

Study on the Influence of Electron Beam Irradiation on the Thermal, Mechanical, and Rheological Properties of Ethylene-Octene Copolymer With High Comonomer Content

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ABSTRACT: Ethylene-octene copolymer (EOC) was irradiated using electron beam irradiation at different dosages (30, 60, 90, and 120 kGy). Effect of irradiation dosage on thermal and mechanical properties was studied. When compared to low density polyethylene, EOC exhibited higher degree of crosslinking reflected in increased gel content, higher elastic modulus (G'), and lower $\tan \delta$ obtained by rheology measurement at 150°C. Crosslinking caused improvement in high-temperature creep and room temperature and also elevated temperature elastic properties. Differential scanning calorimetry revealed that e-beam irradiation has caused a gradual reduction in crystallinity and a presence of a fraction with higher melting temperature. In the case of EOC, as the extent of crosslinking increased, stress at break showed an increasing trend whereas irradiation dosage had an inverse effect on elongation at break. Radiation dosage has positive effect on thermal stability estimated by thermogravimetric analysis. After 30 min of thermal degradation at 220°C, slightly higher C=O peak for crosslinked sample was found by Fourier transform infrared spectroscopy while for room temperature samples no C=O peak was detected. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

The development of Dow's INSITE™ constrained geometry catalyst technology has led to the polymerization of new ethylene-octene copolymers (EOCs) with very low density which designed to be processed like thermoplastics but can be compounded like elastomers. Copolymers with densities less than 0.90 g cm⁻³ synthesized with this technology constitute a unique class of thermoplastic elastomers.^{1,2} In 1993, DuPont Dow Elastomers introduced polyolefin elastomers (POEs) under the brand name ENGAGE™. The exceptional performance of ENGAGE™ is attributed to good control over polymer structure, molecular weight distribution, uniform comonomer composition, and rheology. They are being considered for use in diverse applications such as in footwear applications and are particularly good alter-

native for sealing applications due to their structural regularity and nontoxic composition.³ Foams made from these metallo-cene-based polyolefins are being considered for use in diverse applications as cushioning agents, gaskets, sealants, etc.⁴

Crosslinking technology represents a highly effective way for improving EOC's high temperature properties and extends their applications.⁵ Over these years, crosslinking of polymers has attracted attention of researchers worldwide. Crosslinking in polymers enables them to exhibit a viscoelastic behavior, characteristic of an elastomer, at temperatures above the melting point of the thermoplastic. This is very important property which can be utilized in the manufacture of heat shrinkable components which are widely used in the cable and electric for jointing, splicing, and termination applications.⁶

EOC has been successfully crosslinked using techniques like peroxide crosslinking,^{7–10} silane water crosslinking,^{11–14} and electron beam (β) or gamma (γ) irradiation.^{15–19} Irradiation is very powerful form of energy which can produce deep changes in the polymers. Crosslinking via controlled irradiation is an alternative to dynamic vulcanization to improve the properties of thermoplastic elastomers (TPEs) considerably.²⁰ One of the advantages of irradiation crosslinking is that it can be done on finished products at room temperature.

A number of earlier studies have focused on the effect of irradiation on polyethylene and its blends. Benson et al.¹⁵ studied the effect of molecular weight and composition on thermal and mechanical properties of gamma irradiated EOCs. Cardenas et al.²¹ investigated the effect of e-beam irradiation on thermal and mechanical properties of various blends containing EOCs. But there is a lack of studies on the effect of irradiation dosage on rheological and high temperature mechanical properties. This work is focused on rheological, thermal, and high-temperature elastic and creep properties of e-beam crosslinked EOC with high comonomer content, compared to low density polyethylene (LDPE) without the presence of regular short branching.

EXPERIMENTAL

EOC with 45 wt % of octene content having trade name ENGAGE 8842 was supplied by The Dow Chemical Company, Midland, Michigan, United States. Density of ENGAGE 8842 was 0.8595 g cm^{-3} and melt flow rate was $1.02 \text{ g } 10 \text{ min}^{-1}$ ($190^\circ\text{C}/2.16 \text{ kg}$). LDPE which has been used for the comparison of some properties was Bralene RB 2-62, manufactured by Slovnaft Petrochemicals, Bratislava, Slovak Republic. MFI and density of Bralene RB 2-62 was $2 \text{ g } 10 \text{ min}^{-1}$ and 0.918 g cm^{-3} respectively.

EOC and LDPE sheets (sample size was $12 \times 6 \times 0.2 \text{ mm}^3$) for beta (electron beam) irradiation were prepared using a compression molding machine at 110°C and 130°C for 10 min, respectively. Beta irradiation was performed in normal air at room temperature, in BGS Beta-Gamma-Service GmbH, Germany. It was made sure that the temperature did not exceed 50°C . Source of radiation was toroid electron accelerator Rhodotron (10 MeV, 200 kW). The irradiation was carried out in a tunnel on a continuously moving conveyer with the irradiation dosage ranging from 30 to 120 kGy; in steps of 30 kGy per pass.

