Development of New Thermoplastic Elastomers from Blends of Polyethylene and Ethylene–Vinyl Acetate Copolymer by Electron-Beam Technology

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ABSTRACT: Electron beam-initiated crosslinking of films prepared from a blend of low-density polyethylene (LDPE) and ethylene–vinyl acetate (EVA) containing 45% vinyl acetate, with ditrimethylol propane tetraacrylate (DTMPTA), was carried out over a range of radiation doses (20–500 kGy), concentration of DTMPTA (1–5 parts by weight), and blend compositions. The gel fraction of the films increases with increase in the irradiation dose, DTMPTA level, and EVA content of the blends. The mechanical and dynamic mechanical properties of the films are also changed with the above variables. Reprocessibility studies revealed that the blends irradiated at 50 kGy and below are thermoplastic elastomers with a low permanent set. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1877–1889, 2001

Key words: low-density polyethylene; ethylene–vinyl acetate; ditrimethylol propane tetraacrylate; gel fraction; irradiation; reprocessibility; thermoplastic elastomer

INTRODUCTION

Modification of polymers and polymer blends in the presence of radiation is a relatively new technique for the development of materials with superior properties. Irradiation of polymeric materials by an electron beam results in grafting and subsequently the formation of a three-dimensional network through the union of the macroradicals generated.[1–3] Electron beam-initiated grafting and crosslinking is often easier to employ and control than are conventional chemical methods. Active species, for example, free radicals and ions formed by radiation, tend to react with neighboring atoms, finally producing crosslinking and scission of polymer chains. The final crosslinking to scission ratio determines the net effect.[4–7] Polyfunctional monomers, such as multifunctional acrylate and allylic reactive molecules, blended with the base polymers, increase the crosslinking efficiency and help to achieve crosslinking at much reduced radiation levels without much deterioration of the base polymers.[8,9]

Blending of a thermoplastic and an elastomer gives a class of rubbery materials known as thermoplastic elastomers which possess the good physical properties of elastomers along with the processing characteristics of thermoplastics. Among the various types of thermoplastic elastomers, those prepared by melt-mixing of a crystalline thermoplastic material and an elastomer under a high shearing action have gained considerable attention due to the simple method of preparation and easy attainment of physical properties by varying the blend ratios.[10,11] It was found that addition of small quantities of crosslinking agents during the mixing operation improves the

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final properties of such blends without much affecting the processing characteristics. This type of crosslinking is known as dynamic crosslinking.[12,13] Dynamically vulcanized rubber–plastic thermoplastic elastomers were prepared in this laboratory.[14,15] It is also observed that an optimum quantity of a crosslinking agent is required for the best compromise of the properties. However, the preparation of a thermoplastic elastomer by electron-beam technology has not been reported in the literature. It was the aim of the present article to prepare a thermoplastic elastomer from an immiscible blend of polyethylene and the ethylene–vinyl acetate copolymer crosslinked by electron beam irradiation, as an alternative to the conventional dynamic crosslinking process. In such blends, additional possibilities of intercrosslinking of the blend components at their interface may also exist.

Modification of polymers by electron-beam radiation was described recently. It was observed that rubbers generally can be crosslinked using electron-beam radiation,[16–19] whereas some plastics like polypropylene and poly(vinyl chloride) have a tendency to degrade.[20] The effects of electron-beam radiation on the structures and properties of polyethylene (PE) and ethylene–vinyl acetate (EVA) in the presence of different types of polyfunctional monomers have also been reported.[21–23] The influence of electron-beam irradiation on the mechanical properties of polypropylene–EPDM rubber blends was studied by Harnischfeger et al.[24] Martinez-Padro et al.[25] carried out gamma radiation-induced crosslinking of PE and EVA blends. Possible chemical reactions and alternative irradiation methods were also discussed. Abdel-Bary et al. studied the characterization and possible application of grafted acrylamide onto low-density polyethylene (LDPE), EVA, and their blends.[26] Mateev and Karageorgiev[27] studied the effect of electron-beam irradiation and the content of EVA (13% VA content) upon the gel-forming processes in LDPE–EVA films.

The two polymers in the system under investigation, namely, the blends of EVA with 45% VA content and LDPE, have a structural similarity in the sense that the former is a copolymer of a nonpolar methylenic chain (—CH_2—) with a polar acetate group and the latter is a completely nonpolar methylenic chain. These two polymers differ in the degree of crystallinity (the former is completely amorphous) and also in their polarity. Ditrimethylol propane tetraacrylate (DTMPTA), a tetrafunctional unsaturated monomer, was used to produce high yield of radicals during irradiation. Gel fraction analysis was done to evaluate the extent of crosslinking. Mechanical and dynamic mechanical properties were measured over a range of irradiation doses, DTMPTA levels, and blend ratios. Tension-set and reprocessibility studies were done to establish the thermoplastic elastomeric characteristics of the blends.

EXPERIMENTAL

Materials

The EVA copolymer (LEVAPRENE 450, 45% VA content) was supplied by Bayer (Germany) (density 0.975 g/cm^3, ash content at 950°C 0.26%, and volatility 0.6% maximum). LDPE was supplied by IPCL (Boroda, India) (INDOTHENE 16MA400; density 0.918 g/cm^3, melt index 3 dg/min). DTMPTA (Ebecryl 140), used as a radiation sesitizer, was obtained from UCB Chemicals (Belgium).

Preparation of Samples

EVA, PE, and DTMPTA were mixed in a Brabander Plasticorder, PLE-330, at 130°C and 60 rpm rotor speed. PE was first allowed to melt, followed by EVA and DTMPTA for 2 min. The mixes so obtained were sheeted out under conditions through the open-mill set at a 2-mm nip gap. It was remixed in the Brabander Plasticorder for another 2 min.

