

## Vinyl acetate content and electron beam irradiation directed alteration of structure, morphology, and associated properties of EVA/EPDM blends

Subhendu Ray Chowdhury,<sup>1</sup> Bhuwanesh Kumar Sharma,<sup>2</sup> Prakash Mahanwar,<sup>2</sup> Kuppa Sivasankara Sarma<sup>1</sup>

<sup>1</sup>Radiation Technology Development Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

<sup>2</sup>Department of Polymer and Surface Engineering, Institute of Chemical Technology, Matunga, Mumbai, India

Correspondence to: S. Ray Chowdhury (E-mail: rcsubhen@barc.gov.in or rcsubhendu@gmail.com)

**ABSTRACT:** A series of ethylene vinyl acetate/ethylene-propylene diene elastomer (EVA/EPDM) blends with four types of EVAs with various vinyl acetate (VA) content, are prepared without and with crosslinker, trimethylol propane triacrylate (TMPTA). These are irradiated by electron beam (EB). As the VA content increases, the gel content, i.e., degree of crosslinking of EVA/EPDM blends, is increased. With increase in VA content, the modulus and tensile strength are decreased but elongation at break is increased due to increase in amorphousness. On EB irradiation, modulus and tensile strengths are increased but at the cost of elongation at break. Crystallinities of all blends are decreased with increase in VA and EB crosslinking. The thermal stability of EVA/EPDM blend is decreased with increase in VA content but increased after EB irradiation. Scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) show that with increase in VA content the miscibility of two polymers keeps on increasing, which even become more after EB irradiation. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43468.

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### INTRODUCTION

Ethylene vinyl acetate (EVA) is an important copolymer of ethylene and vinyl acetate (VA). Varying the VA content, EVA can be tailored for application as rubber, thermoplastic elastomer, and plastic.<sup>1</sup> These are extensively used for electrical insulation purpose, cable jacketing, water proofing, corrosion protection, and packaging component. The amount of VA controls rheology, crystallinity, mechanical, thermal and electrical properties, and flame retardancy of the EVA molecules.<sup>2,3</sup>

EVA has a good barrier property, low-temperature excellent toughness, stress-crack resistance, waterproof properties, ultraviolet radiation, weather resistance, and excellent mechanical properties.<sup>4</sup> However, ethylene-propylene diene elastomer (EPDM) has high crosslinking ability, excellent heat resistance, ozone resistance, impact strength, and flexibility, which is a perfect material in many areas such as wire and cable insulation, automotive, O-ring, gasket, etc.<sup>5</sup> For combining above mentioned properties, few EVA/EPDM blends and composites have already been prepared and studied.<sup>1,5–7</sup> However, almost all studies are made based on one kind of EVA. As the quantity of VA changes the properties of EVA including rheology, the degree of compatibility of various EVA with EPDM should be different

leading to variable properties. Yuan Hu and coworkers<sup>8</sup> has studied the effect of vinyl acetate content and electron beam (EB) irradiation on the flame retardancy, mechanical, and thermal properties of pure intumescent flame retardant ethylene-vinyl acetate copolymer. It has been found that EVA with different VA content shows different properties. Althman has reported the effect of VA content on the mechanical, thermal, and dynamic properties of high density polyethylene (HDPE)/EVA blends.<sup>9</sup> Martín-Alfonso has investigated the influence of vinyl acetate (VA) content on the rheological properties and microstructure of polymer gels based on conventional and high-oleic sunflower vegetable oils and ethylene-vinyl acetate copolymer (EVA).<sup>2</sup> Some reports again have shown that different vinyl acetate content toughens other polymers such as poly(lactic acid), polypropylene (PP) in different degrees.<sup>10,11</sup> Thus, it is evident that the VA content in EVA is significantly affecting the properties of EVA based blends. Obviously, the effect of VA of EVA on the EVA/EPDM blend morphology, interface, and driven properties are very important, which are left unstudied.

However, since EPDM and EVA reportedly have excellent crosslinking efficiency and degree of crosslinking of EVA depends on VA content, the study of crosslinked EVA/EPDM blends with various EVAs should be interesting and useful. However, there is

very little available literature. Mishra *et al.* has studied the dynamic and static crosslinking behavior of EVA/EPDM blends with one kind of EVA using dicumyl peroxide (DCP).<sup>12</sup> They have not studied other related properties.

Last two decades, radiation technology is being used extensively and they have become very common and useful technique for radiation crosslinking of polymers. However, recently, the market of electron beam has rapidly grown up compared to gamma irradiation due to some limitations of gamma irradiation e.g., difficulties in large-scale irradiation, time consumption, safety towards handling of isotopes, etc. The electron beam crosslinking improves the mechanical, thermal, chemical, electrical insulation, and environmental properties of polymer blends and composites, which makes them suitable for wide area of applications e.g., automotive, wire and cable insulation, constructions, etc.<sup>13</sup>

In this study, we have prepared EVA/EPDM blends with various VA containing EVAs with and without crosslinking agents. Blends are irradiated by electron beam radiation. The effect of VA content and EB irradiation on the structure, morphology and properties namely, mechanical, crystallization, thermal stability, and flame retardancy of the blends are studied. With increase in VA content, the miscibility of EVA/EPDM is increased. Upon crosslinking, the miscibility of EVA/EPDM is increased more. This is reflected in Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and mechanical properties. Thermal stability and crystallinity are decreased with VA increase. However, upon crosslinking, thermal stability is increased and crystallinity is decreased. Flame retardancy (Limiting Oxygen Index, LOI) is increased with VA content and EB crosslinking.

## EXPERIMENTAL

### Materials

Various ethylene-vinyl acetate copolymers (EVAs), Elvax 460, Elvax 265A, Elvax 40L-03, and LEVAMELT700, with vinyl acetate (VA) content 18, 28, 40, and 70 wt % are purchased from Dupont and Lanxess in form of pellets.

The melt flow index (MFI) and densities of the above EVAs are 2.5, 3.0, 3.0, and 4.0 g/10 min, and 0.940, 0.951, 0.967, and 0.980 g cc<sup>-1</sup>, respectively.

Ethylene-propylene diene elastomer (EPDM), NORDEL IP 3722P grade, with 71% ethylene content and 0.5% ENB, Mooney Viscosity, ML 1 + 4 at 125 °C (ASTM D1646) 18 and density of 0.87 g cc<sup>-1</sup> is supplied by Dow chemical. The trimethylol propane triacrylate (TMPTA), the crosslink promoter, is purchased from Sigma-Aldrich.

### Preparation of Blends and Test Specimens

EPDM is melt mixed with each EVA separately in 50/50 weight ratio with and without TMPTA in brabender type batch mixer at 120 °C and 70 rpm for 5 min. The crosslinker TMPTA is used in 1 phr (parts per hundred parts of resin). For further study, dumb-bell shaped specimens are prepared by compression molding at 140 °C and 5 ton in an electrically heated press.

The 50/50 blend of various EVAs and EPDM will be written as EVA18/EPDM, EVA28/EPDM, EVA40/EPDM, and EVA 70/EPDM. The first part represents the type of EVA and second part EPDM, the blend partner. Only 50/50 blends are prepared that is why no composition is mentioned. All blends are irradiated in electron beam as discussed later at 100 kGy (kilo Grey) dose in absence and presence of TMPTA. Those will be denoted as EVA/EPDM-100 and EVA/EPDM-T-100, respectively. EVA/EPDM-100 means blend irradiated at 100 kGy without crosslinker. EVA/EPDM-T-100 means blend irradiated at 100 kGy with 1 phr TMPTA. The reason of irradiation at 100 kGy is explained in the “gel content analysis” part.

### Electron Beam Irradiation

The compression molded dumb-bell shaped specimens of 2 mm thickness are irradiated by high-energy electron beam in an inert environment using 2 MeV electron beam accelerator at a radiation dose of 50, 100, 125, and 150 kGy (kilo Grey) at dose rate of 1 kGy/pass and 1 mA beam current. The distance of the sample from the scan horn is 20 cm and the conveyer speed is set at 0.94 m min<sup>-1</sup>.

