

# Structure-Property Relationship in Terms of Dynamic Mechanical Properties of High Energy Radiation Treated Industrially Important Thermoplastic Elastomer Blend

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Received 11 August 2015; accepted 8 September 2015; published 11 September 2015

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## Abstract

A series of low-density polyethylene (LDPE)/ethylene propylene diene terpolymer (EPDM) blends with various compositions have been prepared by melt mixing followed by injection molding. These specimens are irradiated at 40, 80, 120 and 160 kGy electron beam radiation. The gel content increases with increase in EPDM and as well as EB dose. Storage modulus ( $E'$ ) and loss modulus ( $E''$ ) are decreased with increase in EPDM content. Storage modulus continues to increase and loss modulus keeps on decreasing with radiation dose. Interestingly, damping property is found to be more for EPDM rich blends, which again decreases upon irradiation. Morphology of fractured surface of LDPE/EPDM shows that with increase in EPDM content, the size and depth of the cavity becomes larger and deeper indicating higher ductility. But, EB crosslinking makes the surface smoother and the smoothness keeps on increasing with increase in dose rendering stiffness to the samples.

## Keywords

LDPE, EPDM, Electron Beam Crosslinking, DMA, SEM, Gel Content

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## 1. Introduction

Blending of a thermoplastic with an elastomer leading to a thermoplastic elastomer has become a practice for last forty years. Due to their advantages in processing of thermoplastic, with elastomer of excellent physical properties, it is gaining wide varieties of applications. This is a widely used technique nowadays in industries. There are various thermoplastics, which are unique for easy processing, availability, and low cost. Among the polyolefins, low density polyethylene (LDPE) and linear low density poly ethylene (LLDPE) are widely used plastics in the packaging and consumer industries because of their advantages like higher tensile strength, stress crack resistance, flexibility, thermal, chemical and excellent dielectric properties [1] [2] whereas EPDM elastomer exhibits high crosslinking ability, radiation resistance, thermal resistance, impact strength, flexibility and dynamic damping properties [3]. Thus, by judicious selection of properties of LDPE and EPDM scientists have made blends of above two, to get selected combination of properties [4] [5]. That is why; LDPE/EPDM blends have got their application in automobile, wire and cable insulation and construction applications [6] [7].

Mechanical, thermal, rheological and morphological properties of PE/EPDM blends have been investigated and reported [8]-[11]. M.M. Abdel-Aziz [12] is the first scientist to investigate the effect of gamma radiation on mechanical properties of LDPE/EPDM blends. Again, Mohammad E. has crosslinked the LDPE/EPDM blend by DCP (dicumyl peroxide) and studied mechanical, thermal, morphological and electrical properties [13]. Similar kinds of reports are available on HDPE/EPDM and EB crosslinked HDPE/EPDM [14] [15]. But, as per our knowledge there is no reported literature on the effect of electron beam irradiation on dynamic mechanical thermal analysis (DMA) of LDPE/EPDM system. Dynamic mechanical properties are important for some applications, where materials have to face high temperature environment along with high energy radiation exposure but has to maintain mechanical performance to retain them useful. In this environment LDPE/EPDM may be a suitable candidate for medium radiation dose and temperature range. On the other hand, EB irradiation has become an important process in the development of new materials with improved technical properties. The process is neat, residue free, selective, flexible, uniform, easily controllable, economical and most effective in crosslinking of polymers in large scale. This process has been effectively utilized in the power cable industry for crosslinking of polyolefins [16]. Recently high-energy electron beam radiation (EBR) has been used in the dynamic vulcanization of polymer blends leading to thermoplastic elastomer vulcanizations (TPV) [17]. High energy electron beam irradiation of polymers leads to formation of macro-radicals which react with each other to form inter and intramolecular crosslinking leading to a three dimensional network structure [18] [19]. If the dose is higher *i.e.* free radical production is extensive, then chain scission may occur, which will lead to degradation of polymers [20]. The objective of the work is to investigate the effect of radiation dose and blend composition on the gel content (crosslinking), dynamic mechanical properties, phase morphology and to establish their correlations.

## 2. Experimental

LDPE (MFI 4 gm/10 min, density of 0.922 gm/cc) in form of pellets has been supplied by Reliance Petrochemicals. EPDM (pellet form, Mooney viscosity, ML1+4 at 125°C 20, NORDEL IP 4520, ethylene content = 50% with 4.9% of ENB, MFI 10 gm/10 min and density of 0.88 gm/cc) is supplied by Dow chemical. These are used to prepare blends. LDPE is blended with EPDM in different compositions using twin screw extruder with the temperature profile of 120°C: 140°C: 160°C: 180°C at 80 rpm without any crosslinker. Both components are mixed in various weight proportions to prepare blends (100/0, 70/30, 50/50, 30/70, 0/100). For study purpose dumbbell shaped samples are prepared by injection molding at 180°C. The codes of the samples are provided in **Table 1**. In the sample code “L” stands for LDPE and “E” stands for EPDM. The injection molded specimens

**Table 1.** Blend compositions.

Samples	1	2	3	4	5
LDPE	100	70	50	30	0
EPDM	0	30	50	70	100
Sample code	L 100	LE73	LE55	LE37	E 100

“L” stands for LDPE and “E” stands for EPDM.

are irradiated by high energy electron beam in an inert environment using 2 MeV, 20 kW electron beam accelerator (Model ILU-6) under forced air cooling at a radiation dose of 40, 80, 120 and 160 kGy (kilo Grey). Only one side of the sample is exposed to irradiation, as the thickness of the sheet is 2 mm, which is thin enough for penetration of the electron beam of 2 MeV energy. The distance of the sample from the scan horn is 20 cm and the conveyer speed is set at 0.94 m/min. The dose rate is 10 kGy/pass and beam current is 1 mA.

### 3. Characterization

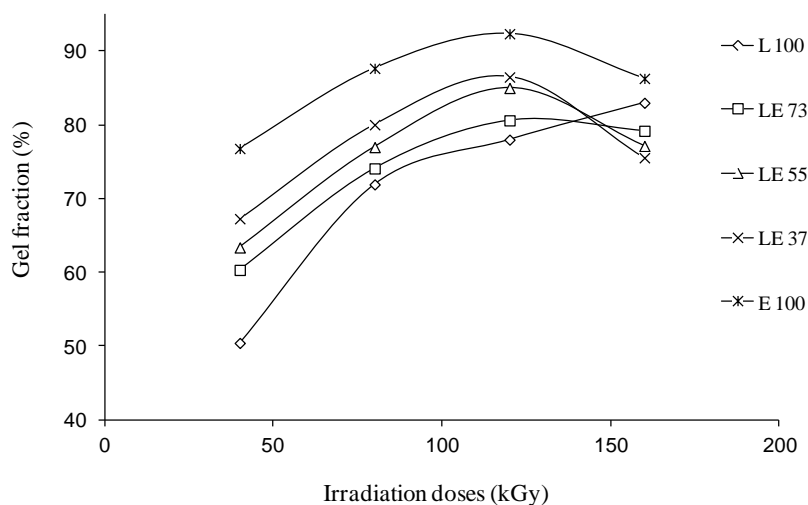
Gel fractions are measured by solvent extraction technique using xylene as solvent. The samples are extracted in hot Xylene for 48 hrs at 110°C. Extracted samples are dried in a vacuum oven at 80°C till constant weight. The gel content (% gel fraction) is determined using the following formula:

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

The FTIR spectra of both unirradiated and irradiated samples (2 mm thick) have been recorded on a Bruker-Alpha's Platinum ATR model. Samples are characterized on Attenuated total reflection (ATR) mode in wave number ranging from 500 - 4000  $\text{cm}^{-1}$ . Dynamic mechanical thermal analysis (or Dynamic mechanical analysis) is carried out for LDPE-EPDM blends to determine the viscoelastic properties of the samples. The test is performed in tension mode using EPLEXOR 150 N (Gabo Qualimeter) instrument. The temperature range is -150 to 80°C with a heating rate 3°C/min. The dimension of test samples is 20 mm  $\times$  6 mm  $\times$  2 mm. The Analysis is investigated on temperature sweep mode at constant frequency of 1 Hz to find out storage modulus ( $E'$ ), loss modulus ( $E''$ ) and loss tangent ( $\tan\delta$ ) for unirradiated and irradiated blends. The samples of LDPE/EPDM blends fractured in liquid nitrogen are characterized by SEM (scanning electron microscopy) using JEOL, JSM-5400 model. To increase the conductivity, fractured surfaces are gold sputtered before investigation under the scanning electron microscope.

### 4. Results and Discussion

The susceptibility of LDPE, EPDM and various LDPE/EPDM blends, towards radiation induced cross-linking process, in absence of crosslinker, is estimated from the gel fraction determination. Results are presented in **Figure 1**. Higher is the gel content greater will be the amount of crosslinking, as gel content is the measurement of amount of crosslinking [21] [22]. There is no gel formation observed for control systems. It is clear from the **Figure 1** that neat LDPE shows 50.43%, 71.94%, 78.01% and 83.01% gel fraction at 40, 80, 120 and 160 kGy EB doses respectively. On the other hand, for pure EPDM, the gel contents are 76.81%, 87.69%, 92.38% and 86.32% at the same doses respectively. Thus, it is revealed that the gel content *i.e.* crosslinking ability is increased steadily with increase in radiation doses up to 120 kGy for both polymers (LDPE and EPDM). That

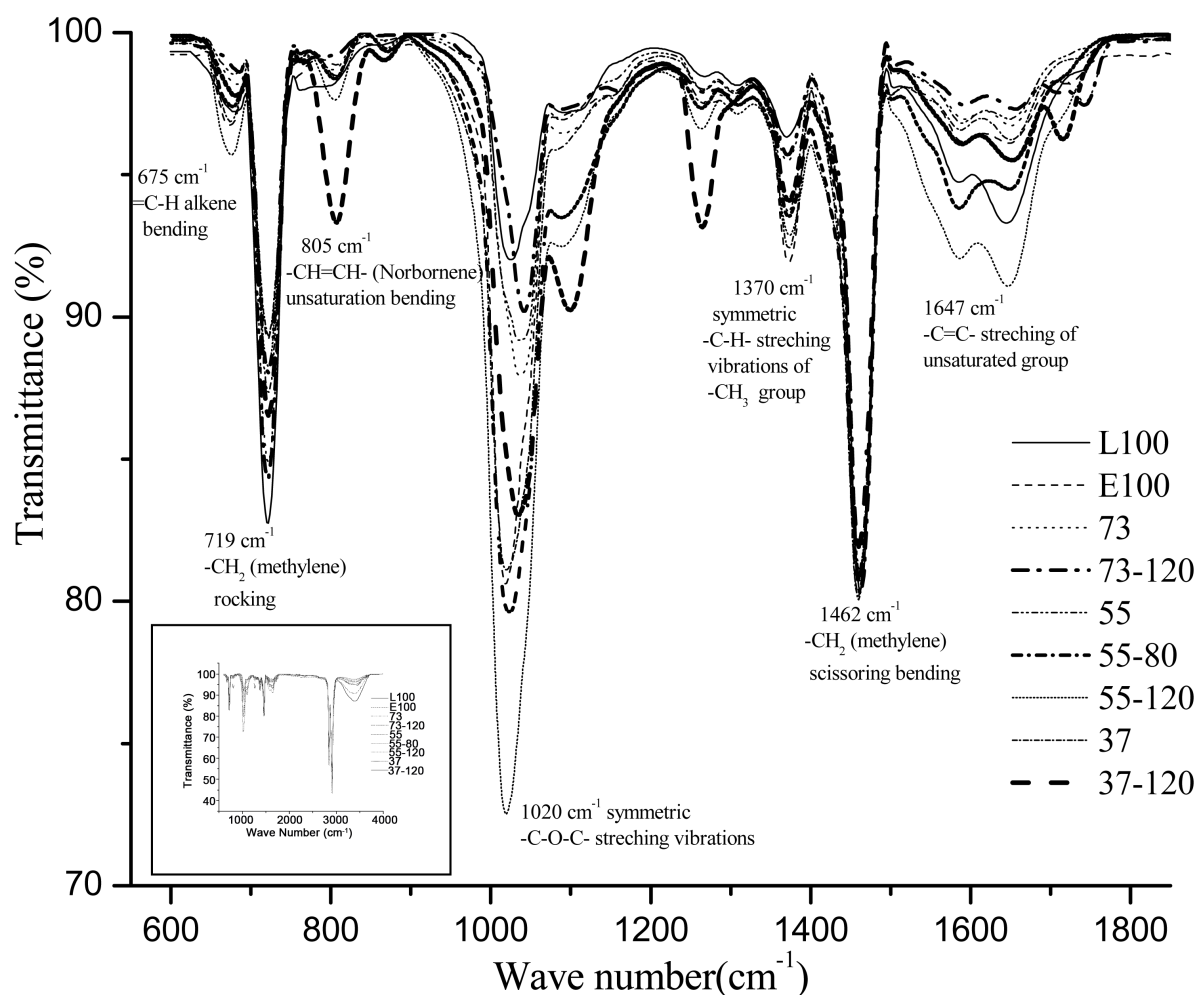


**Figure 1.** Variation of gel fraction with blend composition and electron beam irradiation dose.

proves up to 120 kGy, in both the polymers, crosslinking process dominates over the chain scission process. Similar increasing trend is noticed even at 160 kGy for LDPE. This is due to its higher crystallinity and lower speed of crosslinking. Interestingly, the gel content of EPDM is decreased at 160 kGy. At this higher dose EPDM is degraded. From the figures it is again obvious that, at a certain dose, EPDM shows higher gel fraction than LDPE and that is true for all studied doses. That is due to higher crosslinking ability of EPDM than LDPE. The crosslinking ability of EPDM is more due to higher amorphousness and molecular structure of EPDM [23].

