Engineering Properties of Electron Beam-Crosslinked Ethylene Methyl Acrylate Copolymer

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ABSTRACT: Effect of electron beam on mechanical, thermal, and morphological properties of ethylene methyl acrylate copolymer, grade Elvaloy 1335 has been investigated. The copolymer was subjected to varying doses of electron beam radiation with different proportion of the sensitizer trimethylolpropane trimethacrylate (TMPTMA). It was observed that with increase in electron beam dose, the physicomechanical properties of the crosslinked copolymer improve, reaches an optimum level and subsequently deteriorates. The thermal properties as envisaged from thermogravimetric analysis and differential scanning calorimetric studies revealed stability of the crosslinked irradiated samples over that of the unirradiated ones. The thermal stability was also found to attain the maximum at the same level of radiation and sensitizer. The morphological studies showed consistency with the mechanical properties. Based on the overall study, it may be concluded that ethylene methyl acrylate copolymer with 1 phr TMPTMA at 60 kGy radiation dose is the optimum condition within the range studied in this investigation. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 75–83, 2010

Key words: electron beam radiation; crosslinking; physicomechanical properties; thermal properties

INTRODUCTION

Radiation-induced grafting and crosslinking are an advanced technique to modify a polymer without the aid of any curing agent. Radiation processing with electron beam is a modern development because of some of its unique advantages. Several authors have reviewed the radiation processing of polymers with electron beam. One investigation on electron beam curing of aliphatic unsaturated polyesters was carried out by Ebe and Sasaki.[1] The mechanistic study on converting to pressure-sensitive adhesive was carried out, and it was concluded that the pressure-sensitive adhesive nature of the electron beam-cured mixture of aliphatic unsaturated polyesters and *N*,*N*-diethylaminoethyl methacrylate could be attributed to the formation of flexible graft polymers entangled in a loosely crosslinked network. The grafting of styrene on commercially available fluoropolymer films by the preirradiation method has been investigated by Lappan et al.[2] Several studies on the effects of radiation on fluorocarbon elastomer were reported by Banik and Bhowmick.[3] It has been observed that with rise in radiation dose, an increase in degree of crosslinking results, which leads to an increase in modulus and T_g with a corresponding decrease in elongation at break, set properties, and tan δ. The thermal stability also improved on irradiation.[4] Radiation crosslinking of unplasticized polyvinyl chloride in the presence of additives revealed modification of the polymer.[5,6] The effect of electron beam radiation at various doses on EVA sensitized with varying percentages of trimethylolpropane trimethacrylate (TMPTMA) was reported by Datta et al.[7] The presence of residual unsaturation was found in irradiated pure TMPTMA. However, when used in blends, they observed that all unsaturation present in TMPTMA were used up to form the three-dimensional crosslinked network structure. A thorough study on the incorporation of TMPTMA and TAC on ethylene vinyl acetate copolymer was done by Chaki et al.[8]

Although a considerable quantity of investigation has been carried out on electron beam crosslinking of EVA, no such systematic work with ethylene methyl acrylate has been reported so far. Realizing the potential use of ethylene methyl acrylate copolymer, it is felt that there is enough scope to develop a new technology on the crosslinking of ethylene methyl acrylate based on electron beam radiation. It has been found that some polyfunctional monomers (sensitizer) especially acrylates and methacrylates

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are very useful to enhance the crosslinking reaction through electron beam radiation without much degradation of the polymer.[9] Therefore, it appears that studies on varying concentration of sensitizer will also be an interesting area from process engineering point of view.

In this study, Elvaloy 1335 has been selected as the base polymer, which is ethylene copolymer, containing 35% methyl acrylate, and with MFI 3. It was subjected to varying doses of radiation at different sensitizer level. The sensitizer used in this case was TMPTMA, and the results were analyzed with respect to their physicomechanical, thermal, and morphological properties. The influence of crosslinking induced by electron beam both in the presence and absence of sensitizer on the above properties has been studied, and henceforth, the radiation dose and sensitizer level have been optimized to achieve modified EMA copolymer having best possible physicomechanical properties.

EXPERIMENTAL

Materials

Elvaloy 1335 was supplied by M/s DuPont Specialty Elastomers, Belgium. An antioxidant, Irganox 1010 (hindered phenol type), was supplied by Ciba Specialty Chemicals, Switzerland, and TMPTMA was supplied by Sartomer Chemicals.

Preparation of samples

Hundred parts by weight of Elvaloy 1335 was mixed with 3 parts by weight of Irganox 1010 and a proportionate quantity of TMPTMA in a Haake Rheocord (Model Haake Rheocord system 40) at a temperature of 80°C. Elvaloy was first allowed to melt in the mixer followed by the antioxidant and TMPTMA. The mix so obtained was sheeted out through an open mill at 2 mm nip gap.

The sheets were then compression molded between aluminum foils at 110°C at a pressure of 140 kgf/cm^2 in an electrically heated press. Aluminum foils were used to reduce the shrink marks on the molded surface. The moldings were cooled under compression to maintain the overall dimensional stability of the samples.

