# Molecular Structure and Physical Properties of E-Beam Crosslinked Low-Density Polyethylene for Wire and Cable Insulation Applications

## Susan Dadbin,<sup>1</sup> Masoud Frounchi,<sup>2</sup> M. Haji Saeid,<sup>1</sup> Fazel Gangi<sup>2</sup>

<sup>1</sup>Radiation Processing Center, Atomic Energy Organization, P.O. Box 14155-4494, Tehran, Iran <sup>2</sup>Polymer Engineering Group, Department of Chemical Engineering, Sharif University of Technology, Tehran, Iran

Received 10 June 2001; accepted 1 December 2001

ABSTRACT: Crosslinking of homemade low-density polyethylene (LDPE) was performed by electron-beam (EB) irradiation. The gel content of the EB-exposed LDPE was determined by the solvent-extraction method. The degree of crosslinking was also evaluated by a hot set measuring test. The results obtained from both the gel-sol and the hot set methods showed that the degree of crosslinking was dependent on the deposited energy in LDPE samples. Increasing the absorbed dose increased the degree of network formation. The LDPE with higher molecular weight yielded higher efficiency of crosslinking at the same irradiation dose. The effect of irradiation dose on the molecular weight between crosslinks (M<sub>c</sub>), glass-transition temperature, and free volume were calculated. Mechanical test results showed that the tensile strength of the samples increased with increase in the irradiation dose up to 150 kGy and then slightly decreased with further increasing the deposited energy. The elongation at break decreased with increasing the absorbed

## **INTRODUCTION**

Ionizing radiation can profoundly alter the molecular structure and macroscopic properties of polymeric materials. The most important chemical reactions leading to changes in mechanical properties of polymers are those involving chain scission and crosslinking. Polymers with a high concentration of quaternary carbon atoms along the chain primarily undergo scission, mostly because of the steric inhibition of radicalradical recombination. Polymers such as polyethylene, lacking this structural feature, primarily undergo crosslinking.1-3 In the wire and cable industry, the most commonly used plastics for electrical insulation for building wire are polyethylene (PE) and polyvinyl chloride (PVC).<sup>4</sup> These thermoplastics form the largest tonnage for insulating wire and cable conductors. For modern applications, however, some of the physical properties of the thermoplastics should be improved.

dose. The results obtained from differential scanning calorimetry exhibited a small reduction in the melting point and the degree of crystallinity of the EB-exposed LDPE samples compared to those of the untreated samples. The effect of crosslinking on the electrical properties of the irradiated samples was insignificant. The dielectric constant of the treated samples remained nearly constant within the irradiation dose range, although the dissipation factor increased slightly with increasing the absorbed dose. The results obtained from characterizing the EB-induced crosslinking of homemade polyethylene, including LH0030 and LH0075, showed the higher molecular weight polyethylene (LH0030) as a preferred option for wire and cable insulation. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 1959–1969, 2002

**Key words:** electron beam; crosslinking; LDPE; wire and cable insulation; crosslink density; free volume; dielectric constant

Crosslinking of thermoplastics alters the materials to those that no longer melt and also resist temperatureinduced deformation or flow.<sup>5</sup> By linking the macromolecules into a network by crosslinking, the toughness, impact resistance, chemical resistance, and working temperatures are improved.<sup>6</sup> The low cost of polyethylene and its excellent crosslinking efficiency make it the best choice for using it as wire insulation, especially for power cables. Crosslinking of polyethylene improves the maximum permissible conductor temperature and also the maximum allowable temperature in the case of overcurrent and soldering.<sup>7</sup> It also makes it possible to use them at temperatures higher than their inherent softening point for a long period of time by choosing an adequate antioxidant.<sup>8–10</sup>

Three crosslinking processes are used in the wire and cable industry: (1) conventional peroxide continuous vulcanization (CV); (2) silane crosslinking; and (3) the newer electron-beam (EB) process.<sup>11</sup> However, growing fuel costs for steam generation plants, coupled with pollution control problems in the peroxidecuring process and slow crosslinking rates as well as the high cost in the silane process, have caused the wire industry to show interest in EB processing.<sup>12</sup>

Correspondence to: M. Frounchi (frounchi@sina.sharif.ac.ir).