The gel content of the e-beam crosslinked EOC and LDPE samples was determined by evaluation of the content of insoluble fraction of crosslinked material after solvent extraction according to ASTM D2765-01. About 0.3 g of crosslinked sample was wrapped in a 120 mesh stainless steel cage and extracted in refluxing xylene for 6 h. Sample was then dried in vacuum at 55°C and weighed. Percent (%) gel content was calculated as per the given formula.

$$\text{Gel content} = \frac{\text{Final weight of sample}}{\text{Initial weight of sample}} \times 100 \quad (1)$$

Thermal properties of irradiated EOC samples were analyzed by a Perkin–Elmer DSC-1. Temperature calibration was performed

using indium standard. Nitrogen atmosphere was employed during the experiment at heat flow rate being 20 mL min^{-1} . Heating rate for the differential scanning calorimetry (DSC) experiments was $20^\circ\text{C min}^{-1}$.

Advanced Rheometric Expansion System ARES 2000 (Rheometric Scientific, Piscataway, NJ, USA) equipped with 25-mm parallel plates geometry was used to determine storage modulus G' , loss modulus G'' , and complex viscosity η^* in the frequency range $0.1\text{--}100 \text{ rad s}^{-1}$ at constant temperature (150°C) and strain (1%).

Elastic properties were measured by residual strain experiments conducted using an Alpha Tensometer 2000 instrument. Microtensile samples with dimensions according to ISO 12086 were used for tensile experiments. Hysteresis experiments for the residual strain evaluation were carried out at a cross-head speed of 10 mm min^{-1} , where the cross-head was allowed to return to the original position after reaching to a pre-set strain of 100%. Tensile experiments till rupture were carried out at a different cross-head speed of 100 mm min^{-1} and tensile modulus, stress at break, and elongation at break was noted.

To study the effect of crosslinking on elastic properties, residual strain experiments were also carried out above the melting temperature (about 50°C) of the virgin copolymer. For this, the samples were stretched to 100% elongation for 5 min and kept in a hot air oven (Memmert UFE 400) maintained at 70°C . The samples were then cooled to room temperature and the residual strain values were noted.

Tensile samples were cut out of the crosslinked sheets and used for the tensile creep experiments according to ISO 899 standard. Creep test was carried out in Memmert UFE 400 oven with digital temperature control. Creep was recorded through the glass window using SONY SLT-A33 camera capable of HD 1920×1080 video (25 frames/s). This video was later analyzed at proper time intervals. Effect of irradiation dosage on creep behavior of crosslinked EOC was studied.

Thermal stability of crosslinked EOC samples was studied using a Q500 instrument (TA Instruments). Thermogravimetric analysis (TGA) experiments were carried out in nitrogen atmosphere at a heating rate of $20^\circ\text{C min}^{-1}$ in the selected temperature range of $25\text{--}600^\circ\text{C}$.

The Fourier transform infrared (FTIR) spectroscopy of the pure and crosslinked EOC samples was carried out by using the Nicolet 320 Avatar FTIR spectrometer in attenuated total reflectance (ATR) mode. The samples were scanned from 4000 to 400 cm^{-1} .

RESULTS AND DISCUSSIONS

DSC thermograms of irradiated EOCs are shown in Figure 1. There is a clear difference in the position of melting peaks and peak areas. Only one melting peak around 43°C is seen in the case of unirradiated EOC sample while there is a second peak at around 56°C in the case of EOCs irradiated with 90 and 120 kGy dosages. This may be ascribed to the formation of high-melting fraction (chains with high molecular mass) due to increased crosslinking. Inset of Figure 1 reveals that crystallinity

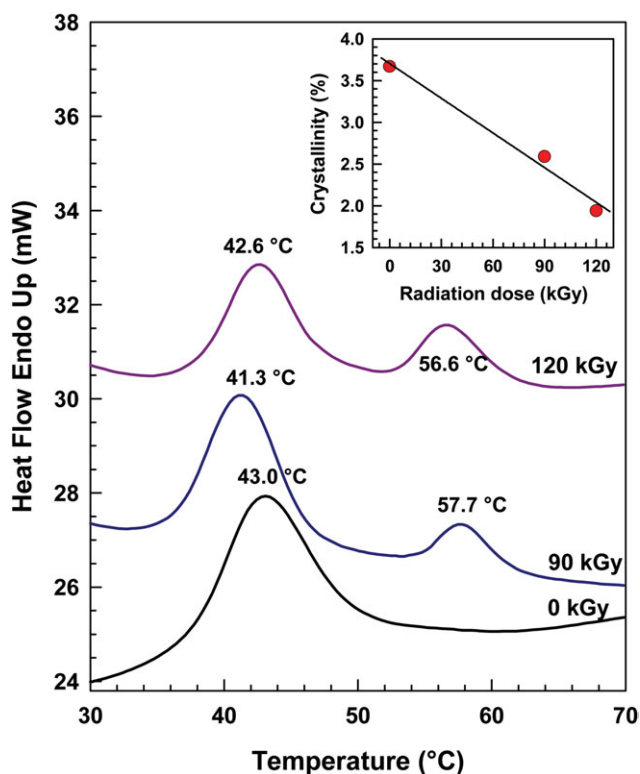


Figure 1. DSC thermograms of EOC samples at 20°C/min and crystallinity vs. radiation dosage (inset). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreases with radiation dosage. Crosslinking and chain branching inhibit the growth of crystals and the whole crystallization process by disturbing the reorganization and chain folding.