So, it is expected that with increase in EPDM content in blends, gel fraction would keep on increasing. That is the finding throughout the experiments, which has been discussed later. Interestingly, as in LDPE and EPDM, the gel contents of LDPE/EPDM blends are also in increasing trend with increase in irradiation dose up to 120 kGy. But at 160 kGy, all LDPE/EPDM blends degrade showing reduced gel fractions. Chain scission is initiated in blends due to presence of EPDM component. In LE 73 blends the percentage of gel fraction are observed to be 60.34%, 74.11%, 80.63% and 79.21% for different electron beam doses (40, 80, 120 and 160 kGy). In LE55 blends, the gel fractions are higher than that of LE 73 blends due to greater amount of EPDM content in blends. The increased gel content in LE 55 blends are 63.39%, 77.00%, 85.02% and 77.15% at 40, 80, 120 and 160 kGy. It is again seen that LE 37 blend shows higher degree of change in gel fraction compared to LE 73 and LE 55 blends. The values of gel fractions for LE37 blends are 67.29%, 80.04%, 86.51% and 75.56 % at the above mentioned doses.

FTIR spectra of LDPE, EPDM and various unirradiated and irradiated LDPE/EPDM blends are taken and represented in **Figure 2**. As during crosslinking new  $-C-C-$  bonds are formed but LDPE and EPDM possess



**Figure 2.** FTIR of unirradiated and irradiated LDPE/EPDM blends.

plenty of C-C bonds, so expectedly no new peak corresponding to  $-C-C-$  bond formation will appear rather the intensity corresponding to various modes of C-C bond vibration will alter, producing signal of radiation crosslinking. However, new bonds corresponding to chain scission may appear. A prominent strong peak appears at  $719\text{ cm}^{-1}$  (Figure 2), which is assigned as  $-CH_2$  rocking vibration peak [3]. This peak is present both in LDPE and EPDM. For LDPE, the transmittance is found least that means the absorbance is highest due to presence of large number of  $-CH_2$  groups. Interestingly, it is noticed that upon crosslinking absorbance intensity of  $-CH_2$  rocking vibration is increased due to formation of new  $-C-C-$  bonds. That is reflected for all three blends and the effect is highest in LE37, due to highest amount of crosslinking in EPDM phase (as shown in gel content, Figure 1). Similar effect is observed at  $2840$  and  $2916\text{ cm}^{-1}$ , which are ascribed to  $-CH_2$  symmetric and asymmetric stretching [24]. Again a high intensity peak appears at  $1370\text{ cm}^{-1}$ , which is due to  $-C-H$  symmetric stretching of  $CH_3$  group [24]. This absorbance is least for LDPE and highest for EPDM due to different degree of freedom in crystalline and amorphous phase of former and later respectively. Upon cross linking transmittance corresponding to this peak of all blends become more, due to less freedom of  $CH_3$  group in a compact crosslinked network structure and the difference of the transmittance before and after crosslinking *i.e.* reduction of absorbance depends on blend composition and gel content, *i.e.* degree of crosslinking. On crosslinking same trend is observed for peak  $1462\text{ cm}^{-1}$  which is the characteristics of  $-CH_2$  scissoring vibration. Interestingly, very strong peaks appear at  $1020\text{ cm}^{-1}$  and  $1274\text{ cm}^{-1}$  ascribed for symmetric and asymmetric stretching of  $-C-O-C-$  [3]. After crosslinking absorbance of these two peaks are reduced due to cleavage of  $-C-O-C-$  bond by high energy radiation and formation of new  $-C-C-$  bonds. EB irradiation occurs in inert environment, thus the above oxides must have formed during thermal processing of polymers. However, it is beneficial that during irradiation these previously formed oxides are broken though the effect in LE 55 is not convincing.

Absorbance at  $675\text{ cm}^{-1}$  and  $1647\text{ cm}^{-1}$ , which are due to stretching of  $-C=C-$  bond, are increased after irradiation [24]. This is the evidence of chain scission during irradiation. Upon irradiation, the increase in absorbance intensity is found highest for LE55, leaving LE 73 and LE37 very very less. It is again noticed that after long time exposure to radiation ( $120\text{ kGy}$ ) still peak of norbornene unsaturation of EPDM occurs at  $805\text{ cm}^{-1}$  [25] for all blends. Thus, though norbornene double bond contributes to radiation crosslinking *i.e.* property development, but the contribution is much much lesser than  $-C-H$  bond's contribution because of its small quantity (4.9% of ENB) and incomplete crosslinking. The schematic diagram of crosslinking and chain scission based on the FTIR spectra is represented in Figure 3(a) and Figure 3(b).

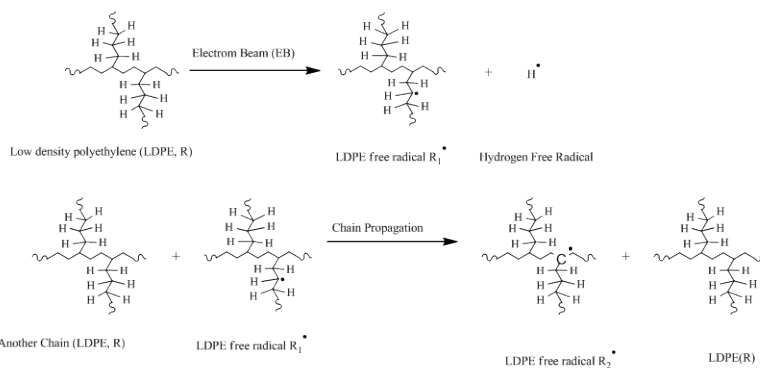
The dynamic mechanical properties (storage modulus, loss modulus and  $\tan\delta$ ) of pure LDPE, EPDM and LDPE/EPDM blends before irradiation are reported in Figures 4(a)-(c). To understand the change quantitatively storage modulus, loss modulus as well as transition temperatures are tabulated in Table 2. The storage modulus ( $E'$ ) for LDPE at sub ambient temperature of  $-140^\circ\text{C}$  is  $3780\text{ MPa}$ , which drastically reduces to  $2120\text{ MPa}$  at  $-75^\circ\text{C}$ . This further reduces to around  $327\text{ MPa}$  at  $25^\circ\text{C}$  prevalent for semicrystalline polymer. Thus, it is obvious that the storage modulus exhibits two step reduction; one near the  $\gamma$  transition region and other near the  $\beta$  transition region. (The details on relaxation are discussed later in this section). Neat EPDM also exhibit similarly two-step reduction in dynamic (storage) modulus [Table 2 and Figure 4(a)]. At  $-140^\circ\text{C}$  the elastic (storage) modulus of EPDM is  $1720\text{ MPa}$ , which reduces to  $926$  and  $9\text{ MPa}$  at  $-75^\circ\text{C}$  and  $25^\circ\text{C}$  respectively.

The storage moduli of all blends are decreased with temperature following similar fashion as LDPE and EPDM due to increase in flexibility. Again, it is interesting to note that the modulus of neat EPDM is significantly lower than that of neat LDPE in the whole range of temperature studied. This is due to the greater stiffness originated from compact organized crystalline structure of LDPE. The blends, on the other hand, exhibit storage moduli in between the two neat polymers in the whole temperature range. Figure 4(a) shows that the storage moduli of blends decrease with the increase in EPDM contents. From the table it is seen that, at  $-140^\circ\text{C}$ , the storage modulus of blends decreases with increase of EPDM content in blends (from LE73 to LE37). Storage modulus is a measurement of rigidity and stiffness of the samples [26]. If EPDM content increases in blend, stiffness and rigidity due to amorphous nature of EPDM decreases.