Journal of Applied Polymer Science, Vol. 86, 1959–1969 (2002) © 2002 Wiley Periodicals, Inc.

In the EB process crosslinking is induced by the interaction of high-energy electrons with the polymeric material, resulting in a product with properties that are similar or identical to those obtained by the peroxide (CV) process. Unlike CV, EB crosslinking occurs quickly, thereby allowing higher throughput.

In the present study we have investigated the effect of various EB doses on the crosslinking of two kinds of homemade high molecular weight, low-density polyethylenes (LDPEs). The degree of crosslinking was evaluated by both the solvent-extraction and the novel hot set methods. The variation of density of the samples with irradiation dose was determined. The molecular weights between crosslinks and free volume were also predicted and their relation concerning the absorbed dose was studied. The effects of the crosslinking on the mechanical properties of the LDPE samples were measured using a stress-strain technique. Variations of the melting point and degree of crystallinity with crosslink density of the samples were investigated through dynamic scanning calorimetry (DSC). The dielectric constant and dissipation factor of the samples were determined according to ASTM D-150 test method on an Ando electrical test machine (Japan).

## **EXPERIMENTAL**

## Materials

Low-density polyethylene (LH0030) of density of 0.9226 g/cm<sup>3</sup> and melt flow index of 0.35 g/10 min and LDPE (LH0075) of density of 0.921 g/cm<sup>3</sup> and melt flow index of 0.89 g/10 min were purchased from Bandar Imam Petrochemical Co. (Iran).

## Sample preparation

The LDPE granules were preheated in an electrically heated press for 5 min, and then compression molded according to ASTM D-1928 into rectangular sheets (dimensions:  $150 \times 150 \times 2$  mm) at  $150^{\circ}$ C under pressure of 1500 psi for 3 min. The mold was cooled with water at the rate of nearly 15°C/min. The sheets were removed from the mold when the temperature reached below 50°C.

## Irradiation

Irradiation of the LDPE sheets was carried out using an electron accelerator (Rhodotron TT200, Belgium) with energy of 5 MeV under various irradiation doses (50-250 kGy).

## **Density measurement**

The density of samples was measured using a Toyoceike automatic densitometer model DH-100 (Japan).

## Melt flow index

Melt flow index (MFI) of the samples was determined according to ASTM D-1238 using a Zwick 4100 apparatus (Germany). The MFI for polyethylene samples was measured in grams per 10 min when the tests were run at the temperature of 190°C under the weight of 2.16 kg.

## Gel content

The gel content of the electron beam-treated samples was determined using the solvent-extraction method according to the ASTM D-2765 method. The samples were refluxed with hot xylene for 20 h then the remaining insoluble sample was dried in a vacuum oven to a constant weight.

## Hot set test

The hot set test was carried out in a hot set oven Heraes UT 6050 HS (Germany). The samples in the form of dumbbells were placed in the hot set oven under a definite static load at 200°C and the elongation between two marks was measured after 15 min.

## Thermal analysis

Thermal analysis of the samples was carried out on a Shimadzu DSC-50 thermal analysis system (Shimadzu, Kyoto, Japan). The test was performed under nitrogen environment and the rate of heating of 10°C/ min. The melting temperature, degree of crystallization, and the decomposition temperature of the samples were determined from the DSC thermograms.

## Mechanical properties

The stress-strain properties were determined according to ASTM D-638 on an Instron model 4411 testing machine (UK). The test procedure was carried out at a crosshead speed of 50 mm/min and room temperature conditions.

## **Dielectric properties**

The dielectric constant and dissipation factor of both the exposed and the untreated samples were measured according to ASTM D-150 using an Ando insulation resistance measuring set at temperature of 23°C and frequency of 1 MHz.