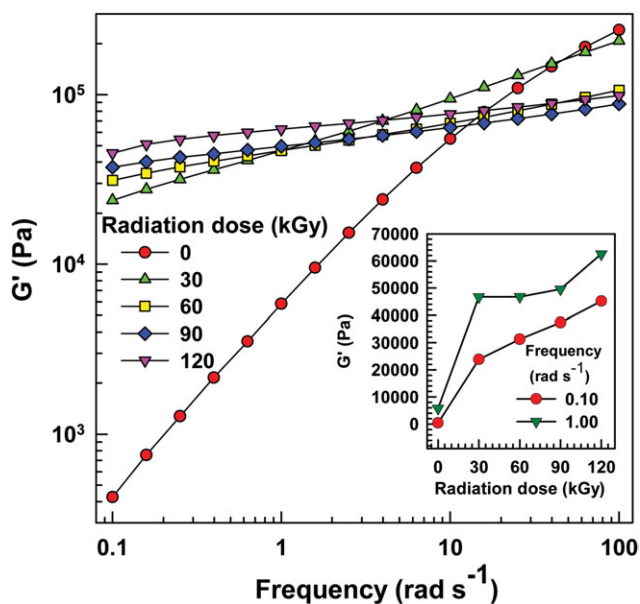


Figure 2. Elastic modulus (G') at 150°C vs. frequency for irradiated EOC samples and increase in G' as a function of radiation dose (inset). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

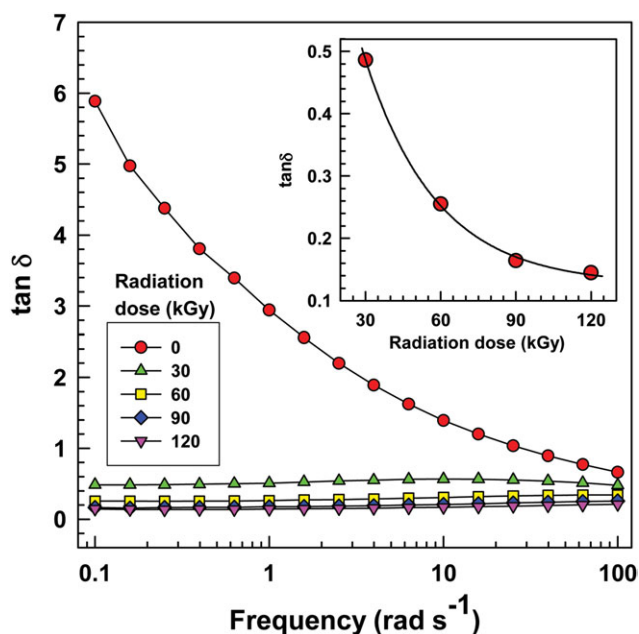


Figure 3. $\tan \delta$ at 150°C as a function of frequency for irradiated EOC samples and the inset is the effect of radiation dose on $\tan \delta$ (at 0.1 rad s^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The rheological properties of e-beam irradiation crosslinked EOC are shown in the following figures. Frequency dependence of elastic modulus, G' of irradiated samples is illustrated in Figure 2. At low frequency, time is large enough to unfold the chains and relax slowly which reduces the modulus. But at higher frequency, the entangled chain had less time for reorientation and results in higher G' values; similar behavior was observed by Mir et al.²² An increase in radiation dosage significantly increases low frequency elastic modulus (see inset in Figure 2). At low frequency range, longer chains are contributing more toward the elasticity of the polymer. As the radiation dosage increases, presence of shorter chains decreases, i.e., longer and crosslinked chains are formed. This is obvious from the Figure 2 that, as the radiation dosage increases, G' increases at lower frequency range. But at higher frequencies, shorter chains are responsible for the elasticity. This is the reason why G' values are decreasing with the radiation dosage at higher frequencies when the number of shorter chains is relatively smaller. In this case G' curves were higher than G'' . This showed that a strong connection was developed between the polymer chains by irradiation.

Figure 3 depicts the effect of radiation dosage and frequency on $\tan \delta$. There is a large decrease in $\tan \delta$ with increasing frequency for 0 kGy. Then $\tan \delta$ is almost independent of frequency level for the radiation above 30 kGy. As shows also in Figure 2, initially there is a large change in polymer structure (compare $\tan \delta$ at 0.1 rad s^{-1} for 0 and 30 kGy, the values were about 6 and 0.5, respectively), then the change is rather moderate in range 30–120 kGy. The effect of radiation dose on $\tan \delta$ at the frequency 0.1 rad s^{-1} for samples 30–120 kGy is illustrated in the inset of Figure 3. There is an exponential decrease