Radiation

The molded Elvaloy samples in the form of rectangular sheets were radiated by an electron beam accelerator at Nicco Corp., Cable Division, Shyamnagar, India. Radiation doses of 30, 60, 90, 120, and 150 kGy were used. The formulations of the samples are given in Table I and specification of the electron beam accelerator in Table II.

TABLE I
Formulation of Samples

Elvaloy 1335 (parts by weight)	TMPTMA (parts by weight)	Radiation dose (kGy)	Sample code
100	0	0	E000
100	0	30	E003
100	0	60	E006
100	0	90	E009
100	0	120	E012
100	0	150	E015
100	1	0	E100
100	1	30	E103
100	1	60	E106
100	1	90	E109
100	1	120	E112
100	1	150	E115
100	2	0	E200
100	2	30	E203
100	2	60	E206
100	2	90	E209
100	2	120	E212
100	2	150	E215
100	3	0	E300
100	3	30	E303
100	3	60	E306
100	3	90	E309
100	3	120	E312
100	3	150	E315
100	4	0	E400
100	4	30	E403
100	4	60	E406
100	4	90	E409
100	4	120	E412
100	4	150	E415

Characterization

Physicomechanical properties

Tensile strength, elongation at break, and modulus at 100% elongation were measured on dumbbell specimens according to ASTM D 412 in a Zwick-1445 Universal Testing Machine at a strain rate of 50 mm/min at 27°C ± 2°C. The average was taken on four samples and the experimental error was ±5%.

The tear strength was measured on trouser-shaped specimen following ASTM D 412 in a Universal Testing machine model no. ZMGI-25. Hardness of the prepared samples was measured by Durometer on Shore A scale.

Estimation of gel content

An idea of the crosslink density of the samples was made by measuring the gel content in a Soxhlate apparatus using ethyl acetate as a solvent. Absolutely dry samples were subjected to fractionation for 72 h

TABLE II
Specification of Electron Beam Accelerator

Energy range (MeV)	1–3
Beam power (kW)	0.5–150
Beam energy spread (%)	50–99.9
Average current (mA)	0.5–50
Accelerating voltage frequency	100 kHz–0.1 MHz
Duration	Any number of passes
Pulse current (max)	50 mA
Pulse current (min)	0.5 mA
Power supply voltage (V)	440
Power supply voltage frequency (Hz)	50
Consumption of power (kW)	0.5–150
Manufacturer	RDI, USA
Model no.	369/3 MeV/50 mA/220 mm Dynamitron Oscillator Model 375

at 65°C and dried in an air oven at 80°C until a constant weight is obtained.

The initial weight of the sample is taken as W_1 and the final weight as W_2. The gel content is then approximated as $W_2/W_1 * 100$.

IR spectra

IR spectra were taken on sample sheets using Perkin–Elmer (model Paragon 1000 PC) spectrophotometer by attenuated total reflectance mode.

Thermal properties

Thermogravimetric analysis

The thermogravimetric measurements were carried out in a thermogravimetric analyzer, model no. TGA Q50 V6.1 within the temperature range of 27–600°C and at a heating rate of 10°C/min in an inert atmosphere of nitrogen.

Differential scanning calorimetry

The differential scanning calorimetric measurements were carried out on a DSC apparatus, model DSC Q100 V8.1, within the temperature range of −150 to +150°C. The rate of heating was maintained at 10°C/min.

Morphology

The morphological studies were carried out on a scanning electron microscope (model Jeol JSM-5800, Japan). The fractured surface of a tensile fracture specimen was inspected for morphology. The scale of magnification was 500×.

RESULTS AND DISCUSSION

Physicomechanical properties

Figure 1 shows the variation of tensile strength with changes in electron beam radiation dose. It is evident that with sensitizer level as parameter, the tensile strength of the samples increases sharply for all sensitized levels reaching a maximum at 1 phr TMPTMA level and 60 kGy radiation dose (E106). It is interesting to note that for samples with 1 phr TMPTMA level, the maximum tensile strength is obtained at 60 kGy radiation dose, whereas the samples with higher sensitizer level show their maximum tensile strength at comparatively low radiation dose. As the present optimization involves two parameter system namely radiation dose and sensitizer level, on a closer examination it reveals that the magnitude of increase in tensile strength in case of 1 phr TMPTMA level is appreciably higher compared with other counterparts. Thus, even at the expense of a slight increase in radiation dose from the optimization point of view, samples with 1 phr TMPTMA level with 60 kGy radiation dose may be recommended as most acceptable combination. It is needless to mention that system without sensitizer attains the maximum tensile strength at a much higher radiation dose of 90 kGy.

Figure 2 represents the changes in elongation at break with variation in electron beam radiation dose. As expected, with increase in radiation dose, a steady fall in percent elongation of all the samples irrespective of sensitizer level is exhibited.

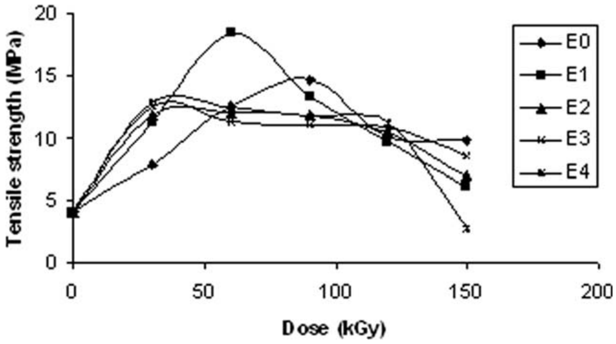


Figure 1 Variation of tensile strength with radiation dose.