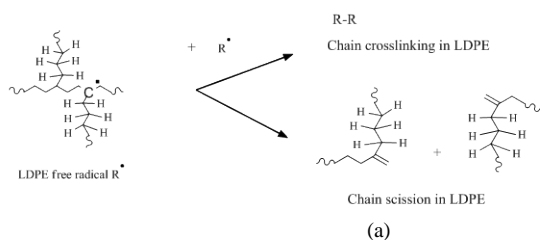
The alterations of dynamic mechanical properties of neat polymers and blends, with radiation dose and temperature are illustrated in Figures 5(a)-(c), Figures 6(a)-(c) and Figures 7(a)-(c) for LE73, LE55 and LE37 respectively.

Upon irradiation storage modulus of LE73 increases, which continues to increase with dose up to  $120\text{ kGy}$  (Figure 5(a)). For irradiated samples, the trend of decrease of storage modulus with temperature is similar as unirradiated one (Table 2). It is noticed that in gel content analysis that crosslinked network is formed upon ir-

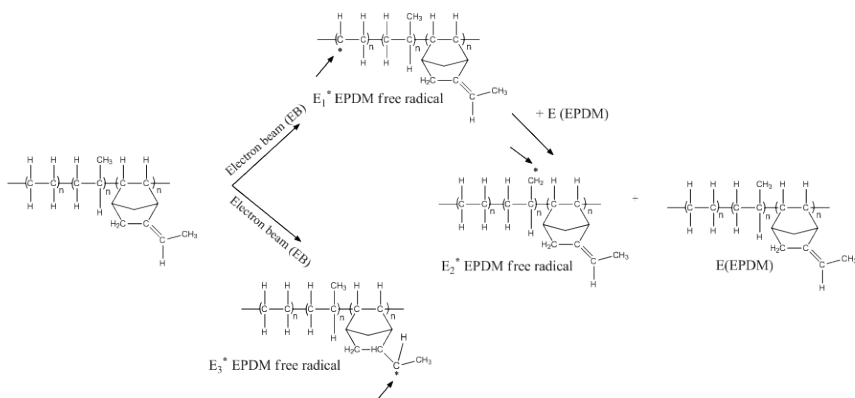
Electron beam (EB) crosslinking and chain scission in low density Polyethylene (LDPE)



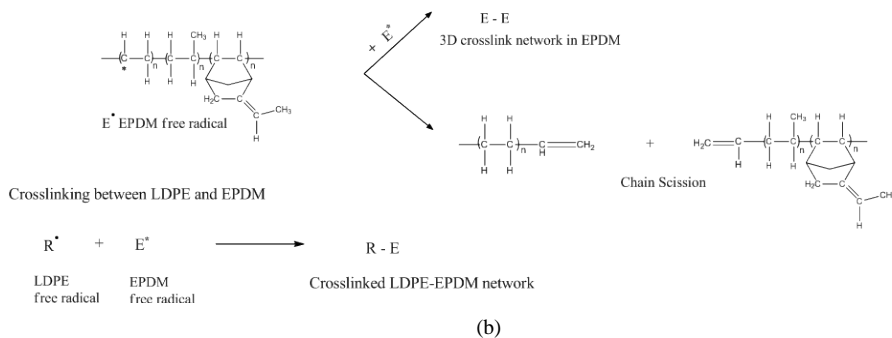
All -C-H bond in LDPE can form LDPE free radicals by direct electron beam (EB) radiation or by chain propagation reaction. All LDPE free radicals ( $R_1^\bullet, R_2^\bullet, \dots$ ) can be represented by  $R^\bullet$ . These all macromolecular free radicals ( $R^\bullet$ ) can either form three dimensional network through -C-C- bond(chain crosslinking) or lead to chain scission.



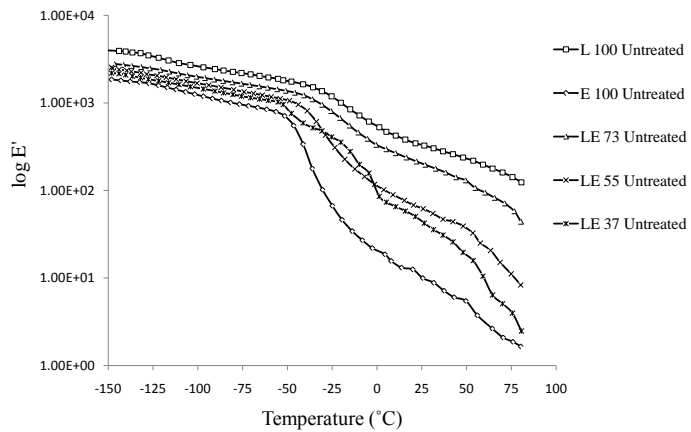
Electron beam chain crosslinking and scission in Ethylene Propylene Diene Elastomer (EPDM)



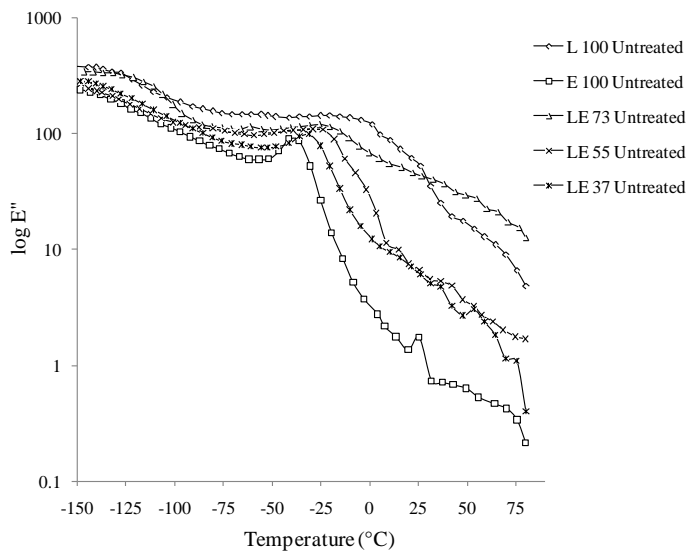
Similarly, all -C-H bond in EPDM can generate EPDM free radicals ( $E_1^\bullet, E_2^\bullet, E_3^\bullet, \dots$ ) by direct electron beam irradiation or chain propagation reaction. We can represent all free radicals by  $E^\bullet$  which can either form 3D network by -C-C- bond or undergo chain scission.



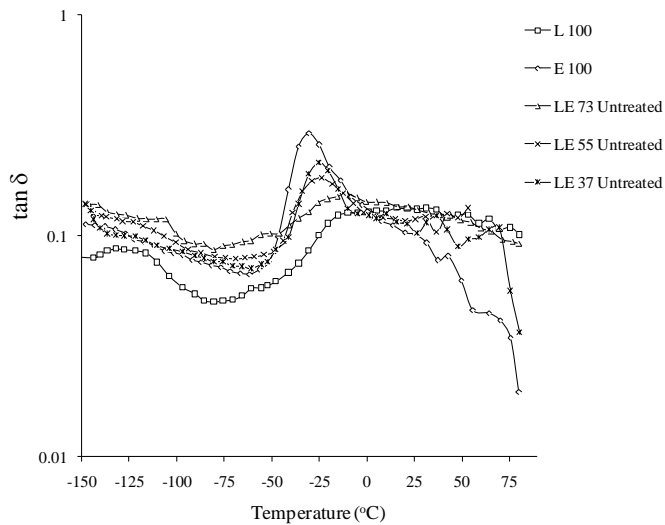
**Figure 3.** (a) Schematic diagram of radiation crosslinking and degradation of LDPE; (b) schematic diagram of radiation crosslinking and degradation of EPDM and LDPE/EPDM Interphase crosslinking.