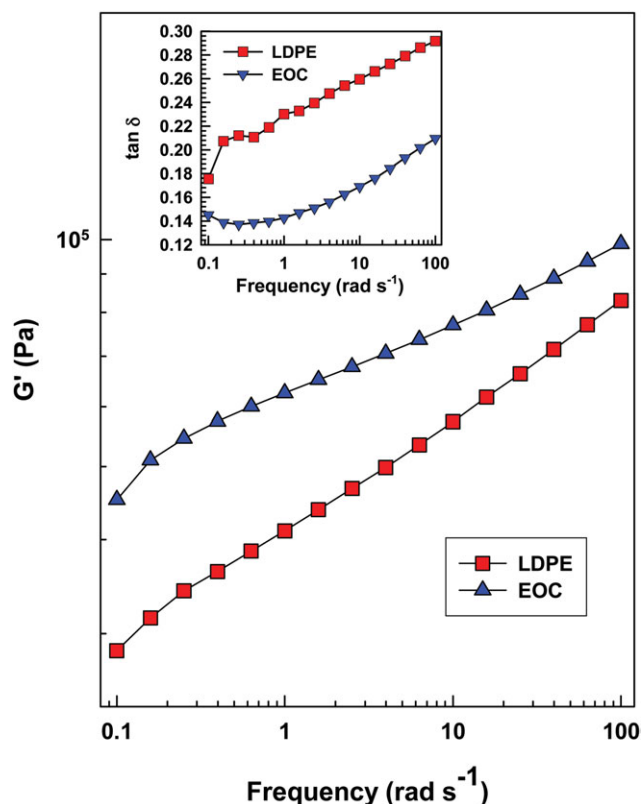


Figure 4. Elastic modulus (G') and $\tan \delta$ at 150°C of LDPE and EOC samples irradiated at 120 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of $\tan \delta$ with radiation dosage. The decrease in $\tan \delta$ means improvement in elasticity.

We have carried out also the rheology analysis of LDPE and compared with that of EOC samples to see the effect of octene branching on crosslinkability. Results for 120 kGy samples are shown in Figure 4. From the comparison of elastic modulus (G') shown in Figure 4, it is clear that EOC has higher modulus than LDPE and better elasticity (lower $\tan \delta$ values at all frequencies), see inset of Figure 4. To support these results, we have analyzed the gel content of EOC and LDPE samples. Figure 5 shows the effect of irradiation dosage on gel content which is proportional to the degree of crosslinking. Structures with low molecular weight which are by-products of chain scission or chain branching may not contribute toward the insoluble fraction. As a result of increase in network formation (cross-linking extent), gel content increases. It is clear from the Figure 5 that samples irradiated with 30 kGy dose were completely dissolved due to low crosslinking degree, in both cases. A gradual increase in gel content was observed thereafter. A maximum gel content of 88% was recorded for EOC irradiated with 120 kGy, while for LDPE, it was only 65%. These two measurements indicate better crosslinkability of EOC compared to LDPE. This can be ascribed to the presence of increased number of tertiary carbon atoms in EOC which arose due to the incorporation of comonomer units to the polyethylene chain structure. This results in reduction in number of consecutive ethylene units (i.e., crystallizable part) which leads to a rise of amorphous

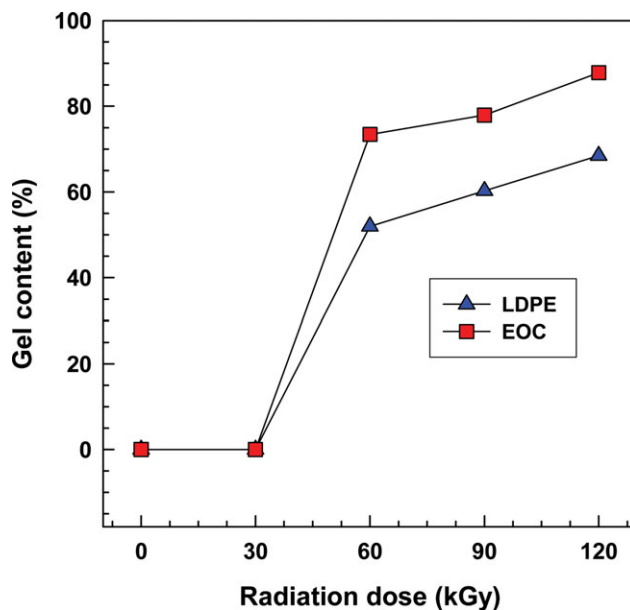


Figure 5. Gel content analysis of irradiated LDPE and EOC samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

region in the copolymer. Hydrogen atoms attached to the tertiary carbon atoms are more easily attacked than the primary and secondary ones. In conclusion, higher degree of crosslinking in the case of EOC can be attributed to the higher presence of tertiary carbon atoms and possibly also to lower crystallinity (higher content of amorphous phase).

