Thermally Recoverable Crosslinked Polyethylene

SURESH KUMAR, M. V. PANDYA

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400-076, India

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ABSTRACT: The thermal recovery of the stored stress in crosslinked polyethylene has been commercially exploited in the preparation of heat shrinkable materials. The study on thermally recoverable crosslinked polyethylene compositions is reported in this paper. Thermally recoverable compositions were prepared by crosslinking of four grades of polyethylenes in air using γ-rays from a Co-60 source. The effect of the irradiation dose on the gel fraction and radiation dose to gelation is studied. The effect of the melt index (MI) and the density of the polyethylene on the gel fraction, radiation dose to gelation, and recovery percentage of the stored stress is also studied. It is observed that the gel fraction is higher in case of the lower MI material and that rate of recovery is higher at higher temperatures. The rate of recovery of the stored stress is higher in case of the 100 kGy irradiated sample. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 823–829, 1997.

Key words: crosslinking; polyethylene; irradiation

INTRODUCTION

Polyethylene when irradiated with E-beams, gamma rays, and other forms of high energy radiation predominantly undergoes crosslinking.[1] Crosslinking is an important phenomenon in polymers. It enables a thermoplastic polymer like polyethylene to exhibit a viscoelastic behavior, characteristic of an elastomer, at temperatures above the crystalline melting point of the thermoplastic. This valuable property is widely exploited commercially in the preparation of heat shrinkable materials.[2] Heat shrinkable components are widely used in the cable and electric for jointing, splicing, and termination applications. At ambient temperatures, the molded crosslinked polymer retains its shape due to the presence of plastic crystalline domains[3] (Fig. 1). At temperatures above the crystalline melting point, the shape retaining plastic crystalline domains melt, and the polymer exhibits a viscoelastic state due to the presence of chain entanglements and interchain bridges produced by crosslinking. The polymer can be stretched to a higher dimension in this state, and, upon cooling in this condition, the polymer solidifies with the reformation of the plastic crystalline domains into a new shape as held during the cooling process. This material, when heated, tries to revert to its original prestretch shape and dimension due to an effect termed as the "memory effect" by Charlesby.[4]

The presence of the crosslinks is thus important in storing the memory of the shape before the stretching process. It is also observed that the crosslinking dose, presence of the crosslinking promoters, extent of stretching, stretch temperature, and recovery temperature are important parameters in the preparation of heat shrinkable products of polyethylene by the irradiation technique.[5]

We have studied the effect of the melt index and the density of the polyethylene on the gel fraction and the extent and rate of recovery of the stored stress. The effect of irradiation dose and the recovery temperature on the extent of recovery is also investigated. The study was carried

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Correspondence to: M. V. Pandya.

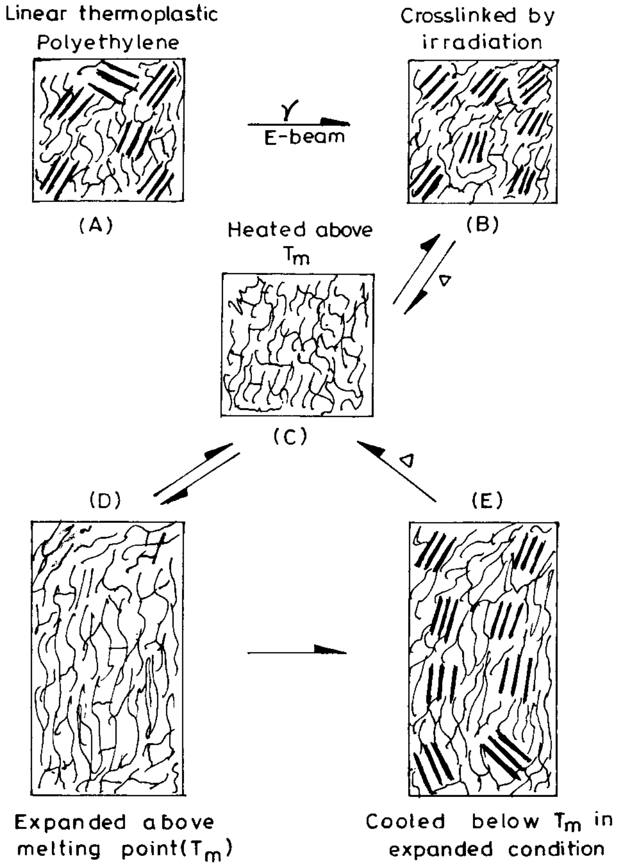

Figure 1 Mechanism of heat shrinkage: (a) molded unstretched thermoplastic polyethylene; (b) molded unstretched crosslinked polyethylene; (c) unstretched crosslinked polyethylene heated above the crystalline melting point; (d) polyethylene stretched above melting point; (e) polyethylene cooled to room temperature in the stretched condition.

