Effect of Irradiation on Mechanical and Structural Properties of Ethylene Vinyl Acetate Copolymers Hollow Fibers

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ABSTRACT: Effect of irradiation on mechanical and structural properties of ethylene vinyl acetate copolymers (EVA) hollow fibers was studied by the tests such as determination of gel content, density, tensile, FTIR, SEM, and DMA. These effects were discussed based on dose and irradiation environment. The results of gel content depicted that irradiated EVA in ambient conditions had tendency to chain scission while the crosslinking overcame in irradiated samples under nitrogen. Density insignificantly enhanced with irradiation dose. In tensile test, irradiation induced increase in tensile strength and decrease in elongation at break (especially in samples irradiated in nitrogen). Also, changing in layer orientation could be observed by SEM images. In addition, irradiation caused altering peak intensity in FTIR spectrum. DMA results demonstrated that irradiation broaden the elastic zone. Totally, irradiation enhances features especially in irradiated EVA18 in nitrogen. Since, according to stabilization of induced deformation and improvement of mechanical properties (that created by radiation), the irradiated samples can be used in different applications. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 2085–2092, 2011

Key words: ethylene vinyl acetate copolymer; gamma radiation; crosslinking; irradiation effects; chain scission

INTRODUCTION

High-energy irradiation, gamma ray or electron beam (EB), is a well-known tool for the modification of polymers. In polymer irradiation, two phenomena occur at the same time: crosslinking and chain scission. The generation of a crosslinked network between the polymer chains may enhance thermal and chemical resistance as well as stress cracking and dimensional stability. On the other hand, degradation resulting from ionizing irradiation may adversely affect the engineering properties of the polymer. The balance of crosslinking and scission reactions in polyolefin chains, exposed to high-energy radiation processes that produce free radicals, may result in good properties and new applications. These processes have the advantages of being clean and continuous with very good controllability.[1–3]

Ethylene vinyl acetate copolymer (EVA) is a random copolymer consists of ethylene and vinyl acetate (VA) as a repeating unit. It is available as a plastic, thermoplastic elastomer, and rubber depending on the VA content in the copolymer. EVA containing 28% VA is a thermoplastic elastomer, and 50% VA is a rubber. To improve its properties and form EVA in special shape, the crosslinking of EVA is a useful method. High-energy irradiation (^{60}Co γ–rays or EB) is a method for crosslinking of EVA.[4,5] On the other hand, for the device which should be sterilized after packing, irradiation is an effective method for avoiding problem of recontamination. Black and Charlesby performed one of the earliest studies on gamma irradiation of polymers. They showed the changes in chemical structure and physical properties of polyethylene upon irradiation with gamma rays. Irradiation causes some events like macromolecular chain split, creation of low mass fragments, free radicals production, oxidation and crosslinking.[6,7] Factors such as temperature of irradiation, irradiation dose, dose rate, presence or absence of air or another gases, thickness of samples are effective on polymeric material properties.[8]

In this study, tests such as determination of gel content, density, tensile, Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), as well as dynamic mechanical analysis (DMA) were used to evaluate the changes in the mechanical and structural properties of EVA18 and EVA28.

EXPERIMENTAL

Materials and sample preparation

EVAs, containing 18% VA and 28% VA, with density of 0.938 g/cm^3 and 0.95 g/cm^3, respectively,

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were supplied by Hyundai Petrochemical Co. in the form of granules. EVA18 and EVA28 were melted in coextruder at 175°C and 140°C, respectively. Air was injected in the center of the molten filament to produce the hollow structure. Then hollow fiber entered in the cold water bath to stabilize its shape.

Sample irradiation

The ^{60}Co-γ-irradiation source was performed using a 22,844 Ci activity ^{60}Co source (Atomic Energy Institute, Iran). The EVA samples were γ-irradiated at ambient conditions with a dose rate of 5.3 Gy/s. For this study three doses (25, 80, and 120 kGy) were selected. Also, to evaluate the irradiation environmental effect, samples were put in receptacle contain nitrogen and irradiated with dose of 80 kGy. Unirradiated samples (control) were also investigated.

Determination of gel content

For investigation the influence of gamma rays on the gelation of EVA, this test was performed. After being irradiated, the samples were cut into thin slices and placed in a basket made of a 120-mesh stainless steel net. According to ASTM D 2765, the gel content of the samples was determined through extracting the irradiated sample (w_1) in the basket for 12 h with boiling xylene stabilized by 0.5% IRGAFOS168 (an antioxidant) to prevent oxidation. Then, the basket was washed with acetone and the sample was dried in a vacuum oven at about 60°C to constant weight of w_2 (insoluble residue). The average gel content (wt %) in the test was calculated as $(\frac{w_2}{w_1}) \times 100$. Usually, three samples were analyzed to determine the average gel content for a given set of irradiation conditions.

