

Structure–Property Relationship of Electron-Beam-Modified EPDM Rubber

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ABSTRACT: Electron-beam-initiated grafting of trimethylolpropane triacrylate (TMPTA) onto the bulk ethylene propylene diene monomer (EPDM) was carried out with varying concentrations of TMPTA at a constant irradiation dose of 100 kGy and over a wide range of irradiation doses (0–500 kGy) at a fixed concentration (10%) of TMPTA. The rubber was also modified in the bulk by tripropylene glycol diacrylate (TPGDA, 10%) and tetramethylol methane tetraacrylate (TMMT, 10%) at an irradiation dose of 100 kGy. The modified rubbers were characterized by IR spectroscopy, crosslinking density measurements, and mechanical, dynamic mechanical, and electrical properties. The IR studies indicated increased peak absorbances at 1730, 1260, and 1019 cm^{-1} due to increased >C=O and C—O—C concentrations up to certain levels of TMPTA and irradiation dose. These are accompanied by an increase in the crosslinking density. The tensile strength of the samples increases gradually with increasing both the concentration of the monomer and radiation dose up to a certain level. The values of the modulus also increase at the expense of the elongation at break. An increase in the number of double bonds from two in the case of the diacrylate to four in the case of the tetraacrylate also brings about an increase in the tensile strength and moduli values. The elongation at break, however, decreases. The DMTA measurements indicate changes in the glass transition temperature, T_g , and $\tan \delta_{\text{max}}$ on modification. The T_g shifts to a higher temperature with a simultaneous lowering of the $\tan \delta_{\text{max}}$ values as the TMPTA level is increased. A similar trend is observed when the irradiation dose is increased and the nature of the monomer changes from di- to tetraacrylate. The dielectric loss tangent registers an increase on modification by irradiation of TMPTA while the permittivity is decreased. All the results could be explained on the basis of the structural modification and crosslinking density. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 323–337, 2000

Key words: EPDM, Electron Beam, Radiation, Modification, Rubber Dynamic Mechanical Properties, Mechanical Properties, IR

INTRODUCTION

The industrial applications of radiation processing have been growing rapidly in recent years.

The main fields are the manufacturing of radiation crosslinked heat-shrinkable materials, wire and cables, and automobile parts.

Some advanced research work on radiation grafting and crosslinking of polymers has been reported recently. The effect of monomer and substrate structure on the graft modification of ethylene–propylene rubber (EPR) by γ -radiation was investigated by Haddadi-asl et al.¹ They also described the effect of additives on the same sys-

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tem.² Kudoh et al.³ reported low-temperature γ -ray irradiation effects on poly(methyl methacrylate) (PMMA), polyethylene (PE), polytetrafluoroethylene (PTFE), etc.

Electron-beam-initiated grafting of monomers onto polymers is a relatively new technique. It has certain advantages over conventional grafting processes, such as absence of any catalyst residue and complete control of temperature. Furthermore, being a solvent-free system and a source of an enormous amount of radicals and ions, this technique has gained commercial importance in recent years. The treatment of polymers by electron beam was reviewed.⁴ The modification of polyethylene and ethylene vinyl acetate (EVA) using this technique was reported by Tikku et al.⁵ and Datta et al.,⁶ respectively. Chaki et al.⁷ described the effect of MMA on the grafting efficiency and the physical properties of PE in the presence of electron-beam irradiation. Banik et al. studied the structural modification of fluoroelastomers by electron beam and also its impact on the dynamic mechanical properties.^{8–10} Konar and Bhowmick discussed the surface properties of polymers modified by dibutyl maleate and vinyltrimethoxysilane and by triallyl cyanurate.¹¹ In our earlier communications, we reported the influence of trimethylolpropane triacrylate (TMPTA) and the irradiation dose on the surface properties of ethylene propylene diene monomer (EPDM) rubber-modified by electron-beam irradiation.^{12,13} Preliminary results of electron-beam-modified EPR are interesting.¹⁴ Crosslinking of EPDM by a conventional technique and electron-beam irradiation is expected to generate different types of network, which could be reflected on the properties.¹⁵ In our present article, we discuss the influence of the electron-beam irradiation dose and concentration and the nature of the polyfunctional monomers on the mechanical, dynamic mechanical, and electrical properties of EPDM rubber. An attempt was made to correlate the structure analyzed by IR spectroscopy and the crosslinking density with the above-mentioned properties.

EXPERIMENTAL

Materials

EPDM rubber (Keltan 520-DCPD containing rubber, density = 0.86 g/cm³, diene content = 4.5 mol %, viscosity-average molecular weight = 1.93

$\times 10^5$ g/g mol, ethylene/propylene ratio = 58 : 42 mol/mol) was supplied by DSM Chemical Zwolle (The Netherlands). Dicumyl peroxide (DCP, Di-cup, 98% pure) was procured from Hercules Inc., Wilmington, DE (U.S.A.). TMPTA (flash point > 100°C Cleaveland open cup; boiling point >100°C; specific density 1.11 g/cm³) was obtained from UCB Chemicals, Drogenbos, (Belgium). Tripropylene glycol diacrylate (TPGDA, flash point >100°C Cleaveland open cup; boiling point >100°C; specific density 1.05 g/cm³) was also obtained from UCB Chemicals. Tetramethylol methane tetraacrylate [TMMT, specific gravity (40°C) 1.165; saponification value (mg KOH/g) 621.0; bromine value (g Br/100 g) 150.9] was supplied by the Shin Nakamura Chemical Co. Ltd., Tokyo, (Japan). *n*-Heptane obtained from E. Merck (India) Ltd. (Mumbai, India) was used.