out on sheet samples crosslinked by gamma rays from a GC-900 laboratory Co-60 source in air at room temperature. The sol–gel-measurements were also carried out, and the Charlesby–Pinner plots are made. An understanding of the effect of the MI of the base polyethylene and the irradiation dose on the gel fraction and the percentage recovery of the stored stress will be useful in development of formulations for heat shrinkable components meeting specific shrinkage performance requirements.

EXPERIMENTAL

Dosimetry

The calibration of the Co-60 laboratory gamma ray chamber GC-900 was carried out by standard Fricke's dosimetry according to ASTM E 1026-84.[6]

Materials Selection

In all four grades of polyethylene, two high density and two low density grades were selected for the study. The material details are as given in Table I.

Compounding and Molding

The polyethylenes were compounded with 5 wt % fast extrusion furnace (FEF) carbon black for ultraviolet (UV) stability and weathering resistance and 2.5 wt % triallyl cyanurate (pro-rad) in a screw extruder with an L/D ratio of 20. The details of the temperature profile maintained on the extruder for the compounding of the polyethylene samples are shown in Table II. The polyethylene compounds were injection molded into sheets (10 × 7 × 0.1 cm) at a temperature of 180°C.

Irradiation

The molded polyethylene samples were crosslinked to different extent by irradiation with γ-rays from a Co-60 source at a dose rate of 2.03 kGy/h. The irradiation was carried out between 30–160 kGy. The irradiated samples were conditioned for seven days in air at room temperature to allow for the complete decay of the free radicals.

Sol–Gel Measurements

The gel content of the conditioned gamma-ray-irradiated polyethylene samples was determined gravimetrically, using a 12 h soxhlet extraction cycle with xylene as the solvent.[7] Irganox 1330 was added at 0.5 wt % to inhibit polymer degradation during the extraction. Approximately 1 g of the irradiated polymer sample was cut into small pieces and placed in a preweighed stainless steel fine wire mesh. After the extraction cycle, the sample was washed with acetone and vacuum dried to constant weight. The gel fraction was calculated as the percentage ratio of the final weight

Table I Material Details

Sample	Melt Index (g/10 min), 2.16 kg, 190°C	Density (g/cm^3) at 25°C
LD-1	12	0.926
LD-2	17	0.924
HD-1	6	0.950
HD-2	12	0.946

Table II Processing Conditions

	Zone			
Sample	Feed (°C)	Compression (°C)	Metering (°C)	Die Head (°C)
LD	90	140	160	90
HD	100	150	180	110

of the polymer to its initial weight. The Charlesby–Pinner plots were also plotted, and the radiation dose to gelation was determined.

Stretching

The conditioned irradiated samples were heated at 150°C for 3 min and stretched at this temperature from 3 to 9 cm using a tensile type stretching apparatus. The samples were then cooled in this stretched condition to room temperature using a water spray. The samples were removed from the stretching assembly and conditioned at ambient temperature for 24 h.

Recovery Studies

The stretched samples were shrunk in an ethylene glycol bath maintained at 115, 120, 130, and 140°C. The samples were removed at time intervals ranging from 15 to 10 min, depending on the rate of shrinkage, and quickly cooled to room temperature by immersion in water at room temperature. The shrunk dimensions of the sample were determined at ±0.1 mm accuracy using a vernier caliper. The percentage recovery was calculated as the percentage ratio of the shrinkage at any given time to the maximum possible shrinkage. The maximum possible shrinkage is the shrinkage at which the size of the shrunk sample is equal to that of the original unstretched sample, as follows:

$$\text{percentage recovery at time } t = \frac{\left(\begin{array}{r}\text{maximum stretched size}\\ -\text{ size at time } t\end{array}\right)}{\left(\begin{array}{r}\text{maximum stretched size}\\ -\text{ original unstretched size}\end{array}\right)} \times 100$$

The percentage recovery of the stored stress is 100 when the size at time t is equal to the original unstretched size. The percentage recovery of the stored stress is a better index for comparing shrinkage data as compared to the percentage shrinkage, as the latter is a function of the percentage stretch.

