Electron Beam Irradiation of Ethylene-propylene Terpolymer: Evaluation of Trimethylol Propane Trimethacrylate as a Crosslink Promoter

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ABSTRACT: The effect of electron beam irradiation on ethylene-propylene terpolymer (EPDM) was investigated. A 50-part oil-extended EPDM with high termonomer (ENB) content (iodine number of base polymer) 19, was selected for this study. An increase in irradiation dose from 0 to 200 kGy resulted in increased crosslinking, measured by an increase in gel contents and better swelling resistance. The effect of the multifunctional monomer trimethylol propane trimethacrylate (TMPTMA) as a crosslink promoter was studied using IR spectroscopy. The IR studies revealed enhanced peak absorbances at 1725, 1257, and 1023 cm^{-1} as a result of the increased concentration of C = O and C-O-C groups and reduced absorbance at 1630 cm^{-1} due decreased concentration of C = C groups with TMPTMA level in the irradiated samples. The presence of TMPTMA increased the level of crosslinking at a given irradiation dose, which was manifested by improvement in tensile properties. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 968–975, 2005

Key words: crosslinking; electron beam irradiation; EPDM; gels; trimethylol propane trimethacrylate

INTRODUCTION

Radiation processing of thermoplastic elastomeric systems based on rubber–plastic blends has attracted interest in the past. Spenadel and colleagues[1,2] studied radiation-induced crosslinking in thermoplastic elastomers based on ethylene-propylene rubber (EPDM) and polyethylene (PE) or polypropylene (PP) plastics. Van Gisbergen et al.[3] described the morphology fixation of dispersed EPDM phase in a PP matrix via electron beam irradiation. Recently Zaharescu et al.[4] reported on gamma processing of EPDM–PP blends.

Organic polymers can be characterized according to their response to high energy radiation.[5,6] One group consists of polymers like EPDM[7] that show predominant crosslinking, whereas the other group, which includes polymers like PP, predominantly undergoes degradation through molecular chain scission. However, these responses of polymeric materials to high energy radiations can be manipulated with additives like crosslink promoters and chain scission sensitizers. Various multifunctional monomers like triallyl cyanurate (TAC),[8] trimethylol propane triacrylate,[9] and trimethylol propane trimethacrylate (TMPTMA)[10–12] have been used as crosslink promoters in electron beam induced crosslinking of polymers. In this article we report on the effect of electron beam irradiation on a particular grade of EPDM selected for our future studies on radiation processing of rubber–plastic blends, over a range of radiation doses, and to evaluate the efficiency of the crosslink promoter TMPTMA by monitoring the development of gel, swelling behavior, and physical properties and correlating the same with radiation dose and TMPTMA levels.

EXPERIMENTAL

Materials

EPDM (EP 96) of ML(1 + 8) at 120°C, 53; ethylene content, 73%; paraffinic oil extension, 50 part; termonomer ENB content (iodine number of base polymer), 19; was supplied by JSR, Japan. TMPTMA was generously donated by Sartomer, Inc.

Preparation of samples

EPDM was mixed along with TMPTMA and a small amount of DCP (0.2% wt.) in a Brabender Plasticorder, PL2207 for 5 min at 40°C and 60 rpm rotor speed. The mixed samples were then compression molded to rectangular sheets of 1-mm thickness at 125°C for 5 min. The small amount of the added peroxide resulted in smooth sheets of uniform thicknesses. The molded specimens containing 0, 2, 4, 6, and 8 parts of TMPTMA were subjected to electron beam irradiation

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TABLE I
Peak Assignments in HATR Spectra of Irradiated Samples

Observed peak (cm^{-1})	Peak assignment
1725	C═O stretch
1630	C═C stretch
1460	CH_2 scissor
1375	CH_3 stretch
1257	Asymmetric C—O—C stretch
1120	Asymmetric C—O—C stretch
1023	Asymmetric C—O—C stretch

of 20, 40, 80, 120, and 200 kGy in air at the Bhabha Atomic Research Centre (Mumbai), with electron energy 2 MeV.