## **RESULTS AND DISCUSSION**

## **Theoretical aspects**

The glass-transition temperature  $(T_{o})$  of a crosslinked polymer can be quantitatively correlated with the mole fraction of the crosslinker agent ( $X_c$ ) in chemical crosslinking reactions by the following equation, proposed by DiBenedetto<sup>13</sup>:

$$(T_g - T_{g0})/T_{g0} = (1.2X_c)/(1 - X_c)$$
(1)

where  $T_{g0}$  is the glass-transition temperature of the uncrosslinked polymer. The mechanism of crosslinking in polyethylene under interaction of high-energy electrons can be visualized by the following scheme<sup>14</sup>:

$$\begin{array}{rcl} -(CH_2-CH_2)-&+&e\rightarrow -(CH_2-CH_2)^{*-}\rightarrow -(CH_2-\dot{C}H)-&+&H\cdot\\ -(CH_2-CH_2)-&+&H\cdot\rightarrow -(CH_2-\dot{C}H)-&+&H_2\\ -(CH_2-\dot{C}H)-&&-(CH_2-CH)-&\\ -(CH_2-CH)-&&-(CH_2-CH)-&\end{array}$$

where \* represents the molecule-exited state. Radicals in both the crystalline and amorphous regions can be identified. Radicals formed in the crystalline regions have much lower mobility and longer lifetimes because macromolecular diffusional movement is strongly restricted; such radicals can migrate slowly to the amorphous region, where they subsequently react.<sup>15</sup> In EB crosslinking  $X_c$  can be defined as the mole fraction of ethylene units that crosslink the molecular chains. Thus the molecular weight of the chain between two crosslinks ( $M_c$ ) can be correlated with the molecular weight of the monomer unit ( $M_0$ ) by

$$M_c = M_0 / X_c \tag{2}$$

For ethylene  $M_0 = 28$  so that  $M_c = 28/X_c$ . Substituting relation (2) into eq. (1) yields

$$(T_g - T_{g0})/T_{g0} = (1.2M_0)/(M_c - M_0)$$
 (3)

The number of crosslinks in a unit volume ( $\nu$  mol/ cm<sup>3</sup>) is called *crosslink density* and is correlated with  $M_c$  by

$$\nu = \rho / M_c \tag{4}$$

where  $\rho$  is the density of polymer. Hence,

$$(T_g - T_{g0})/T_{g0} = (1.2M_0\nu)/(\rho - M_0\nu)$$
(5)

The above relation indicates that increasing crosslink density results in increasing glass-transition temperature. The glass transition of a polymer is a measure of chain mobility. Thus increasing the crosslink density of a polymer restricts the molecular chain movements, which is an anticipated conclusion. It is interesting to correlate the changes in free-volume content of the polymer with increase in crosslink density. The following relation can be written between  $T_g$  and the free-volume content  $V_f^{16}$ :

$$(V_{f0} - V_f) / V = \alpha (T_g - T_{g0}) / T_g$$
(6)

where  $V_{f0}$  is the free volume at  $T_{g0}$ ;  $\alpha$  is the freevolume expansion of polymer; and V is the total volume, which consists of volume occupied by polymer molecules ( $V_0$ ) and free volume ( $V_f$ ), such that  $V = V_f$ +  $V_0$ . For polyethylene,  $\alpha = 5.4 \times 10^{-4} \text{ K}^{-1}$ . Combining eqs. (3) and (4) yields a relation between free volume and crosslink density:

$$(V_{f0} - V_f) / V = \alpha T_{g0} (1.2M_0 \nu) / (\rho - M_0 \nu)$$
(7)