Preparation of the Samples

EPDM was premixed with 0.2 phr DCP (the minimum suitable level to obtain a smooth surface) on an open-roll mill (6 \times 13 in., Schwabenthan, Germany) at 25°C before electron-beam irradiation. The mix was then further compounded with TMPTA (1, 2, 5, 10, and 20% by weight) in a Brabender Plasticorder, PLE-330, at 30°C for 3 min at a 60 rpm rotor speed. The mixes were then sheeted out from the roll mill. Finally, the sheets were compression-molded at a temperature of 150°C and at a pressure of 5 MPa for 45 min (the optimum cure time), as obtained from the rheometric studies using a Monsanto rheometer, R-100, under a hot press to obtain rectangular sheets of dimensions 150 \times 120 \times 2 mm. For infrared (IR) spectroscopic measurements, thin films of 0.3-mm thickness were prepared by compression molding the above unvulcanized mix at 150°C and 10 MPa pressure for 45 min. EPDM mixes were also prepared separately with TPGDA (10%) and TMMT (10%) and molded following a similar procedure. The control sample (without any monomer) was made by mixing EPDM with 0.2 phr DCP following the above procedure.

Irradiation of the Samples

The molded rectangular EPDM samples (both control and bulk-modified) were irradiated in air by an electron-beam accelerator (Model ILU-6) at Bhabha Atomic Research Centre (BARC), Mumbai. Irradiation doses of 0–500 kGy were used. The specifications of the electron-beam accelera-

Table I Specifications of the Electron-Beam Accelerator

Energy range	0.5–2.0 MeV
Beam power over the whole energy range	20 kW
Beam energy spread	±10%
Average current (E 1.5 MeV)	15 mA
Dose rate	5400 kGy/h

tor are given in Table I. The designation of the samples is given in Table II.

Characterization of the Samples

Infrared (IR) Spectroscopy

IR spectra on thin films of thickness 0.3 mm were taken on a Perkin–Elmer Model 843 IR spectrophotometer. A total of four scans were taken for each sample with a resolution of 1 cm^{-1} . IR spectra of the liquid TMPTA were taken by casting a thin film on the KBr cell, while irradiated solid TMPTA samples were mixed with KBr to produce pellets, which were then analyzed by IR spectra. The absorbances were normalized with respect to the peak absorbance at 1460 cm^{-1} , which was constant. Hence, any experimental error arising from a disparity in the TMPTA concentration was minimized.

Volume Fraction of Rubber in the Swollen Gel and Crosslinking Density

Previously weighed samples were allowed to swell in *n*-heptane at 40°C for 12 h, the equilibrium swelling time (which was determined from a plot of mass uptake against time). The samples were then removed, weighed, and dried to a constant weight in a vacuum oven at 70°C for 6 h. The volume fraction of the rubber in the swollen gel (V_r) was determined on the basis of simple additivity rule of volumes as follows:

$$V_r = \frac{(D - FH)/\rho_r}{(D - FH)/\rho_r + A_0/\rho_s} \quad (1)$$

where H is the weight of the test specimen; D , the deswollen weight of the test specimen; F , the weight fraction of the insoluble components; A_0 , the weight of the absorbed solvent; ρ_r , the density of the rubber; and ρ_s , the density of the solvent. The ρ_r of EPDM = 0.86 g/cc , and the ρ_s of *n*-heptane = 0.68 g/cc .

The crosslinking density was calculated according to the Flory–Rehner equation¹⁶ using the values of V_r as follows:

$$-\ln(1 - V_r) + V_r + \chi V_r^2 = \frac{\rho}{M_c} \times V_s (V_r^{1/3} - V_r/2) \quad (2)$$

where χ is the Flory–Huggins polymer–solvent interaction parameter; ρ , the density of the rubber; M_c , the molecular weight between crosslinks; and V_s , the molar volume of the solvent. The crosslink density was evaluated as $[1/(2M_c)]$.¹⁶ The unit of M_c is kg/mol. Hence, the unit of crosslink density is expressed as mmol/kg RH.

Measurement of Properties

Dynamic Mechanical Thermal Analysis (DMTA) Measurements

DMTA studies were performed using a dynamic mechanical thermal analyzer (Polymer Laboratories, Model MK-II) at a heating rate of $2^\circ\text{C}/\text{min}$ in a dual-cantilever bending mode at a frequency of 3 Hz and a strain amplitude of $64\ \mu\text{m}$ (peak-to-peak displacement) in the temperature range of -50 to 100°C . The data were analyzed using DMTA MK-II software.

Mechanical Properties

The tensile strength, modulus, and elongation at break were measured (on a dumbbell-shape test piece punched by a C-type die) employing a cross-head speed of $500\text{ mm}/\text{min}$ at 27°C according to the ASTM D-412-92 (1993) method using a Zwick UTM (Model 1445). The results are the average of three samples. The error in tensile strength measurement was $\pm 5\%$.