RESULTS AND DISCUSSION

Gel Fraction Measurements

Figure 2 is a plot of the gel fraction of the various polyethylenes gamma ray irradiated in air at room temperature with respect to the irradiation dose. It is observed that the gel fraction increases with the irradiation dose in all the samples. However, the rate of increase in the gel fraction decreases beyond a particular dose. It is also observed that the gel fraction is higher in case of the higher density samples as compared to the low-density samples for the same irradiation dose.

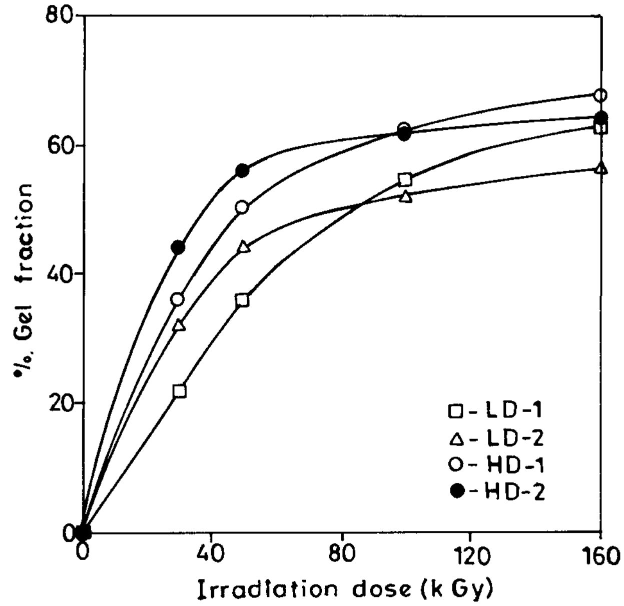

Figure 2 Plot of gel fraction against irradiation dose.

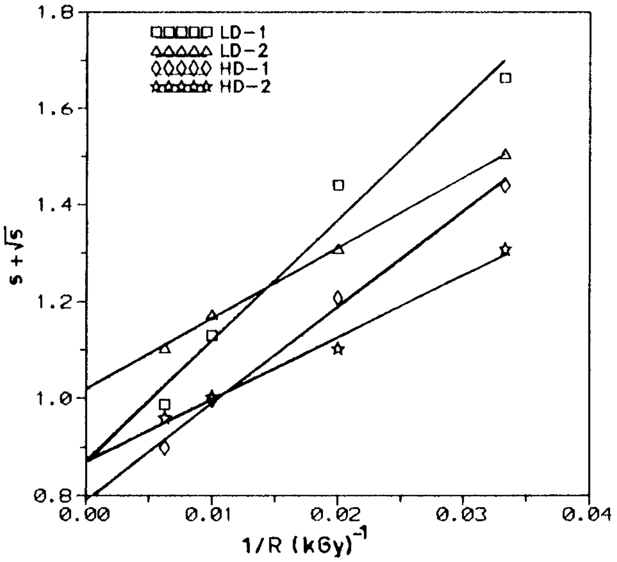

Figure 3 Charlesby–Pinner plots for γ-irradiated polyethylenes.

The lower MI material shows a lower gel fraction initially but attains a higher ultimate gel fraction.

Polyethylene is a thermoplastic consisting of a continuous amorphous phase in which the crystalline domains are distributed. On irradiation with gamma rays, it predominantly under goes crosslinking in the amorphous regions.[8–9] The probability of free radicals being generated at the adjacent sites is higher in the amorphous regions. The amorphous region includes the interlamellar volume and the defect sites in the lamellae.[10] The higher density polyethylenes are more crystalline as compared to the low-density polyethylene. The higher crystallinity leads to a greater proximity of the crystal lamellae, which also anchor the amorphous segments. The proximity of the amorphous segments increases the extent of cross-linking in the higher density samples. In case of the higher MI material, the wider molecular weight distribution results in an increase in the amorphous content, which initially increases in the statistical probability of crosslinking. However, at higher doses, the probability of crosslinking increases in the more uniformly distributed macromolecular chain lengths of the lower MI polyethylene. The increase in the crosslinking results in an increase in the gel fraction.