(a)



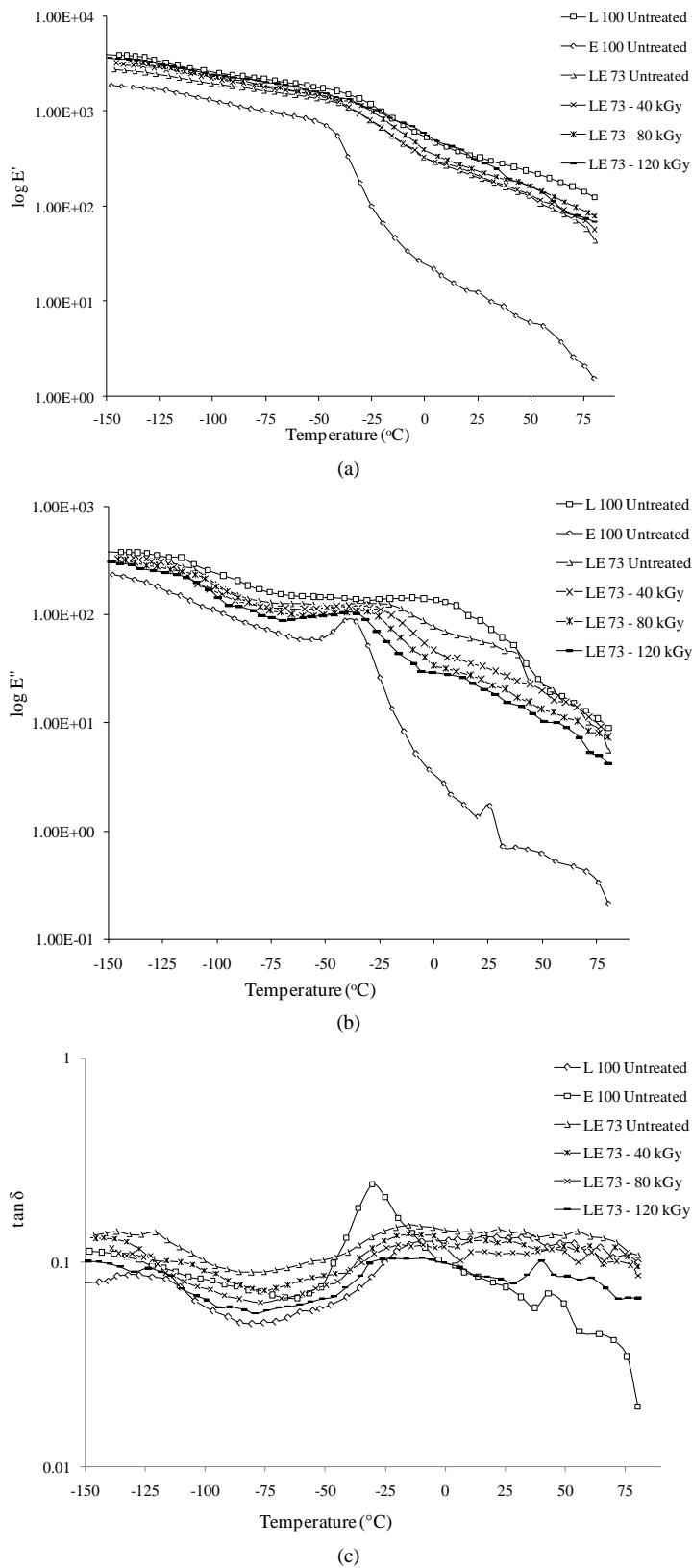
(b)



(c)

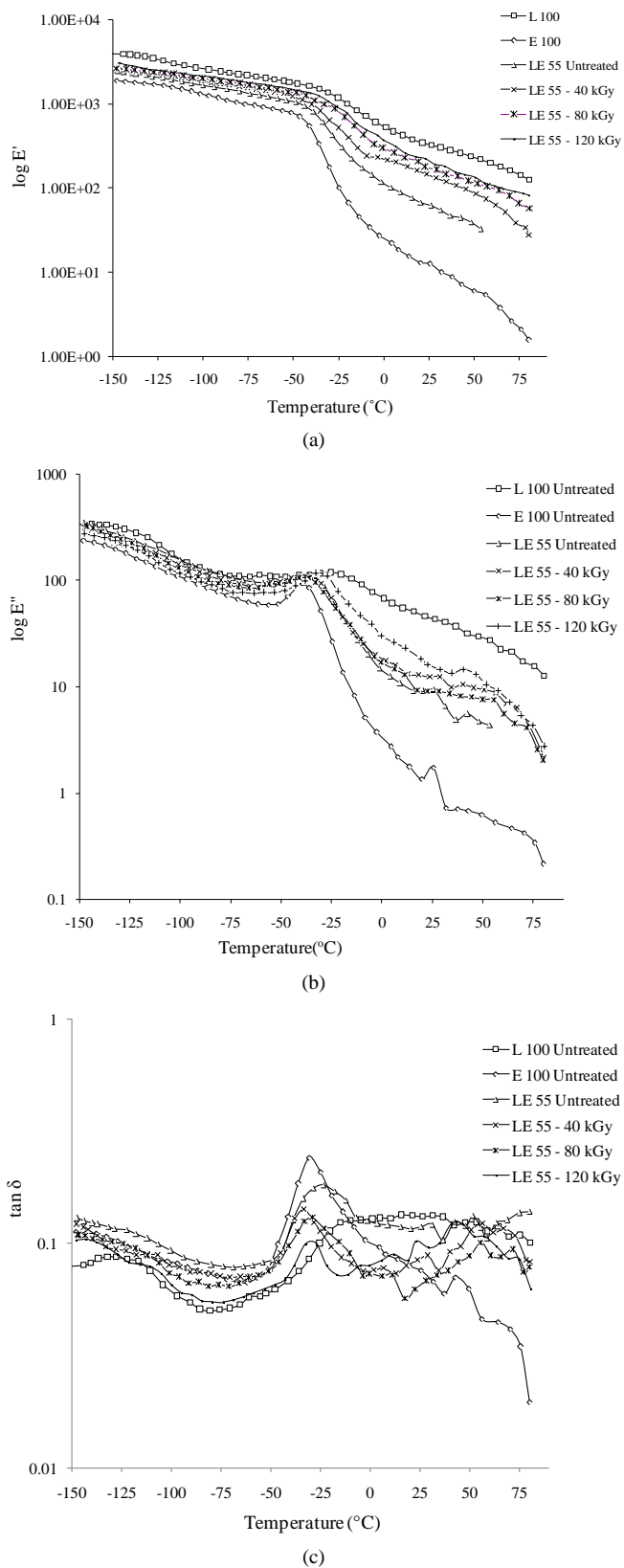
**Figure 4.** (a) Variation of storage modulus of blends with composition and temperature; (b) variation of loss modulus of blends with composition and temperature; (c) variation of  $\tan \delta$  of blends with composition and temperature.



