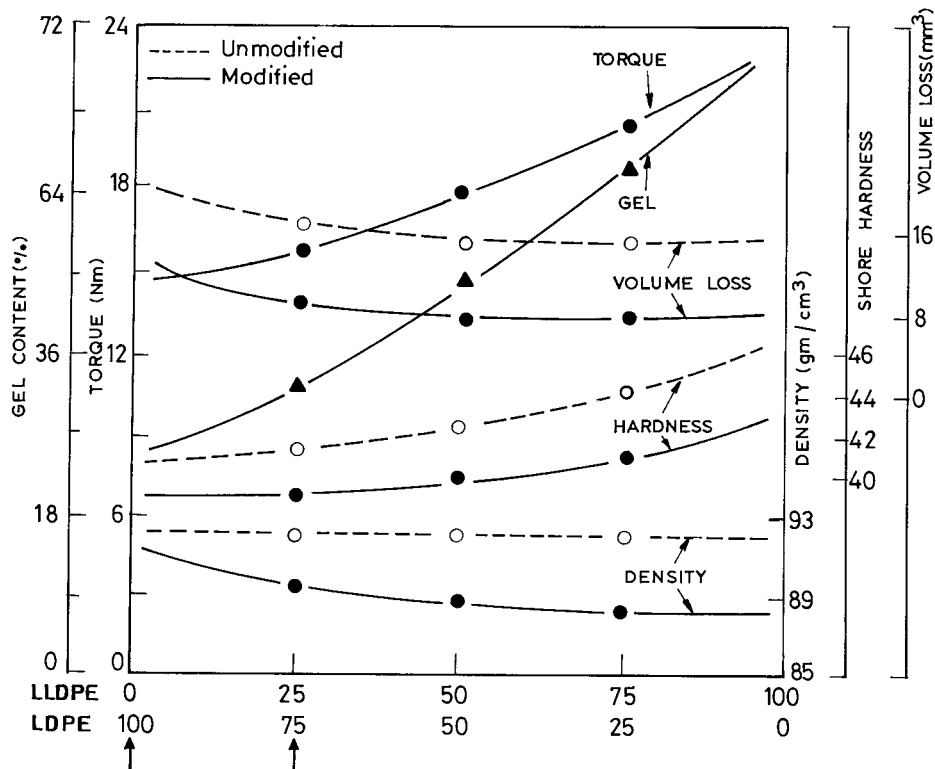

Figure 7 Correlation of gel content, torque, and physical properties with composition of LDPE and LLDPE (arrow indicating compositions under study).

Table V   Effect of Gel Content on Mixing Torque and Physical Properties

Sample	Gel Content (%)	Maximum Torque (Mg)	Density (g/cm³)	Hardness (Shore D)	Volume Loss (mm³)
LDPE	0	180	0.920	41	26
	10	200	0.920	40	24
	24	300	0.910	39	20
	36	320	0.906	37	12
	70	370	0.906	37	12
LDPE/LLDPE					
(75/25)	0	260	0.921	43	20
	17	260	0.921	42	18
	33	350	0.911	41	13
	49	440	0.908	41	8
	77	480	0.908	40	8

creases. The molecular process taking place during the extension of a semicrystalline polymer beyond the yield point is the unfolding of lamellar-like folded chain crystals.[15,16] Due to the high crosslink density, the mobility of the long-chain molecules is restricted, thus hindering the unfolding process, leading to a decrease in the elongation at break.

The effect of the gel content on the moduli of elasticity is shown in Figure 6 and Table IV. A decrease in modulus can be observed, reaching a limiting value for the gel above 50% for both LDPE and the blend, the values being correspondingly higher for the modified blend. Although the Young's modulus variation is not as clearly parallel with the changing of the sample's crystallinity, the decrease in crystalline content leads to the softening of the material and, hence, the decrease of the initial modulus.

Physical Properties

The effect of gel content on the mixing torque and physical properties such as density, hardness, and volume loss on abrasion is presented in Figure 7 and Table V. The densities of both LDPE and its blend with LLDPE decrease continuously with the gel content. This behavior can be attributed to the reduction of crystallinity in both series of samples because of network formation. The interlinking of polymer chains by crosslinking restricts the mobility and, hence, the ordering of the chains. Nevertheless, the network itself corresponds to a denser struc-

ture than that of the amorphous phase. Thus, network formation and crystallinity reduction are competitive factors, and as is evident, network formation dominates in both cases, leading to a decrease in density. The changes in hardness with gel content show a behavior similar to that for density. The explanation is essentially the same as that given in connection with changes in density. Volume loss on abrasion improves as expected on crosslinking.

CONCLUSIONS

1. The use of polyethylene in powder form ensures homogeneity in crosslinking.
2. Chemical modification leads to bonding between the long-chain molecules.
3. The nature of the network depends on the type of polyethylene used, the concentration of peroxide, and the conditions employed during processing.
4. A small amount of LLDPE (25 wt %) incorporated into LDPE increases the rate and extent of crosslinking.
5. The modified blend forms a relatively denser network.
6. Mechanical properties of the modified blend are superior.
7. The modified blend system LDPE/LLDPE (75 : 25) can be substituted for the conventional LDPE in applications such as wire, cable insulation, and hot-water pipes.

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