Determination of density

Fiber density was measured by a flotation method with dichloromethane and acetone at 25°C. The density was calculated from the formula (1):

$$d_m = \varphi_1 d_1 + \varphi_2 d_2 \quad (1)$$

where φ and d are the volume fraction and density of components, respectively. The density at 25°C for dichloromethane is 1.33 g/cm^3 and for acetone is 0.79 g/cm^3.

Mechanical properties

Tensile strength and elongation at break were measured with a universal testing machine (GOTECH) at room temperature with a crosshead speed of 300 mm/min and a gauge length of 50 mm.

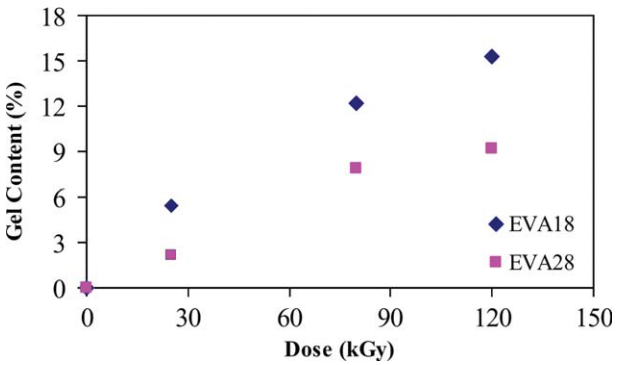


Figure 1 Variation of gel content as a function of irradiation dose for irradiated EVA at ambient condition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

IR spectroscopy

The structural modifications were revealed by FTIR spectral investigation on an Equinex 55, Bruker. The results show characteristic bands. The absorbance changed during irradiation.

Scanning electron microscopy

A XL30 scanning electron microscope (Philips, Netherlands) was used for obtaining electron micrographs of samples prepared by cryofracturing in liquid nitrogen. The accelerating voltage of the beam was 16 kV. The magnification of images is 5000.

Dynamic mechanical analysis

The DMA was performed on a NETZCH 242C instrument in a tensile mode at the frequency of 1 Hz with the heating rate of 5°C/min from −80 to 80°C.

RESULTS AND DISCUSSION

Determination of gel content

Figure 1 shows the relationship between the gel content and irradiation dose for EVA. Unirradiated samples were discovered to be soluble in hot xylene, but the solubility of irradiated samples was reduced gradually. During irradiating polymer, chain scission and crosslinking happen simultaneously. So, according to analyze the relationship between the dose and the gel fraction in terms of the relative amounts of crosslinking and scission, the theory recommended by Charlesby and Pinner was used.

Considering the Charlesby–Pinner equation, the relationships between chain scission (p_o) and crosslinking (q_o) events can be declared by equation:[3]

$$S + S^{1/2} = \frac{p_o}{q_o} + \frac{1}{q_o \overline{X}_n D} \quad (2)$$

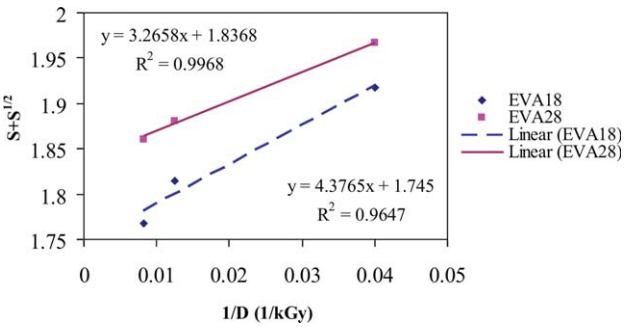


Figure 2 Curve resulting from Charlesby–Pinner equation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

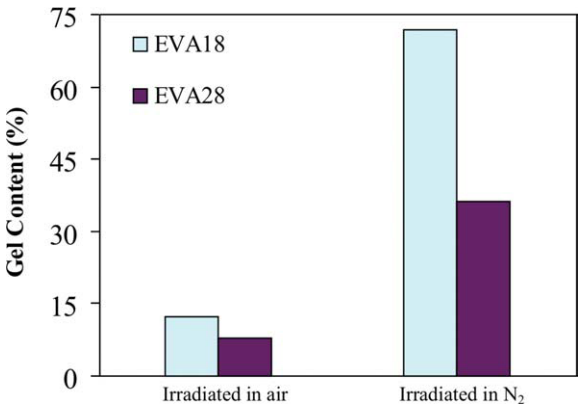


Figure 3 Variation of gel content as a function of irradiation environment for irradiated EVA at 80 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where S is the sol fraction, D is irradiation dose and $\overline{X}_n$ represents the initial number-average degree of polymerization. The relationship between $S + S^{1/2}$ and $1/D$ shown in Figure 2 is basically linear. According to p_o/q_o results ($p_o/q_o > 1$), irradiated EVA in air has a tendency to chain scission rather than form crosslinks. The more p_o/q_o relationship in EVA28 may specify that EVA with a higher VA content is more susceptible to chain scission.