Tensile stress–strain curves of the pure and crosslinked EOCs are depicted in Figure 6. A gradual decrease in elongation at

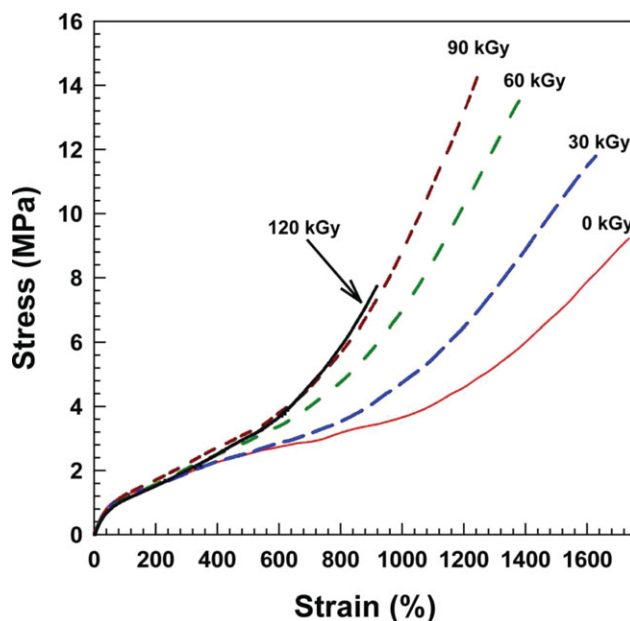


Figure 6. Stress–strain curves of EOC samples at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Effect of Irradiation Dosage on Tensile Properties

Radiation dose (kGy)	Stress at break (MPa)	Elongation at break (%)
0	9.2	1740
30	11.8	1630
60	13.7	1400
90	14.7	1260
120	7.7	920

break has been observed while stress at break has shown an increase, except in the case of the highly irradiated (120 kGy) EOC. Increase in crosslinking is the reason for these two phenomena. For majority of the samples, elongation before failure has gone up to as high as 1000%. No yield points were noted in any of the measurements because of extremely low crystallinity. There was no significant effect of crosslinking observed in the case of tensile modulus. Perraud et al. have reported similar results for the e-beam crosslinked poly(ethylene-co-octene).²³ Tensile properties of irradiation crosslinked EOC are summarized in Table I.

Influence of radiation dosage on elastic properties at room temperature is demonstrated in Figure 7. Residual strain (ϵ_r) values obtained from the hysteresis curves from the tensile instrument are being considered as the measure of elasticity. In this case, applied strain was 100%. Residual strain is found to be decreasing with increase in crosslinking via irradiation. In other words, elasticity of EOC is getting improved by crosslinking. Just by the exposure to 30 kGy dosage irradiation, a significant drop of about 30% in the ϵ_r value has been observed. A gradual decrease in ϵ_r (or increase in elasticity) with further increase in irradiation dosage was found.

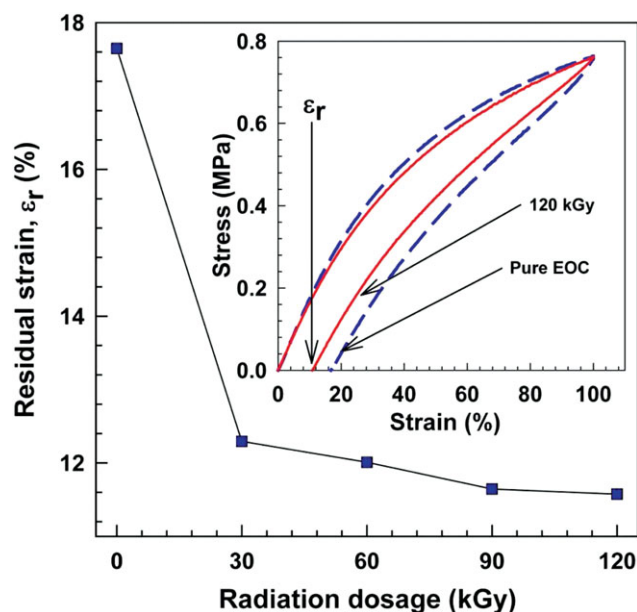


Figure 7. Residual strain of irradiated EOCs at room temperature after stretching to 100%. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

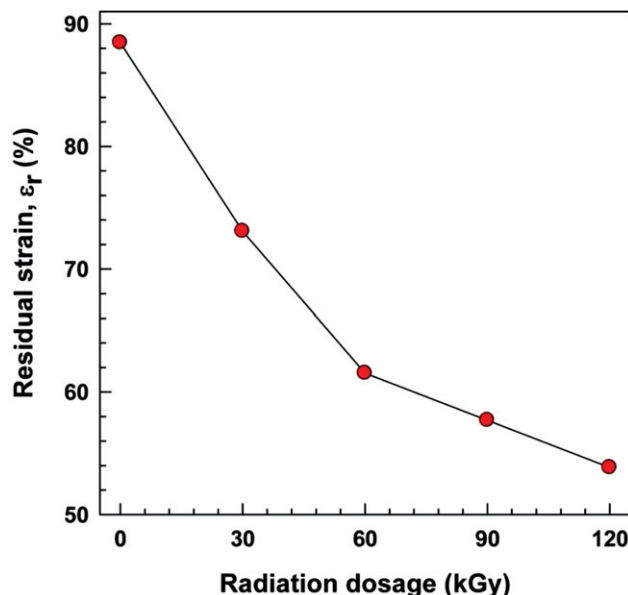


Figure 8. Effect of radiation dosage on residual strain of EOC samples after 5 min exposure to 100% elongation at 70°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tion dosage was found. Original stress–strain hysteresis curves of pure and the most crosslinked EOCs are shown in the inset of the Figure 7, where the position of ϵ_r is clearly marked.