The sheets were compression-molded between Teflon foils for 2 min at 150°C and at a pressure of 5 MPa in an electrically heated press to obtain films of thickness 0.025 ± 0.003 cm. The moldings were cooled under compression to maintain the overall dimensional stability.

Irradiation of Samples

The molded films were irradiated in air at a room temperature of 25 ± 2°C by an electron-beam accelerator (Model ILU-6) at the Bhabha Atomic Research Centre (BARC), Bombay, India. Irradiation doses of 20, 50, 100, 200, and 500 kGy were used. The specification of the electron-beam accelerator was given in an earlier communication.[17] The formulations of the samples are given in Table I.

Measurement of Properties

Gel Fraction

The gel fraction was measured gravimetrically by immersing the samples in xylene at 353 K for

Table I Formulation of the Samples

Sample Code	PE (Wt by Parts)	EVA (Wt by Parts)	DTMPTA (Wt by Parts)	Radiation Dose (kGy × 10^{-1})
PE100	100	0	0	10
PEVA 55000	50	50	0	0
PEVA 55020	50	50	0	2
PEVA 55021	50	50	1	2
PEVA 55023	50	50	3	2
PEVA 55025	50	50	5	2
PEVA 55050	50	50	0	5
PEVA 55100	50	50	0	10
PEVA 55200	50	50	0	20
PEVA 55500	50	50	0	50
PEVA 55101	50	50	1	10
PEVA 55103	50	50	3	10
PEVA 55105	50	50	5	10
PEVA 37100	30	70	0	10
PEVA 46020	40	60	0	2
PEVA 46100	40	60	0	10
PEVA 64020	60	40	0	2
PEVA 64100	60	40	0	10
PEVA 73100	70	30	0	10
EVA 100	0	100	0	10

72 h. The equilibrium swelling time, which was determined from the experiments and calculated from the weight of the sample before and after swelling, was determined as follows:

$$\text{Gel fraction} = w_2/w_1 \quad (1)$$

where w_1 is the initial weight of the film, and w_2, the weight of the insoluble portion of the film. The results reported here are the average of three samples.

Mechanical and Dynamic Mechanical Thermal Analysis

Tensile, hysteresis, and tension-set specimens were punched out from the molded films using ASTM Die-C. The tests were carried out as per the ASTM D 412-98a method in a universal testing machine (ZWICK 1445) at a crosshead speed of 500 mm/min at 25°C. The average of three tests is reported here. Hysteresis loss at 100% elongation was measured by subtracting the area under the force retraction curve from the area under the force–deformation curve. The hysteresis loss ratio reported here was calculated as the ratio of hysteresis loss to the strain energy.

Dynamic mechanical thermal properties were determined on a DMTA (Rheometric Scientific Inc.) under a dual-cantilever mode. The experiments were carried out at frequencies 0.01, 0.1, 1, and 10 Hz. The measurements were taken from −50 to 50°C, at a heating rate of 2°C/min and a double-strain amplitude of 64 μm. The storage modulus and the loss tangent (tan δ) were measured for all samples under identical conditions. The data were analyzed using a COMPAQ Computer (version 1.2).

RESULTS AND DISCUSSION

Gel-fraction Analysis

The gel-fraction values of the films are plotted against irradiation doses [Fig. 1(a)], DTMPTA level [Fig. 1(b)], and EVA content of the blend [Fig. 1(c)]. For a particular blend ratio and monomer level, the gel fraction increases steadily with the radiation dose. The higher values of the gel content at higher radiation doses indicate the formation of three-dimensional network structures. At a constant radiation dose of 100 kGy, the gel content increases steadily with increase in the DTMPTA level. The increase in the gel fraction is only marginal after 3 wt % of DTMPTA concentration in the blend. At a constant irradiation