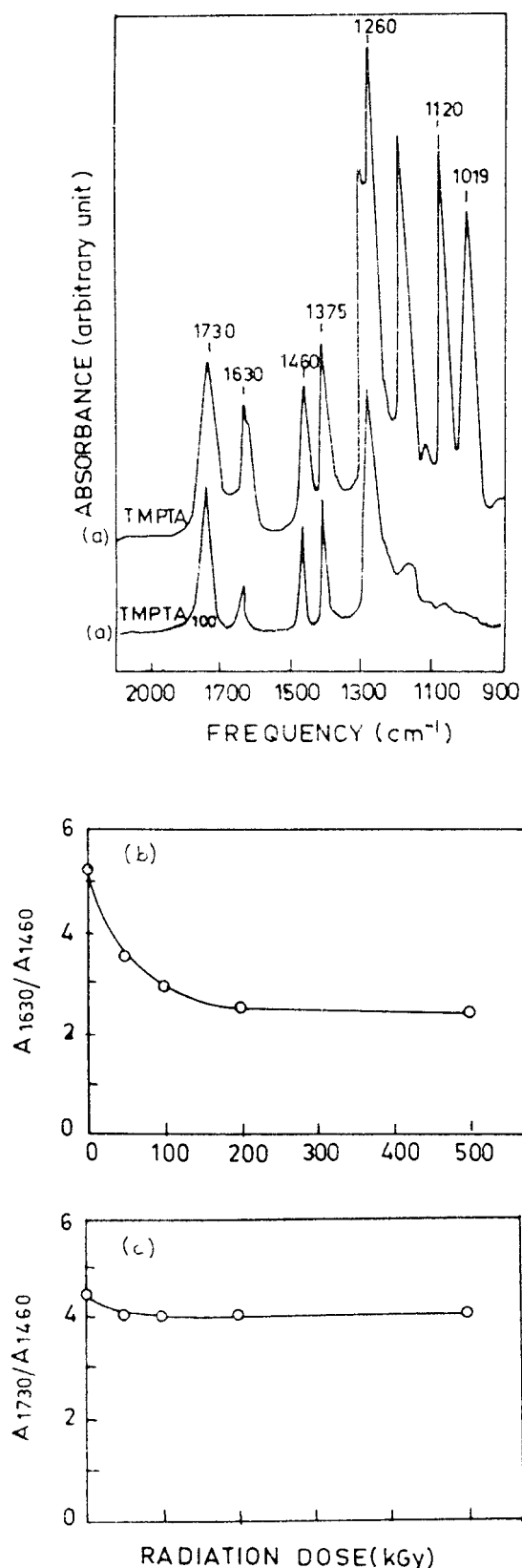
Electrical Properties

The dielectric studies were performed using a dielectric analyzer DEA-2970, coupled to a control-

Table II Designation of the Control and the Modified EPDMs

Rubber System	Designation
Control EPDM rubber	$E_{x/y}$
EPDM bulk-modified with TMPTA	$EB_{x/y}$
EPDM bulk-modified with TPGDA	$DB_{x/y}$
EPDM bulk-modified with TMMT	$TB_{x/y}$

x : monomer level in percent; y : radiation dose in kGy.



ler 2000 (TA Instruments Inc., U.S.A.) using parallel plate sensors from -80 to 100°C at a heating rate of $3^{\circ}\text{C}/\text{min}$ at 10^3 Hz on thin films of thickness 0.3 mm. The dielectric properties (dielectric constant, ϵ' , and loss factor, $\tan \delta$) were obtained from the computer attached to the machine.