Figure 3 is the Charlesby Pinner plot of different polyethylenes irradiated with gamma rays in air at room temperature. The Charlesby-Pinner equation is given as follows:[1]

$$s + \sqrt{s} = p/q + 2/q\mu D$$

where s is the sol fraction, D is the radiation dose expressed in kGy, q is the proportion of units crosslinked, p is the ratio of main chain fractures to chain units, and μ is the weight average of initial degree of polymerization.

A plot of $s + \sqrt{s}$ against $1/D$ is a straight line with a slope of $2/q\mu$ and an intercept of p/q. It is observed that the plot is linear at low doses but becomes slightly nonlinear at higher doses, as previously observed.[9] The value of radiation dose at gelation r_g (i.e., the dose at which $s + \sqrt{s} = 2$) is calculated for all the polyethylenes and is given in Table III. The radiation dose at gelation is the dose of irradiation at which the first insoluble residue is detected in the irradiated polyethylene. It is seen from the Table III that the radiation dose to gelation is higher in case of the lower MI material; i.e., the higher MI material shows the presence of the insoluble residue (gel) first. This is due to the greater amorphous content of the higher MI material.

Principle of Heat Shrinkage

Polyethylene is a thermoplastic consisting of plastic crystalline domains and amorphous domains. A thermoplastic can be melted and reshaped as desired by heating it to a temperature above the melting point of the plastic crystalline domains. The irradiation with gamma rays results in the formation of crosslinks or bridges between the macromolecular chains. When this material is heated to a temperature above the crystalline melting point, the material does not melt and flow; instead, it exhibits a viscoelastic behaviour. The expansion or deformation of the polyethylene in this condition results in the orientation of the macromolecular chains, and elastic stress is developed in the material. If the material is cooled in this elastically stressed condition, the reformation of the plastic crystalline domains freezes the elastic stress in the material. The material retains the expanded shape, even on removal of the deforming force. This material is heat shrinkable,

Table III Radiation Dose to Gelation

Sample	Radiation Dose to Gelation (kGy)
LD-1	22.03
LD-2	14.88
HD-1	16.40
HD-2	11.31

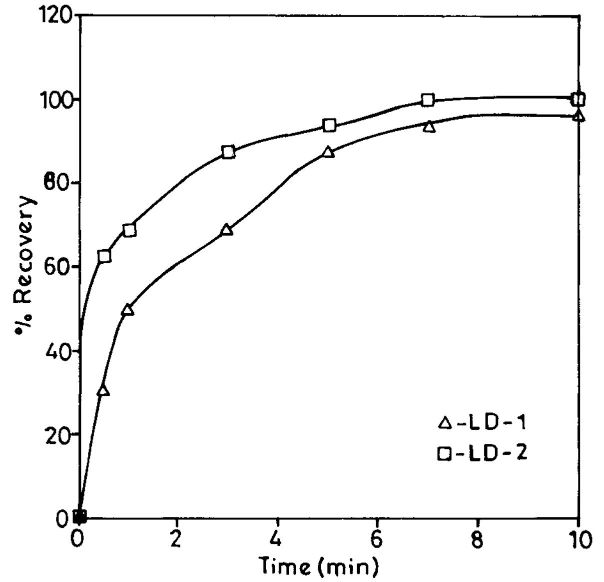

Figure 4 Plot of percentage recovery of stored stress against time for the 80 kGy irradiated LD-1 and LD-2 recovered at 115°C.

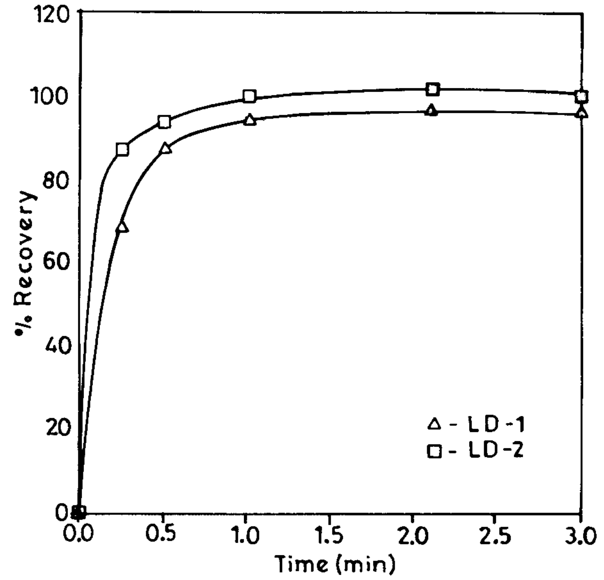

Figure 5 Plot of percentage recovery of stored stress against time for the 80 kGy irradiated LD-1 and LD-2 recovered at 130°C.

and the stored stress can be recovered at any time by heating the material to a temperature above its crystalline melting point stored in it. During the application, the heating results in the melting of the stress freezing plastic crystalline domains, and the stored elastic stress is recovered.