Thus the free-volume content of the polymer diminishes with increase in crosslink density of the polymer. The crosslink density  $\nu$  of the polymer can be predicted from the theory of elasticity, which is expressed by the relation

$$G = \nu R T \tag{8}$$

where *G* is the shear modulus of the polymer, which is approximately one-third of the tensile modulus *E*. The above relation shows that *G* increases with an increase in  $\nu$ . The creep tensile modulus in the hot set test can be calculated from the relation

$$E = \sigma/\varepsilon \tag{9}$$

where  $\sigma$  is the tensile stress and  $\epsilon$  is the tensile creep strain in 15 min. In the hot set test the tensile stress is constant ( $\sigma = 20$  MPa). Hence,  $\epsilon = 20/(3\nu RT)$ . Thus the measurement from the hot set test (i.e.,  $\epsilon$ ) can be used to calculate the crosslink density  $\nu$ . Then, the free-volume change  $(V_{f0} - V_f)/V$  is calculated from eq. (7).

#### **Experimental aspects**

Figure 1 shows the effect of irradiation dose on the density of exposed polyethylene samples, from which one observes that the density of samples shows a trend of very slight increase with increase in irradiation dose. This indicates that the amorphous region in the polymer undergoes a decrease in free-volume content, thus implying a tighter network structure (i.e., higher crosslink density), as predicted from eq. (7). The free-volume calculations presented below (see Tables II and III) confirm these slight volume changes. The specific volume of a semicrystalline polyethylene is

ĩ

$$v = x v_c + (1 - x) v_a \tag{10}$$



Figure 1 Variation of density of the exposed polyethylene samples with irradiation dose.

where x is the mass fraction of crystals and  $v_c$  and  $v_a$  are the specific volumes of the crystal and amorphous regions in polyethylene, respectively. From X-ray dif-

fraction, for polyethylene,  $v_c = 0.989 \text{ cm}^3/\text{g}$ , and from extrapolation of the volume–temperature line for the molten unexposed polyethylene to room temperature



Figure 2 Variation of gel content of the EB-exposed samples versus irradiation dose.

 TABLE I

 Hot Set Results at 200°C under 20 N/mm² Load

| Absorbed dose<br>(kGy) | LH0030            | LH0075            |
|------------------------|-------------------|-------------------|
| 0                      | Fails immediately | Fails immediately |
|                        | Fails after 3–5   | Fails after 1–2   |
| 100                    | min               | min               |
|                        | Fails after 11–12 | Fails after 9–10  |
| 150                    | min               | min               |
| 200                    | 156.8%            | 170.6%            |
| 250                    | 77%               | 114.8%            |

(27°C),  $v_a = 1.14 \text{ cm}^3/\text{g}.^{17}$  The density of LH0030 is 0.9226 ( $v = 1/\rho = 1.084$ ). Thus slight changes in the volume of the amorphous region account for slighter changes in the density of the semicrystalline polymer. The mass fraction of crystallinity for LH0030 will be x = 0.37 from eq. (10). As shown later, this result is consistent with DSC measurements (see Fig. 5 below).

Figure 2 exhibits the relationship between the gel content of the EB-exposed samples and irradiation dose. The extent of gel formation in the exposed samples is strongly dependent on the dose values. The higher gel content corresponds with a higher portion of the network structure in the amorphous region of the polymer, which is insoluble in solvents. The sol content corresponds with the linear portion of the polymer in both amorphous and crystalline regions. It should be noted, by way of reminder, that the crystalline portion of the polymer is soluble in xylene at 140°C, which is inferred from the zero gel content of uncrosslinked polyethylene. Further, from melting point and enthalpy of fusion measurements of crosslinked polyethylene (see DSC results), it is concluded that the crystalline regions remain effectively intact, that is, uncrosslinked. Thus the higher the gel content, the higher the degree of crosslink density in amorphous regions. The gel content increases rapidly up to a dose of 100 kGy and then the extent of gel formation slows down with further increase in dose rates. This could be attributed to the restricted movement of radical species at the tighter network, which makes the rate of crosslinking slower at the higher dose values.