### Characterization

**Determination of Gel Fraction (% Gel Content).** Gel fractions of irradiated blends are measured by solvent extraction technique using xylene as solvent. The samples are extracted in hot xylene for 48 h at 110 °C. Extracted samples are dried in a vacuum oven at 80 °C until constant weight. The gel content (% gel fraction) is determined using the following formula:

$$(\%) \text{ Gel content} = \frac{\text{Weight after extraction}}{\text{Weight before extraction}} \times 100.$$

**Fourier Transform Infrared Spectroscopy (FTIR).** The FTIR spectra of neat polymers and their unirradiated and irradiated blends (2 mm thick) have been recorded on a Bruker-Alpha's Platinum ATR model.

Samples are characterized at Attenuated total reflection (ATR) mode at room temperature (25 °C) and 50% ± 5 humidity, wave number ranging from 400–4000 cm<sup>-1</sup>. The number of scans and spectral resolution are set to 24 sec and 4 cm<sup>-1</sup>, respectively.

**Mechanical Properties. Tensile properties.** Tensile testing is carried out using a Universal Testing Machine (LLOYD Instrument LR 50 K) following ASTM D 638. The cross head speed is 50 mm min<sup>-1</sup> at 25 °C. Sample dimensions are length overall (LO) × We (width narrow section) × T (thickness) = 115 mm × 5 mm × 2 mm. The average of four replicas is reported here.

**Hardness.** Hardnesses of irradiated and unirradiated blends are measured using Shore “A” Durometer following ASTM D 2240.

The specimen is first placed on a hard flat surface. The indenter for the instrument is then pressed into the specimen making sure that it is parallel to the surface. The hardness is read within 1 sec of firm contact with the specimen. The test specimens are 6.4 mm thick.

**Differential Scanning Calorimetry (DSC).** Differential scanning calorimetric (DSC) analysis is carried out at heating and cooling

rate of  $10^{\circ}\text{C min}^{-1}$  in  $\text{N}_2$  atmosphere using TA Instrument's differential scanning calorimetric thermal analyzer (DSC, Q-100).

Melting temperature ( $T_m$ ), crystallization temperatures ( $T_c$ ), heat of fusion ( $\Delta H_m$ ), and % crystallinity are calculated from the DSC curves. The degree of crystallinity ( $X_c$ ) is calculated from heat of fusion under the melting endotherm, using following formula:

$$X_c = \frac{\Delta H_m}{\Delta H_m^0} \times 100$$

where  $\Delta H_m$  is the melting enthalpy of sample and  $\Delta H_m^0$  is the melting enthalpy of 100% crystalline sample.  $\Delta H_m^0$  for both 100% crystalline EVA and EPDM is taken as  $239 \text{ J g}^{-1}$ , which is the  $\Delta H_m^0$  of crystalline low density polyethylene (LDPE).<sup>13</sup> The crystallinities of the EVA and EPDM are originated mainly from long chain hydrocarbon of the above two polymers.<sup>13,14</sup>

**Thermogravimetric Analysis (TGA).** Thermogravimetric analysis (TGA) of the virgin EVAs (various VA content), EPDM, and their blends before and after crosslinking is carried out using a Perkin Elmer Pyris -1 Thermo-Gravimetric Analyzer (TGA) under  $\text{N}_2$  atmosphere at a heating rate of  $10^{\circ}\text{C min}^{-1}$ . To compare the nature of degradation of various samples, onset temperature ( $T_i$ ), degradation temperature ( $T_d$ ), temperature corresponding to 30% mass loss ( $T_{30}$ ), temperature corresponding to 50% mass loss ( $T_{50}$ ), and temperature corresponding to 90% mass loss ( $T_{90}$ ) are calculated from TGA graphs.

**Flame Retardancy (Limiting Oxygen Index, LOI).** Limiting oxygen index (LOI), which corresponds to the minimum concentration of oxygen needed for the combustion of a material in specified conditions, is measured using an Limiting Oxygen Index (LOI) chamber (Dynisco Polymer test instrument) in oxygen–nitrogen atmosphere. The sample dimension for LOI measurement is kept  $100 \text{ mm} \times 6.5 \text{ mm} \times 3 \text{ mm}$  according to ASTM D 2863-77 standard.

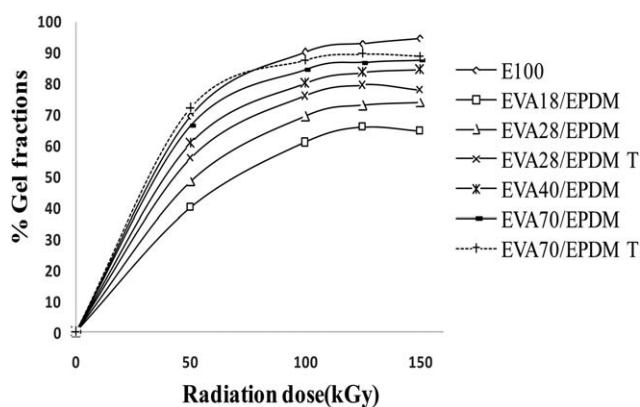
This test method provides for the measurement of the minimum concentration of oxygen in a mixture of oxygen and nitrogen that will just support flaming combustion of plastics. In this procedure, the test specimen is subjected to flame through vertical support in a mixture of oxygen and nitrogen. By testing a series of specimens in different oxygen concentrations, the minimum oxygen concentration is determined.

**Surface Morphology (Scanning Electron Microscope, SEM).** The EVA/EPDM blends fractured in liquid nitrogen are characterized by Scanning Electron Microscope (SEM) using JEOL, JSM-6380 LA model. To enhance the conductivity fractured surfaces are gold sputtered prior to examining surface morphology.

## RESULTS AND DISCUSSION

### Gel Fractions Analysis

The crosslinking ability of EVA/EPDM blends containing different vinyl acetates (VAs) in presence and absence of TMPTA crosslinker is measured from gel fraction analysis. The variation in gel fraction of the above samples with electron beam radiation dose is presented in Figure 1. It is reported that higher is the gel fraction, higher will be the crosslinking, as gel fraction is



**Figure 1.** Variation in gel fraction of EVA/EPDM blends with vinyl acetate content and EB radiation dose.

the measurement of amount of crosslinking.<sup>15</sup> For pure EPDM and EVA/EPDM blends with various VA content, the gel content increases up to 125 kGy, beyond which the change is not considerable. A sharp change is noticed for all blends and pure EPDM up to 100 kGy. From 100 kGy to 125 kGy, a little change is noticed. Again, pure EPDM shows higher gel fractions compared to all EPDM/EVA samples because of higher crosslinking ability of the former, which is due to the higher amorphousness and molecular structure.<sup>16</sup> Interestingly, the gel fraction of EVA/EPDM blends gradually increases with increase in vinyl acetate content (VA) of used EVAs suggesting the crosslink efficiency of blends is directly proportional to the vinyl acetate content. This is due to increase in amorphousness of EVA with higher VA content (Table I).<sup>8</sup> It is also seen that the TMPTA added EVA/EPDM blends show higher gel fractions compared to without ones due to increase in degree of crosslinking in presence of crosslinker.<sup>17</sup> In this Figure 1, TMPTA containing EVA28/EPDM and EVA 70/EPDM are reported. TMPTA containing EVA28/EPDM and EVA40/EPDM blends lie in between other two blends and follow the same trend as described above.

### Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra of EPDM, EVAs of various VA content, their unirradiated, and electron beam irradiated blends are displayed in Figure 2(a,b). In this study, the effect of vinyl content (VA) and electron beam crosslinking on absorbance of different functional groups of EVA/EPDM blends have been investigated.