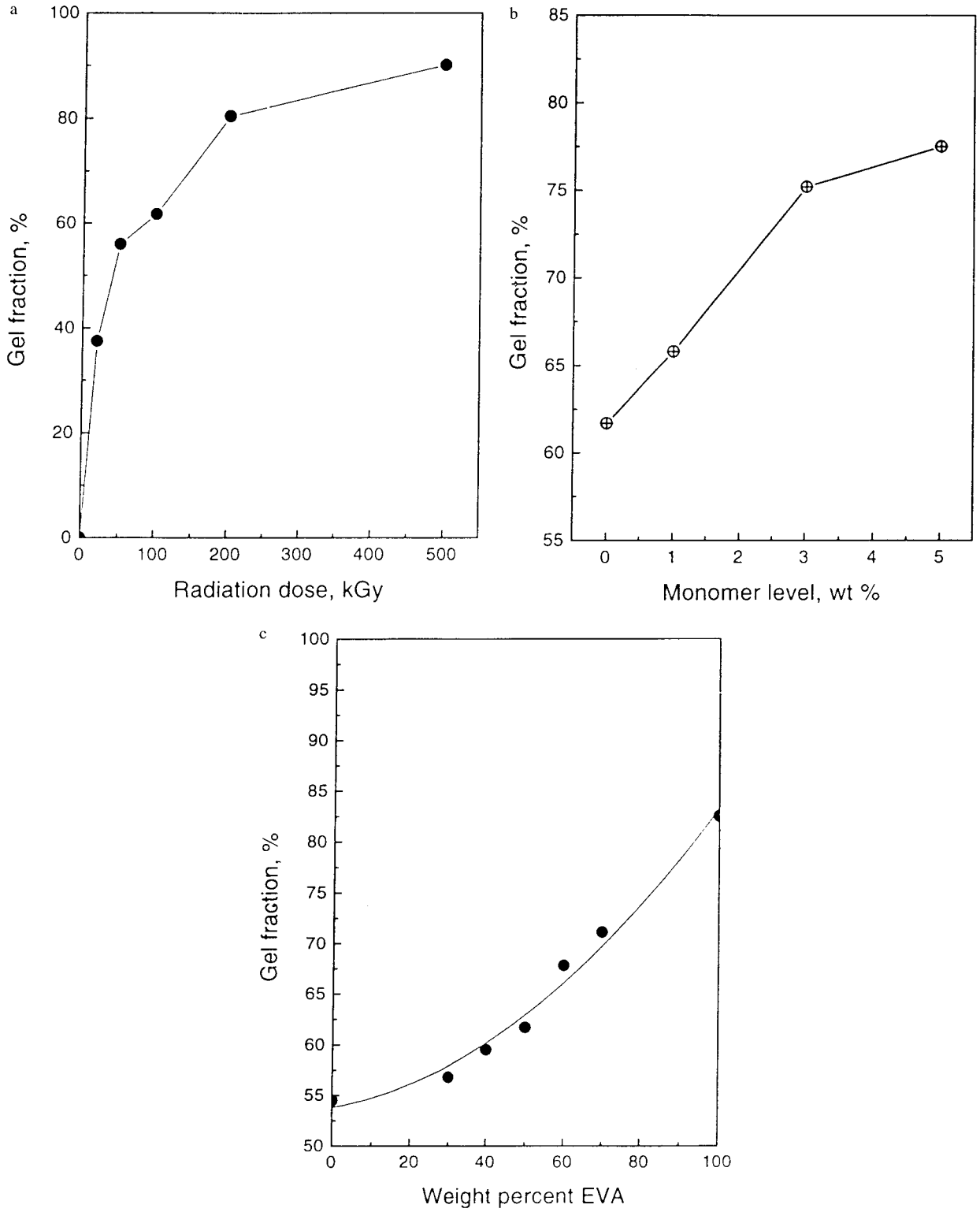

Figure 1 Gel fraction against (a) radiation dose for 50 : 50 PE : EVA blend without DTMPTA, (b) DTMPTA level for 50 : 50 PE : EVA blend irradiated at 100 kGy, and (c) EVA content of the blends irradiated at 100 kGy without DTMPTA.

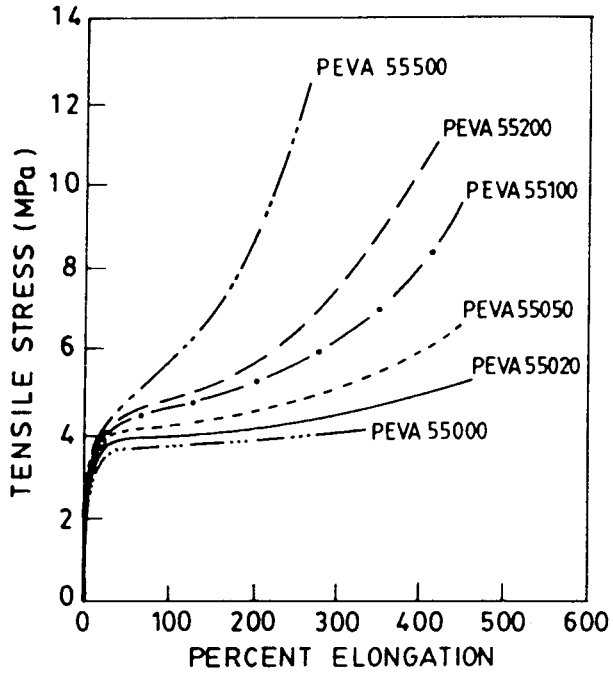

Figure 2 Stress–strain curves for the films of 50 : 50 PE : EVA blend, irradiated at irradiation doses without DTMPTA.

dose of 100 kGy, the gel content increases with increase in the EVA content of the blend.

At higher irradiation doses or higher concentration of DTMPTA, a large number of radicals are formed, which would lead to a higher gel fraction by radical combinations. However, at a very high dose of irradiation or DTMPTA levels, there are also possibilities of chain scission and or the degradation of polymers. A balance is stuck at optimum levels. Hence, the gel fraction does not change to a significant extent after an irradiation dose of 200 kGy and 3 wt % of DTMPTA. Increase in the EVA proportion makes the blend more amorphous in nature, which, in turn, increases its efficiency toward crosslinking at a particular radiation dose. Also, EVA can easily form free radicals at lower radiation doses compared to PE.[23,26]

Mechanical Properties

Effect of Radiation Dose

Figure 2 depicts the stress–strain properties of a 50 : 50 PE and EVA blend irradiated at different radiation doses. The tensile properties of the blend irradiated at different radiation doses are given in Table II. As the radiation dose is increased, the modulus of the blend is improved due to an increased gel fraction. The elongation at break is initially increased and then decreased sharply with the radiation dose as compared to that of the control sample. The tensile strength is also increased with the irradiation dose. The initial increase in elongation at break and increase in tensile strength may be due to increase in the interfacial interaction, which eliminates the possibility of formation and propagation of crack at interfaces during stretching. It may be pointed out that the tensile strength of pure PE and EVA passes through a maximal at an intermediate radiation dose while the elongation at break decreases with increase in the radiation dose.[21–23]

To understand the modulus and strength of the electron-beam crosslinked PE/EVA blend, the same parameters were calculated theoretically using an approach similar to that of Takayanagi et al.[28] and assuming a two-phase material combining series and parallel elements. Since the LDPE used in this study has a high MFI (low viscosity at mixing temperature), the parallel-model upper bound was considered as follows:

$$\sigma_{PEVA} = \phi_1\sigma_{PE} + \phi_2\sigma_{EVA} \quad (2)$$

Table II Stress–strain Properties of the Films from 50 : 50 Blend of PE and EVA Irradiated at Different Irradiation Doses

Sample Code	Tensile Strength (MPa)	Elongation at Break (%)	Modulus (MPa)		
			100%	200%	300%
PEVA 55000	4.2	340	3.54	3.78	4.08
PEVA 55020	5.3	470	4.04	4.27	4.58
PEVA 55050	6.7	450	4.25	4.60	5.22
PEVA 55100	9.5	440	4.72	5.31	6.20
PEVA 55200	11.0	430	5.10	5.83	7.21
PEVA 55500	12.1	265	5.60	8.52	—