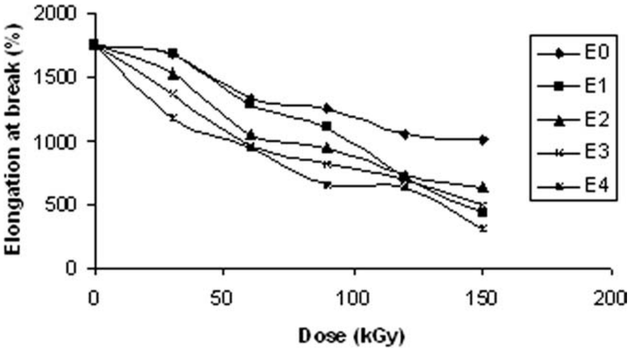


Figure 2 Variation of elongation at break with radiation dose.

Figure 3 represents the changes in modulus with electron beam radiation dose. In all the cases, a continuous rise in magnitude is observed with increase in radiation dose. This case therefore does not show any abnormality from the conventional systems, where tensile strength at 100% elongation always increases with increase of radiation dose.

Postulation of reaction schemes

The increase in tensile strength up to the optimum limit with variation in radiation dose may be attributed to the crosslinking of the polymeric chains and formation of a large network structure.[10] Electron beam when incident over the material under study knocks off electrons and generates ions or free radicals, a phenomenon called ionizing radiation. These radicals generated, react with TMPTMA present in the system by a mechanism, which can be postulated as shown in Scheme 1.

When electron beam is incident over ethylene methyl acrylate polymer molecules, the base polymer can interact among themselves to produce a crosslinked giant structure, which may be postulated as shown in Scheme 2.

These two crosslinking reactions (Schemes 1 and 2) simultaneously contribute to the rise in gel content and hence the crosslink density as evidenced from Figure 4. It is to be noted that the samples without any sensitizer, increase of gel content is much slower compared with sensitized systems.

The modulus and tensile strength at a given elongation of a cured sample are proportional to the

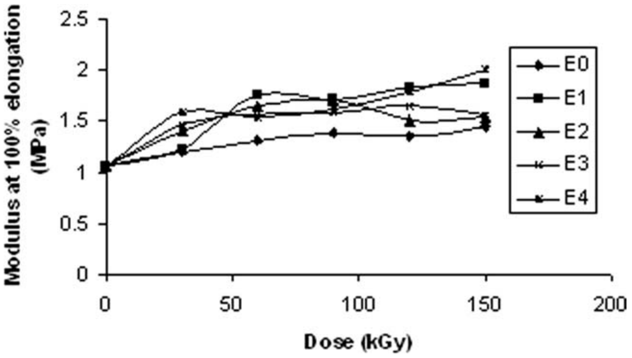
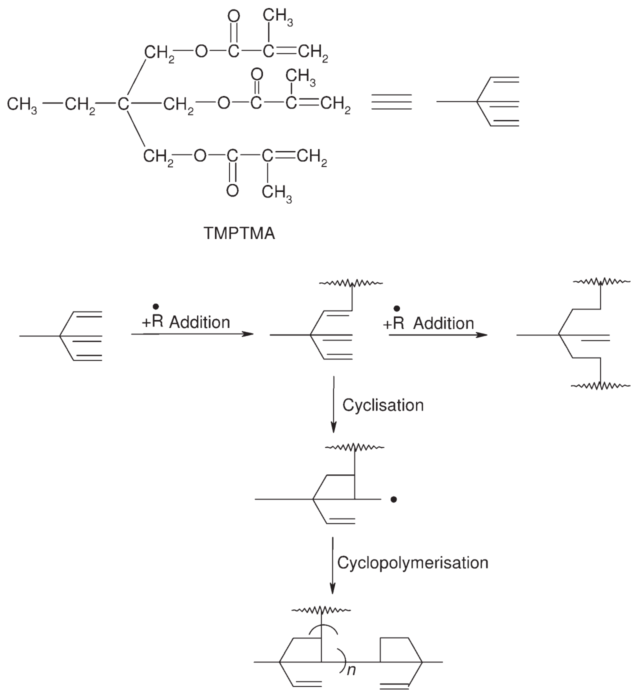
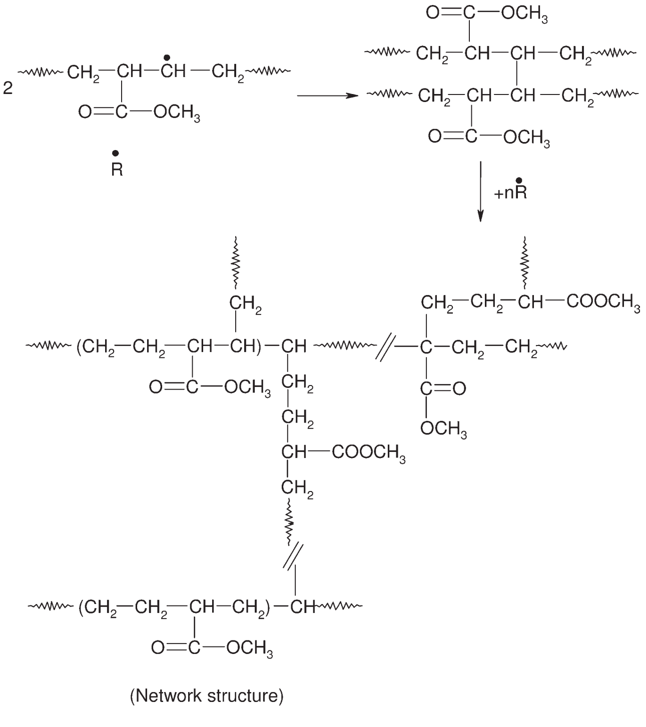