In other words, the free-volume content in the amorphous regions of the polymer becomes less available for the movement of the radical species. Thus 1963

there should be a critical level of EB irradiation dose at which the free-volume content reaches a critical value. Tightening the network of the amorphous region by overdosing of the polymer above the critical dose reduces the free-volume content below the critical (optimum) level. The gel content at 250 kGy reaches the highest value of 81.15%, which is higher than was predicted, considering the average amorphous content of polyethylenes (i.e., 65%). This may be explained based on the crystalline-amorphous structure models such as random-reentry or switchboard models. In this model the chain-folded macromolecules lie parallel to each other within the crystal but, at folding zones, threadlike macromolecules reenter to adjacent amorphous regions, thus firmly holding together the whole structure. Then the two-phase crystallineamorphous polyethylene is pinned together by the macromolecules, which pass from one region to another and back again many times. Thus it may be concluded that crosslinking of the molecules extending from amorphous to crystalline regions will intermingle some of crystalline regions into the crosslinked network. The gel content percentage in LH0030 samples is greater than that in LH0075 samples at the same irradiation dose. This is because the longer the macromolecules, the more effective the pinning of the two crystalline-amorphous phases. The hot set test results (Table I) and crosslink density calculations (Tables II and III) also suggest higher crosslink density for the LDPE with longer polymer chains or higher molecular weight.

A typical DSC thermogram of a treated polyethylene sample showing melting point, enthalpy of fusion (area under the melting point peak), and the degradation temperature is depicted in Figure 3. Variations of melting point with the absorbed irradiation dose are shown in Figure 4. Only a slight reduction is observed in the melting point of the EB-treated samples compared with that of the untreated sample. The percentage of crystallinity in Figure 5, which is proportional to the area under the melting point peak on the DSC thermogram, shows no trend so that only small deflections from the untreated polyethylene are observed. However, all measured crystallinity percentages of the exposed samples are less than that of the untreated polyethylene. This could be the result of reduction in free volume of the amorphous regions, as

 TABLE II

 Crosslink Density and Free-Volume Change of LDPE (LH0030) with EB Irradiation

| Dose rate<br>(kGy) | Creep modulus<br>(MPa) | Crosslink density <i>v</i><br>(mol/L) | Molecular weight<br>between crosslinks<br><i>M<sub>c</sub></i> (g/mol) | $(T - T_g)/T_g$ (%) | $(V_{f0} - V_f)/V$ (%) |
|--------------------|------------------------|---------------------------------------|--|---------------------|------------------------|
| 200                | 12.76                  | 1.09662                               | 841.68   | 4.13                | 0.00223                |
| 250                | 25.95                  | 2.23018                               | 413.96   | 8.71                | 0.00470                |

1964

| Dose rate<br>(kGy) | Creep modulus<br>(MPa) | Crosslink density <i>v</i><br>(mol/L) | Molecular weight<br>between crosslinks<br>$M_c$ (g/mol) | $(T - T_g)/T_g$ (%) | $(V_{f0} - V_f)/V$ (%) |
|--------------------|------------------------|---------------------------------------|---|---------------------|------------------------|
| 200                | 11.72                  | 1.00724                               | 915.27  | 3.81                | 0.00206                |
| 250                | 17.43                  | 1.49796                               | 615.30  | 5.78                | 0.00312                |

TABLE III Crosslink Density and Free-Volume Change of LDPE (LH0075) with EB Irradiation

was discussed earlier using eq. (10). These results also suggest that the effect of the electron beam on the crystalline part of the polymer is minor. The minor changes in melting point of the polymer could be the result of minor defects created in crystals by the irradiation. The temperature, at which degradation apparently starts, decreases with increasing the irradiation dose (Fig. 6). This is probably attributable to the higher degree of freedom of mobility of polymer chains in a linear uncrosslinked structure than that in a crosslinked network structure. The flow model of Eyring correlates the relation between rate of mobility of polymer chain segments and absolute temperature T.