Figure 3 depicts variation of gel content as a function of irradiation environment. It is observed that gel content noticeably increases with irradiation in nitrogen. According to studies, crosslinking overcomes when gel fraction increases significantly.[3,6] Hence it seems that crosslinking conquers in irradiated samples under nitrogen.

Therefore, the irradiation environment drastically affects the response of a polymer to radiation exposure. Most polymers that crosslink in an inert environment, will have a tendency to undergo chain scission when oxygen is available during irradiation.[9]

Determination of density

Table I shows density insignificantly increase with irradiation dose in both environments. It can be the result of variation in volume due to exit of gases (such as CO_2, CO and CH_4). These gases can be generated by decomposition of produced radical components. Proposed decomposition mechanism in papers is demonstrated in Scheme 1.[10] As observed in Table I, irradiated sample in nitrogen has more density than irradiated sample in air.

Mechanical properties

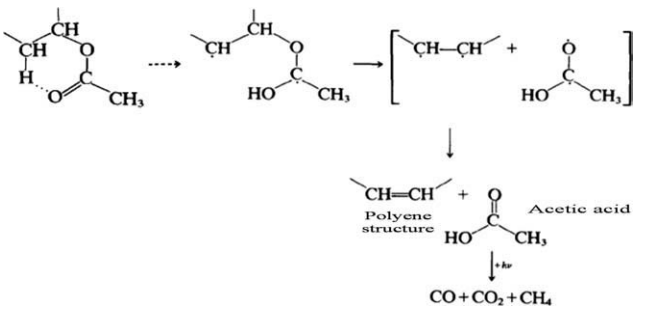
Polymers under irradiation show various behavior based on their nature. In general, for flexible polymers that experience crosslinking as a result of irradiation, the mechanical properties tend to increase while the strain to failure decreases. In polymers susceptible to scission, mechanical properties decrease with dose.[9] Since EVA is a flexible polymer, its behavior is predictable under irradiation lead to crosslinking and/or chain scission.

Figure 4 shows variation of tensile strength as a function of irradiation dose. It is observed that tensile strength insignificantly increases because of chain scission overcome. Changes in tensile strength of EVA28 are less than EVA18, because of more chain scission occurrence in EVA28 than EVA18. This confirms the result of gel content experiment, according to more p_o/q_o. As shown in Figure 5, elongation at break has a tendency to decrease with irradiation dose. Generally, elongation depends on molecular weight between crosslinking junctions. The decrease in elongation at break may be due to the lowering of molecular weight caused by the scission of molecules.

Figure 6 shows tensile strength for irradiated samples in different conditions. As demonstrated, tensile

TABLE I
Density of Irradiated Samples in Different Conditions

Irradiation condition	Non-irradiated	Irradiated at 25 kGy in air	Irradiated at 80 kGy in air	Irradiated at 120 kGy in air	Irradiated at 80 kGy in N_2
EVA18	0.938	0.941	0.946	0.961	0.969
EVA28	0.950	0.963	0.980	0.984	1.007



Scheme 1 Decomposition of radical component into CO_2, CO and CH_4.

strength intensely enhances with irradiation in nitrogen. It should be mentioned that in air, chain scission and in nitrogen crosslinking are dominant. Elongation at break declines in both conditions compared with non-irradiated EVA18 (see Fig. 7). While specimens are irradiated in air, decrease of elongation at break is caused by scission of molecules which discussed above. But in irradiated EVA in nitrogen, reduction of elongation at break is due to stretching of crosslinked samples. In this case, the slippage of chains will not be easy.

FTIR studies

Chemical structural changes in EVA can be depicted by IR bands. The IR spectra of EVA show the typical bands of VA at 1734, 1234, 1018, and 607 cm^{-1}, and ethylene at 2915, 2846, 1460, 1367, and 720 cm^{-1}. These peaks are in good agreement with the literature values.[11] Absorption peak at 3438 cm^{-1} relates to hydroxyl or carboxyl group probably due to slight oxidation during the sample preparation.

Figure 8 shows IR spectra of unirradiated and irradiated samples in air. The carboxyl group (3438 cm^{-1}) can be decomposited into CO_2, CO and CH_4 (as shown in Scheme 1), so related peak nearly disappears with more radiation dose.