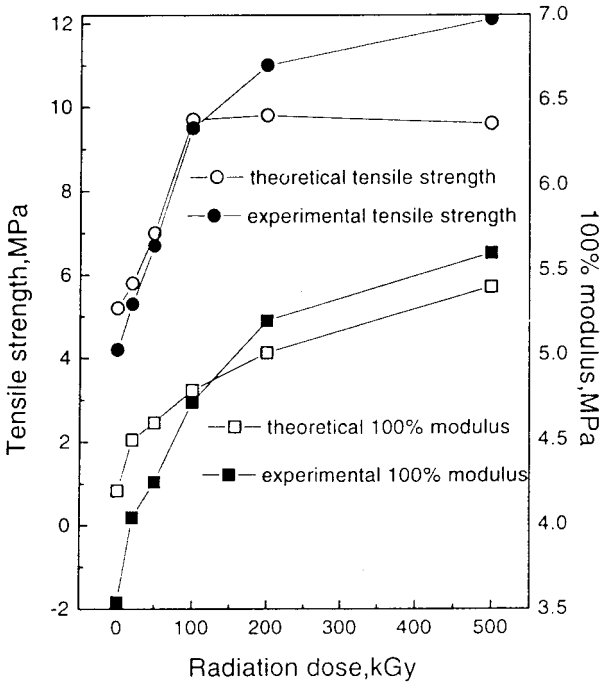

Figure 3 Theoretical and experimental moduli and tensile strengths of the films of 50 : 50 PE : EVA blend without DTMPTA.

where σ_{PEVA} is the modulus of the blend at a particular radiation level; ϕ_1 and ϕ_2, the volume fractions of the PE and EVA in the blend; and σ_{PE} and σ_{EVA}, the modulus of PE and EVA, respectively, at the same radiation dose. Similarly, the tensile strength was theoretically evaluated. These are shown in Figure 3. It is shown that the theoretical value of the modulus is in accord with the experimental one especially at higher radiation doses. Similarly, the experimental tensile-strength values match those of the theoretical values at low irradiation doses. However, at higher doses, the experimental values are much higher, indicating the existence of interfacial crosslinking between PE and EVA, which is not accounted for in the model.

The hysteresis loss ratio and permanent set of the 50 : 50 blend without any monomer are plotted against the radiation dose (Fig. 4). The gel fraction increases with increase in the radiation dose, and the elastic properties of the material increases, which is reflected in the decrease in hysteresis loss and increase in the recovery property of the films. Hence, the same nature of variation of the permanent set and hysteresis loss ratio with the radiation dose was observed.

Effect of Monomer Levels

Figure 5 reveals the effect of the monomer level on the properties of a 50 : 50 PE/EVA blend irradiated at 100 kGy. The modulus increases and the elongation at break decreases with increase in the monomer level. However, the tensile strength passes through a maxima at a 3 wt % monomer level before a final decrease. The hysteresis loss ratio and permanent set are found to decrease with increase in the monomer levels.

The modulus of a vulcanizate is proportional to the number of crosslinks formed. At a particular radiation level and blend composition, as the number of crosslinks increases with increase in the monomer level, the modulus increases. However, at a higher crosslink density, the network is so dense that there is little energy dissipation in the matrix and the energy supplied is utilized to break the bonds, as a result of which the elongation at break decreases. Monomers like DTMPTA also act as a plasticizer, giving efficient contact between the phases and chains as well.[17] A failure property like tensile strength is a function of the crosslink density and energy dissipation. Initially, plasticization and crosslinking are the dominating factors to give a steady increase of the tensile strength with the monomer levels. But

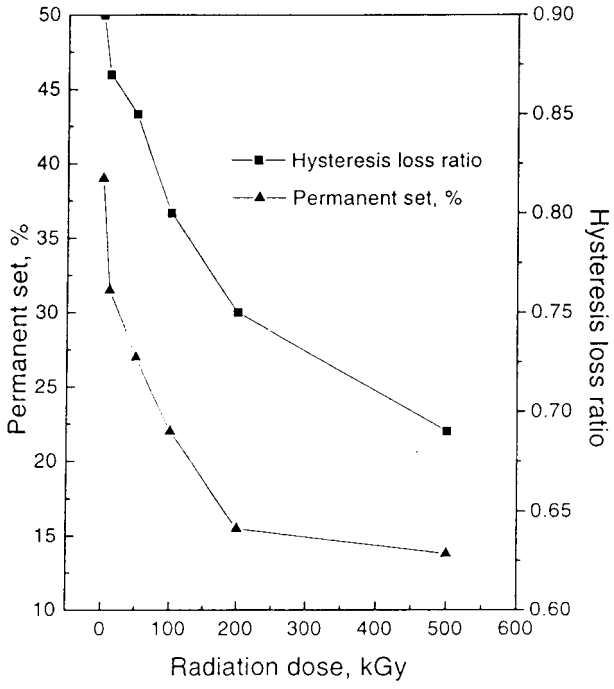

Figure 4 Variation of hysteresis loss ratio and permanent set with radiation doses for 50 : 50 blend.