Recovery Studies

Figures 4 and 5 are plots of the percentage recovery of stored stress against time at 115 and 130°C, respectively for the 80 kGy irradiated LD-1 and LD-2 sample. It is observed that the LD-2 sample undergoes a 100% recovery, whereas the LD-1 sample recovers to 94% only. The residual 6% stress is not recoverable even on prolonged heating.

In the higher MI material, the widening of the molecular weight distribution leads to a decrease in the crystallinity, causing an increase in the amorphous content. The increase in the amorphous content results in a more uniform distribution of the crosslink density throughout the bulk of the polymer. The uniform distribution of crosslink density, in turn, leads to a more uniform recovery of the stored stress, resulting in a 100% recovery. In the case of the lower MI material, the uniformity of the crosslink density is somewhat lower due to the presence of more crystalline regions, resulting in the nonrecovery of some of the stored stress. The lower crystallinity of the higher MI material will also result in the faster melting of the stress freezing crystalline plastic forces, increasing the overall recovery rate.

Figures 6 and 7 are plots of percentage recovery against time for the LD-2 and HD-2 samples irradiated to different doses recovered at 120 and 140°C, respectively. It is observed that the recovery is faster at higher doses in both the samples.

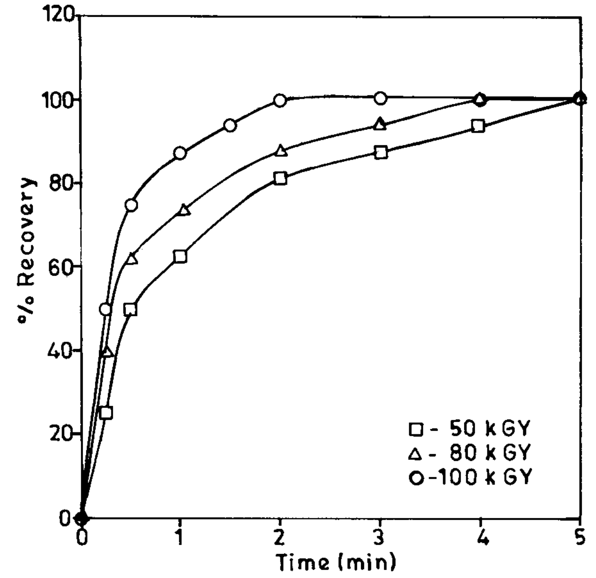

Figure 6 Plot of percentage recovery of stored stress against time for LD-2 irradiated to different doses and recovered at 120°C.

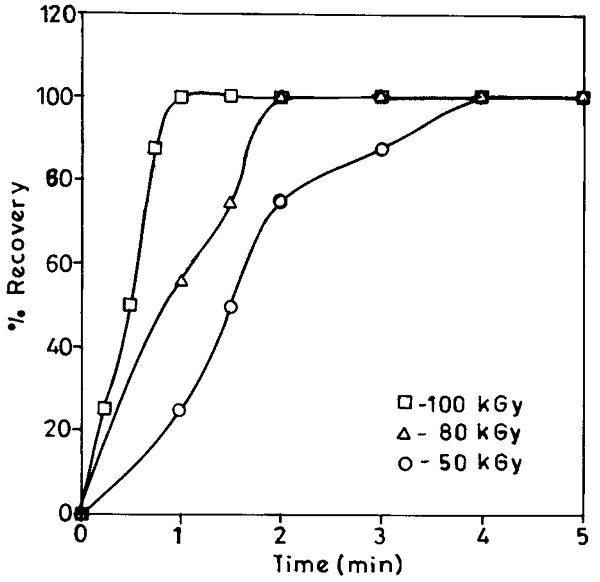

Figure 7 Plot of percentage recovery of stored stress against time for HD-2 irradiated to different doses and recovered at 140°C.