Figure 3 Variation of modulus at 100% elongation with radiation dose.



Scheme 1 Crosslinking by TMPTMA.



Scheme 2 Self-crosslinking of ethylene methyl acrylate and network formation.

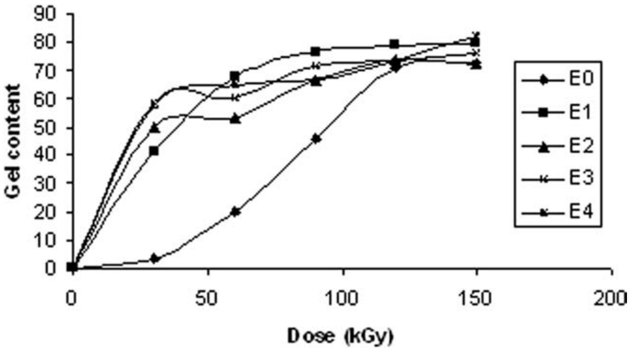


Figure 4 Variation of gel content with radiation dose.

number of crosslinks formed. As the radiation dose increases, the crosslink density increases. Tensile strength, being a function of crosslink density, rises until an optimum level of sensitizer and radiation is reached in all the cases of sensitized and unsensitized samples.[11] Beyond the optimum level of radiation, the tensile strength decreases in all the cases. This is attributable to the process of chain scission, which comes into play at higher crosslink densities as can be depicted in Scheme 3.[12]

Tensile strength and elongation at break depend on the degree of strain-induced crystallization, which in turn depends on the polymer chain length and the degree of crosslinking. Generally, it is found that larger polymer chains can exhibit higher strain-induced crystallization and better strength properties compared with shorter ones. Crosslinking of the polymer chains reduces the tendency of chain slippage during straining. This contributes to a rise in tensile strength up to a certain level. Beyond the optimum point, the decrease in chain length due to chain scission leads to a decrease in tensile strength. The modulus, on the other hand, more strongly depends on the crosslink density and is found to increase with increase in the degree of crosslinking.

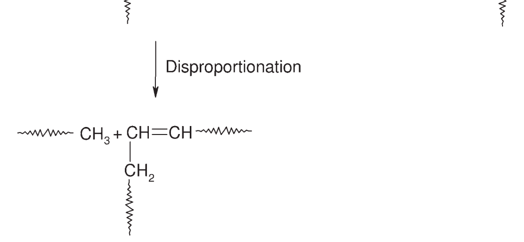
The gradual decrease in percent elongation at break may be attributed to the gradual formation of more and more stiff, hard crosslinks within the polymer matrix with increasing radiation dose (also exhibited in the curve of rising gel content), which consequently reduces the possibility of chain slippage. At the higher radiation dose, when crosslink density is high, decoiling of the polymer chains is prevented even on application of more load, resulting in brittle fracture, which is depicted by the continuous fall in elongation over the entire range of radiation.

I. R study

Figure 5 shows the normalized ATR spectra of E000 to E115 in the region of 2000–600 cm^{-1}. A range of 0–150 kGy irradiation has been considered under investigation. The curve of E000 (pure ethylene methyl acrylate) shows a peak at 1734 cm^{-1}, which may be attributed to the carbonyl stretching of the ester group. This peak is, however, present in all the cases from E000 to E115. As per agreement with literature values,[13] the peak values around 1592 cm^{-1} may be attributed to the stretching vibration of $>C{=}C<$ conjugated with $>C{=}O$ of the methacrylate group in TMPTMA. As the radiation dose increases, a distinct diminution of this peak from 30 to 60 kGy is observed (E103 and E106). Again from 120 to 150 kGy (E112 to E115), the peak starts developing. In the first instance, the diminution of 1592 cm^{-1} peak probably corresponds to the consumption of trans-vinylene group of TMPTMA either through grafting or crosslinking reaction. At 60 kGy dose, the near flattening of the peak indicates a significant consumption of vinylene group in the above process. In this context, Nethsinghe and Gilbert[14] also reported that there was no such peak corresponding to unsaturation when PVC was modified with TMPTMA.