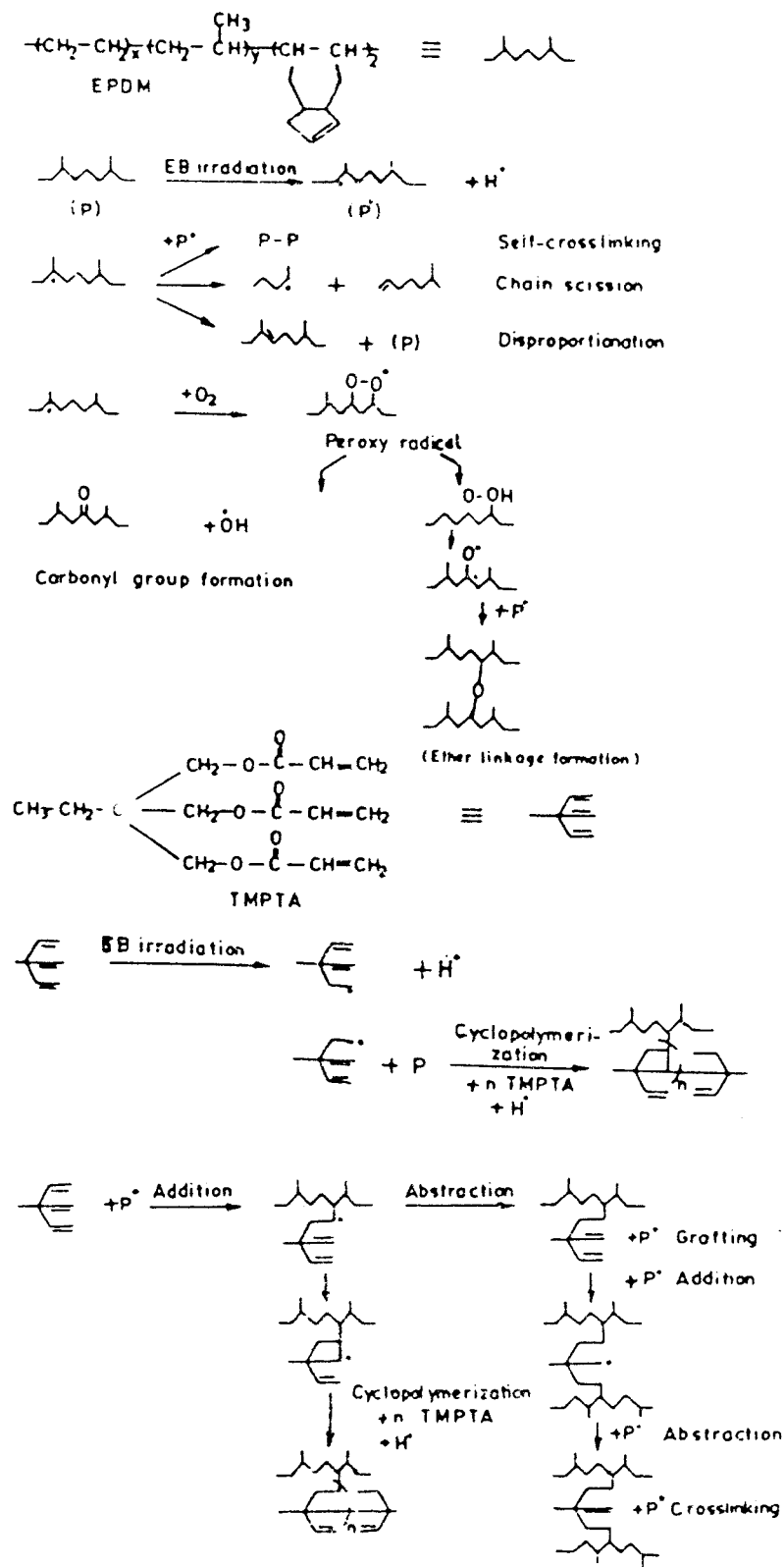
RESULTS AND DISCUSSION

Structural Aspects: IR Studies

IR spectra of the unirradiated TMPTA and the TMPTA irradiated to various doses were taken and the representative spectra are shown in Figure 1(a). The peak at 1630 cm^{-1} due to the >C=C< stretching vibration of the control TMPTA decreases with a radiation dose up to 100 kGy. Liquid TMPTA becomes solid on irradiation. The peak absorbance of 1630 cm^{-1} , when normalized with respect to 1460 cm^{-1} due to >CH_2 scissor vibration and plotted against irradiation dose, indicates that the absorbance ratio decreases sharply with irradiation dose up to 100 kGy [Fig. 1(b)]. Similar behavior was also observed with other polyfunctional acrylates, namely, TPGDA and TMMT.⁹ During irradiation, a large number of free radicals is generated on the TMPTA molecules. As a result, TMPTA may undergo several reactions, namely, polymerization, cyclopolymerization, crosslinking, grafting, and cyclization, as shown in Scheme 1. All these reactions utilize the double bonds in TMPTA as can be seen from the decrease in the absorbance ratio. The ratio between the absorbances at 1730 and 1460 cm^{-1} does not change with irradiation dose [Fig. 1(c)], as the carbonyl groups have no active role in the polymerization or crosslinking of the TMPTA molecules.

The representative IR spectra of the EPDM rubber bulk-modified with various contents of TMPTA and irradiated to a constant dose of 100 kGy are shown in Figure 2. The main peaks of interest are observed at 1730 , 1630 , 1460 , 1375 , 1260 , 1120 , and 1019 cm^{-1} as given in Table III. The peak absorbances are plotted against the concentration of TMPTA in Figure 3(a-f). It can be observed that with increasing concentration of

Figure 1 (a) IR spectra of the control TMPTA and TMPTA irradiated to 100 kGy dose and change of absorbance ratios (b) A_{1630}/A_{1460} and (c) A_{1730}/A_{1460} of TMPTA against radiation dose.



Scheme 1 Reaction scheme showing electron-beam irradiation of EPDM and plausible mechanism of interaction of TMPTA with EPDM.

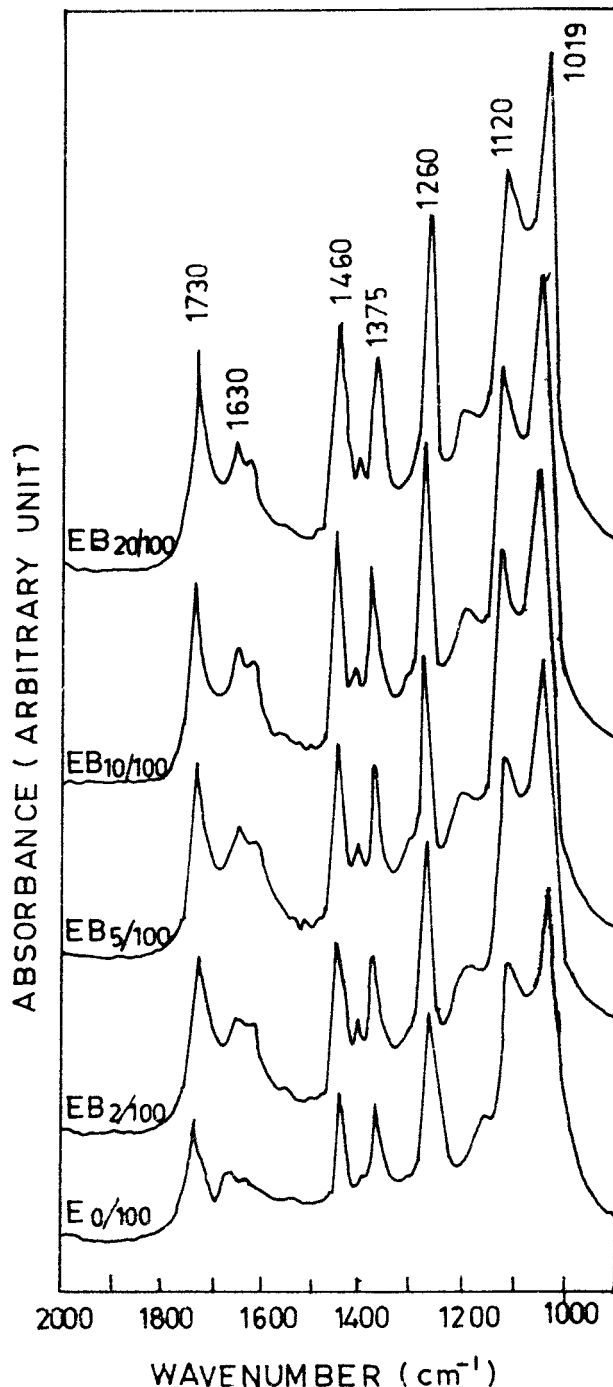


Figure 2 IR spectra of EPDM bulk modified with different concentrations of TMPTA at a constant irradiation dose of 100 kGy.

TMPTA the peaks at 1730, 1630, 1460, 1375, 1260, and 1019 cm^{-1} are steadily increased in the initial stages. This increase is, however, marginal beyond 10% of the TMPTA level, as indicated from the slopes in the figures.

These effects may be explained with the help of the reaction mechanisms (Scheme 1), as follows: During irradiation, a large number of free radicals is generated on the EPDM backbone. These radicals, being highly reactive, undergo aerial oxidation to produce carbonyl and ether linkages along the rubber chain. They may also cause crosslinking and chain scission of the EPDM rubber, which are discussed in a later section. Similarly, the active free radicals produced on the TMPTA molecules themselves cause the molecules to graft onto the rubber. This grafting of TMPTA together with the carbonyl and ether groups (1730, 1260, and 1019 cm^{-1}) generated on the rubber itself causes the carbonyl and ether absorptions to increase.