Residual strain values above the T_m of the pure EOC (43°C) were also measured and are shown in Figure 8. For this, a temperature of 70°C was used, when there are no crystals present. At room temperature the crystals play the role of tie points for amorphous chains. Above T_m only crosslink chemical bonds are holding amorphous chains together during mechanical stretching. Then after 100% elongation at 70°C one can clearly see a big difference among the samples (at room temperature the difference was much smaller). The residual strain values at 70°C are much higher compared to room temperature. High temperature testing is common practice in industry and has a great importance for the customers.

Creep is an important property for polymers that are being used under constant stress for a long duration of time such as pipes, storage tanks, etc. Crosslinking can enhance the creep resistance of polymers. Effects of crosslinking on creep compliance of EOC are illustrated in Figure 9. Figure 9 shows the influence of irradiation dosage on creep behavior of EOC at 150°C under 0.1 MPa stress. Pure EOC and samples with low crosslinking undergo a rapid and high creep behavior. As the crosslinking increases, more network is formed in the whole polymer system. These crosslinks hold the polymer chains more firmly in the case of highly crosslinked EOC samples. Almost no creep was observed in the case of EOC irradiated with 120 kGy dosage. There is a transition from a high-creep to a low-creep which is noticeable between samples irradiated with 30 kGy and 60 kGy. This relates well with the fact that there was no gel content found in the case of samples irradiated with 30 kGy dosage but in case of 60 kGy the gel content was 73% (see Figure 5).

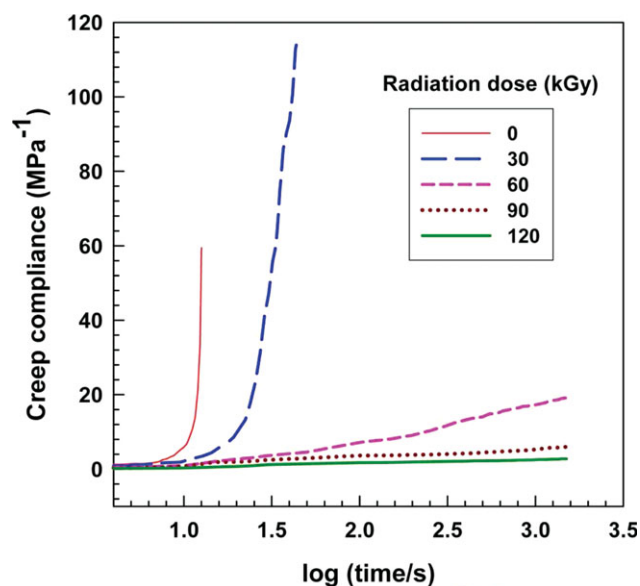


Figure 9. Effect of radiation dose on creep compliance of EOC samples at 150°C under 0.1 MPa stress. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Thermal stability of crosslinked and uncrosslinked EOCs is shown in Figure 10. As we can see from the figure, thermal stability increases as the crosslinking increases. Virgin EOC starts to decompose rapidly at around 300°C while EOC irradiated with 120 kGy dosage was thermally stable up to around 350°C. For a comparison, we have evaluated the temperatures at which 50% of weight loss occurred. These temperatures have been noted as 385, 391, 405, 407, and 409°C, respectively, for the EOCs irradiated with 0, 30, 60, 90, and 120 kGy dosages.

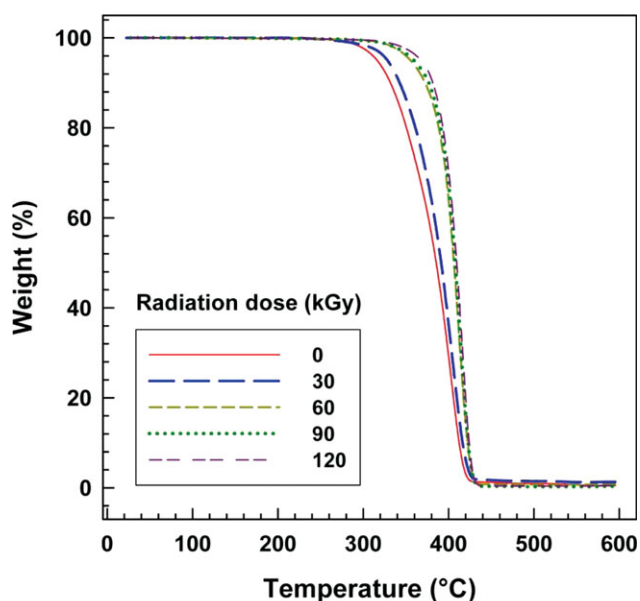


Figure 10. Effect of radiation on thermal stability of ethylene-octene copolymer. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