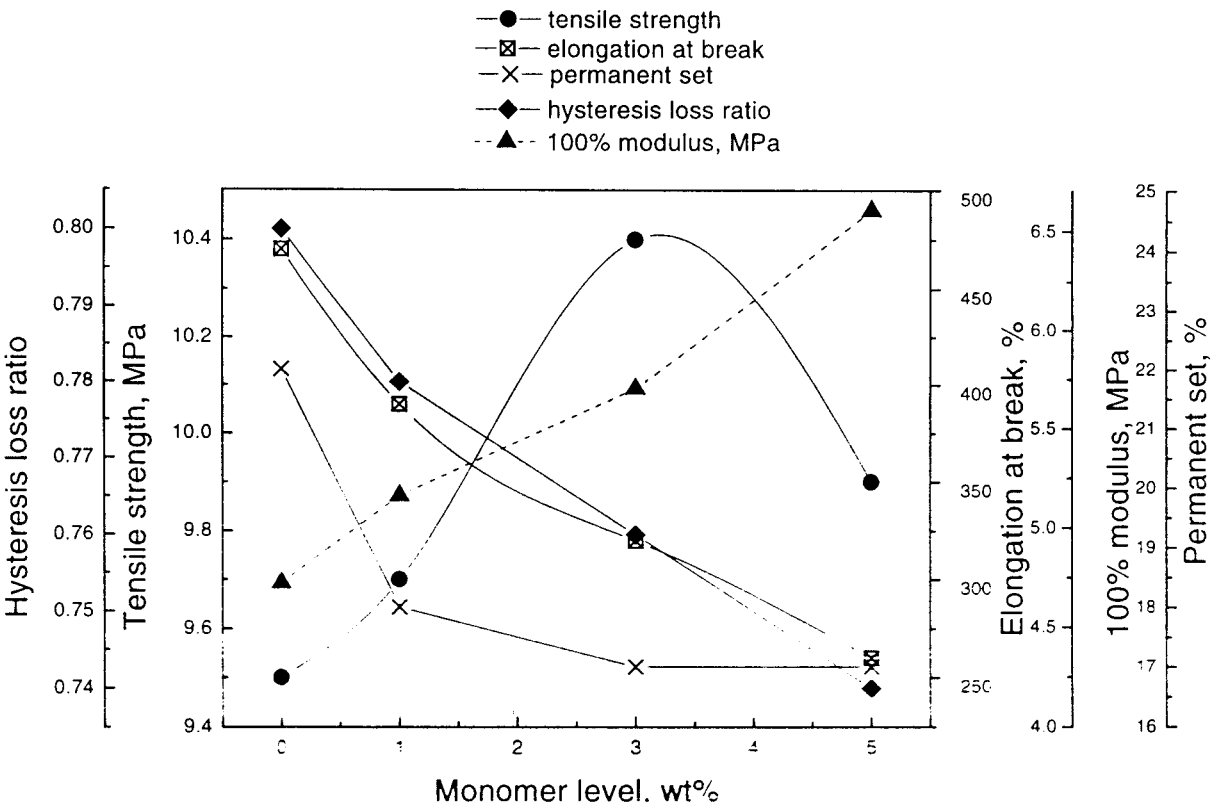

Figure 5 Variation of mechanical properties against DTMPTA levels for 50 : 50 blends irradiated at 100 kGy.

after achieving a certain number of crosslinks, the energy-dissipation factor overshadows the others. Hence, the failure properties become poorer. A decrease in the hysteresis loss ratio and permanent set can be explained by increase in the gel fraction.

Effect of Blend Ratio

The effect of the blend ratio on the properties was investigated at 100 kGy and 0 wt % monomer concentration (Table III). The tensile strength and 100% modulus increase with increase in the PE content of the blend due to the increased crystallinity of the blends.[29] But with increase in the EVA content, the effective energy-dissipation process becomes easier, which gives rise to an increase in the elongation at break. As the EVA content of the blend increases, the crosslink density increases, which, in turn, decreases the hysteresis loss ratio and permanent set of the blends.

Table III Mechanical Properties of Different Blend Compositions Irradiated at 100 kGy

	Theoretical		Experimental				
Blend	Tensile Strength (MPa)	100% Modulus (MPa)	Tensile Strength (MPa)	100% Modulus (MPa)	Elongation at Break (%)	Hysteresis Loss Ratio	Permanent Set (%)
PE 100	—	—	11.4	8.60	310	0.90	48
PEVA 73100	10.4	6.3	10.5	6.27	370	0.86	42
PEVA 64100	10.1	5.58	10.3	5.67	440	0.84	28
PEVA 55100	9.7	4.79	9.5	4.72	470	0.80	22
PEVA 46100	9.4	3.99	9.0	3.67	520	0.76	19
PEVA 37100	9.1	3.12	8.4	2.70	570	0.74	15
EVA 100	—	—	8.0	0.66	670	0.17	5

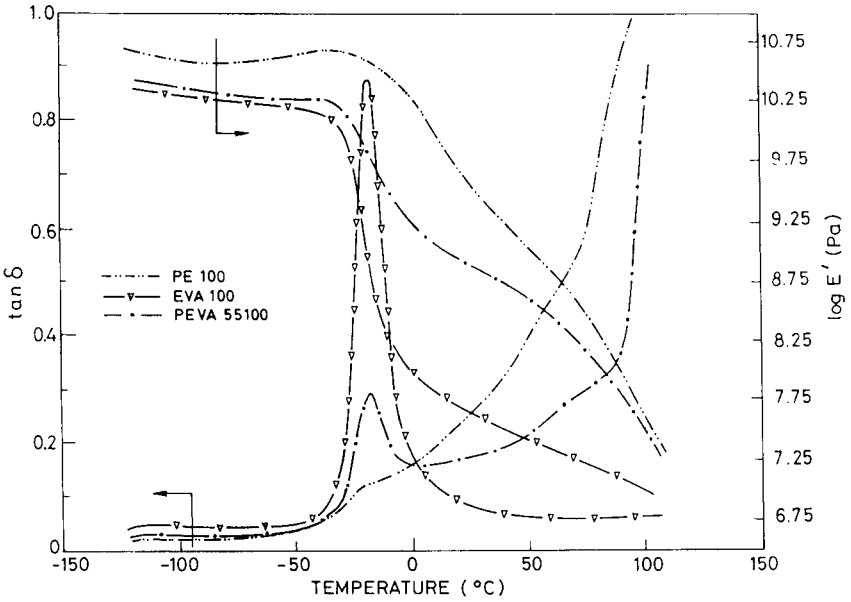

Figure 6 DMTA spectra of PE10, PEVA55000, and EVA10 at fixed frequency of 0.1 Hz.