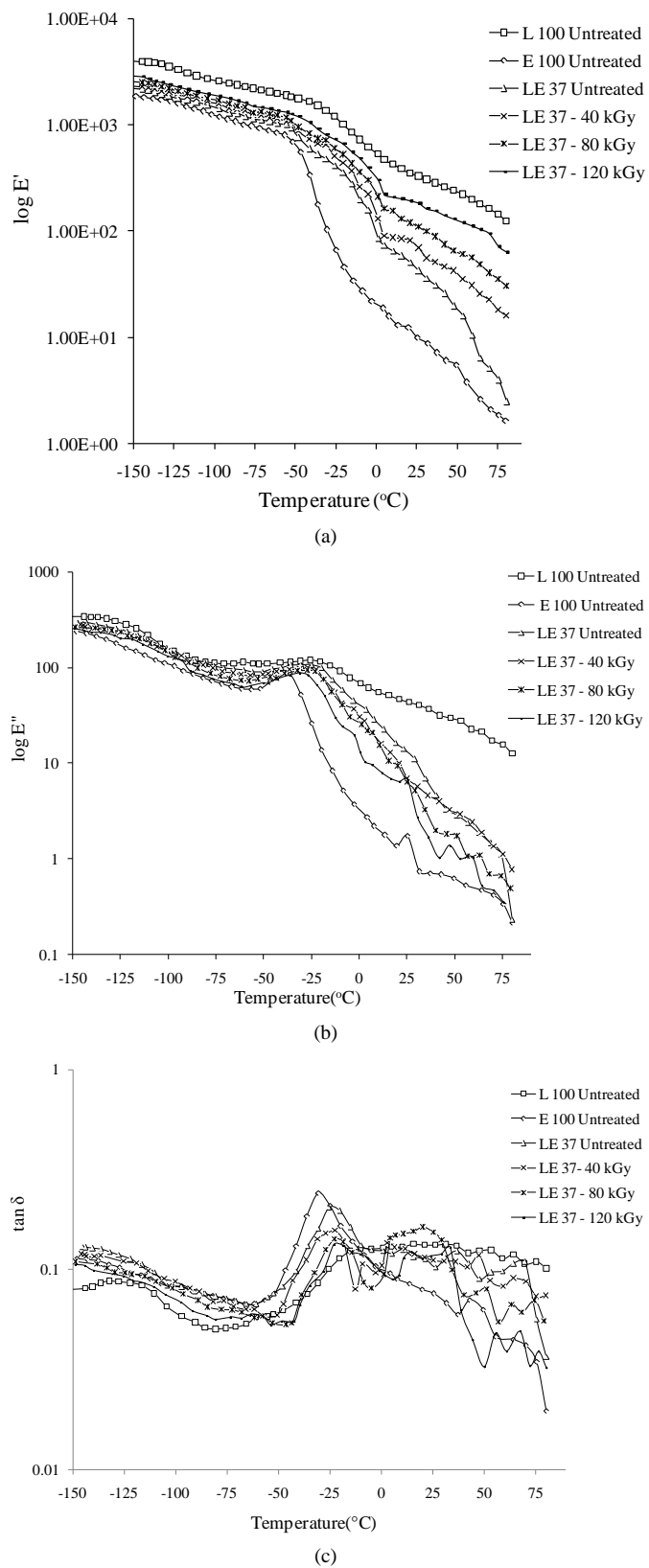


**Figure 5.** Variation in dynamic mechanical properties of LE73 blends with temperature and radiation dose (a) variation in storage modulus (b) variation in loss modulus (c) variation in  $\tan \delta$ .





**Figure 6.** Variation in dynamic mechanical properties of LE55 blends with temperature and radiation dose (a) variation in storage modulus (b) variation in loss modulus (c) variation in  $\tan \delta$ .



**Figure 7.** Variation in dynamic mechanical properties of LE37 blends with temperature and radiation dose (a) variation in storage modulus (b) variation in loss modulus (c) variation in  $\tan \delta$ .

**Table 2.** Storage modulus ( $E'$ ), loss modulus ( $E''$ ) and transition temperature of neat LDPE, neat EPDM and their blends before and after electron beam irradiation.

Samples	$E'$ (-140°C) (MPa)	$E'$ (-75°C) (MPa)	$E'$ (+25°C) (MPa)	$E''$ (-140°C) (MPa)	$E''$ (-75°C) (MPa)	$E''$ (+25°C) (MPa)	Temp. corresponding to $\tan\delta_{\max}$ (LDPE)	Temp. corresponding to $\tan\delta_{\max}$ (EPDM)
L100	3780	2120	327	374	150	54	-132, -15	-
E100	1720	926	9	227	73	2	-	-30
LE 73	2570	1610	197	339	129	55	-130	
LE 73 40 kGy	3130	1820	240	330	115	31	-15.4 -132	
LE 73 80 kGy	3320	1910	215	315	109	24	-15.2 -131	
LE 73 120 kGy	3600	2030	340	290	94	22	-15.2 -134 -14.9	
LE 55	2350	1345	62	314	109	11	-128	-23.6
LE 55 40 kGy	2460	1552	141	282	96	10	-127.8	-33.2
LE 55 80 kGy	2530	1665	176	290	92	8	-129.7	-29.9
LE 55 120 kGy	2860	1820	224	262	78	13	-127.3	-32.1
LE 37	2096	1196	18	294	104	9	-129	-25
LE 37 40 kGy	2230	1230	69	255	97	7	-128	-22.5
LE 37 80 kGy	2425	1293	108	259	84	5	-129	-22.3
LE 37 120 kGy	2700	1480	180	234	76	7	-129	-22.1

radiation, degree of crosslinking depending on irradiation dose and blend composition. This three dimensional interchain crosslinked network makes the materials stiffer and rigid, which provide greater resistance to dynamic deformation. That's why irradiation leads to increase in storage modulus in the whole range of temperature studied degree depending on irradiation doses. All crosslinked samples show reduced storage moduli with temperature due to same reason as unirradiated, *i.e.* increase in chain mobility at high temperature.

Loss modulus measures the energy dissipated as heat, representing the viscous portion.

Neat LDPE shows multiple loss peaks in temperature range  $-140^{\circ}\text{C}$  to  $80^{\circ}\text{C}$ , from 374 MPa, the loss modulus reduces to 150 MPa at  $-75^{\circ}\text{C}$ , which again reduces to 54MPa at  $25^{\circ}\text{C}$  (**Figure 4(b)**). On the other hand, the loss modulus of EPDM reduces drastically from 227 to 73 MPa while temperature increases from  $-140^{\circ}\text{C}$  to  $-75^{\circ}\text{C}$ . This value again goes down to 2 MPa at  $25^{\circ}\text{C}$ . This drastic reduction is due to rubbery nature of the polymer. The blends lie in between LDPE and EPDM in loss modulus vs. temperature sweep graph. Like storage modulus, loss modulus also increases with increase in LDPE content in the blends. This observation is very similar with the reported literature on the DMA study of LLDPE/PDMS blends [27]. All blends follow similar trend in changing loss modulus with temperatures, which are very similar to two neat polymers (**Figure 4(b)**).