Reappearance of the peak beyond 90 kGy (i.e., 90, 120, and 150 kGy) is a significant observation, which may be explained by the following hypothesis. At lower radiation dose (30–60 kGy), the electron density is lower. At higher electron density (free electrons being highly unstable), there is a substantial surge in free radical generation at the vinylene group of TMPTMA. These activated sites may react to produce either homopolymerization of methacrylate moiety of TMPTMA, its cyclization, grafting or crosslinking in the polymer main chain.

The substrate of the sensitizer becomes sterically hindered and immobile because of the bulky nature of reacted TMPTMA, which prevents them from getting involved in any further crosslinking or grafting reaction. If the linear homopolymerization of



Scheme 3 Termination reaction by combination and disproportionation.

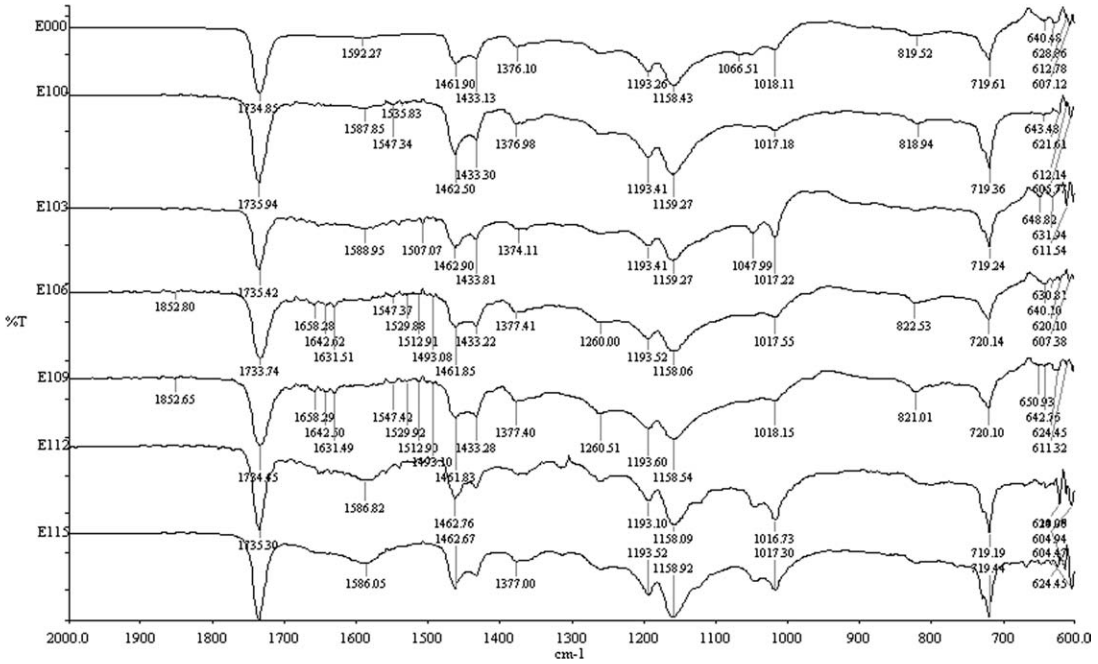
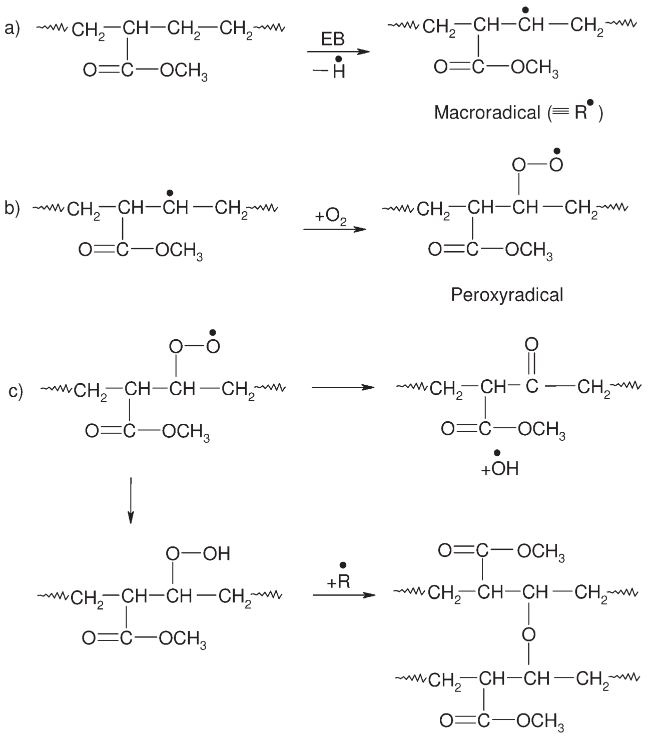


Figure 5 ATR of unsensitized and sensitized samples.

TMPTMA predominates and gets immobile, then there may be a substantial quantity of free vinylene group remaining unreacted in the system, which leads to an increase in the peak intensity of 1592 cm^{-1}. The self-crosslinking of the base polymer also becomes predominant at higher radiation dose, and it may be inferred that from 90 kGy onward, a situation arises where the possibilities of unreacted vinylene group concentration increases. The peak around 1433 cm^{-1} corresponds to the asymmetric bending of $-CH_2$ group, 1376 cm^{-1} due to $-C-H$ bending of CH_3, 1193 cm^{-1} due to $-C-O-C-$ asymmetric stretching of saturated aliphatic ester, 1159 cm^{-1} due to $-C-O-$ stretching of the esters, and 1018 cm^{-1} due to ether linkage. The formation of ether linkage is indicative of some oxidation reaction taking place because of aerial oxygen and producing a peroxyradical, the reaction of which has been depicted in Scheme 4.