Measurements

Horizontal attenuated total reflection (HATR) spectroscopy. IR-HATR spectra of the samples were taken using a Perkin–Elmer Paragon 1000 Model spectrophotometer in the HATR mode.

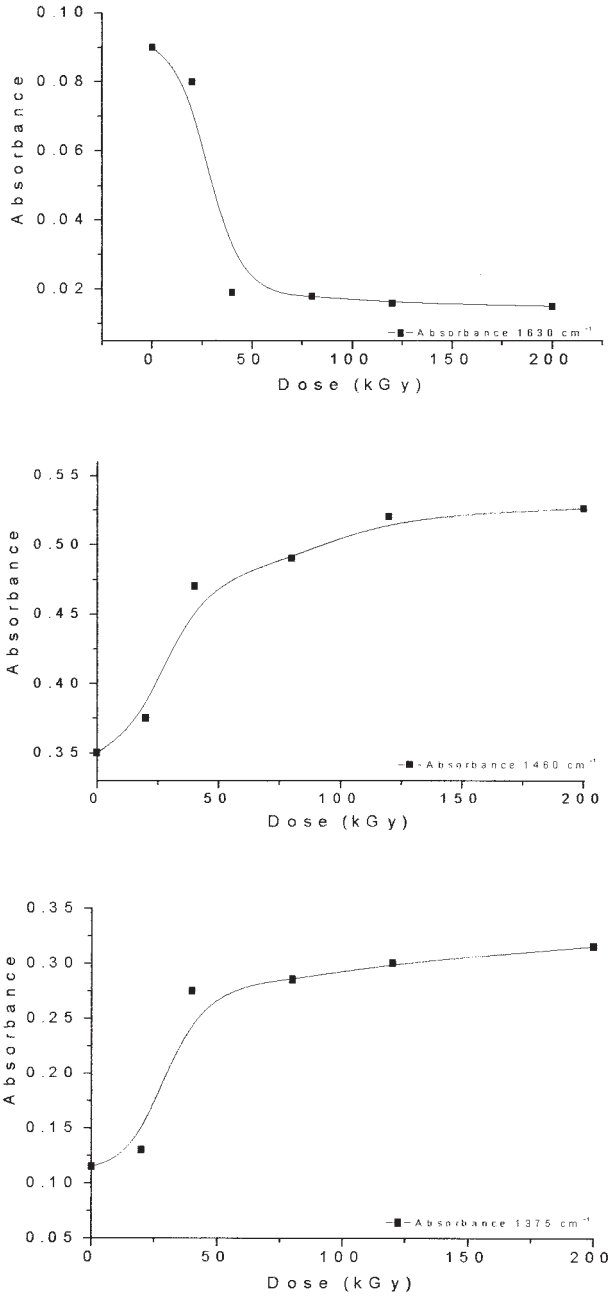
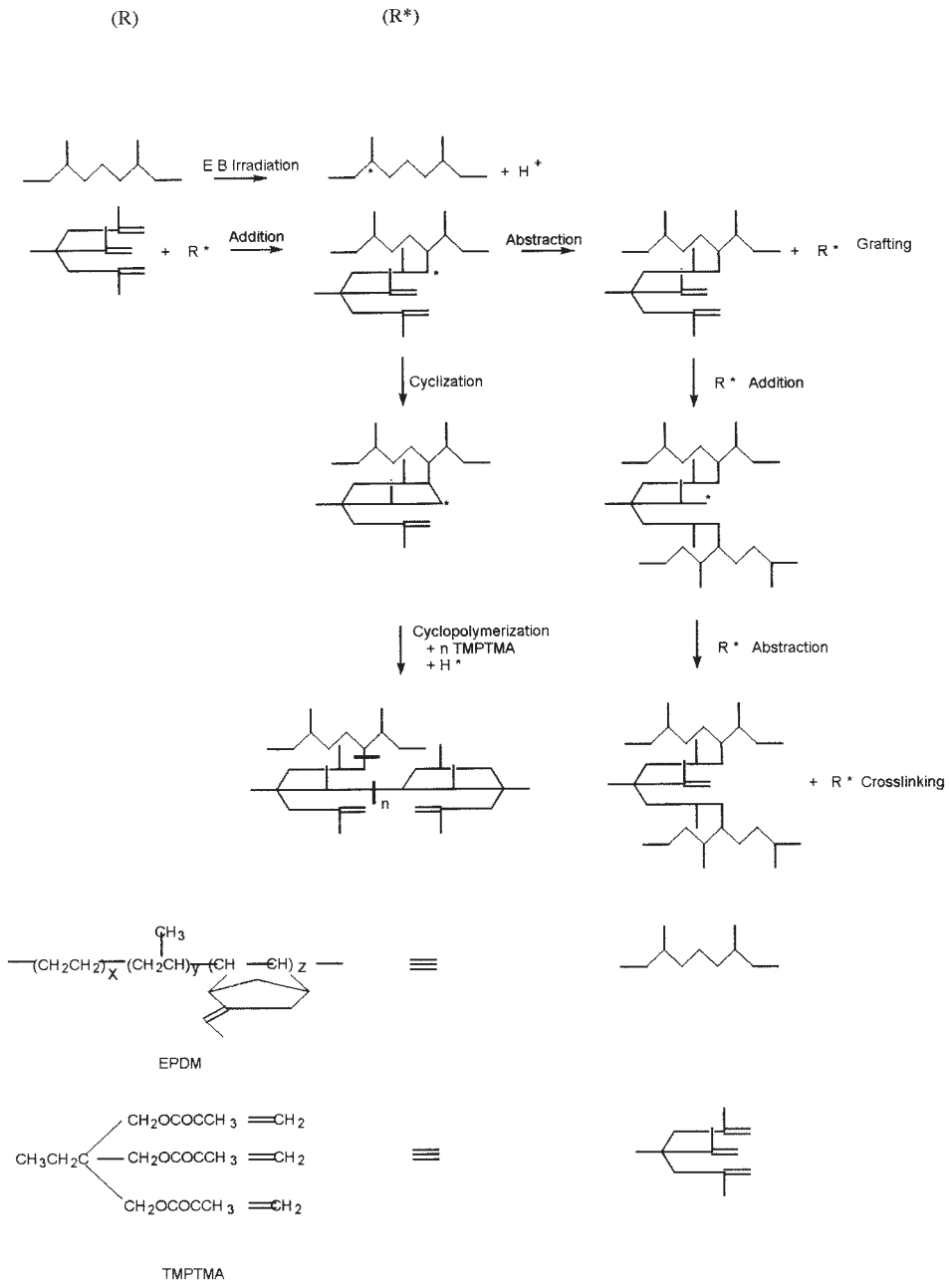