The theoretical calculation of the modulus and tensile strength of the blends at 100 kGy for different blend proportions was done (Table III). It is apparent that the values of the theoretical modulus and tensile strength are in accord with the experimental values within experimental error, except for PEVA37100, where there is a negative deviation. As the theoretical values were calculated using the upper-bound model, it is clear that the compositions up to 60% EVA have PE as a continuous matrix. This is possible because of the high MFI or low viscosity of PE.[29]

Dynamic Mechanical Thermal Analysis

Dynamic mechanical thermal analysis (DMTA) of various irradiated samples was performed. The investigation of internal friction over a wide range of temperatures has proved to be very useful in studying the structure of polymer blends and the variation of properties.[30]

Figure 6 shows the dynamic mechanical spectra of LDPE, EVA, and their 50 : 50 blend irradiation at a 100-kGy irradiation dose. Control LDPE exhibits three different relaxation peaks termed α, β, and γ, where the α-peak occurs at around 100°C (the tan δ value is so high that it cannot be fitted on the same scale), a not so prominent β-peak at an intermediate temperature (around -20°C), and γ-relaxation at a temperature around -120°C. The mechanism of α-transition is believed to be due to the vibration–rotational motion within the crystalline zone.[31] The β-relaxation is associated with the branch points containing the side group. The β-peak becomes prominent if the concentration of the side groups exceeds a certain limit.[32] The γ-transition is associated with the crank-shaft motion of the polymethylene groups of the main backbone.[31]

Control EVA, on the other hand, exhibits two main relaxations in the temperature range of -130 to 120°C. The β-transition occurs at -17°C. The relatively broad γ-damping peak occurs at around -130 to -120°C. It may be pointed out that that the uncrosslinked LDPE and EVA show β-peaks at -20 and -25°C, respectively.[33] The slight shift in these peaks in the present investigation is due to the effect of crosslinking and crystallinity. The melt-mixed blends of EVA–LDPE also exhibit peaks at -120, -19, and around 100°C, respectively. The effects of irradiation dose, blend proportion, and DTMPTA content on the dynamic mechanical properties are discussed in the next section in the temperature range of -50 to 50°C, where a maximum change of properties was observed.

Effect of Radiation Dose

The effect of radiation dose on tan δ is shown in Figure 7 and the results are tabulated in Table IV. With increase in the radiation dose, the glass

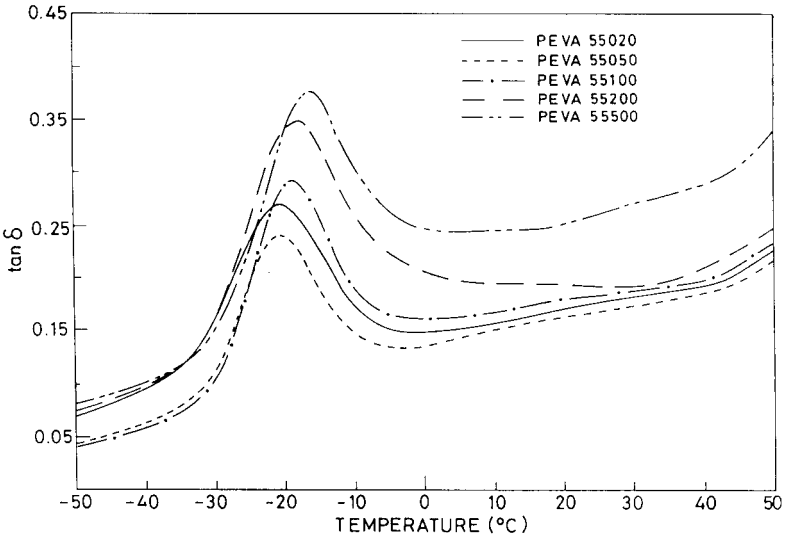

Figure 7 Variation of tan δ with temperature for 50 : 50 PE : EVA blend without DTMPTA at a fixed frequency of 0.1 Hz.

transition temperature (T_g, corresponding to the β-transition) gradually shifts toward a higher temperature. The degree of crosslinking increases with increase in the radiation dose, which, in turn, increases the potential barrier to cause the relaxation. The tan δ_{max} corresponding to the T_g initially decreases, reaches its minimal at 50 kGy, and then increases sharply (Fig. 8). The initial decrease in tan δ_{max} may be due to increase in the crosslinking. At higher radiation levels, an increased movement of chain branches takes place, possibly due to the elimination of the VA group.[34] The dynamic storage modulus initially increases with the radiation levels, reaches its maximum value at a radiation dose of 50 kGy, and then decreases with increase in the radiation levels. An initial increase in the storage modulus is probably due to the crosslinking and improvement in interfacial adhesion. At higher radiation doses, the gradual decrease in the storage modulus may be due to the change in the molecular architecture caused by the radiation.