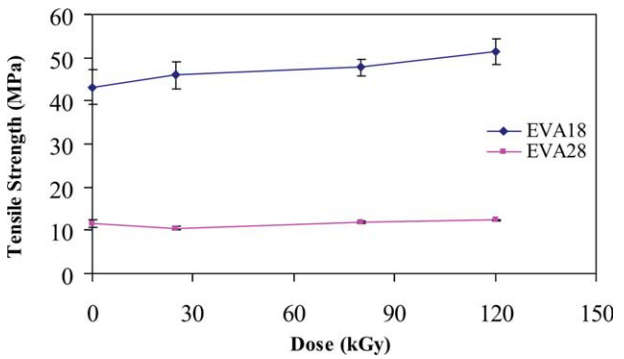


Figure 4 Variation of tensile strength as a function of irradiation dose for irradiated EVA at ambient condition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

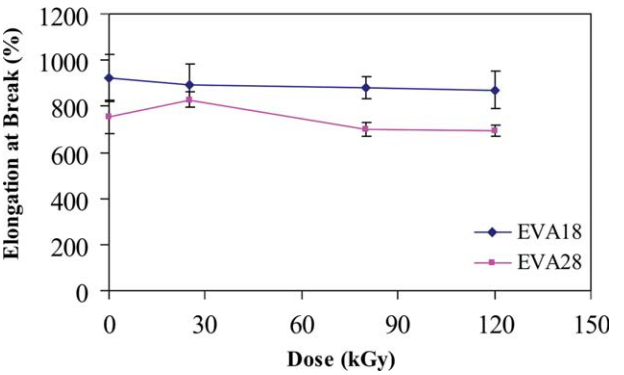


Figure 5 Variation of elongation at break as a function of irradiation dose for irradiated EVA at ambient condition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Absorption peaks created at 1114 cm^{-1} is due to C—O—C linkage and at 948 cm^{-1} is due to creation of peroxy radicals or formation of vinylene group and allyl free radical in ethylene parts. The structures like ketone and lactone can be observed at 1715 and 1770 cm^{-1}, respectively. These peaks are evidence to oxidation of irradiated samples in air. Scheme 2 displays proposed oxidation mechanism in studies.[12] It should be noted that the intensity of these peaks in Figure 8 are so weak. The formation of ketone structure might be acquired during the acetaldehyde evolution or be obtained during the H_2O deprivation reaction of the hydroperoxide. The lactone formation is the consequence of the back-biting process in the VA units by the acetate groups. However the intensity of ketone and lactone reported by Jin et al.[13] is also insignificant.

Figure 9 shows IR spectra of irradiated samples in air and nitrogen. As considered, the peaks which demonstrated by oxidation of irradiated samples in air decrease with irradiation in nitrogen (shown in the figure by arrows). Also IR spectral region of 720–730 cm^{-1} (which analyzes crystalline phase)

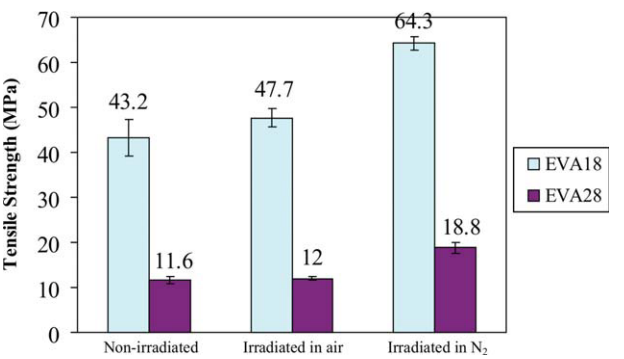


Figure 6 Variation of tensile strength as a function of irradiation environment for irradiated EVA at 80 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

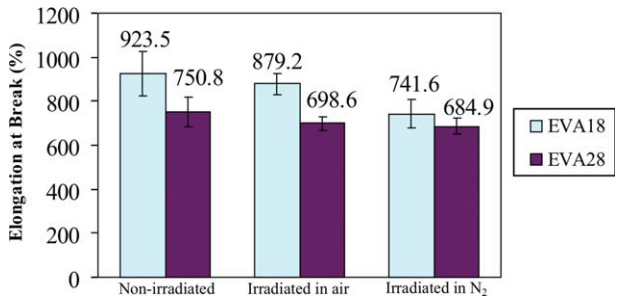
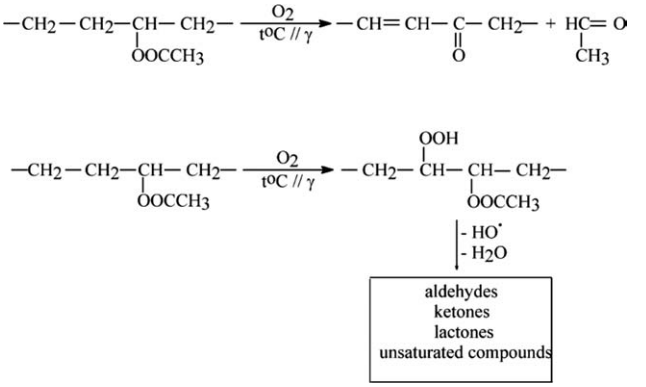


Figure 7 Variation of elongation at break as a function of irradiation environment for irradiated EVA at 80 kGy. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reduces in result of irradiation in nitrogen that proves crosslinking of chains. In addition, intensity of absorption peak at 3438 cm^{-1} of irradiated sample in nitrogen reduces more than irradiated sample in air. It confirms more increase of density in irradiated sample under nitrogen.