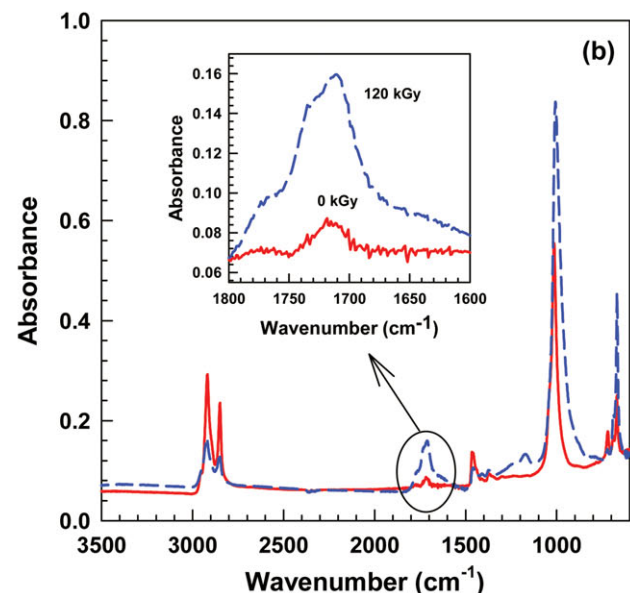
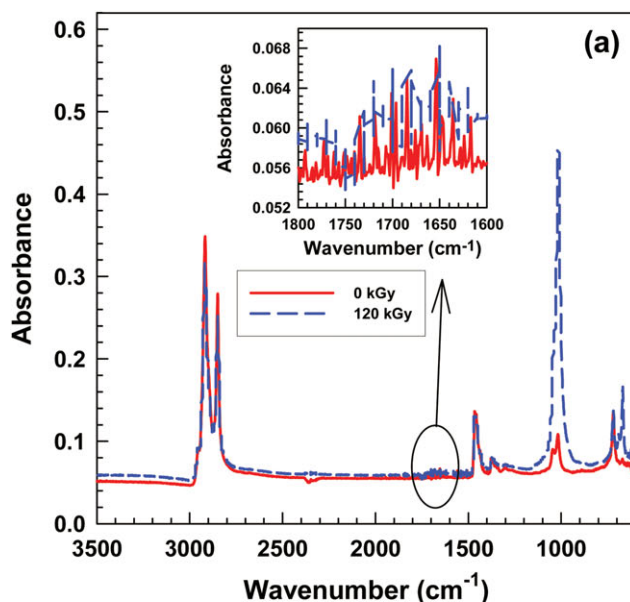


Figure 11. FTIR spectra of pure and irradiated EOC samples: (a) at room temperature, (b) after 30 min at 220°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

FTIR results illustrated in Figure 11(a, b) demonstrate the effect of temperature on oxidation of nonirradiated (0 kGy) and irradiated (120 kGy) EOC samples. For this, samples were exposed to a temperature of 220°C for 30 min. Figure 11(a) depicts FTIR spectra of pure and irradiated EOCs at room temperature which show no significant peak in the carbonyl region (1700–1770 cm⁻¹). This implies that e-beam irradiation (below 50°C) did not cause any oxidation to the copolymer. But, in the case of high temperature exposed samples [Figure 11(b)], prominent peak can be observed in the carbonyl region owing to the presence of carbonyl groups caused by oxidation. Carbonyl yield is much higher for irradiated EOC samples probably due to the