While formation of blends there is no chemical reaction between EVA and EPDM. Due to physical interaction, they mix with each other. Therefore, when EPDM and EVA phases are mixed, the functional groups experience restriction in vibrational motion and consequently absorption intensities become less. That is why the intensities of the functional groups are reduced. Greater the miscibility higher will be the reduction of intensities of a functional group. In EVA/EPDM systems, we have mentioned about the symmetric and asymmetric stretching of  $-\text{C}-\text{O}-\text{C}-$  group, carbonyl stretching of acetate group. The absorption intensities of these functional groups in pure EVAs are more than EVAs in blends. As VA content increases in EVA, the degree of reduction becomes more revealing the fact that the interaction i.e., miscibility of EPDM with EVA with higher

**Table I.** DSC Parameters of Various EVAs, EPDM, and Unirradiated and Irradiated EVA/EPDM Blends

Samples	T <sub>g1</sub> T <sub>g2</sub>	T <sub>m1</sub> T <sub>m2</sub> (°C)	T <sub>c1</sub> T <sub>c2</sub> (°C)	ΔH <sub>m</sub> (J/g) Peak 1 Peak 2	% Crystallinity (X <sub>c</sub> ) Peak 1 Peak 2
EPDM	-9.02	- 54.00	- 31.41	- 23.60	- 9.87
EVA18	-13.04	89.45 54.29	68.46 31.67	22.30 5.40	9.33 2.25
EVA18/EPDM	-10.57	89.16 53.82	69.06 32.64	5.52 12.55	4.61 10.5
EVA18/EPDM 100	-10.66	87.81 53.96	62.76 24.83	7.64 8.70	6.39 7.28
EVA18/EPDM T 100	-10.80	85.74 51.38	62.38 26.00	1.84 4.64	1.53 3.88
EVA28	-13.95	76.76 51.26	53.93 33.03	10.35 2.61	4.33 1.10
EVA28/EPDM	-10.15	77.29 52.81	56.43 33.80	2.84 15.20	2.37 12.71
EVA28/EPDM 100	-10.29	77.82 53.17	47.94 24.70	1.38 4.08	1.15 3.41
EVA28/EPDM T 100	-10.36	72.49 50.67	47.05 25.39	1.11 5.29	.928 4.42
EVA40	-14.09	- 52.54	- 29.61	- 4.05	- 1.69
EVA40/EPDM	-11.46	- 54.45	- 25.28	- 11.44	- 9.57
EVA40/EPDM 100	-10.45	- 50.65	- 25.16	- 11.88	- 9.94
EVA40/EPDM T 100	-10.68	- 50.28	- 25.74	- 8.77	- 7.33
EVA70	-18.68	- -	- -	- -	- -
EVA70/EPDM	-16.45	- 52.21	- 28.94	- 8.80	- 7.36
EVA70/EPDM 100	-12.31	- 53.51	- 26.12	- 5.38	- 4.50
EVA70/EPDM T 100	-14.53	- 52.17	- 26.14	- 7.17	- 6.0

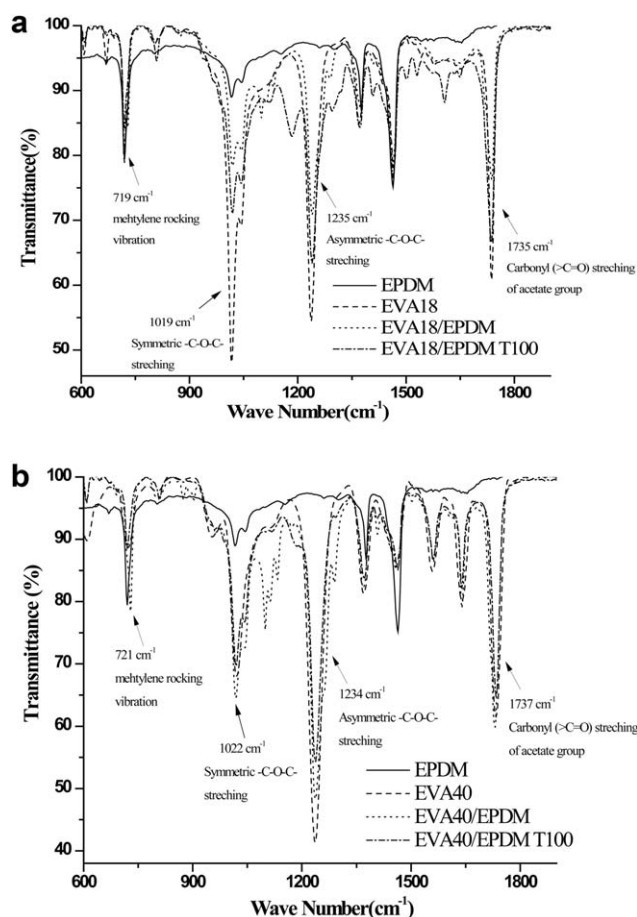
VA is higher. FTIR spectrum of neat EPDM shows peaks at 719, 1014, 1376, and 1464 cm<sup>-1</sup>. Pure EVAs show peaks around 719 cm<sup>-1</sup> due to methylene (-CH<sub>2</sub>) rocking vibration, 1017–1022 cm<sup>-1</sup> due to symmetric -C-O-C- stretching, 1235–1237 cm<sup>-1</sup> due to asymmetric -C-O-C stretching and 1735–1737 cm<sup>-1</sup> due to carbonyl stretching (>C=O) of acetate group.<sup>18</sup> In EVA/EPDM blends, interesting changes in transmittance (reverse of absorbance) have been observed with change in vinyl acetate content. The transmittance at 719 cm<sup>-1</sup> (-CH<sub>2</sub> rocking) is found unchanged or little change for all EVA/EPDM blends compared to pure respective EVA samples (Figure 2). However, transmittances corresponding to -C-O-C symmetric stretching (1019 cm<sup>-1</sup>), -C-O-C asymmetric stretching (1235 cm<sup>-1</sup>), and C=O stretching (1735 cm<sup>-1</sup>) are increased in EVA18/EPDM compared to pure EVA18. It means that those functional groups in blends absorb less amount of energy due to restriction of vibration aroused from interaction with other phase (EPDM), though the reduction of absorption of the C=O stretching is not so high. Similarly, for other three blends (EVA28/EPDM, EVA40/EPDM, and EVA70/EPDM) the absorption corresponding to the above-mentioned characteristic peaks are decreased and the magnitudes of reduction keep on increasing with increase in VA content. For FTIR of EVA40/EPDM is represented in Figure 2(b). The reduction of absorbance corresponding to -C-O-C- symmetric stretching (1022 cm<sup>-1</sup>), -C-O-C- asymmetric stretching (1234 cm<sup>-1</sup>), and C=O stretching (1737 cm<sup>-1</sup>) frequencies with respect to pure EVA40 is more than previous system [Figure 2(a)]. This finding indicates that with increase in VA content in blend the restriction of vibration of the above mentioned functional groups are higher i.e., absorption is less. Thus, FTIRs implies higher degree of miscibility of EVA with higher VA content with EPDM.

Now, for EB crosslinking 3D networks are formed, which again restrict the motion of those functional groups and as a consequence, absorption intensities are reduced.

The schematic diagram of chemical reactions of EVA and EPDM in presence and absence of TMPTA are given in Scheme 1. The absorbance due to -CH<sub>2</sub> rocking at 719 cm<sup>-1</sup> slightly decreases for all blends, due to restriction aroused from crosslinked network formation [Figure 2(a,b)].<sup>18</sup> The absorbance of peaks around 1019 (-C-O-C- symmetrical stretching) and 1235 cm<sup>-1</sup> (-C-O-C- asymmetric stretching) for EVA18/EPDM blend are found much less than pure EVA18, though the change is not much for C=O stretching (1735 cm<sup>-1</sup>). Similar trend has been noticed from EVA28/EPDM to EVA70/EPDM blends. This is due to the same reason. In presence of TMPTA, the crosslinked blends exhibit similar trend of reduction of absorption of the above-mentioned functional groups as cross-linked ones without crosslinker. This finding again suggests an enhancement of compatibility of two phases after crosslinking.