As the concentration of TMPTA increases gradually, the concentration of the active radicals also increases, thereby increasing the grafting and crosslinking level with EPDM. This is evident from the increase in the peak absorbance at 1460 and 1375 cm^{-1} . This is also clear from the plot of crosslinking density versus TMPTA concentration, which shows a similar trend [Fig. 4(a)]. However, there is competition among various reactions during electron beam exposure. For example, with an increasing TMPTA level from 10 to 20%, the TMPTA molecules may preferably engage themselves in reactions such as self-crosslinking, cyclization, and cyclopolymerization, generating new but different molecules. Also, chain scission of EPDM due to high radical concentrations may still be possible. Thus, the changes in the absorbances at higher concentrations of TMPTA become marginal.

The IR spectra of the control EPDM rubber as well as those modified with 10% TMPTA and ir-

Table III Principal Peak Assignments in the Spectra of the Control and the Modified EPDMs

Observed Peak (cm^{-1})	Peak Assignment
1730	>C=O stretching vibration
1630	>C=C< stretching vibration
1460	>CH_2 scissoring vibration
1375	Symmetric C—H stretching vibration of —CH_3
1260	Asymmetric C—O—C stretching vibration
1120	Symmetric C—O—C stretching vibration
1019	Symmetric C—O—C stretching vibration

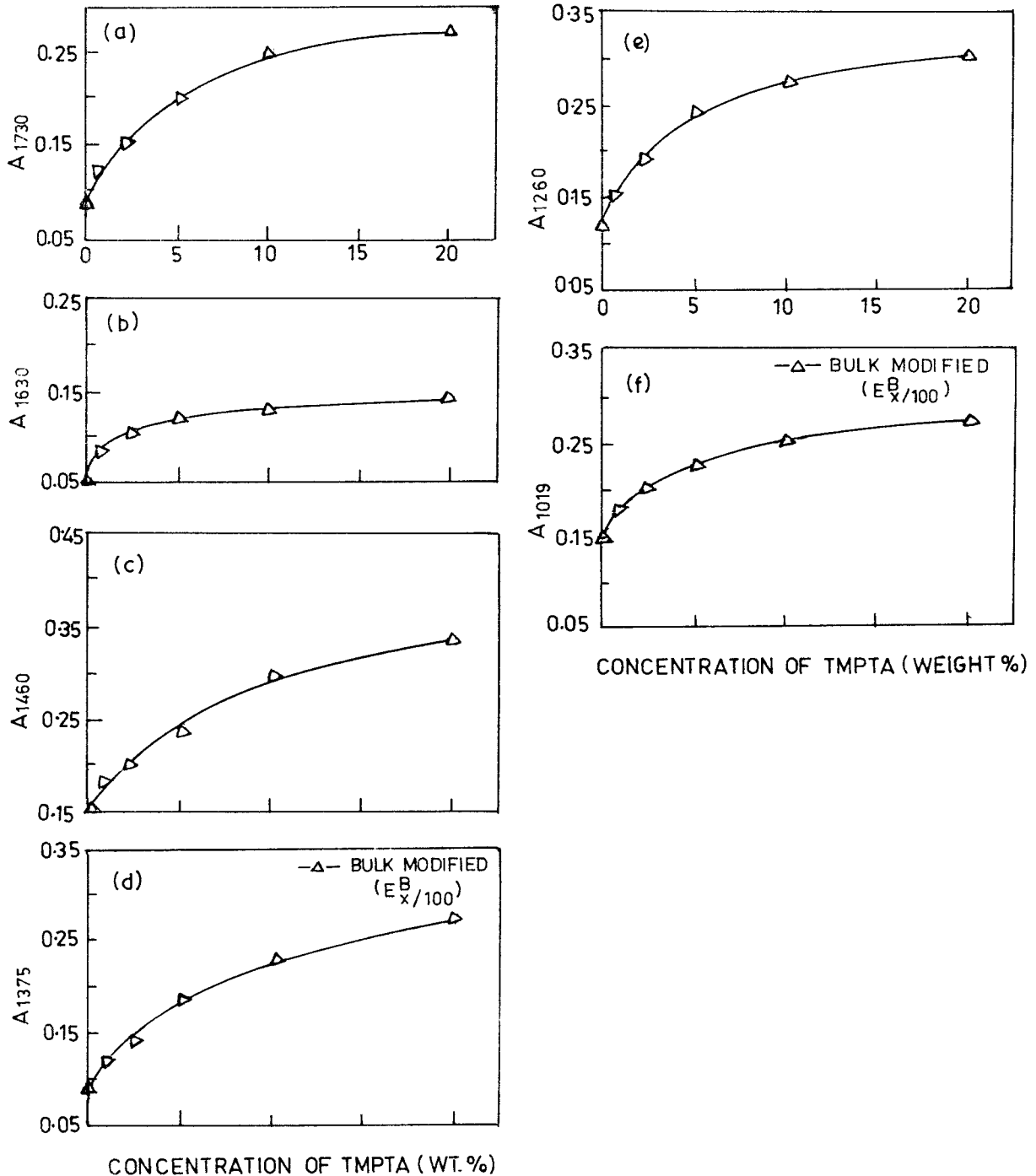


Figure 3 Change of absorbances (a) A_{1730} , (b) A_{1630} , (c) A_{1460} , (d) A_{1375} , (e) A_{1260} , and (f) A_{1019} for EPDM bulk-modified with different concentrations of TMPTA at a constant irradiation dose of 100 kGy.

radiated to various doses from 0 to 500 kGy are shown in Figure 5. The main absorbances are plotted against the radiation dose in Figure 6(a-f). For the control sample, the absorption at 1630 cm^{-1} remains almost constant with irradiation

initially, but shows a marginal increase at higher irradiation doses above 50 kGy. The initial constancy may be due to self-crosslinking through the double bonds as well as generation of double bonds due to chain scission and disproportion-