In Eyring theory, the rate of thermally activated movements of segments of macromolecules in a viscous flow is expressed as an Arrhenius type equation: Rate =  $\alpha \exp(-E/RT)$ , where  $\alpha$  is a constant and *E* is the activation energy required to overcome a potential

barrier for chain segments to move from one position to another.<sup>17</sup> At a high temperature (above 200°C) the rate of movements is large enough to cause tension in a polymer chain, either between physical entanglements in an uncrosslinked linear structure or between chemical crosslinks in a crosslinked network structure. which finally results in chain scission. It is reasonable to assume that chemical crosslinks can impose greater restrictions on chain movements than physical entanglements and thus tension required for chain scission can build up at somewhat lower temperatures in a crosslinked structure. The higher the irradiation dose or the tighter network, the lower the degradation temperature. The other explanation for the decrease in the decomposition temperature with irradiation is freeradical species entrapped in the exposed samples, which promote faster degradation of the polymer at higher temperatures (above 200°C). The higher concentration of these free radicals at higher absorbed



Figure 3 Typical DSC thermogram of the treated polyethylene samples.

0 i. 

**Crystallinity (%)** 





Figure 4 Melting point of the EB-treated samples versus the absorbed irradiation dose.



Figure 5 Crystallinity percentage in the EB-exposed samples versus the irradiation dose.



Figure 6 Degradation temperature of the EB-treated samples versus the irradiation dose.

dose may be responsible for lowering the decomposition temperature in these samples.

The results obtained from hot set measurements are depicted in Table I. The unexposed samples crept rapidly under a constant 20 MPa load, so that failed immediately. By increasing the irradiation dose up to 150 kGy, the samples still failed but the failure occurred at longer time intervals. At 200 kGy an optimum creep elongation percentage (156.8% for LH0030 polyethylene) without failure of the sample was observed. However, at an irradiation dose of 250 kGy the extent of elongation of both kinds of polyethylene samples decreased dramatically (77.07% for LH0030 polyethylene). Considering the high gel content of the latter sample in Figure 2, the reduction in creep elongation should be attributable to the high degree of crosslink density formed at that high dose rate; that is, the higher concentration of crosslinks in the amorphous region leads to a longer resistance time in the hot set creep conditions before the sample failure. In other words, the thermal stability of the samples improves with increasing irradiation dose. Comparison of the gel contents with the hot set values suggests that the optimum elongation percentage in the hot set oven could be obtained at a gel content range of 70 to 80%. From the equations presented above, it is possible to evaluate the tensile creep modulus and free-volume content at the highly crosslinked polyethylene.

The results for LH0030 are shown in Table II. Creep data are available from tensile tests on injectionmolded bars of polyethylene. Creep  $\epsilon$  strain for uncrosslinked polyethylene is given as follows in terms of stress  $\sigma$  (in MPa) and creep time *t* (in hours) at 20°C<sup>17</sup>:

$$\varepsilon = 1.35 \times 10^{-3} \sigma^{1.3} t^{0.11} \tag{11}$$

Thus the creep compliance J(t) can be presented as

$$J(t) = \varepsilon / \sigma = 1.35 \times 10^{-3} \sigma^{0.3} t^{0.11}$$
(12)

In hot set tests, stress is maintained at a fixed value of  $\sigma = 20$  MPa. Substituting this value in eq. (12), expressing *t* in seconds, yields the following equation:

$$I(t) = 1.347 \times 10^{-3} t^{0.11} \tag{13}$$

Creep data at 200°C (the oven temperature in hot set tests) can be obtained by first shifting the data at 20°C to -120°C and then to 200°C using the time–temperature correspondence expressed as<sup>18</sup>:

$$[J(t)]_{T_g} = [J(t/a_{T1})]_{20^{\circ}\text{C}} \text{ and } [J(t)]_{200^{\circ}\text{C}} = [J(t/a_{T2})]_{T_g}$$
(14)



Figure 7 Tensile strength of the EB-treated samples at room temperature versus the irradiation dose.