### Mechanical Properties

**Tensile Properties.** Young's modulus, tensile strength, and % elongation at break of uncrosslinked and crosslinked EVA/EPDM blends have been tabulated in Table II and graphs are represented in Figure 3(a,b). Young's modulus, tensile strength, and % elongation of neat EPDM are 4.80 MPa, 1.71 MPa, and 720%, respectively. Pure EVA18, EVA28, EVA40, and EVA70 exhibit the Young's modulus 18.5, 13.14, 3.54, and 0.748 MPa, tensile strength 8.34, 5.83, 3.54, and 0.394 MPa, and % elongation at break 410, 465, 520, and 595, respectively (Table II). For EVA/EPDM blends, with change in VA content, similar trend has been reflected in all samples, where Young's modulus and tensile strength decrease, however, % elongation increases with



**Figure 2.** (a) FTIR diagram of EVA18, EPDM, and their unirradiated and irradiated blends. (b) FTIR diagram of EVA40, EPDM, and their unirradiated and irradiated blends.

increase in vinyl acetate (VA) content in the blends. With increase in VA content, the crystallinity of EVA is decreased and amorphousness i.e., flexibility is increased. This is the reason of the above findings. All blends show higher elongation but lower modulus and tensile strength than respective EVAs. This is due to incorporation of soft, flexible, and amorphous EPDM phase in blend.

On the other hand, electron beam irradiation significantly influences the Young's modulus, tensile strength, and % elongation of EVA/EPDM blends in absence and presence of TMPTA. The crosslinking effect in presence and absence of TMPTA has been observed for all samples i.e., from higher VA to lower VA containing blends (Table II). Both Young's modulus and tensile strength of all irradiated EVA/EPDM samples are found increased by electron beam crosslinking at 100 kGy but at the cost of % elongation<sup>19</sup> (Figure 3 and Table II). For TMPTA added samples, the increase in modulus and tensile strength are higher. However, the elongation due to more rigidity becomes further less. In TMPTA containing blends, the trend of change of all three properties with VA content is similar to uncrosslinked ones only the values are different.

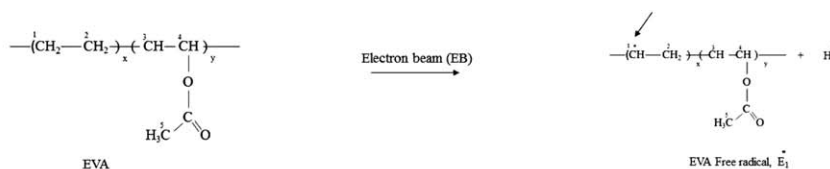
**Hardness.** The "Shore A" hardness values of neat EPDM, EVA with various VA content, their unirradiated and irradiated blends are shown in Figure 4. The similar trend is observed for hardness

as in tensile strength and modulus for EPDM, EVA, and EPDM/EVA blends. For neat EVA samples, the hardness keeps on decreasing with increase of VA content due to decrease in compactness of polymer chains and crystallinity. Similar trend has also been noticed for EVA/EPDM blends, where hardness steadily decreases with increasing VA content.<sup>20</sup> But interestingly, after electron beam irradiation, due to stiff network formation hardness of all cross-linked blends are found higher than uncrosslinked ones. For cross-linked blends, the order of hardness with increase in VA content is similar to uncrosslinked blends. Similarly, the increase of hardness is more in presence of TMPTA like tensile properties.

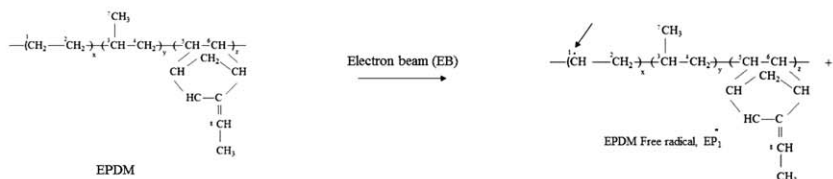
**Differential Scanning Calorimetry (DSC).** Figure 5 shows the DSC diagrams of EPDM, various EVAs and their unirradiated and irradiated blends. Melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), heat of fusion ( $\Delta H_m$ ), and degree of crystallinity ( $X_c$ ) obtained from the DSC thermograms are tabulated in Table I. Pure EPDM shows single broader endothermic peak at 54 °C. Each of both EVA18 and EVA28 show two melting peaks at 89.45, 54.29, 76.76, and 51.26 °C, respectively. However, in EVA40 a single peak is seen at 52.54 °C, whereas for EVA70, no melting peak has been occurred (Table I). The observation indicates that the melting temperatures of EVAs decrease from EVA 18 to EVA28. In EVA18/EPDM and EVA28/EPDM blends, two melting peaks corresponding to EVA and EPDM are obtained. In EVA40/EPDM, only one melting peak is seen at 54.45 °C. The second melting peak of EVA18 and EVA28 and single melting peak of EVA40 are merged with melting peak of EPDM. In EVA70/EPDM blend, a single melting peak corresponding to EPDM is found at 52.21 °C. Electron beam crosslinking reduces the higher melting peak ( $T_{m1}$  in Table I) of EVAs in EVA/EPDM blends, the reduction being more in presence of TMPTA. No change is noticed for second melting peak of EVA and EPDM (Table I).

It is noticed that there is no change of  $T_{m1}$  and  $T_{m2}$  in the blends compared to pure EVAs and EPDM. But when they are crosslinked in presence of TMPTA, a decrease in  $T_{m1}$  for lower VA containing (VA18 and VA28) blends is observed (higher VA containing blends do not show  $T_{m1}$ ), suggesting increased miscibility.<sup>21</sup> However,  $T_{m2}$  does not show any change for all uncrosslinked and crosslinked blends.

With increase in VA content,  $T_c$  of EVA decreases with increase in VA indicating less inclination of high VA containing EVA towards crystallization. For EVA18/EPDM and EVA28/EPDM blends, two crystallization peaks corresponding to EVA and EPDM are obtained, the lower  $T_c$  of EVA being merged with  $T_c$  of EPDM. On the other hand, EVA70/EPDM blend exhibits a single crystallization temperature corresponding to EPDM (Table I). Upon electron beam irradiation in absence and presence of TMPTA, both crystallization temperatures ( $T_c$ ) corresponding to EVA and EPDM are decreased, which are very prominent for EVA18/EPDM and EVA28/EPDM blends. With increase in VA content the  $\Delta H_m$  (heat of fusion), i.e., % crystallinity of EVA decreases due to presence of less hydrocarbon chain.<sup>9</sup> In blends, % crystallinity corresponding to EVA generally decreases but corresponding to EPDM remains unchanged. The % crystallinities corresponding to EVA and EPDM both in

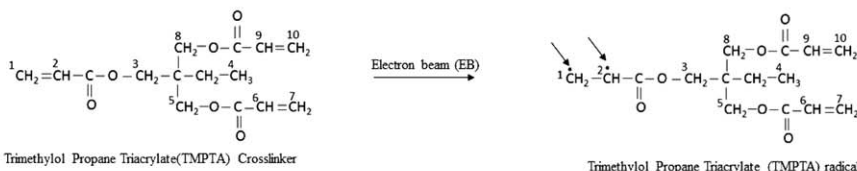
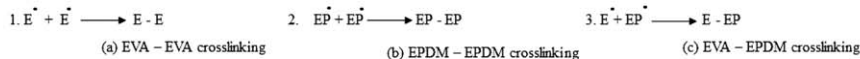


Similarly all -C-H bond in EVA can generate EVA free radicals (E<sub>1</sub>, E<sub>2</sub>, E<sub>3</sub>,.....) by electron beam irradiation. We can represent all free radicals by E which can form Three dimensional (3D) network.