The trend of changes in the tensile properties is also reflected in their tear strength and hardness values as shown in Figures 6 and 7, respectively. The tear strength exhibits a steady decrease, which is a measure of increasing brittleness with rise in crosslink density. The hardness, a surface phenomenon,



Scheme 4 Oxidation by aerial oxygen.

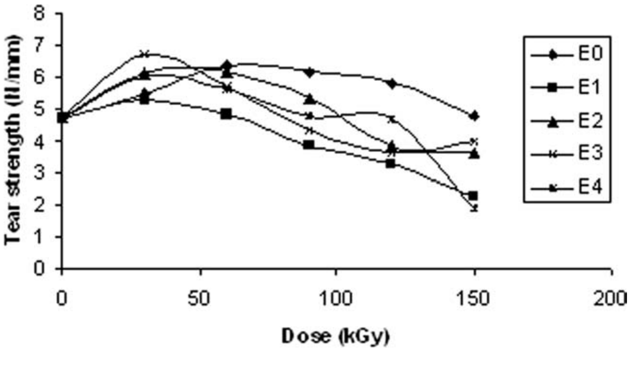


Figure 6 Variation of tear strength with radiation dose.

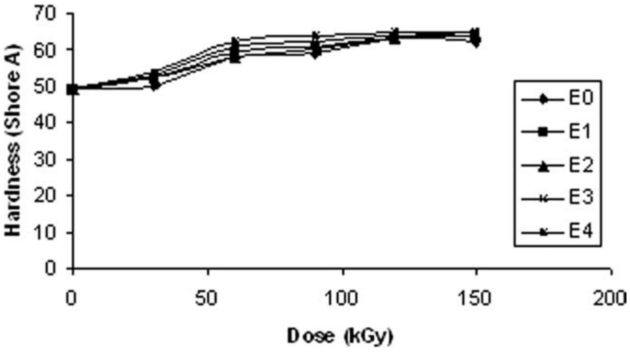


Figure 7 Variation of hardness with radiation dose.

increases marginally over the entire range of radiation studied.

Thermal properties

The thermogravimetric curves of Elvaloy 1335 and its series with 1 phr TMPTMA at different doses of radiation have been shown in Figure 8. It has been observed that Elvaloy 1335 becomes increasingly stable as the radiation dose increases, which bears a direct proportionality with the rise in gel content which is again a measure of crosslink density. The onset of degradation rises on going from E000 to E115 owing to the increased degree of crosslinking thus producing a large network structure. As the crosslink density of the samples increases, the ability to withstand thermal degradation also increases because of the crosslinked network structure. The peak temperature as envisaged from the DTG curves also exhibits ascending order of temperature, which is again indicative of the thermal stability. However, the rise is marginal at higher radiation doses (Table III).[15]

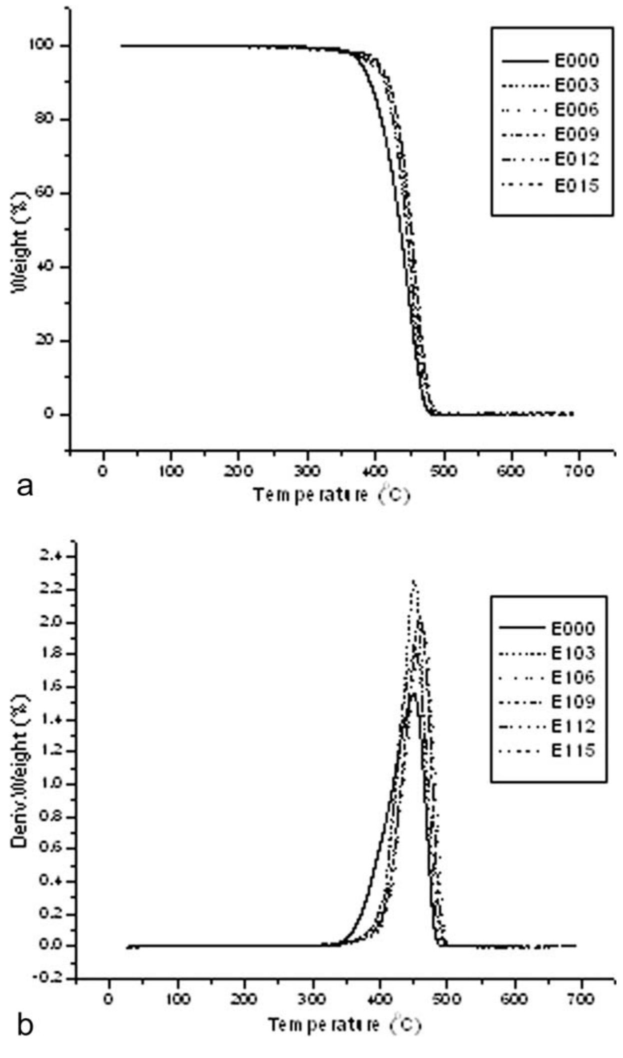


Figure 8 (a) TGA curves at 1 phr TMPTMA incorporation. (b) DTG curves at 1 phr TMPTMA incorporation.