The shift factors  $a_{T1}$  and  $a_{T2}$  are calculated from the Williams–Landel–Ferry equation

$$\log a_{T1} = [-17.4(20 - T_g)] / [51.6 + (20 - T_g)]$$

and

$$\log a_{T2} = [-17.4(200 - T_g)] / [51.6 + (200 - T_g)] \quad (15)$$

In branched polyethylene three relaxations are detected by dynamic measurements. These relaxations are at  $-120^{\circ}$ C ( $\gamma$ -relaxation),  $-10^{\circ}$ C ( $\beta$ -relaxation), and 70°C ( $\alpha$ -relaxation).<sup>17</sup> For polyethylene the  $\gamma$ -relaxation at  $-120^{\circ}$ C is considered as the glass-transition temperature  $T_g$ . Hence, from eqs. (13), (14), and (15) the creep equation for polyethylene at 200°C will be

$$J(t) = 2.398 \times 10^{-3} t^{0.11} \tag{16}$$

However, eq. (16) predicts a creep strain of about 0.002 at 200°C and t = 15 min (0.25 h). This is while the uncrosslinked polyethylene fails rapidly at 200°C in the hot set experiment. The reason for the disagreement between the predictions of eq. (16) and the experimental observations in the hot set measurements is that the crystalline regions of polyethylene are well above the melting temperature (112°C) at 200°C, so that the molecular chains in both amorphous and melted crystalline regions flow freely and rapidly. Thus, the creep eqs. (11) and (16) are valid only in temperatures well below the melting temperature of polyethylene. On the other hand, highly crosslinked polyethylene shows a substantial amount of elongation at 200°C in hot set measurements, so that the crosslinked amorphous region of polyethylene is able to hold the structure together, even though the crystalline region is melted and lies in a liquid state.

The variation of tensile strength of the samples at room temperature with irradiation dose is shown in Figure 7. The tensile strength at break increased from 15.609 MPa for unexposed LH0030 polyethylene to a maximum value of 18.257 MPa, with increasing the dose to 150 kGy, and then slightly decreased with further increases in dose. The elongation at break decreased from 558.67% for unexposed LH0030 polyethylene to a value of 447.93%, with increasing the dose to 150 kGy, and then slightly decreased with further increases in dose. It is noteworthy that a 400% elongation at break is desirable for wire and cable coating applications. Although all samples showed somewhat of a decrease in elongation at break with an increase in the absorbed dose (Fig. 8), the decreasing trend became more pronounced at the higher dose value of 200 kGy. The results suggest that, up to an optimum dose



Figure 8 Elongation at break of the EB-exposed samples versus the irradiation dose.

rate of 150 kGy, the crosslinking of molecular chains in the amorphous regions of polyethylene tightens the integrity of crystalline and amorphous regions and renders a stronger structure. In this more integrated structure, crystals reinforce the leathery crosslinked amorphous part of the polymer, imparting higher strength and higher thermal stability with sufficient ductility. Of course, the gain in strength is achieved at the expense of some loss in elongation attributed to the restricted movement of polymer chains. Furthering the crosslink density of the network at higher dose renders a very tight network, which severely restricts the mobility of polymer chains and thus causes further reduction in ductility of the polyethylene.

The results of electrical tests (dielectric constant and dissipation factor) are shown in Tables IV and V, respectively. The dielectric constant remains un-

TABLE IV Variation of Dielectric Constant of Crosslinked LDPE with Irradiation Dose

| Dielectric constant |  |  |
|---------------------|--|--|
| LH0030              | LH0075   |  |
| 2.31                | 2.30   |  |
| 2.31                | 2.29   |  |
| 2.29                | 2.31   |  |
| 2.33                | 2.30   |  |
| 2.30                | 2.28   |  |
|                     | Dielectric<br>LH0030<br>2.31<br>2.31<br>2.29<br>2.33<br>2.30 |  |

changed with crosslinking. The increase in dissipation factor may be caused by the formation of some polar groups upon irradiation of samples in the presence of air. However, dissipation factors for crosslinked samples still are well below the allowed maximum limit of  $5 \times 10^{-4}$  for wire and cable insulation applications.