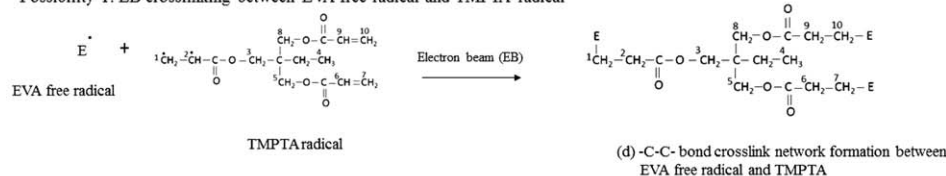
Similarly all -C-H bond in EPDM can generate EPDM free radicals (EP<sub>1</sub>, EP<sub>2</sub>, EP<sub>3</sub>,.....) by electron beam irradiation. We can represent all free radicals by EP which can form Three dimensional (3D) network.

The EB crosslinking between EVA and EPDM may take place via both intra as well as interphase interaction.

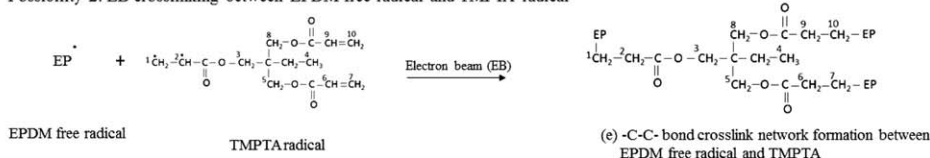


The free radical formation may take place from carbon 1 to carbon 10 positions but the probability of free radical generation is more at Carbon-1,2,6,7,9 and 10 positions. All TMPTA free radicals can be represented as TMPTA radical.

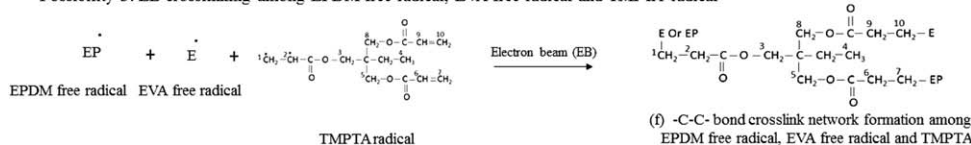
Possibility 1: EB crosslinking between EVA free radical and TMPTA radical



Possibility 2: EB crosslinking between EPDM free radical and TMPTA radical



Possibility 3: EB crosslinking among EPDM free radical, EVA free radical and TMPTA radical

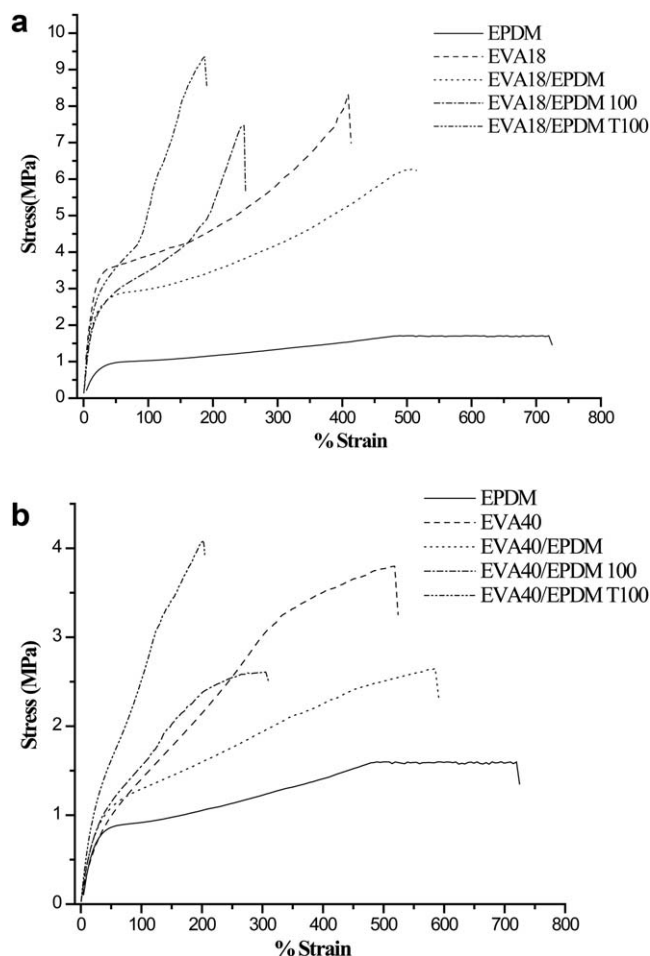


**Scheme 1.** Crosslinking reactions of EVA and EPDM in presence and absence of TMPTA.

the blends, are decreased upon crosslinking for both cases in presence and absence of TMPTA. However, the effect of TMPTA is found to be system dependent.

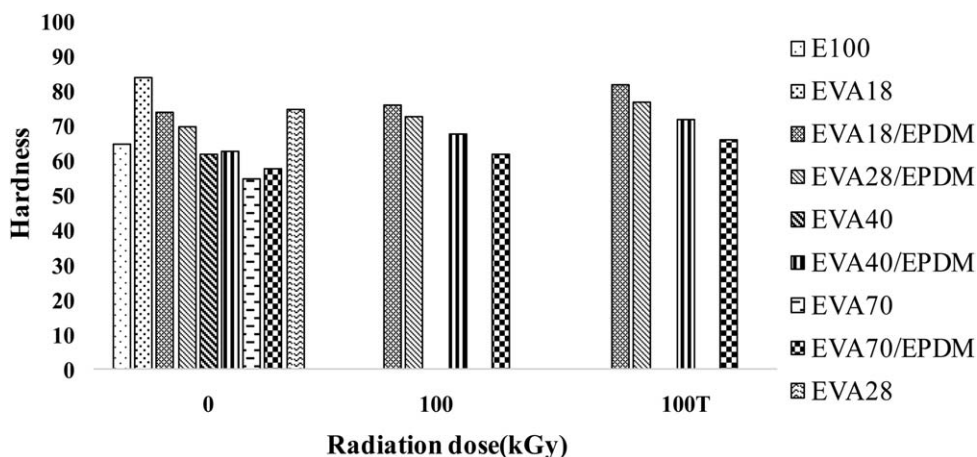
Again, the glass transition temperatures ( $T_g$ s) obtained by differential scanning calorimetric (DSC) have been used to deter-

mine the miscibility of EVA/EPDM blends. The glass transition temperatures of pure EPDM, different EVAs and their unirradiated and irradiated blends have been tabulated in Table I. The glass transitions of EVA18/EPDM and EVA70/EPDM blends have been represented in Figure 5(d,e). The pure EPDM shows the glass transition at  $-9.02^\circ\text{C}$ . The glass transitions for pure



**Figure 3.** (a) Stress–strain graph of EVA18, EPDM, and EVA18/EPDM blends before and after irradiation. (b) Stress–strain graph of EVA40, EPDM, and EVA40/EPDM blends before and after irradiation.

EVA18, EVA28, EVA40, and EVA70 have been found to be  $-13.04$ ,  $-13.95$ ,  $-14.09$ , and  $-18.68$  °C, respectively. In our case, for all blends uncrosslinked and crosslinked, only one  $T_g$  appears in between the  $T_g$ s of EPDM and EVA, indicating the miscibility of the blends [Table I and Figure 5(d,e)].