Table IV Dynamic Mechanical Properties of 50 : 50 Blend Irradiated at Different Radiation Doses

Sample Code	T_g (°C)	tan δ_{max}	Log E' (Pa) 25°C	Log E' (Pa) 50°C
PEVA 55000	−21	0.297	8.90	8.46
PEVA 55020	−21	0.280	8.96	8.60
PEVA 55050	−20.5	0.255	9.06	8.72
PEVA 55100	−19	0.310	8.92	8.66
PEVA 55200	−18	0.375	8.88	8.56
PEVA 55500	−16	0.390	8.86	8.46

Effect of Monomer Concentration

DMTA of the 50 : 50 blend irradiated at 100 kGy reveals a decrease in the loss tangent at the T_g

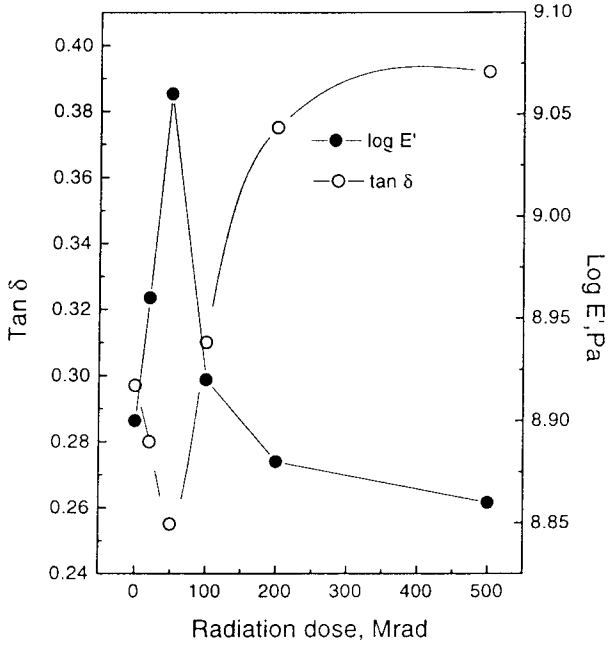

Figure 8 Variation of tan δ and log E' with radiation doses for 50 : 50 blend.

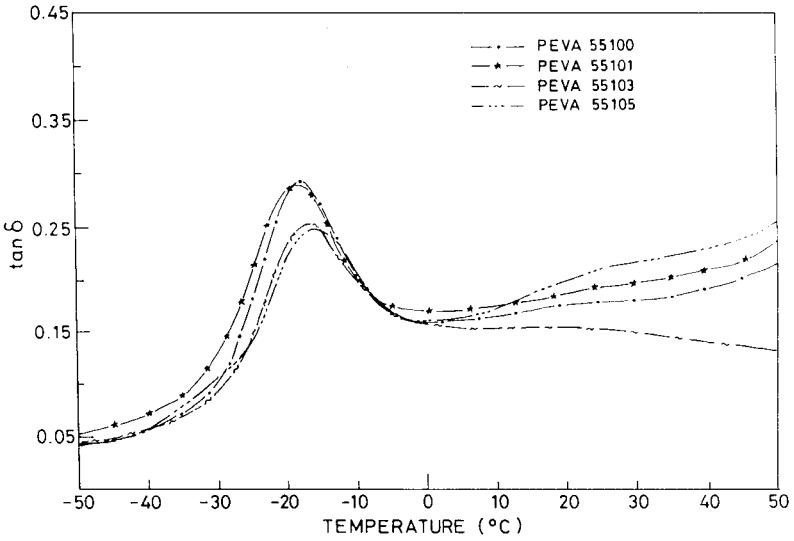

Figure 9 Variation of tan δ against temperature for 50 : 50 blend irradiated at 100 kGy for different DTMPTA levels at a fixed frequency of 0.1 Hz.

with increase in the monomer level (Fig. 9). Due to the increase in crosslinking with increase of the monomer level, free segmental motions involving cooperative diffusional motion of the side chains are restricted. Moreover, at higher monomer levels, the T_g shifts slightly to a higher temperature.[17] With increase in the monomer levels, the storage modulus gradually increases and attains its maximum value for 3 wt % of the monomer concentration (Table V). At a higher monomer level, although the gel fraction increases, the possibility of chain scission and disproportionation also increases, which is reflected in the decrease in the storage modulus at 5 wt % of the DTMPTA concentration.

Effect of Blend Ratio

Figure 10 gives the variation of tan δ against temperature for different blend proportions irradiated at 100 kGy. As the EVA content of the blend increases, tan δ_{max} (at T_g) increases. But at room temperature and above, the tan δ value increases with increase in the PE content of the blend (Table VI). Finally, it tends to a maxima at higher temperature due to the melting of the PE crystallites (α-transition). The storage modulus, on the other hand, increases with increase in the PE content of the blend (Table VI).

Table V Dynamic Mechanical Properties of the Films of 50 : 50 Blends Irradiated at 100 kGy for Different DTMPTA Levels

Sample Code	T_g (°C)	tan δ_{max}	Log E' (Pa)		
			T_g	25°C	50°C
PEVA 55100	−19.0	0.31	9.92	8.92	8.66
PEVA 55101	−19.0	0.297	9.98	9.08	8.76
PEVA 55103	−18.5	0.26	10.18	9.30	9.06
PEVA 55105	−17.5	0.255	9.96	8.98	8.60

Reprocessibility Studies

Reprocessibility studies were performed on the samples. The results are given in Table VII. It is observed that the blends irradiated at a 50-kGy radiation dose and below can still be reprocessed. The samples subjected to a higher irradiation dose are not good for additional processing. They are weak and show melt fracture. To establish the thermoplastic elastomeric behavior, reprocessibility studies at five processing cycles were carried out. Tensile properties were measured on the reprocessed films.