Figure 1 Variation in absorbances at (a) 1630 cm^{-1}, (b) 1430 cm^{-1}, and (c) 1375 cm^{-1} with radiation dose (0–200 kGy).



Scheme 1 Plausible mechanism of TMPTMA promoted crosslinking of EPDM.

Gel content. The gel content of the irradiated samples was evaluated using a Soxhlet extraction procedure in boiling *o*-xylene for 24 h. Duplicate samples were used to assess the gel content.

Swelling studies. The swelling behavior of the samples was investigated using the standard ASTM procedure in ASTM oil 3 for 72 h at 70°C.

Mechanical properties. The tensile strength and the elongation at break of the irradiated samples were measured at a strain rate of 500 mm/min using dumbbells punched out of the irradiated sheets. Tension set values of dumbbells with 50% strain were reported after an aging period of 24 h at 125°C.

RESULTS AND DISCUSSION

IR study

The IR-HATR spectra were taken for specimens containing 0 to 8 parts TMPTMA. The main peaks in the spectra were observed at 1725, 1630, 1460, 1375, 1257, 1120, and 1023 cm^{-1}. Their assignments are listed in Table I. Figure 1 shows the peak absorbances of the specimens with 8 parts TMPTMA irradiated with 0, 20, 40, 80, 120, and 200 kGy dose. The absorbance at 1630 cm^{-1} due to C = C stretching vibration dropped sharply up to 40 kGy, probably due to depletion of the C = C bonds during crosslink formation and grafting

TABLE II
Gel Content and Volume Swell in the Irradiated Samples

Sample	% Gel	% Volume swell
E0/0	12	—
E0/20	30.7	—
E0/40	45	800
E0/80	47.5	543
E0/120	49.4	489
E0/200	55.3	386
E2/0	15	833
E2/20	43.5	578
E2/40	52.6	503
E2/80	55.7	380
E2/120	57.02	364
E2/200	60.5	332.5
E4/0	16	756
E4/20	49.7	552
E4/40	55.7	455
E4/80	59.02	363
E4/120	61.9	331
E4/200	63.7	299
E6/0	18	624
E6/20	50.1	443
E6/40	57	371
E6/80	61	340
E6/120	62	285
E6/200	64	270
E8/0	18	575
E8/20	51	378
E8/40	57	350
E8/80	62.5	290
E8/120	62.5	215
E8/200	65	175

Note. The samples are designated as EX/Y, where X and Y indicate the multifunctional monomer level in percentages and radiation dose in kGy, respectively.

compared to those generated during molecular chain scission and disproportionation reactions in EPDM (Scheme 1). However, above 40 kGy the substantial increase in the rate of molecular chain scission and disproportionation reactions compared to that of consumption of the C = C bonds in crosslink formation made the absorbance value almost constant. The absorbances at 1460 and 1375 cm^{-1} due to $–CH_2–$ scissor vibration and $–CH_3$ stretching vibration, respectively, increased sharply up to 40 kGy, probably due to enhanced grafting and crosslinking reactions in EPDM promoted by TMPTMA, and also manifested by the increase in gel contents with irradiation (Table II). Figure 2 shows the peak absorbances against the concentration of TMPTMA for specimens irradiated at 80 kGy at 1725, 1257, and 1023 cm^{-1}. The absorbances increased with the increase in TMPTMA concentration. During irradiation the large number of free radicals generated on the EPDM molecules, being highly reactive, scavenged oxygen, resulting in the generation of carboxyl and ether functionalities in the EPDM. This also resulted in simultaneous crosslinking and molecular chain scission in the rubber (Scheme 1). Figure 3 shows the peak absorbance ratios of TMPTMA against that at 1460 cm^{-1} plotted against radiation dose. Initially the 1630 cm^{-1}/1460 cm^{-1} absorbance ratio decreased with dose before attaining almost constant values. With irradiation a large number of radicals were also generated on TMPTMA, which underwent polymerization, cyclopolymerization, crosslinking, and cyclization, particularly at higher concentration as shown in Scheme 2. These reactions led to the consumption of *trans*-vinylene bond in TMPTMA, resulting in the reduction of 1630 cm^{-1}/1460 cm^{-1} absorbance ratio. However, the 1725 cm^{-1}/1460 cm^{-1} absorbance ratio as given in Figure 3 remained constant with radiation dose as the carbonyl groups in TMPTMA had no role in these reactions. With increase in TMPTMA concentration from 0 to 8%, the concentration of the active radicals also increased resulting in increased grafting, crosslinking, and higher gel contents.

Development of gel in irradiated systems

The competing crosslinking and scission reactions at given TMPTMA and dose levels primarily determined the level of gels in the irradiated systems. Up to 200 kGy, the gel contents registered a monotonous increase. However, as the TMPTMA levels were raised to 2 parts, the amount of gel at a given dose level sharply increased, probably due to crosslink promotion by TMPTMA. With the increase in the concentration of TMPTMA, the concentration of active radicals also increased; leading to enhanced crosslinking and greater gel content in EPDM. Scheme 1 depicts a plausible mechanism for crosslink promotion in EPDM by TMPTMA. Table II lists the gel values. With increased concentration of TMPTMA above 2 parts, the gel contents also increased. However, the development of gels slowed down above 4 parts TMPTMA. The maximum gel content of 65% wt attained at 200 kGy with EPDM containing 8 parts of TMPTMA was the maximum attainable gel in this grade of EPDM rubber, with 50 parts paraffinic oil extension. The swelling resistances also improved with irradiation and with increased concentration of TMPTMA due to enhanced crosslink generation.