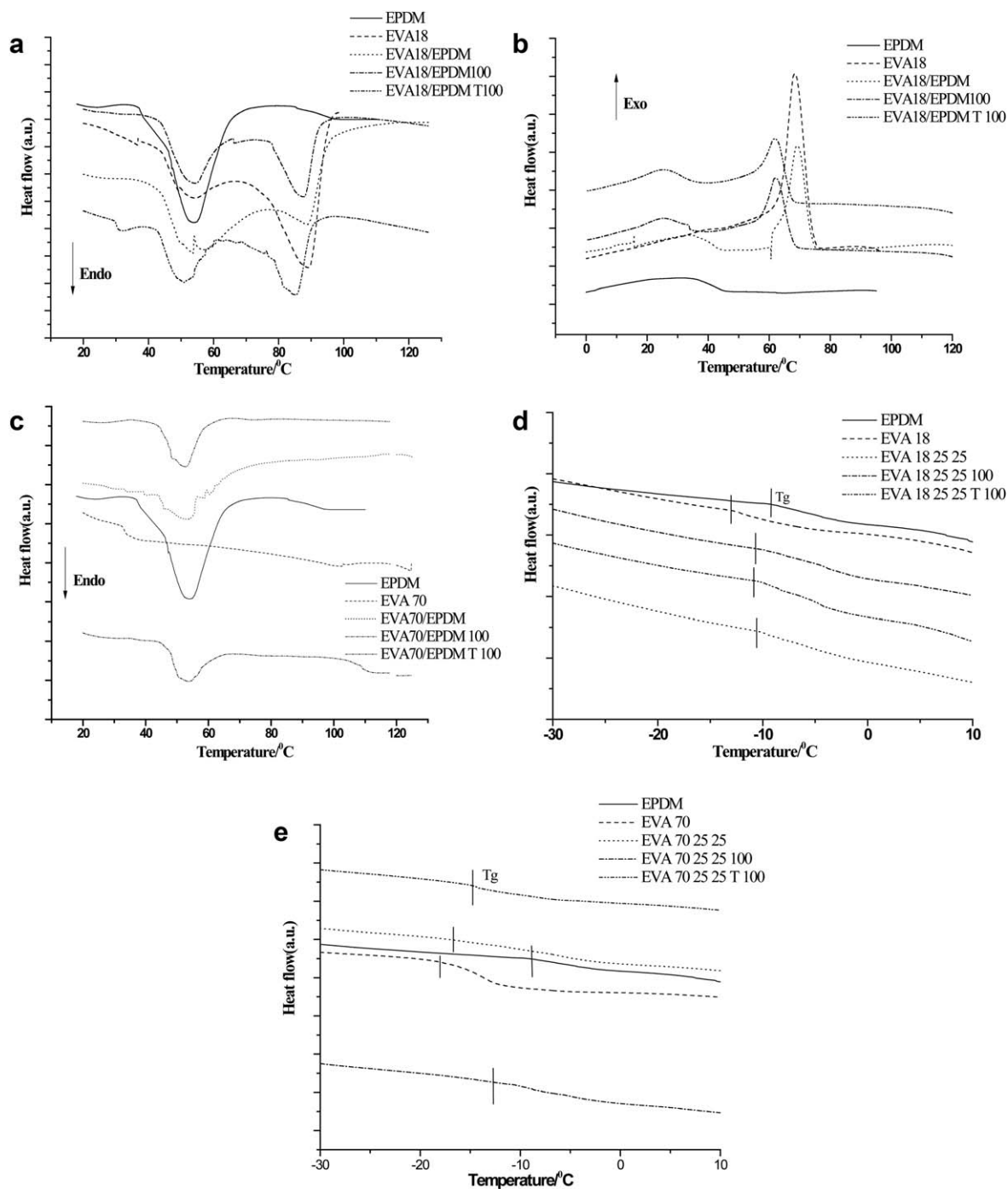
**Figure 4.** Effect of VA content and EB radiation dose on hardness of EVA/EPDM blends.

**Table II.** Tensile Properties of Various EVAs, EPDM, and Unirradiated and Irradiated EVA/EPDM Blends

Samples	Young's modulus (MPa)	Tensile strength (MPa)	% Elongation
EPDM	4.80	1.71	720
EVA18	18.5	8.34	410
EVA18/EPDM	12.8	6.25	510
EVA18/EPDM 100	17.23	7.46	246
EVA18/EPDM T 100	22.39	9.37	187
EVA 28	13.14	5.83	465
EVA28/EPDM	9.67	3.96	554
EVA28/EPDM 100	12.25	4.69	290
EVA28/EPDM T100	14.23	6.85	215
EVA 40	3.54	3.54	520
EVA40/EPDM	3.92	2.45	595
EVA40/EPDM 100	5.58	2.86	308
EVA40/EPDM T100	6.65	4.06	202
EVA70	0.748	0.394	595
EVA70/EPDM	2.60	0.85	654
EVA70/EPDM 100	3.27	1.70	467
EVA70/EPDM T100	4.32	2.21	383

The criteria for the miscibility of the polymer blends is the appearance of a single glass transition temperature ( $T_g$ ) usually at a point between the  $T_g$ s of both the pure constituents or shifting of both the  $T_g$ s closer.<sup>21,22</sup> However, in this case, from the change of  $T_g$  values it is difficult to make out the degree of miscibility or change of miscibility as EVAs are having close  $T_g$  values and blend partner of EVA is common that is EPDM.

**Thermogravimetric Analysis (TGA).** Thermogravimetric analysis (TGA) of neat polymers and blends are summarized in Table III and representative graphs of EVA18/EPDM and EVA70/EPDM systems are provided in Figure 6(a,b). Table III displays onset temperature ( $T_i$ , temperature corresponding to 1% weight loss), degradation temperatures ( $T_{d1}$  and  $T_{d2}$ ), and

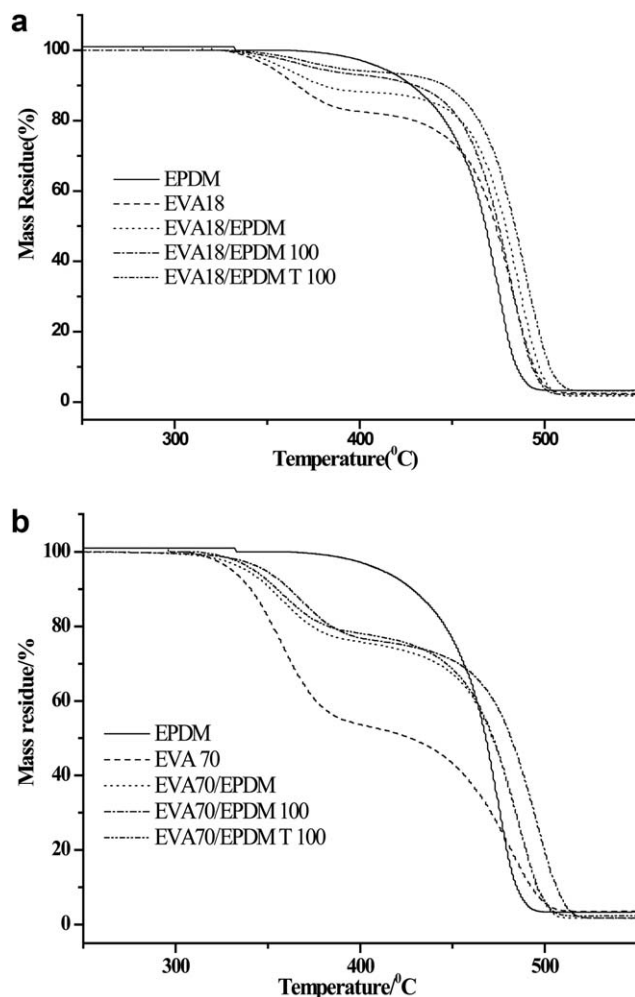


**Figure 5.** (a) DSC (heating mode) of EPDM, EVA18, and their unirradiated and irradiated blends. (b) DSC (cooling mode) of EPDM, EVA18, and their unirradiated and irradiated blends. (c) DSC (heating mode) of EPDM, EVA70, and their unirradiated and irradiated blends. (d) Low temperature DSC of EPDM, EVA18, and their unirradiated and irradiated blends. (e) Low temperature DSC of EPDM, EVA70, and their unirradiated and irradiated blends.