The original 50 : 50 blend (irradiated at 0, 20, and 50 kGy) have tensile strength in the range of 4.2–6.7 MPa and elongation at break in the range of 340–480%. The tensile strength is a function of the irradiation dose and monomer level as discussed earlier. It is interesting to note that the permanent set lies within 50% for all the samples. The lowest value is achieved for PEVA55025. At a 20-kGy irradiation dose when the monomer level is varied, there is a marginal decrease in the

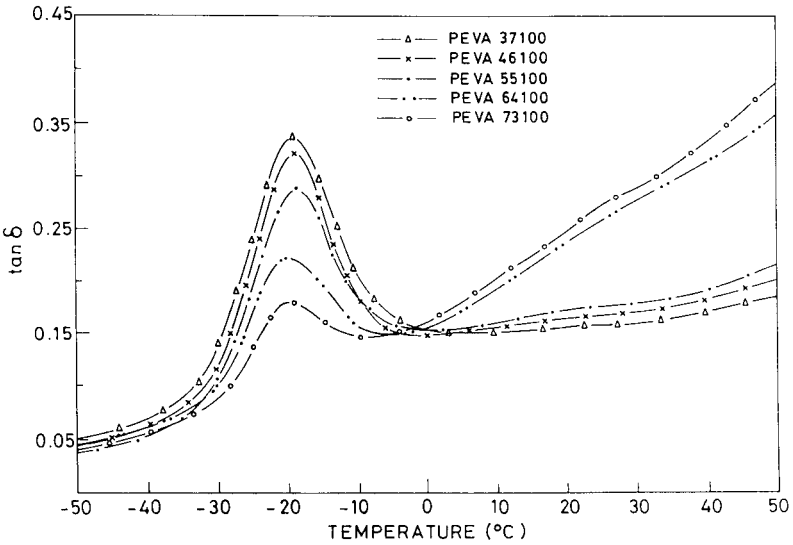

Figure 10 Variation of tan δ against temperature for the different blend proportions without DTMPTA irradiated at 100 kGy.

tensile strength although the elongation at break is reduced after the fifth processing cycle. At a constant radiation dose, the lowering of properties is dependent on the monomer level and blend ratio. The decrease in properties is probably due to the breakdown of the chains particularly for EVA, when these are processed at a higher temperature of 150°C. The blends containing more PE as a result display better processibility and a lower reduction in properties. But the permanent set increases, as the blends become more plastic in nature. For the sample irradiated at 50 kGy, the elongation at break decreases to 90% after the fifth processing cycle, probably due to the crosslinking of the EVA and PE phase to a significant extent.

CONCLUSIONS

The gel fraction, mechanical and dynamic mechanical properties, and reprocessibility of EVA–LDPE blends were investigated and the following conclusions were drawn:

1. The gel fraction of the films increases with increase in the irradiation dose, monomer level, and EVA content of the blend.
2. The tensile strength and modulus increase, while the elongation at break initially increases followed by a decrease with increase in the radiation dose at a constant monomer level and blend ratio. The hysteresis loss ratio and permanent set decrease with increase in the radiation dose due to an increase in the gel fraction.
3. Radiation-induced crosslinking improves the interfacial adhesion of the PE–EVA blends. Theoretical calculations reveal that the blends up to PEVA46100 have predominantly PE as the continuous phase.
4. The modulus increases, but the elongation at break decreases with increase in the

Table VI DMTA Results for Different Blend Proportions Irradiated at 100 kGy

	tan δ			Log E' (Pa)		
Sample Code	T_g	25°C	50°C	T_g	25°C	50°C
EVA 100	0.945	0.080	0.080	8.93	7.67	7.47
PEVA 37100	0.367	0.162	0.195	9.70	8.84	8.56
PEVA 46100	0.345	0.180	0.205	9.79	8.86	8.60
PEVA 55100	0.310	0.245	0.227	9.92	8.92	8.66
PEVA 64100	0.237	0.260	0.327	10.04	9.00	8.74
PEVA 73100	0.185	0.270	0.370	10.14	9.16	8.80
PE 100	0.115	0.265	0.387	10.58	9.60	9.10

Table VII Permanent Set and Reprocessibility Studies on Different Films

		Original		First Cycle		Second Cycle		Third Cycle		Fourth Cycle		Fifth Cycle	
Sample Code	PS (%)	TS (MPa)	EB (%)	TS (MPa)	EB (%)	TS (MPa)	EB (%)	TS (MPa)	EB (%)	TS (MPa)	EB (%)	TS (MPa)	EB (%)
PEVA 55000	38	4.2	340	4.1	300	4.0	280	4.0	250	3.9	230	3.7	230
PEVA 55020	31	5.3	470	5.4	440	5.2	420	5.1	400	5.1	380	5.0	370
PEVA 55021	28	6.3	480	6.1	420	5.8	390	5.6	360	5.3	320	5.3	310
PEVA 55023	27	6.6	370	6.4	260	5.1	230	5.1	210	4.9	180	4.8	160
PEVA 55025	24	6.3	280	5.8	230	5.2	210	5.1	190	4.8	170	4.7	170
PEVA 64020	33	6.7	430	6.7	410	6.4	400	6.4	400	6.2	390	6.1	360
PEVA 46020	23	5.1	590	5.0	530	5.1	420	4.9	410	4.6	400	4.5	400
PEVA 55050	27	6.7	450	6.3	220	6.0	170	5.6	110	5.3	100	5.2	90

TS, tensile strength; PS, permanent set; EB, elongation at break.

DTMPTA content of for the 50 : 50 blend at a constant radiation dose, while the tensile strength increases steadily up to a 3 wt % DTMPTA level followed by a decrease. The hysteresis loss ratio and permanent set decrease with the monomer level due to increase in the gel fraction.

5. The tensile strength and modulus of the blends increase with increase in the PE content of the blends, while the elongation at break decreases. The hysteresis loss ratio and permanent set decrease with increase in the EVA content of the blends.
6. The dynamic mechanical spectra of the blends indicate both their immiscibility and two-phase structure.
7. The changes in crosslinking and molecular architecture are reflected in the dynamic mechanical properties, namely, the tan δ and the storage modulus (E') due to the variation of irradiation doses, DTMPTA levels, and blend ratios.
8. From the reprocessibility studies, it was found that the blends irradiated at 50 kGy and below can be reprocessed. The decrease in properties after the processing cycles is probably due to the change in molecular architecture at a high temperature of 150°C. Although the processibility of the compositions containing a greater amount of PE is better, they suffer from a poor permanent set.

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