Effect of irradiation on mechanical properties

Mechanical properties of the irradiated sheets are shown in Figure 4. At a given level of TMPTMA, the tensile strengths increased up to 20 kGy dose of irradiation followed by a drop at higher levels due to the predominating effect of chain scission reactions. Datta et al.[13] had reported similar crosslink promotion with TMPTMA in EVA, more so in higher vinyl acetate-

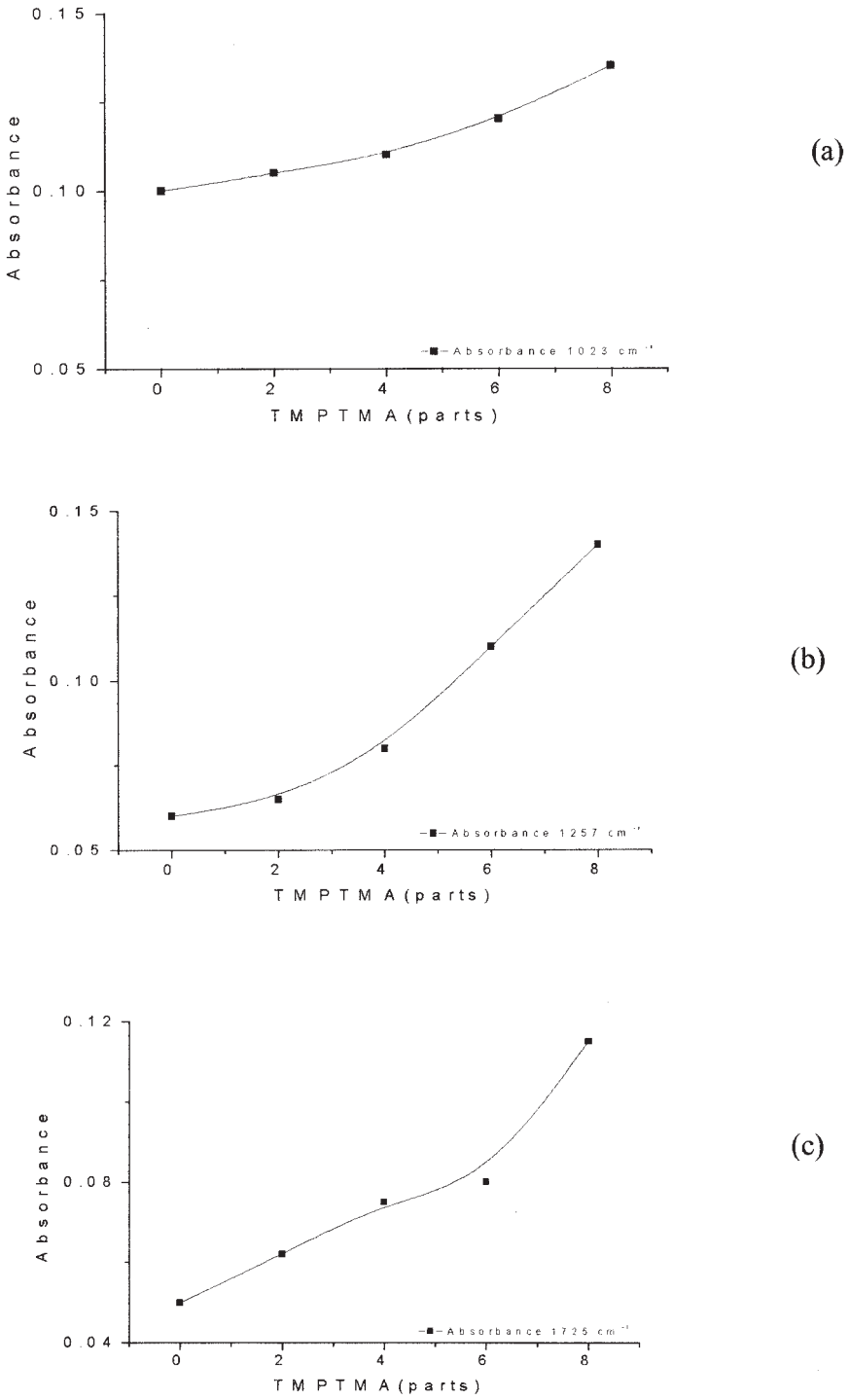


Figure 2 Variation in absorbances at (a) 1023 cm^{-1}, (b) 1257 cm^{-1}, and (c) 1725 cm^{-1} with concentration of TMPTMA (0–8 parts) at 80 kGy.