It is seen that at  $-140^{\circ}\text{C}$  loss modulus ( $E''$ ) of blends (LE73, LE55 and LE37) reduces to with increase of radiation doses (40 to 120 kGy, **Figure 5(b)**, **Figure 6(b)**, **Figure 7(b)** and **Table 2**). Similar trend of decrease of loss modulus of all above blends are also noticed at  $-75^{\circ}\text{C}$  and  $25^{\circ}\text{C}$  (**Table 2**). Higher degree of crosslinking introduces higher degree of elasticity in blends. An elastic system would dissipate less energy as heat [28]. So after crosslinking, loss is less. The ratio of loss modulus to storage modulus is referred as internal damping or loss tangent ( $\tan\delta$ ). It tells us how good a material will be at absorbing energy. It is a measurement of how well a material can get rid of energy and it is reported as the tangent of the phase angle. The changes of loss tangents with temperature for all samples are represented in **Figure 4(c)**. The temperature corresponding to  $\tan\delta_{\max}$  is

considered as glass transition temperature (T<sub>g</sub>). All T<sub>g</sub> values are reported in **Table 2**.

From **Figure 4(c)**, it is obvious that in the whole temperature range  $\tan\delta$  (internal damping) of EPDM is more than LDPE due to the flexible rubbery nature of the former. All blends exhibit higher  $\tan\delta$  value (internal damping) than both LDPE and EPDM in lower temperature range (approximately  $-150^{\circ}\text{C}$  to  $-50^{\circ}\text{C}$ ). It is very unique that, at the lower temperature range,  $\tan\delta$  of LE73 and LE55 are higher than LE37. This synergism occurs due to combined effect of segmental motion of LDPE chains in the glass transition region (T<sub>g</sub> is around  $-132^{\circ}\text{C}$ ) and flexibility of amorphous chain of EPDM. The  $\tan\delta_{\max}$  value for EPDM is 0.292, which again reduces to 0.21 for LE 37 sample with a strong peak at the same position. The  $\tan\delta_{\max}$  for LE55 again becomes 0.18. Thus, the reduction of EPDM content in blend decreases the peak height of  $\tan\delta_{\max}$  indicating lower damping property of blend around glass transition region of EPDM. Generally, LDPE exhibits three different relaxation peaks,  $\alpha$ ,  $\beta$  and  $\gamma$  where  $\alpha$  peak occurs at the highest temperature around  $80^{\circ}\text{C}$ ,  $\beta$  and  $\gamma$  peak occur at  $-15^{\circ}\text{C}$  and  $-132^{\circ}\text{C}$  respectively. As our samples are run up to  $80^{\circ}\text{C}$ , thus  $\beta$  and  $\gamma$  appear prominently in our case. Accordingly to Takayangi, the  $\gamma$  relaxation is due to relaxation of  $-\text{CH}_2$  units in the amorphous region and molecular mechanism is same as the  $\alpha$  relaxation, which is associated with  $-\text{CH}_2$  unit for crystalline region. This is considered as T<sub>g</sub> (glass transition temperature) [29].  $\beta$ -relaxation is associated with side branching of polyethylene. Oakes and Rabinson interpret the  $\beta$  peak in LDPE as being due to the relaxation of branch point containing the side  $-\text{R}$  [30].  $\beta$  peak seems to be a combination of more than one transition [31]. On the other hand, T<sub>g</sub> (temperature corresponding to  $\tan\delta_{\max}$ ) for EPDM appears with a prominent intense peak at  $-30^{\circ}\text{C}$ . But for all three blends (LE73, LE55 and LE37) transition corresponding to T<sub>g</sub> of LDPE does not appear recognizable. It is reported that T<sub>g</sub> of LDPE is masked due to interaction between blend components [32] [33]. If the slope changing points are considered as T<sub>g</sub> of LDPE, then the values for LE73, LE55 and LE37 will be reported as  $-130^{\circ}\text{C}$ ,  $-128^{\circ}\text{C}$  and  $-129^{\circ}\text{C}$  respectively. Again, due to overlapping of  $\beta$  relaxation zone of LDPE and T<sub>g</sub> of EPDM a wide peak in LE73 appears at  $-15.4^{\circ}\text{C}$  due to higher amount of LDPE in blend (**Table 2**).

In LE55, a prominent peak, corresponding to T<sub>g</sub> of EPDM occurs at  $-23.6^{\circ}\text{C}$ . For LE 37, that peak appears at  $-25^{\circ}\text{C}$  but with less peak height and peak area than those of pure EPDM. From these observations it reveals that LDPE/EPDM blends are partially compatible as the T<sub>g</sub> of EPDM is increasing depending on LDPE content [34].

On crosslinking all three blends LE73, LE55 and LE 37 show almost similar behavior in changing damping property with irradiation dose and temperature (**Figure 5(c)**, **Figure 6(c)**, **Figure 7(c)**. and **Table 2**). For all blends, damping property ( $\tan\delta$ ) values keep on decreasing with irradiation dose in whole range of temperature. For all blends transition peak heights are also reduced upon crosslinking depending on radiation dose. Damping property is reduced due to restricted molecular mobility in crosslinked network.