Scheme 2 Proposed oxidation mechanism.

SEM images

Figure 10 shows fracture surfaces of the samples in different irradiation conditions. Shape of these surfaces changes based on overcoming crosslinking or chain scission. According to studies,[14] when chain

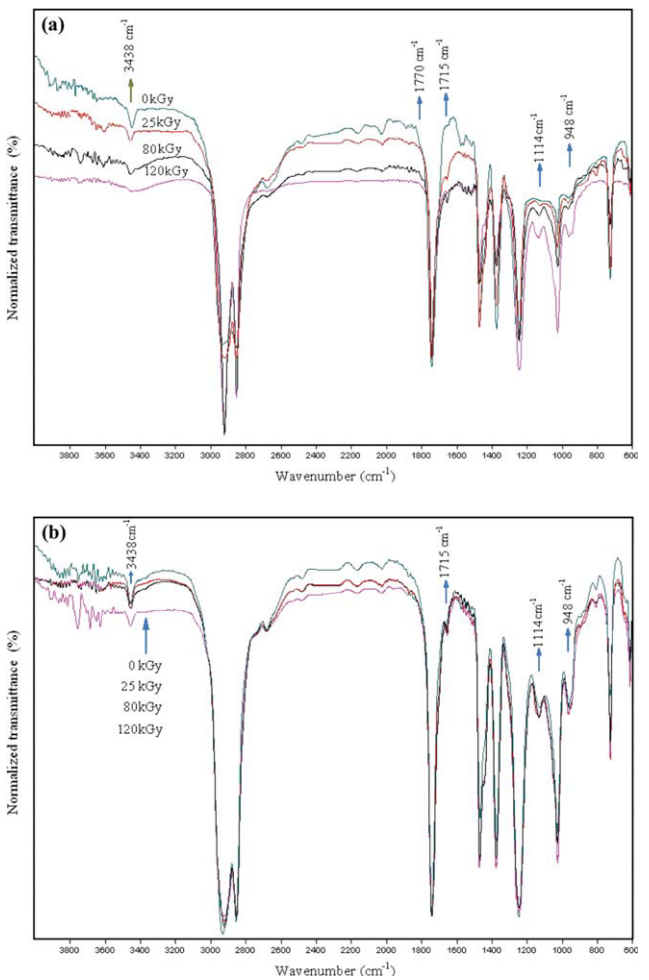


Figure 8 IR spectra of samples as a function of irradiation dose: (a) EVA18; (b) EVA28. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

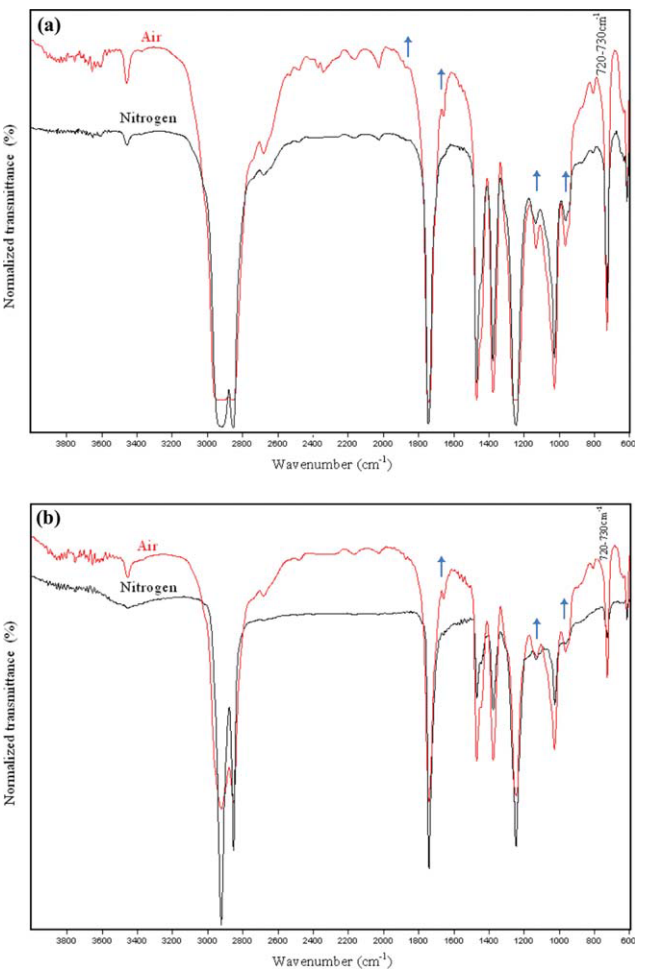


Figure 9 IR spectra of samples as a function of irradiation environment: (a) EVA18; (b) EVA28. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