containing grades. However, in the irradiation of PE at a given dose, the tensile strength did not change markedly with TMPTMA wherein the crystallinity of the polymer had possibly hampered the efficiency of the monomer in crosslink promotion (Tikku et al.[10]).

In our samples the elongation at break values also dropped as the doses increased. Above 2 parts; TMPTMA resulted in decreased tensile values. This was probably due to a reduced efficiency of TMPTMA in crosslink promotion above a concentration of 2 parts, as it probably engaged in other side reactions[9] at a given radiation dose (Scheme 2). Figure 4c shows the variation in tension set values, which decreased with radiation dose as a result of enhanced crosslinking. However, above a TMPTMA concentration of 2 parts, the set properties started to deteriorate. A similar

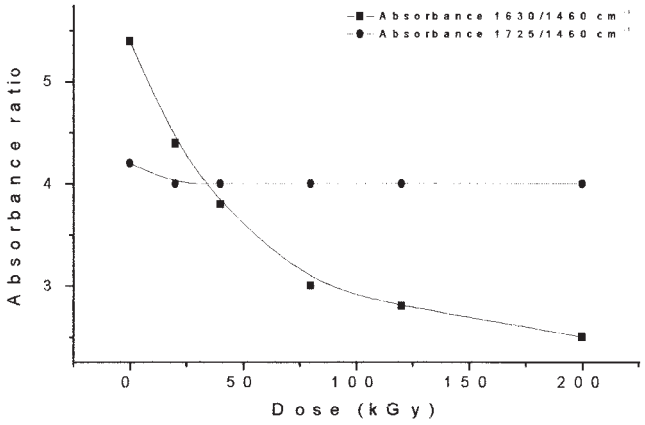
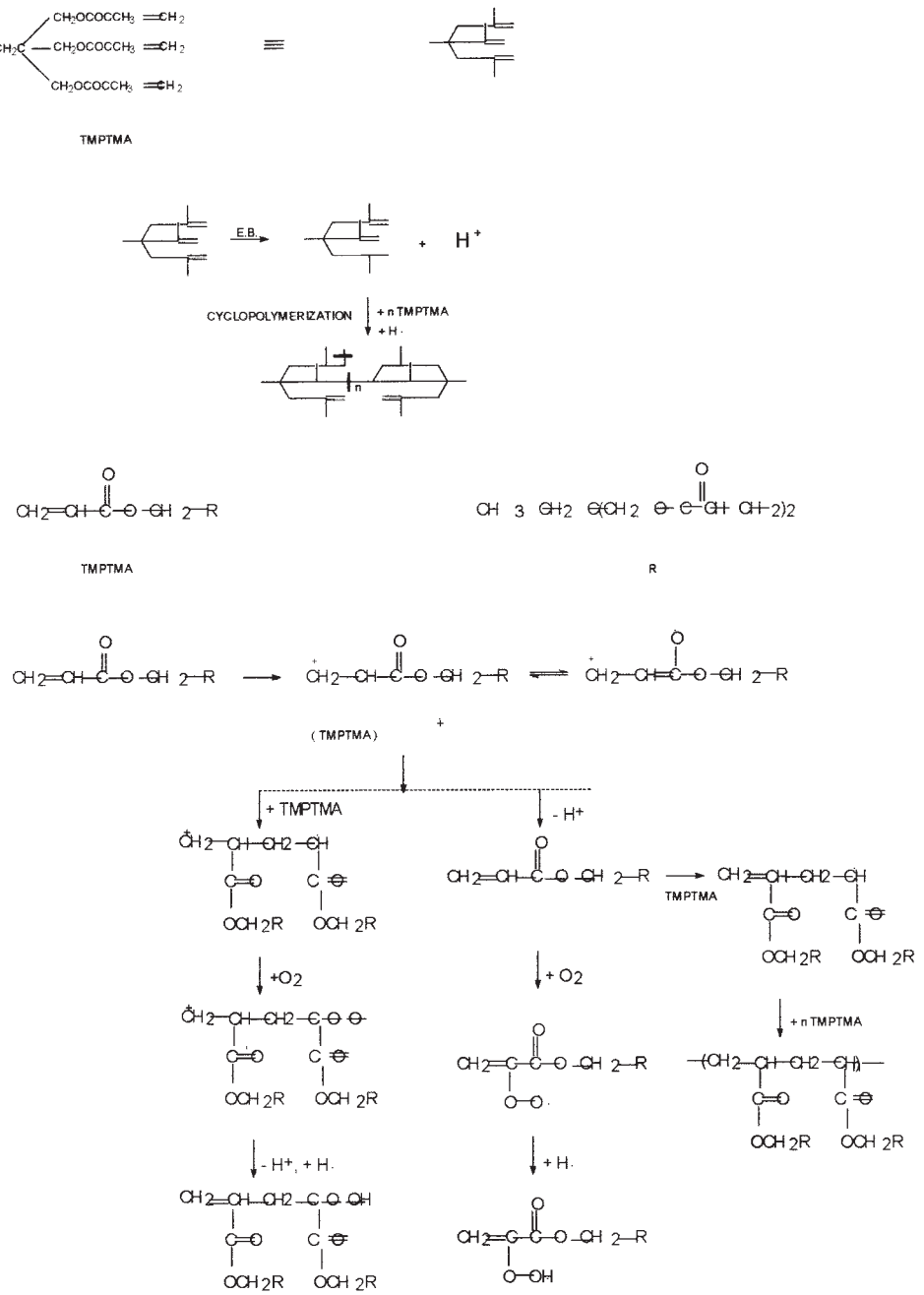