temperatures corresponding to 30, 50, and 90% weight loss ( $T_{30}$ ,  $T_{50}$ , and  $T_{90}$ ) of neat EPDM, neat EVAs (18, 28, 40, and 70% VA contents), and their blends before and after EB irradiation. The TGA graphs of neat EPDM shows single step degradation, while all neat EVA (EVA18 to EVA70) and their blends display two step degradation [Figure 6(a,b)]. The first step degradation temperature ( $T_{d1}$ ) of EVA is assigned to the evolution

of acetic acid in the temperature range from 330 °C to 345 °C and the second step degradation to the pyrolysis of the polyethylene segments.<sup>8</sup> Both first and second steps degradation temperatures of EVA keep on decreasing with increase of vinyl acetate content, which is due to decrease in crystallinity and gas barrier properties of EVAs.<sup>23</sup> Similarly, the values of  $T_i$ ,  $T_{30}$ , and  $T_{50}$  gradually decrease from EVA18 to EVA70 though  $T_{90}$  values





**Figure 6.** (a) Thermogravimetric analysis (TGA) graph of EPDM, EVA18, and their unirradiated and irradiated blends. (b) Thermogravimetric analysis (TGA) graph of EPDM, EVA70, and their unirradiated and irradiated blends.

do not change much. The first step degradation temperatures ( $T_{d1}$ ) are found almost same from EVA18/EPDM to EVA40/EPDM blends. However, for EVA70/EPDM blend, it significantly decreases compared to other ones, while the second step degradation temperature ( $T_{d2}$ ) for EVA18/EPDM and EVA28/EPDM and  $T_{50}$  and  $T_{90}$  for all blends are found unchanged. Though  $T_{d2}$ s are found higher for EVA 40/EPDM and EVA 70/EVA, this is also an indication of higher miscibility, which is hinted by FTIR study. That increase of  $T_{d2}$  generally happens due to increase in barrier property of volatile organic constituents and decrease in heat transfer (these are the two main controlling factors for degradation of polymers), which are originated from two such polymer phases in blends, which are miscible is higher magnitude.<sup>24,25</sup>

Thermal stability of EVA/EPDM blends in both absence and presence of TMPTA is increased by EB irradiation. The onset temperature ( $T_i$ ) increases by 10–15 °C for all blends, TMPTA containing samples showing higher change. Similarly, the degradation temperatures (both  $T_{d1}$  and  $T_{d2}$ ) are increased up to

more than 10 °C from EVA18/EPDM to EVA70/EPDM blends after normal crosslinking. However, there are no significant improvements of  $T_{30}$ ,  $T_{50}$ , and  $T_{90}$ . These changes become higher in presence of TMPTA for all systems except EVA70/EPDM, which does not show much change.

**Limiting Oxygen Index (LOI).** Figure 7 represents the LOI values of pure EPDM, pure EVAs, and their blends. Greater LOI value counts higher flame retardancy. From the histogram (Figure 7), it is found that LOI value of EVA regularly increases with increase in vinyl (VA) contents. Same trends are seen for different EVA/EPDM blends, where LOI is found to increase with increasing VA contents in blends. The LOI values of EVA/EPDM blends with 18%, 28%, 40%, and 70% VA contents are found as 23.5%, 24%, 25.2%, and 26.8%, respectively.

Flaming combustion can be divided into physical and chemical processes. Chemical process involves generation of volatile products, which needs breaking of covalent bonds.<sup>26</sup>

As polymer is very big molecules with high molecular weight, so its boiling point is very high. Thus, intramolecular (backbone) and intermolecular chemical bonds of polymers must be broken to generate volatile fuel species. This process requires a large and continuous supply of thermal energy for ignition and sustained burning.<sup>26,27</sup>

EVA is copolymer of ethylene and vinyl acetate. When EVA is heated and undergoes thermal degradation the first product evolved is acetic acid. Interestingly, this deacetylation reaction starts at 560 °K. According to Mc Neill *et al.*, this result is due to the fact that every short sequence of vinyl acetate (VA) in the copolymer requires its own initiation step,<sup>28</sup> unlike EPDM. That is why EVA is more flame resistant (higher LOI value) than EPDM. Naturally, with increase in VA content in EVA, the LOI of EVA will be higher (Figure 7). Thus, LOI of EVA/EPDM (50/50) blend is higher than pure EPDM and LOI values of blends keeps on increasing with the VA content increase in the used EVAs.

However, electron beam irradiation leads to raise the LOI for all samples. EB irradiation in presence of TMPTA shows greater LOI of the blends than those in absence of TMPTA. The flame retardancy of the irradiated sample is found higher due to strong cross linked network formation, which reduces the volatile combustible products, thus increasing the flame retardancy.<sup>29</sup>

**Surface Morphology (SEM).** Surface morphologies of cryogenically fractured surfaces of unirradiated and irradiated EVA/EPDM blends containing different EVAs are investigated by SEM and pictures are presented in Figure 8(a–f). The micrograph of unirradiated EVA18/EPDM blend fracture surface shows rough surface with large domain size (fractured cavities). EVA28/EPDM fracture surface exhibits comparatively smaller cavities with more number of flow lines suggesting smaller domain size of the dispersed phase. Interestingly, the size of domains keeps on decreasing with increase of vinyl acetate content the smallest domains being seen in EVA40/EPDM. The EVA70/EPDM fracture surface appears like a fractured surface of a single thermoplastic elastomer [Figure 8(d)].

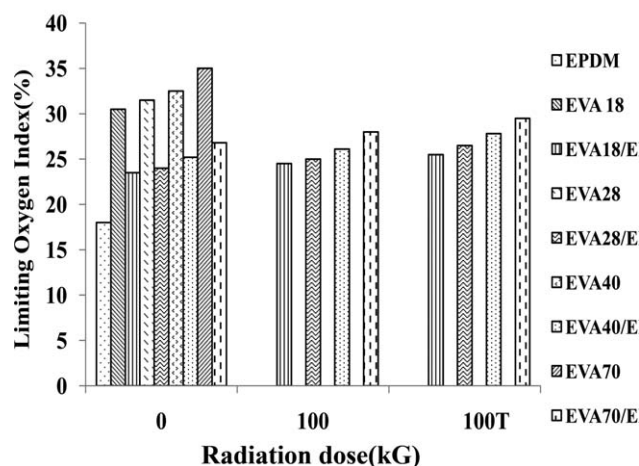
**Table III.** TGA Parameters of Various EVAs, EPDM, and Unirradiated and Irradiated EVA/EPDM Blends