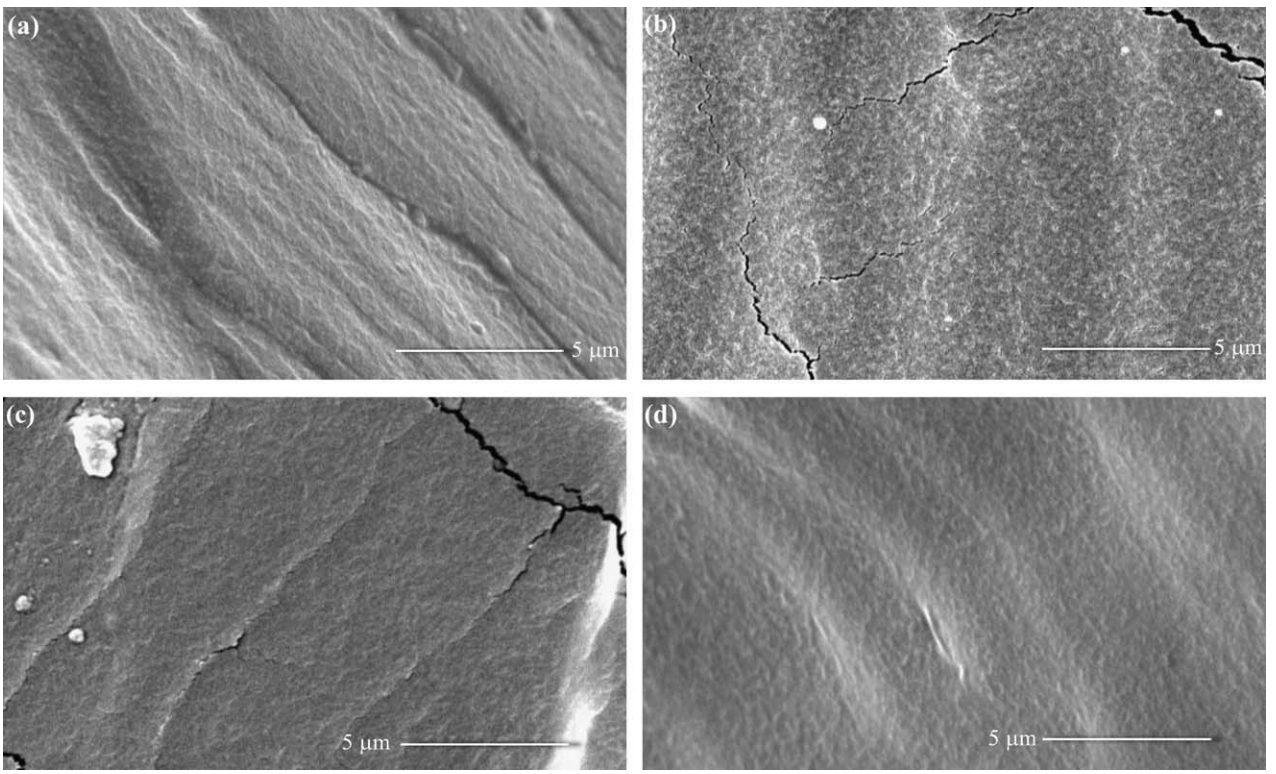


Figure 10 SEM images of a fracture surface of irradiated EVA at 80 kGy: (a) EVA18, in air; (b) EVA18, in nitrogen; (c) EVA28, in air; (d) EVA28, in nitrogen.

scission conquers, a shape of layer orientation (terrace configuration) is seen. Whereas the crosslinking created by three-dimensional structure reduce orientation, therefore layers are bent or twisted. As shown in Figure 10(a,c), EVA is susceptible to chain scission under air irradiation. The bent layers in Figure 10(b,d) prove that crosslinking overcomes in nitrogen irradiation. Also it is considered that orientation in EVA18 is more than EVA28. That is because of EVA which generally has more crystalline region with decrease of VA. Crystallinity can improve orientation of layers.

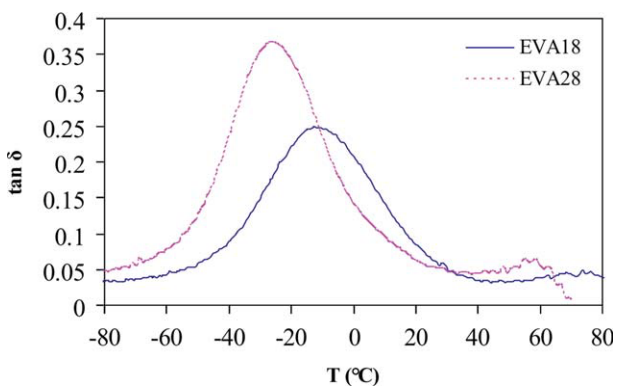


Figure 11 Loss factor versus temperature for non-irradiated samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