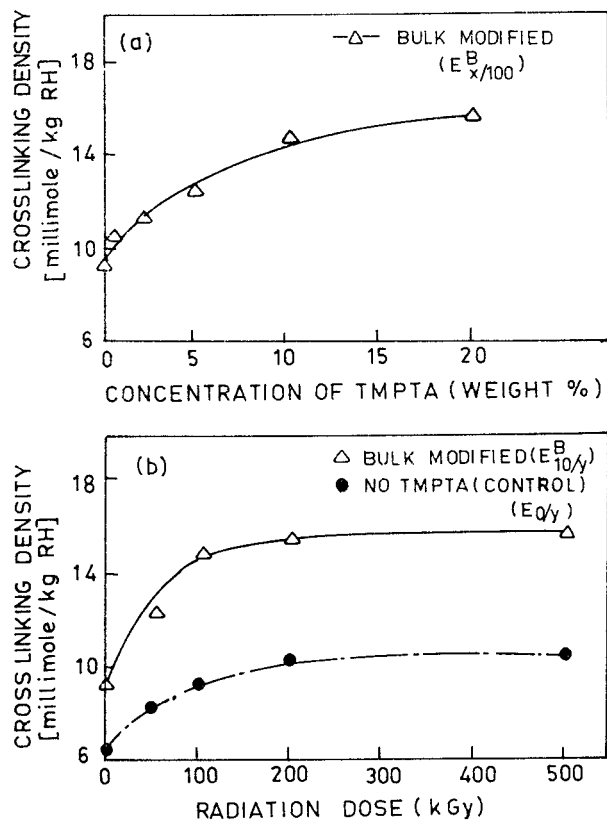


Figure 4 Plot of crosslinking density against (a) concentration of TMPTA and (b) irradiation dose.

ation of EPDM (Scheme 1). At higher radiation doses, however, the scission reactions predominate as a result of which double bonds are formed at the chain ends and the absorption increases. The absorbances at 1460 and 1375 cm^{-1} for the control rubber decrease gradually with irradiation, probably due to the breakdown of the rubber chains on scission which increase with increase in irradiation dose on account of the large amount of macroradicals generated in the rubber. Irradiation of the samples causes the absorptions at 1730, 1260, and 1019 cm^{-1} to initially increase up to 50 kGy, after which there is a slight decrease in the absorbances. The initial increase is due to the aerial oxidation of the EPDM free radicals to carbonyl and ether groups (Scheme 1). The predominance of the scission reactions at higher doses above 50 kGy causes the slight decrease in the absorption values.

On the other hand, when the same absorbances are plotted against irradiation dose for the samples modified with TMPTA in the bulk (Fig. 6), a different picture is revealed. The absorption at 1630 cm^{-1} gradually decreases, probably due to the uti-

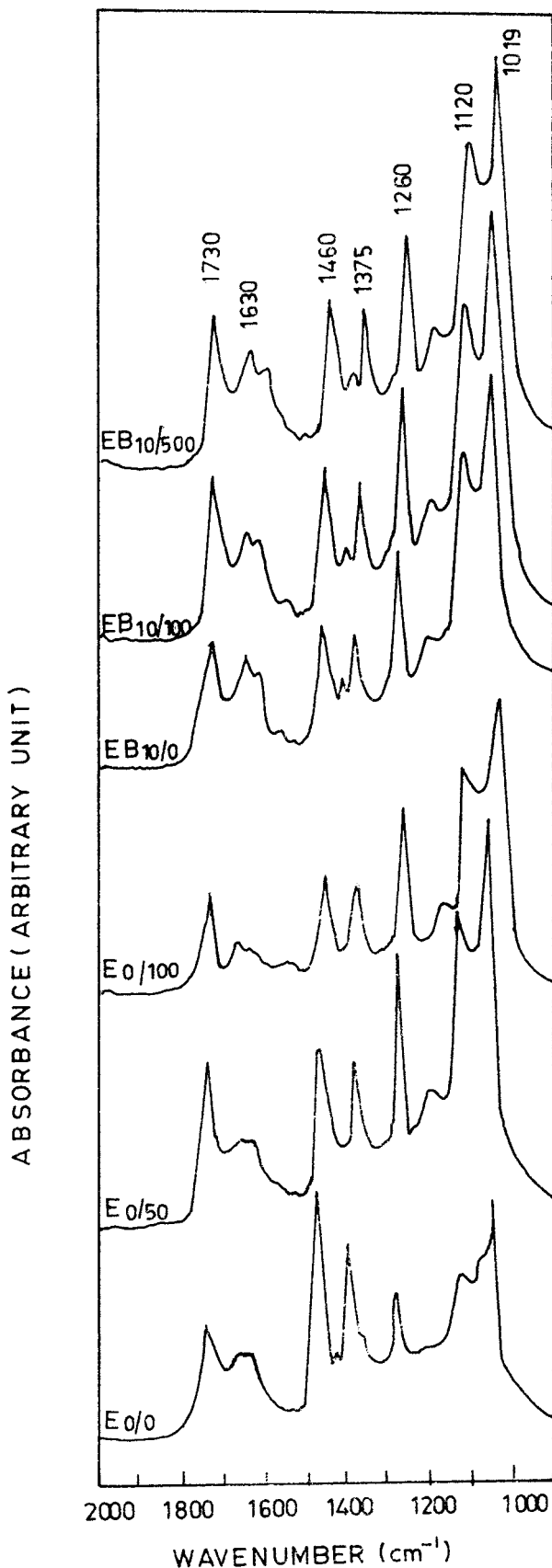
lization of the vinylic unsaturation of TMPTA on irradiation due to grafting. However, the absorbances at 1460, 1375, 1730, 1260, and 1019 cm^{-1} all register a gradual increase with irradiation up to a certain level, that is, 200 kGy beyond which there is a slight drop in the absorbance values. The much higher absorbance values at 1730, 1260, and 1019 cm^{-1} for the TMPTA-modified samples over the control ones is due to a combined effect of the aerial oxidation of the EPDM free radicals and the grafting of TMPTA onto EPDM. Furthermore, it was reported earlier⁸ that the introduction of a polyfunctional monomer into the rubber suppresses the scission reactions to some extent. Hence, in this case, increase in the absorbances continues up to a much higher dose level. However, at very high irradiation doses beyond 200 kGy, the preponderant factor is the scission of the rubber which causes the rubber chains to break down into segmental moieties, as a result of which some of the polarity may be lost. It may be mentioned that the crosslinking density increases sharply with irradiation dose in the initial stages and changes marginally at higher irradiation doses for both the control and the bulk-modified samples [Fig. 4(b)].