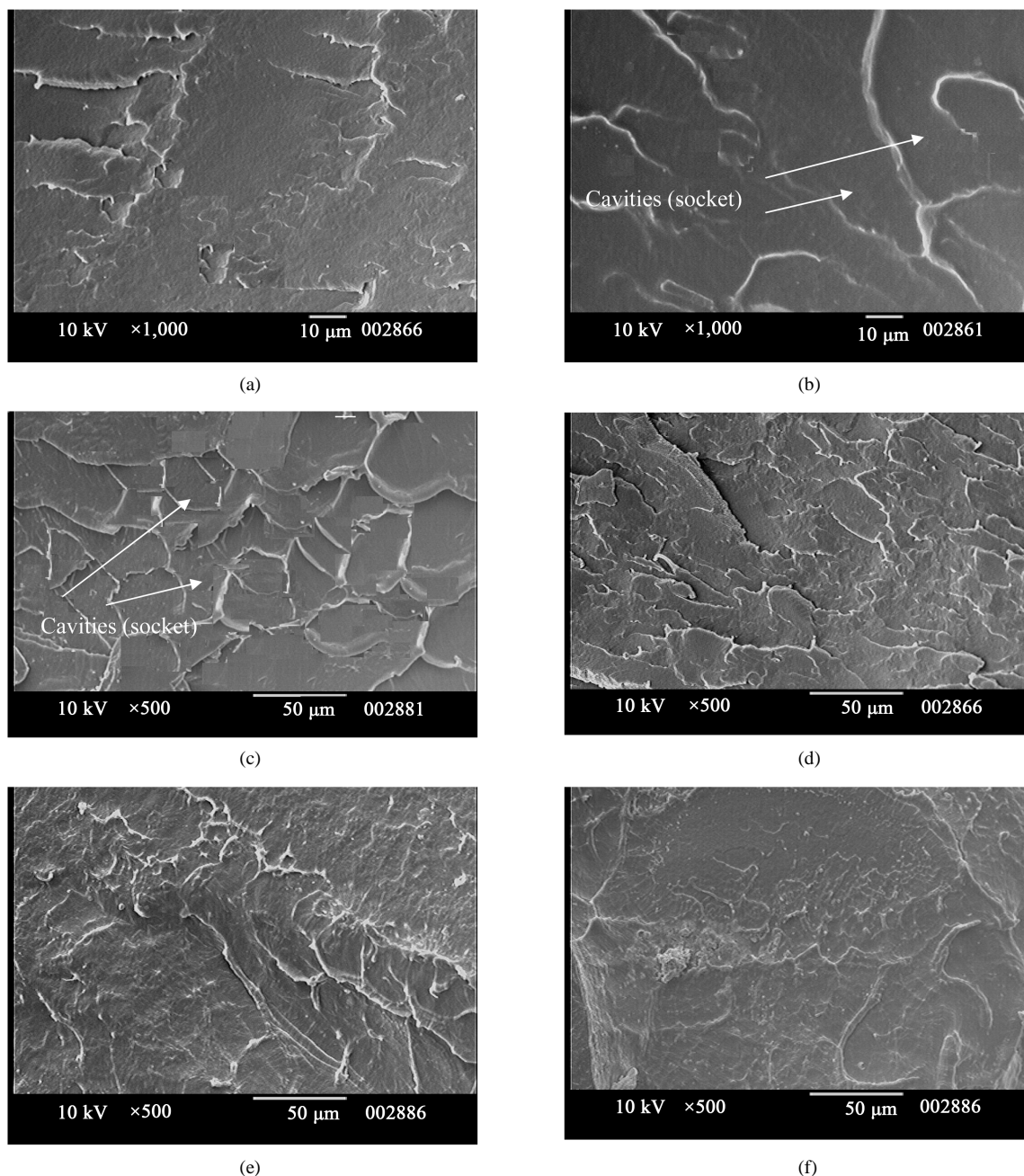
For crosslinked LE73 transition occurs around  $-130^{\circ}\text{C}$  and  $-15^{\circ}\text{C}$  like uncrosslinked one. Both are due to LDPE. Second transition merges with the glass transition of EPDM ( $-30^{\circ}\text{C}$ ). Due to higher quantity of LDPE in blends  $\beta$  transition dominates in LE73 blends masking the glass transition of EPDM. After crosslinking there is no change of transition temperatures (**Table 2**).

$\gamma$  transition ( $-130^{\circ}\text{C}$ , T<sub>g</sub>s of LDPE) in LE55 and LE 37 does not change much after crosslinking, though in blends there is no sharp peak of LDPE before and after crosslinking.

In LE 55, the transition at  $-23.6^{\circ}\text{C}$  (ascribed to T<sub>g</sub> of EPDM), shifts towards lower temperature on crosslinking at 40, 80 and 120 kGy. This may be due to higher intraphase crosslinking than interphase crosslinking in blend, which reduces the compatibility. The second peak of LDPE ( $-15^{\circ}\text{C}$ ) is merged with this peak. In LE 37, second transition occurs at  $-25^{\circ}\text{C}$ , which remains almost unchanged after crosslinking at all three doses.

Morphologies of fractured surfaces of unirradiated and irradiated LE 73, LE 55 and LE 37 blends are investigated by SEM and pictures are provided in **Figures 8(a)-(f)**. In LE 73 blend, the fractured cracks and fissures can be seen across the coarse surface where small domains are dispersed in matrix indicating less ductile surface of blend (**Figure 8(a)**). Surface of LE 37 may be considered as a more ductile fracture in which matrix yielding is considerably high (a higher degree of plastic deformation) (**Figure 8(b)**). Such kind of morphology may also be considered as ball and socket type structure, where cavity behaves like a socket and other phase is like ball. These sockets are continuous phase in which dispersed domains are balls [35]. This is the typical characteristics of ductile surfaces. In LE37, EPDM, being higher in amount, becomes matrix and LDPE is the dispersed phase [36] (**Figure 8(b)**).

In LE 55 untreated, both components are in same proportions and the fractured surface looks like honeycomb



**Figure 8.** SEM image of fracture surfaces: (a) LE 73 untreated; (b) LE 37 untreated; (c) LE 55 untreated; (d) LE 55 - 40 kGy; (e) LE 55 - 80 kGy; (f) LE 55 - 120 kGy.

(**Figure 8(c)**). Significant interface interaction between plastic and elastomer phase, composition and flow behavior are responsible for this kind of organized symmetrical morphology. Symmetrical cavities (*i.e.* sockets) can be noticed across the fracture surface, which shows high degree of ductility. This type of honeycomb-like structure indicates the considerable degree of miscibility between thermoplastic and elastomer. Due to equal amount of LDPE and EPDM the miscibility is higher, which generates the above mentioned structures. Thus the increase in damping properties and decrease in storage modulus with increasing EPDM content can be understood now by the above discussed morphologies. Moreover, it is noticed that with increasing EPDM content in the blends (**Figures 8(a)-(c)**) the morphology changes from spherical to co-continuous structure, which again supports the change in storage modulus and damping property with change in blend compositions.



However, these organized structures were destructed and surface becomes smoother with disappearance of roughness after irradiation with different doses. The size of cavities continues to reduce with radiation doses. It is seen from the **Figures 8 (c)-(f)** that surface becomes smoother with increase in irradiation dose.

At 40 kGy, the size and depth of cavities of LE55 get reduced and large number of flow patches are generated across the surface and surface starts to become smoother (**Figure 8(d)**). Again, at 80 kGy, surface becomes relatively smoother with further reduction of cavity sizes and depth with shorter flow patches (**Figure 8(e)**). At 120 kGy, surface features alter in the same direction introducing more smoothness. These changes occur mainly due to the presence of micro radicals generated by irradiation. These micro radicals react at the boundary surface of the different phases and consequently the adhesion between two phases due to inter chain and intra chain is increased and more uniform surfaces are produced [37]. This appearance resembles with stiffer surfaces. That is the reason why with increases in radiation doses, storage modulus becomes higher and higher and damping becomes lower and lower [38].

## 5. Conclusion

From the increase in percentage gel of LDPE and EPDM and their blends with increased radiation dose, it is seen that the crosslinking efficiency of EPDM is higher than LDPE. The trend of change of storage modulus with blend composition before and after irradiation is similar (higher the EPDM content less is the modulus), only the values are higher for irradiated samples that keeps on increasing with dose. On irradiation loss modulus continues to decrease with dose for a particular blend. For EPDM rich blend the damping properties is found higher though at lower temperature range LDPE rich blend shows greater damping properties due to synergism of glass transition of LDPE and vibration of amorphous EPDM chains. Upon irradiation damping properties keep on decreasing with dose. EPDM rich blends show more ductile surface with higher matrix yielding, supporting less storage modulus. But irradiation makes surface smooth and smoothness keeps on increasing with irradiation dose revealing increased compatibility (higher stiffness) between two phases through crosslinking.

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