TABLE III
Onset Temperature of Degradation and Peak Temperature

Code	T_{onset} (°C)	$T_{\max}$ (°C)
E000	350	443
E103	365	450
E106	369	453
E109	369	455
E112	375	456
E115	377	459

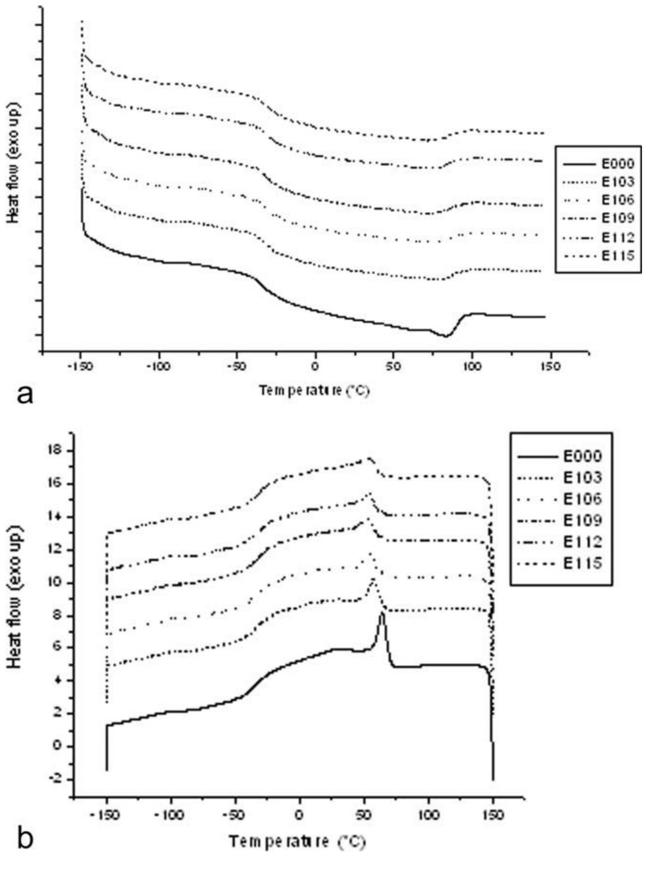


Figure 9 (a) DSC heating curves at 1 phr TMPTMA incorporation. (b) DSC cooling curves at 1 phr TMPTMA incorporation.

TABLE IV
Glass Transition, Crystallization, and Melting Temperature

Code	T_g	T_c	T_m
E000	−80	62	75
E103	−73	58	79
E106	−72	57	80
E109	−68	57	80
E112	−67	54	81
E115	−67	54	82

The differential scanning calorimetric curves, based on constant 1 phr TMPTMA level as shown in Figure 9, exhibit a gradual rise in glass transition temperature with rise in radiation dose. The shift in T_g from −80 to −67°C shows the effect of crosslinking from E000 to E115 (Table IV). As observed from the cooling curves, the crystallization temperature shows a gradual decrease with rising radiation dose from 62 to 54°C for E000 to E115. This may be attributed to the fact that higher crosslinked structures have lesser tendency to crystallize because of restricted mobility to fit into crystal lattice when cooled from the temperature higher than the crystalline melting point (T_m).[16] As E000 is thermoplastic in nature, it shows a sharp and comparatively narrow crystalline melting point but with the commencement of crosslinking (E103 to E115), the peak broadens and represents a transition on account of development of their insoluble and infusible characteristics.

Morphology

The scanning electron micrographs of Elvaloy 1335 in its native state, in association with 1 phr