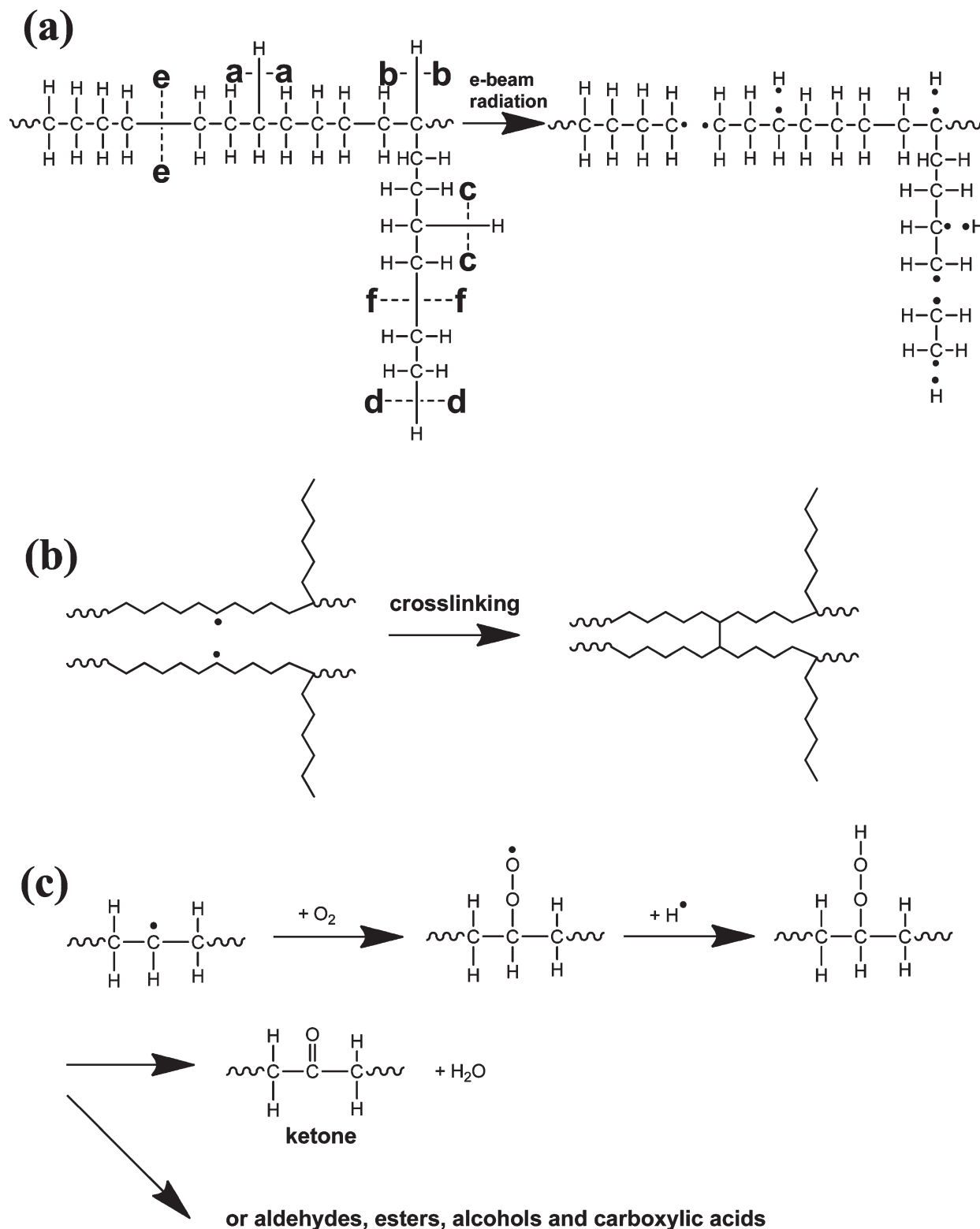


Figure 12. (a) Several possibilities of free radical generation in EOC by e-beam radiation, (b) crosslinking by recombination of two macro-radicals, (c) oxidation mechanism of EOC at elevated temperature.

easier oxidation after irradiation, which is possibly caused by the presence of residual trapped radicals. The radiation takes place at low temperatures (below melting point T_m of EOC). In order to form a crosslink bond the radicals have to come closer

to each other. There is a possibility of the presence of unreacted free radicals because of such low mobility of the macromolecules below T_m . At 220°C these radicals can move much more than at 25°C and can easily react with oxygen.

Figure 12(a) illustrates firstly where the free radicals can be formed on EOC by e-beam radiation. Cases a, b, c, d show breaking of C—H bond. When two such macroradicals come close to each other a crosslink is formed [see example on Figure 12(b)]. One cannot neglect also the possibility of the disruption of C—C bond by e-beam irradiation [see Figure 12(a—case e, f)]. This would result in decrease in molecular weight. And indeed it is well known that pure polypropylene (PP) does not crosslink by e-beam radiation, and that instead of crosslinking a chain scission takes place. Even though the chain scission is possible even for EOC, our results prove that crosslinking reaction prevails over chain scission in case of EOC. From our tensile strength results (see Figure 6) one could conclude that there is an optimum radiation dosage to get the best mechanical properties (in case of EOC it was 90 kGy), further irradiation (120 kGy) resulted in decrease in tensile strength that could relate with chain scission.

Figure 12(c) illustrates post-irradiation oxidation mechanism. Entrapped free radicals (by low mobility below T_m) react at elevated temperature with oxygen forming hydroperoxides. Hydroperoxides are thermally unstable and decompose to ketones, aldehydes, esters, alcohols, and carboxylic acids. The presence of C=O bond was confirmed by FTIR [see Figure 11(b)]. There is a small hint of a C=O peak even for 0 kGy sample, but the peak for irradiated sample is much more pronounced. The irradiated EOCs are more susceptible to high temperature oxidation than the nonirradiated ones.

CONCLUSIONS

EOC has been irradiated using electron beam to investigate the effect of irradiation dose on thermal, rheological, and high temperature elastic and creep properties. High gel content was observed for EOC samples compared to LDPE, due to the lower crystallinity and the presence of hydrogen atoms on tertiary carbon atoms, which enhances crosslinking. Rheological analysis showed that elastic modulus and viscosity increased with radiation dosage. EOC has achieved higher elasticity (lower $\tan \delta$) than LDPE due to increased crosslinking. Increase in radiation dosage has resulted in a decrease in elongation at break and an increase in stress at break. The positive effect of crosslinking was proved by high temperature creep and elastic property measurements. Crosslinking through irradiation improved the thermal stability of EOC. FTIR analysis revealed that e-beam irradiation at room temperature did not cause any oxidation to the copolymer, but after thermal degradation at 220°C the presence of C=O peak was higher for the irradiated sample.

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