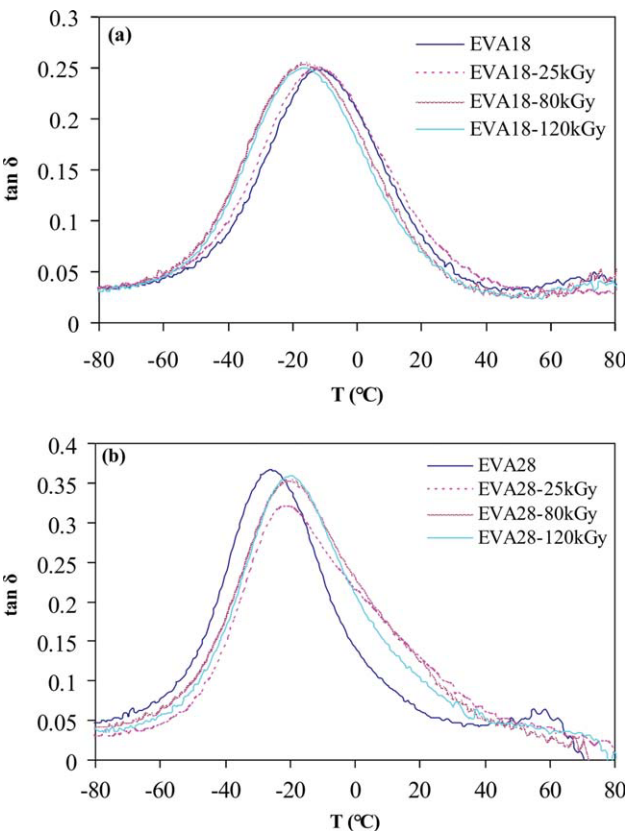


Figure 12 Loss factor versus temperature with different irradiation doses: (a) EVA18; (b) EVA28. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

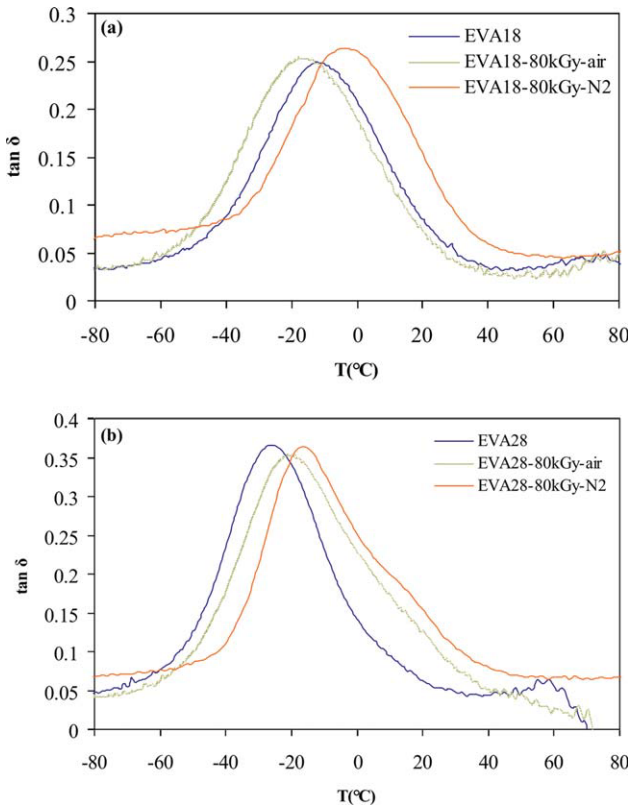


Figure 13 Loss factor versus temperature with different environmental irradiation: (a) EVA18; (b) EVA28. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dynamic mechanical analysis

Figure 11 shows tan δ versus temperature for non-irradiated samples. As known, the temperature at maximum tan δ peak illustrates the glass transition temperature (T_g). The height of the tan δ peak increases with increase of VA content. It is the result of more amorphous phase in EVA with more VA content. The width of the tan δ peak broadens with decrease of VA content. It can be attributed to variety of random structure and different chain length in ethylene that are generated at low VA content.[15] Also it is clear that the position of T_g comes to lower temperature, with higher VA content. It is because of more branching amount and free volume provided with more VA content.

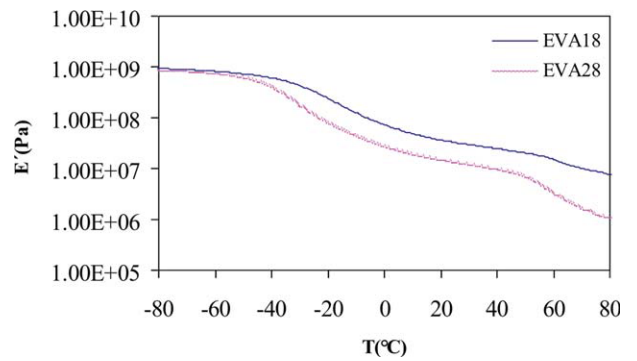


Figure 14 Storage modulus versus temperature for non-irradiated samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