IR-ATR spectra of EPDM rubber sheets modified on the surface with varying concentrations of TMPTA at a constant irradiation dose and with varying irradiation doses at a fixed TMPTA level were reported earlier by us.^{12,13} It is interesting to note that the optimum level of the irradiation dose is 50 kGy at a 10% TMPTA concentration and the optimum TMPTA concentration is 10% at 100 kGy dose. The difference in the optimum values for the *bulk*- and *surface*-modified samples is due to the difference in the concentration of the sensitizer on the surface and in the bulk.

Dynamic Mechanical Properties

Effect of Irradiation Dose

The DMTA for the control EPDM samples ($E_{0/0}$, $E_{0/50}$, $E_{0/100}$, and $E_{0/500}$) is shown in Figure 7(a). The figure shows the damping behavior, as the loss tangent, of the control rubber exposed to different irradiation doses against the testing temperatures. As the temperature is increased, the damping goes through a maximum in the transition region. The damping is low when the segments are completely frozen-in or free to move. Thus, below the T_g , where the deformations are primarily elastic and the molecular slip resulting in viscous flow is low, the damping is low. Also,



above the T_g , in the rubbery region, it is low because the molecular segments are free to move and, consequently, there is little resistance to flow. In the transition region, on the other hand, the damping is high owing to the initiation of the micro-Brownian motion of the molecular chains. Some of the molecular chains are free to move while the others are not. A frozen-in segment can store much more energy for a given deformation than can a free-to-move rubbery segment.¹⁷ Thus, every time a stressed frozen-in segment becomes free to move, its excess energy is dissipated.

The position and height of the loss tangent peak in the dynamic mechanical spectra of a polymer are indicative of the structure and the extent to which a polymer is crosslinked or modified. From Figure 7(a), the damping peak temperature of unirradiated control EPDM rubber is found to be at -33°C . With increase in the radiation dose, there is a slight shift in the glass transition temperature. This is accompanied by a marginal decrease in the $\tan \delta_{\text{max}}$ value as displayed in Figure 8. The shifts in both $\tan \delta$ and T_g are in accordance with the increasing degree of modification, as confirmed from the changes in the IR peak absorbances [Fig. 6(a-f)] and crosslinking density, which register an increase with increase in the irradiation dose [Fig. 4(b)]. The loss tangent data at higher temperatures also indicate that the same is lowered with irradiation dose up to a level of 50 kGy. Beyond this, the $\tan \delta$ values are again higher due to scission reactions. The abrupt increase of the $\tan \delta$ value in the case of the $E_{0/500}$ sample [Fig. 7(a)] is probably due to a considerable softening of the polymer due to degradation at such a high irradiation dose.

Figure 7(b) illustrates the damping behavior of the blends of EPDM with 10% TMPTA at different irradiation doses. It is observed that as the irradiation dose is increased from 0 to 200 kGy there is a steady decrease of the $\tan \delta_{\text{max}}$ value from 1.15 to 0.85 with a corresponding increase in the T_g from -32 to -27°C due to the structural modifications of the rubber (Fig. 8). However, at an extreme dose of 500 kGy, the rubber starts degrading due to chain scission and disproportionation and the T_g is lowered, consequently, with respect to the value of the sample irradiated to 200 kGy, the optimum dose. Due to the

Figure 5 Representative IR spectra of the control and the modified EPDMs (with 10% TMPTA) irradiated to various doses.