Figure 3 Variation in absorbances of TMPTMA with radiation dose (0–200 kGy).

trend was observed in the strength properties of the irradiated samples. At higher concentrations the efficiency of TMPTMA in crosslink promotion decreased on account of side reactions (Scheme 2), resulting in reduced crosslink densities in the irradiated specimens accounting for the deterioration in tensile and set properties.

CONCLUSIONS

The effect of electron beam irradiation on an oil-extended EPDM has been investigated in the presence of trifunctional monomer TMPTMA. EPDM gets



Scheme 2 Plausible mechanism of side reactions of TMPTMA at higher concentrations.

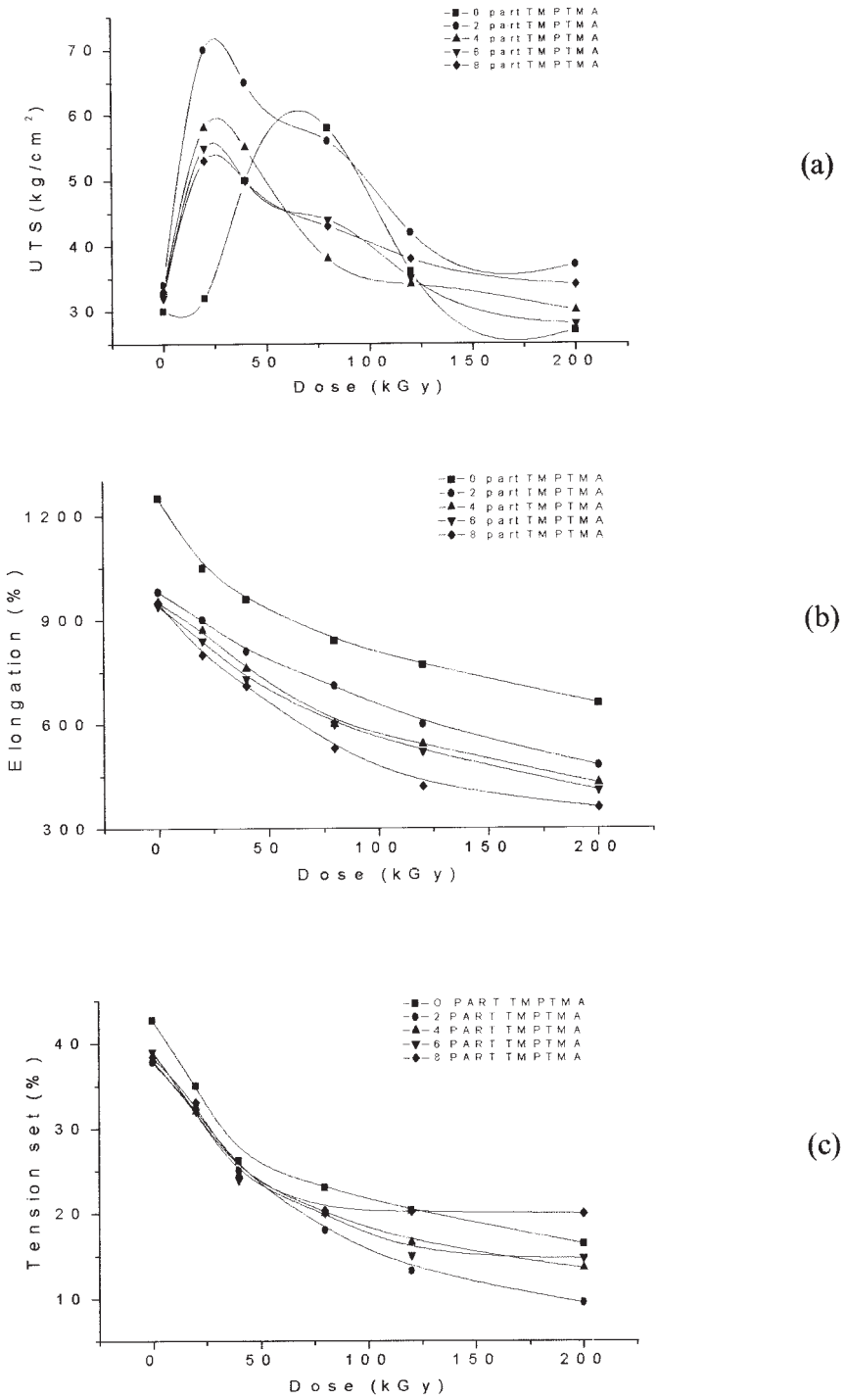


Figure 4 Change in (a) tensile strength, (b) elongation, and (c) tension set with radiation dose (0–200 kGy) and concentration of TMPTMA (0–8 parts).

crosslinked when it is exposed to electron beam. Efficient crosslinking of the elastomer has been possible by crosslink promotion through TMPTMA, whereby the former gets almost 100% crosslinked at about 200 kGy dose with 8 parts of TMPTMA in comparison to the almost 1000 kGy required for the development of equivalent amount of gel in the particular grade of EPDM used in this study in the absence of the crosslink promoter. This is in agreement with Eldred,[7] who had reported a 90% decrease in curing dose using 15 parts of TMPTMA in EPDM. The lower efficiency of crosslink promotion reported in our study is most likely due to the reaction of the monomer with the extender oil in the EPDM used for this study. This could have reduced the amount of monomer available for crosslinking the elastomer. A second possible ex-

planation could be that the extender oil could have simply acted as a diluent, lowering the effective TMPTMA concentration, thereby reducing the rate of crosslinking.

In the presence of TMPTMA, the amount of active radicals increases during irradiation, thereby increasing the grafting of these trifunctional monomers onto the EPDM molecular chains. The mutual termination-by-combination reactions between the grafted monomer radical and an EPDM polymeric chain radical results in the generation of C-C crosslinks. However, with further increase in TMPTMA concentration, the efficiency in such crosslink promotion seems to drop, probably due to side reactions, resulting in reduced crosslink formation in EPDM. Thus, at high concentrations, TMPTMA seems to result in inferior tensile values in the irradiated samples.

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