## CONCLUSIONS

This study showed that polyethylene (LH0030) and (LH0075) efficiently crosslinked under electron beam irradiation. The extent of network formation increased with increasing the absorbed dose to 250 kGy, as verified by gel content and hot set tests. However, the gel content percentage in LH0030 samples is greater than that in LH0075 samples at the same irradiation dose. The higher gel content of LH0030 than that of

TABLE V Variation of Dissipation Factor of Crosslinked LDPE with Irradiation Dose

| Absorbed dose | Dissipation factor ( $\times 10^{-4}$ ) |        |  |
|---------------|---|--------|--|
| (kGy)         | LH0030                                  | LH0075 |  |
| 0             | 0.44                                    | 0.44   |  |
| 100           | 0.89                                    | 1.30   |  |
| 150           | 0.86                                    | 1.10   |  |
| 200           | 0.90                                    | 1.10   |  |
| 250           | 1.20                                    | 1.20   |  |

LH0030 is consistent with the higher crosslink density of LH0030. Thus LH0030, which is higher in molecular weight, yields higher efficiency of crosslinking with the same dose of EB irradiation. The results of mechanical testing showed that the tensile strength of both samples increased with increasing dose and then decreased slightly. Elongation at break decreased steadily with increase in dose. Thermal analysis of the EB-treated samples by DSC showed that the melting temperature and degree of crystallinity decreased with increase in irradiation dose, although to a minor extent. The results of electrical tests (i.e., dielectric constant and dissipation factor) showed no significant change with crosslinking. The results obtained from different tests showed that polyethylene (LH0030) irradiated with 200 kGy fulfills all the specifications required for power cable insulation, such as tensile strength, elongation at break, extent of elongation at hot set test, dielectric constant, and dissipation factor.

#### References

1. Charlesby, A. Atomic Radiation and Polymers; Pergamon Press: Elmsford, NY, 1960.

- Chapiro, A. Radiation Chemistry of Polymeric Systems; Wiley-Interscience: New York, 1962.
- Dole, M. The Radiation Chemistry of Macromolecules, Vol. I; Academic Press: New York, 1972.
- Moscovici, A. In: Kirk Othmer Encyclopedia of Chemical Technology; Othmer, K., Ed.; Wiley: New York, 1995; Vol. 14, p 627.
- 5. Zamore, A. Wire Technol Int 1997, May, 83.
- 6. Lee, D. W. Kunstst Ger Plast 1991, 81, 36.
- 7. Oda. E. Radiat Phys Chem 1981,18, 241.
- 8. Kamel, G.; Knoch, G. Radiat Phys Chem 1981, 18, 1217.
- 9. Widenmann, R. Radiat Phys Chem 1977, 9, 701.
- Jaworska, E.; Kayuska, I.; Strzelczak-Burlinska, G.; Michalik, J. Radiat Phys Chem 1991, 37, 285.
- 11. Silverman, J. In: Radiation Processing of Polymers; Singh, A.; Silverman, J., Eds.; Hanser Publishers: Munich, 1992; p 15.
- Barlow, A.; Biggs, J. W.; Meeks, L. A. Radiat Phys Chem 1981, 18, 267.
- 13. Sperling, L. H. Interpenetrating Polymer Networks and Related Materials; Plenum: New York, 1981.
- 14. Singh, A. Radiat Phys Chem 1999, 56, 375.
- Parkinson, W. W. In: Encyclopedia of Polymer Science and Engineering; Wiley: New York, 1988; Vol. 13, p 671.
- Young, R. J.; Lovell, P. A. Introduction to Polymers; Chapman & Hall: London/New York, 1991.
- McCrum, N. G.; Buckley, C. P.; Bucknall, C. B. Principles of Polymer Engineering; Oxford Science Publications: London, 1997.
- 18. Crawford, R. J. Plastics Engineering; Butterworth Heineman: London, 1998.