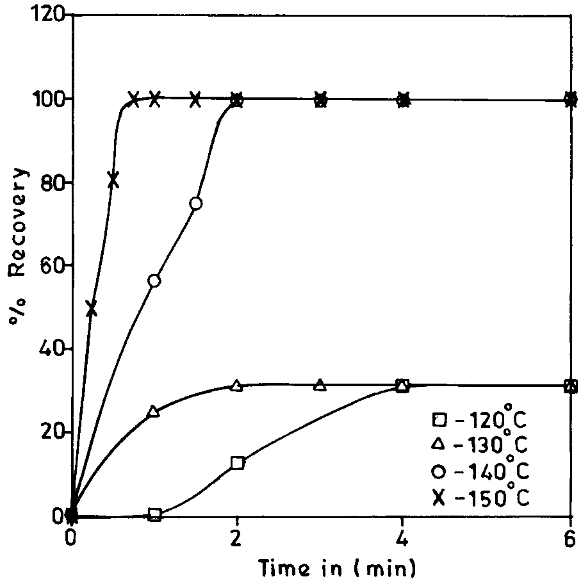

Figure 9 Plot of percentage recovery of stored stress against time at different recovery temperatures for the 80 kGy irradiated HD-2.

At higher doses, the higher crosslink density results in an increase in the elastic character, contributing to the faster recovery. It is also observed that the HD-2 sample requires a higher temperature for recovery as compared to the LD-2 sample. This is due to the higher melting point of the HD sample as compared to the LD sample.

Figure 8 is a plot of the percentage recovery against time for the LD-1 irradiated to different doses and recovered at 120°C. It is seen that the recovery is complete in case of the 100 kGy sample, whereas the 50 kGy and 80 kGy samples attain only 94% recovery. The residual 6% stress is not recoverable even on prolonged heating. A comparison of Figures 6 and 8 also shows that the recovery is faster in case of the higher MI sample.

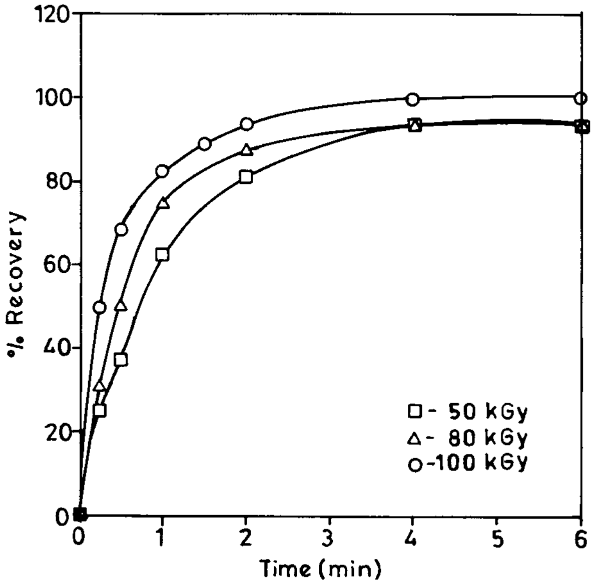

Figure 8 Plot of percentage recovery of stored stress against time for LD-1 irradiated to different doses and recovered at 120°C.

Figure 9 is a plot of the percentage recovery against time for the 80 kGy irradiated HD-2 sample at different recovery temperatures. It is observed that the rate of recovery is higher at higher temperatures. The recovery is only 31% below 130°C, whereas the recovery is 100% at higher temperatures. At temperatures below 130°C, the plastic crystalline domains that are responsible for freezing the stress stored in the elastic amorphous domains do not melt completely; hence, there is only a partial recovery of the stored stress. However, at higher temperatures, there is a complete melting of the crystalline plastic domains, leading to a 100% recovery of the stored stress. The increased chain mobility at higher temperatures also contributes to the higher recovery.

CONCLUSIONS

Polyethylene upon irradiation with γ-rays undergoes crosslinking, and the gel fraction increases with an increase in the irradiation dose. The higher density polyethylene shows a higher gel fraction as compared to the low-density polyethylene. The radiation dose to gelation is lower in case of the higher MI polymer as compared to the lower MI polymer, but the lower MI material attains a higher gel fraction at higher doses. The elastic stress stored in the form of the orientation of the macromolecular chains in the lower MI polyethylene is not fully recoverable at 50 and 80 kGy. The rate of recovery of the stored stress is higher in the case of the polymer irradiated to 100 kGy as compared to the 50 and 80 kGy gamma-ray-irradiated polymer. The recovery of the stored stress is faster and complete at higher temperatures.

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