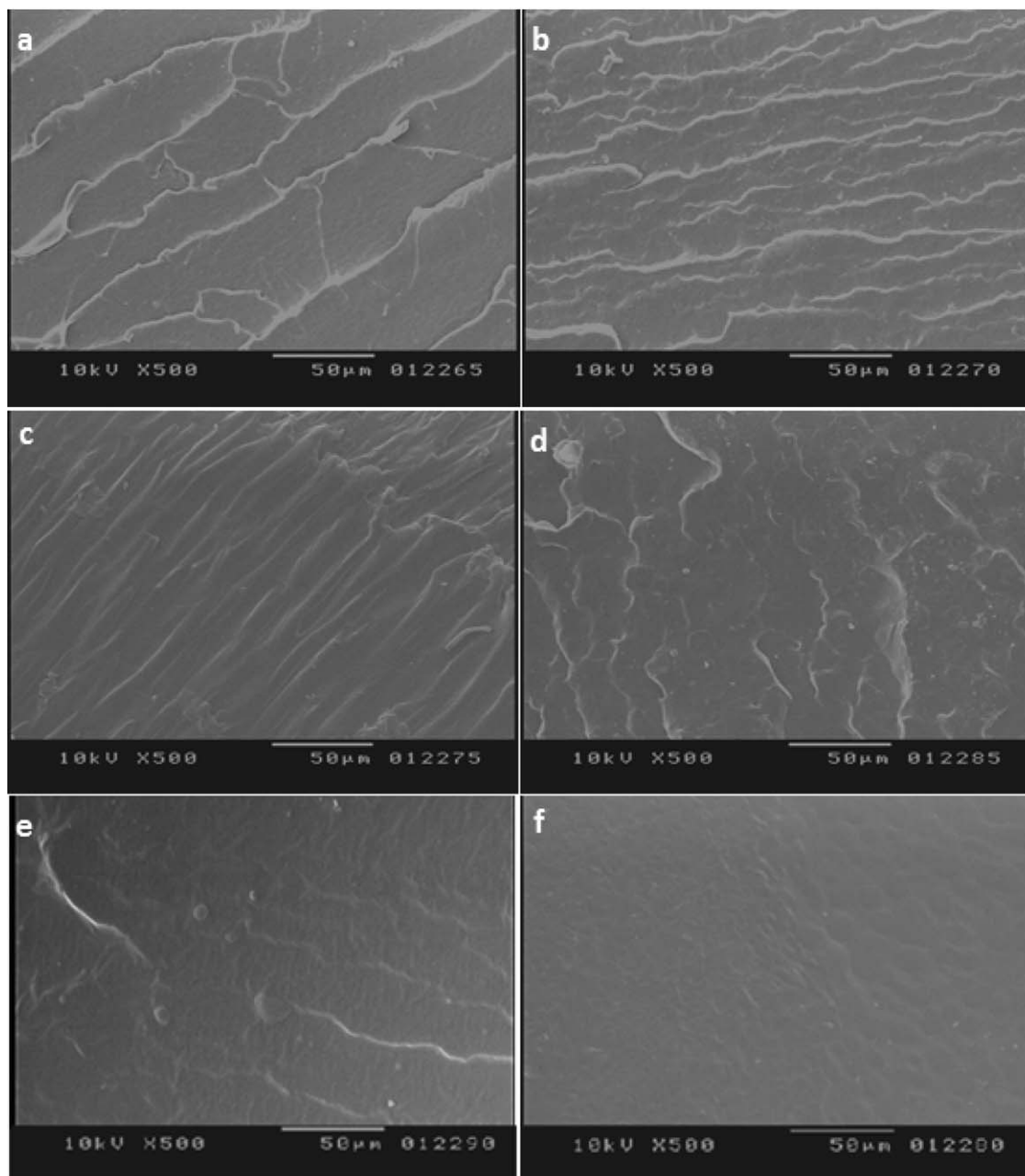
Samples	Onset temperature ( $T_i$ , °C)	Temperature corresponding to 30% weight loss ( $T_{30}$ , °C)	Degradation temperature ( $T_d$ , °C)		Temperature corresponding to 50% weight loss ( $T_{50}$ , °C)	Temperature corresponding to 90% weight loss ( $T_{90}$ , °C)
			$T_{d1}$	$T_{d2}$		
EPDM	383.25	456.13	440.90	-	468.00	484.69
EVA18	337.72	466.37	342.15	462.07	478.60	496.90
EVA18/EPDM	342.99	463.77	340.25	453.36	475.12	493.14
EVA18/EPDM 100	350.05	465.87	346.83	458.88	478.75	496.01
EVA18/EPDM T 100	356.41	468.25	354.70	463.29	481.16	495.86
EVA28	334.26	456.51	338.02	455.83	473.26	493.91
EVA28/EPDM	327.67	461.52	341.40	453.81	474.63	495.04
EVA28/EPDM 100	339.39	464.24	348.29	457.82	476.33	497.06
EVA28/EPDM T 100	345.56	466.65	352.16	461.31	477.20	496.71
EVA40	328.47	435.68	335.24	451.37	456.76	493.24
EVA40/EPDM	320.77	460.66	342.32	460.33	474.88	495.20
EVA40/EPDM 100	333.90	460.58	351.03	466.23	474.43	494.53
EVA40/EPDM T100	340.46	462.92	356.48	471.24	477.22	496.32
EVA70	314.23	362.72	332.35	445.75	426.95	492.58
EVA70/EPDM	312.15	441.88	334.83	462.61	471.53	495.77
EVA70/EPDM 100	325.31	442.87	342.39	467.17	471.75	496.01
EVA70/EPDM T 100	319.71	440.67	338.03	459.33	470.91	495.90

In fracture that is why small cavities are seen. In EVA40/EPDM, the surface appears with symmetrical scaly wave type morphology with continuous flow lines across the fracture surface.<sup>30</sup> From FTIR and TGA, the possibilities of enhancement of miscibility between phases are noticed for higher VA containing blends. Increase in interfacial interaction of the two phases (EPDM and EVA) due to increase in VA content i.e., increase in amorphousness, is responsible for increased miscibility.<sup>24,25</sup> If the interfacial interaction is increased, the interfacial tension is decreased, which inhibits coalescence of the small blend droplets during processing.<sup>25</sup> Thus, in stable morphology small dispersed domains will be seen for higher VA containing blends indicating higher misci-

bility. However, other factors such as blend composition, processing parameters, and rheological properties of various EVAs are the controlling factors of degree of miscibility of EVA and EPDM. Thus, for conclusive explanation of increase in miscibility with increase in VA content, more experimentation is required. The flow patches across the surface also point out towards the higher deformation in blends i.e., ductility, which are in agreement with mechanical properties shown in Table II and Figure 3.<sup>31,32</sup> It is observed that in presence of only 1 phr TMPTA, the miscibility of two polymer phases is not affected considerably. Similar findings are obtained in other system also.<sup>33</sup>

When samples are exposed to EB irradiation, the roughness of fractured surfaces is reduced, where the size of cavities is reduced and surface starts becoming smooth and fine compared to unirradiated ones [Figure 8(e,f)]. The magnitude of smoothness of the surface depends on the initial morphology, thus having effect of VA content. The irradiated surface of EVA40/EPDM exhibits relatively high degree of smoothness and less roughness with less number of cavities compared to irradiated EVA18/EPDM surface [Figure 8(e,f)]. This is because of two reasons, the initial cavity or domain size and degree of crosslinking. The high VA containing blend shows smaller size cavity (domain) and high degree of crosslinking. Thus, the fracture surface of crosslinked sample reveals higher degree of smoothness for higher VA containing blends. The reduction of surface roughness indicates an increase of miscibility of two phases on crosslinking.<sup>14,17,32-34</sup> This alteration of morphology in crosslinked surface suggests some intra or inter phase crosslinking of EVA and EPDM phases.<sup>35</sup> The findings in mechanical property are in agreement with these findings.

**Figure 7.** Effect of VA content and EB radiation dose on limiting oxygen index (LOI) of EVA/EPDM blends.



**Figure 8.** SEM micrographs of unirradiated and irradiated EVA/EPDM blends (a) unirradiated EVA18/EPDM, (b) unirradiated EVA28/EPDM, (c) unirradiated EVA40/EPDM, (d) unirradiated EVA70/EPDM, (e) irradiated EVA18/EPDM-100, and (f) irradiated EVA40/EPDM-100.

## CONCLUSIONS

The overall study deals with the investigation of the effect of vinyl acetate content and electron beam crosslinking on structural, mechanical, crystallinity, thermal stability, flammability, and morphological properties of EVA/EPDM blends. Increase in vinyl acetate (VA) content and EB crosslinking increases the miscibility of EVA and EPDM. This is confirmed by FTIR, TGA, and SEM. The gel fraction (degree of crosslinking) is increased with increase in vinyl acetate (VA) content in blends, TMPTA added samples showing higher gel fraction compared to without one. The Young's modulus and tensile strength are decreased and % elongations are increased with increase in VA

content in blends. However, EB crosslinking has opposite effect on the mechanical properties, the tensile strength and modulus are increased, but elongation is decreased. Similarly, the thermal stability decreases with increasing VA content, however, upon electron beam crosslinking, it generally increases. The percentage of crystallinity of EVA in blends is decreased with increasing VA content and EB crosslinking in absence and presence of TMPTA. The LOI increases with increase of VA content and electron beam irradiation. Thus, fine-tuning of properties of EVA/EPDM system is possible by judicious selection of EVA and incorporation of proper amount of degree of crosslinking into the blends.

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