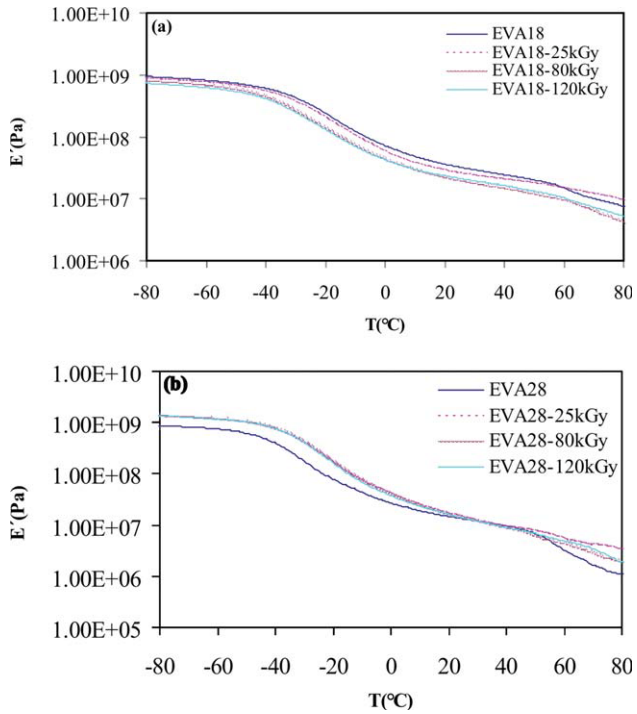


Figure 15 Storage modulus versus temperature with different irradiation doses: (a) EVA18; (b) EVA28. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The changes in tan δ chart for irradiated samples display in Figures 12 and 13. As observed, the maximum tan δ peak do not vary notably with irradiation in air (especially in EVA18) while there is an increase with irradiation in nitrogen. Increase in T_g is a reason for crosslinking.

From Figures 14–16, the storage modulus about $<-50°C$ show the similar values among the samples. It has been reported[16] that the storage modulus below the glass transition region can be hardly affected by changing the crystallinity of the polymer. Since storage modulus above $-50°C$ depends on crystallinity, it enhances by reduce of VA content (see Fig. 14). On the other hand, above $-50°C$, irradiation causes widening of elastic zone. Also crosslinked samples are able to show elastic plateau in these charts (Fig. 16). It is a clear evidence of network structure formation, which is stable under deformation.

CONCLUSIONS

In this study, the effects of irradiation on mechanical and structural properties of EVA are investigated.

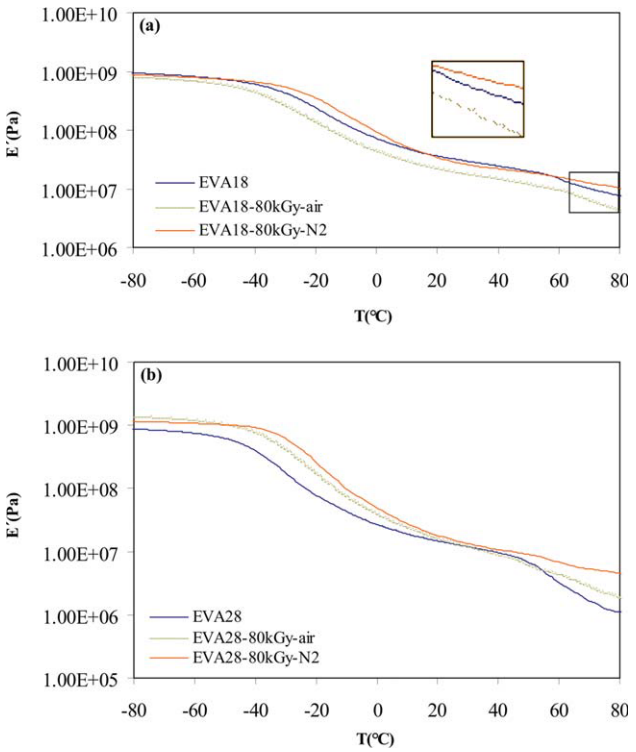


Figure 16 Storage modulus versus temperature with different environmental irradiation: (a) EVA18; (b) EVA28. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

As a conclusion, all these studies show that oxidation, crosslinking and chain scission are the main consequences of gamma irradiation of EVA. The conquest phenomenon can be predicted by Charlesby–Pinner equation. According to this equation, EVA is susceptible to chain scission in air and crosslinking in nitrogen. Totally, properties enhance with irradiation in nitrogen while they do not change importantly with irradiation in air. Results of FTIR show that oxidation more occur under irradiation in air. Finally, by observing the fracture surfaces in the SEM experiment, it was able to observe layers of EVA transforming from terrace configurations (in irradiated samples under air) into bent or twisted shapes (in irradiated samples under nitrogen). In addition, according to DMA results, crosslinked samples are able to show elastic plateau in storage modulus charts.

As, EVA is a biocompatible polymer and can be shaped and sterilized with gamma radiation, it can be used in medical applications.

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