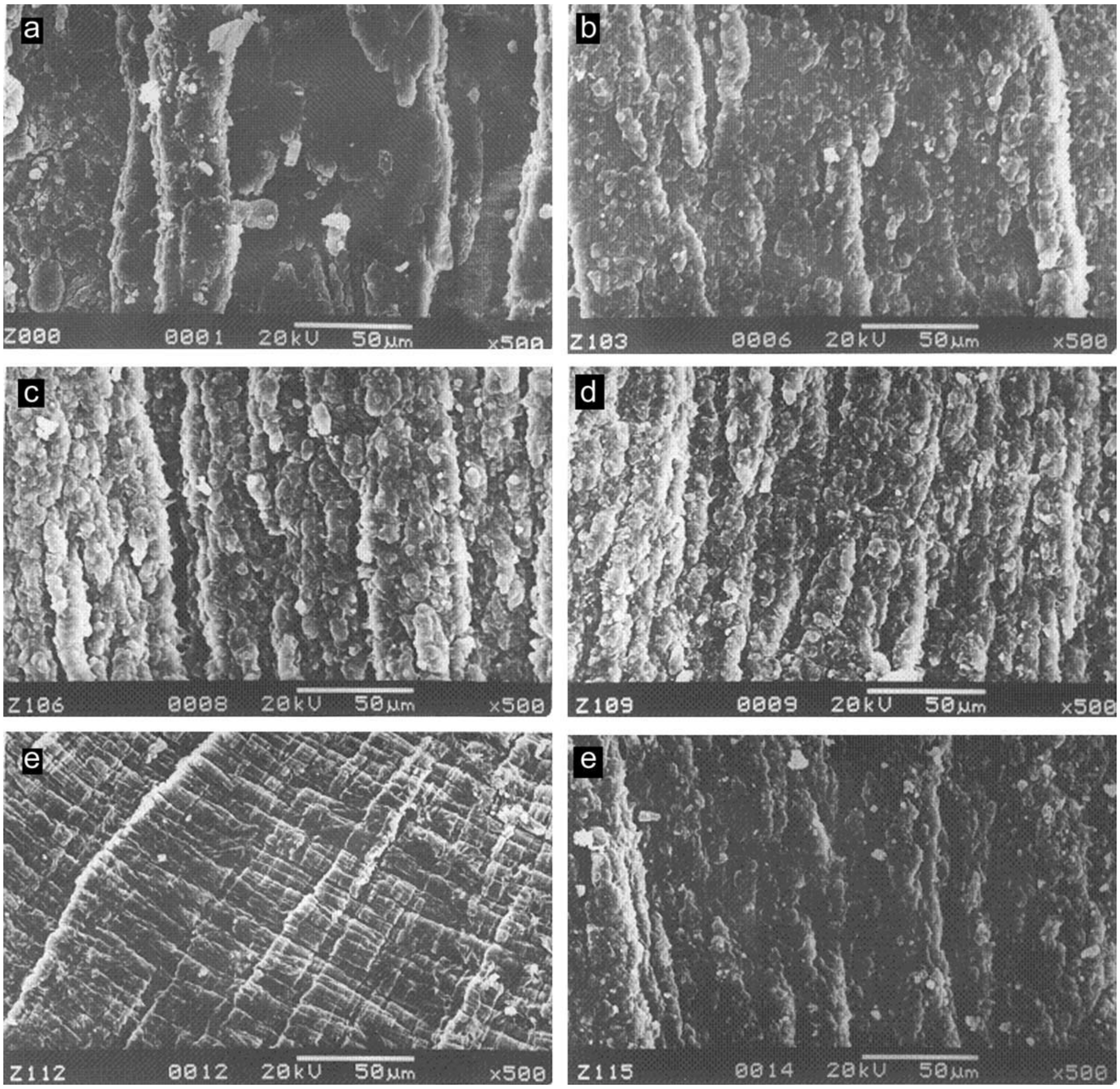


Figure 10 Scanning electron micrographs of unsensitized and sensitized samples with varying radiation dose.

TMPTMA used as sensitizer and at different doses of radiation, have been carried out as shown in Figure 10(a–f). The copolymer of ethylene and methyl acrylate (35% comonomer content) exists in two phases. One is the ethylene-rich crystalline phase, manifested as the dark phase, and the other is the methyl acrylate-rich amorphous phase, manifested as the bright phase. The methacrylate-rich amorphous phase is distributed in different dimensions within the crystalline phase with the smaller ones appearing to be dissolved in it so as to produce diffusing interfaces. The amorphous phases (particularly those of relatively larger dimensions) are more or less arranged in a linear fashion.

Because of polar and bulky structure, the sensitizer mixes predominantly more with the methacrylate-rich amorphous phase and tends to swell the same. However, the amorphous phase is somewhat disintegrated and redistributes itself. At 30 kGy of radiation, the methacrylate phase appears to be crosslinked relatively faster than the ethylene-rich phase as the sensitizer is compatibilized primarily with this. The TMPTMA initiates the crosslinking process in the methacrylate-rich phase and later propagates it through the crystalline one. This crosslinking process forms frequent covalent linkages between the crystalline and amorphous phases and thus improves the compatibility further as is envisaged by the generation of more and more diffused interfacial regions leading to homogenization and improved properties.[17] On increasing the radiation dose, the covalent bridge formation between the phase increases, and hence the homogenization and properties improve further. As we reach higher doses of radiation, the continuity of the process appears to be disturbed. The crosslinking process is an equilibrium reaction between interchain crosslinking (interphases or intraphases) and random chain scission. In this case, it is evident that equilibrium has been reached at an optimum radiation dose of 60 kGy. At higher dose, chain scission and embrittlement of the phases occur as shown by the discontinuity and kink formation resulting in lowering of property as observed.

CONCLUSIONS

The behavior of electron beam-crosslinked ethylene methyl acrylate copolymer, Elvaloy 1335 with 35% methyl acrylate content, reveals optimization with respect to its engineering properties at 1 phr of sensitizer and 60 kGy radiation dose. Four different schemes have been proposed to explain the structural modification behavior. The engineering properties found to be influenced by the rise in gel content and subsequently by the crosslink density. The elongation at break and tear strength of the samples bear a direct proportionality and exhibit a continuous decrease with increase in the radiation dose. On the other hand, the thermal properties exhibit stabilization over unmodified base reference compound. This is subsequently supported by consistent changes in morphology.

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