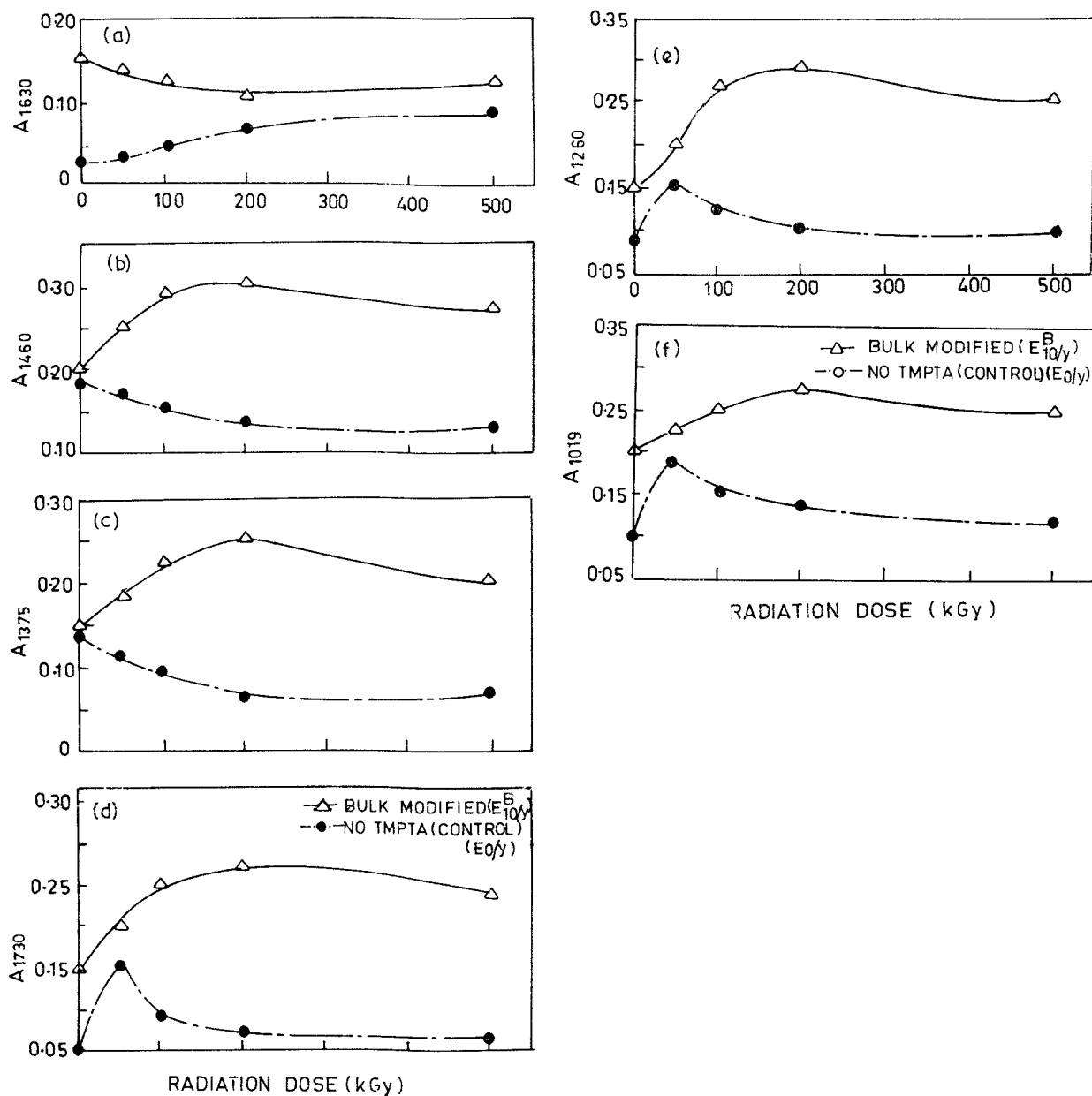


Figure 6 Change of absorbances (a) A_{1630} , (b) A_{1460} , (c) A_{1375} , (d) A_{1730} , (e) A_{1260} , and (f) A_{1019} with irradiation dose for the control EPDM and EPDM bulk modified with 10% TMPTA.

crosslinking of the rubber, the storage moduli, E' , in both the glassy and rubbery regions, on the other hand, increase gradually until a level of 200 kGy, as the capacity of the rubber to store energy increases due to crosslinking. The same, however, falls beyond this level due to a predominance of the scission reactions. The results are in accordance with the IR studies, which indicate that the absorbances at 1730, 1260, and 1019 cm^{-1} due to carbonyl, asymmetric, and symmetric C—O—C

stretching, respectively, increase with the irradiation dose up to a level of 200 kGy (Fig. 6) due to the self-crosslinking of EPDM and crosslinking and grafting of TMPTA with EPDM. A further increase in the radiation dose lowers the above IR absorbances due to the scission reactions.

Influence of TMPTA Concentration

Figures 9 and 10 show the dynamic mechanical characteristics of some representative blends of

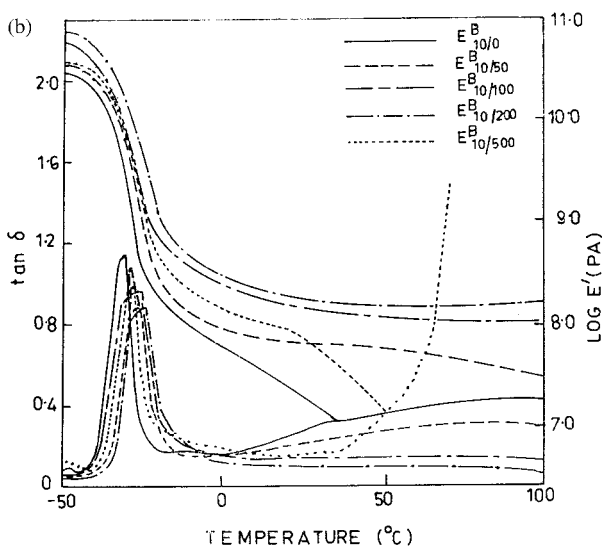
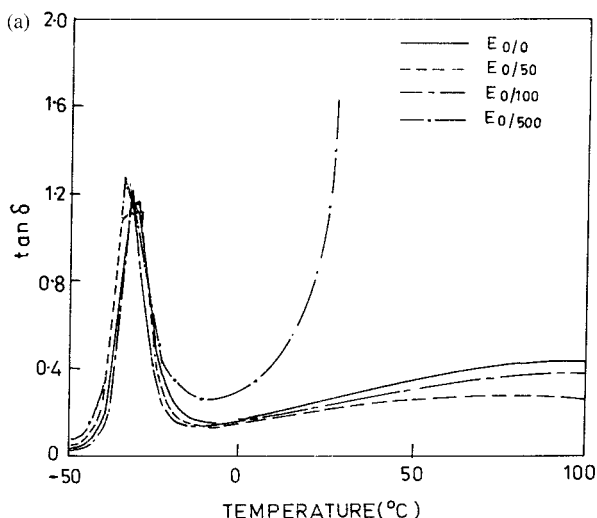


Figure 7 (a) Representative figures showing the variation of $\tan \delta$ with temperature for the control EPDM irradiated to various doses. (b) Plot of $\tan \delta$ and $\log E'$ versus temperature of EPDM modified with 10% TMPTA at various irradiation doses.

EPDM with TMPTA at various concentrations (0, 5, and 10%) at a constant irradiation dose of 100 kGy. It is observed that with an increase in the TMPTA concentration the T_g gradually shifts from -32 to -28°C and the $\tan \delta_{\max}$ decreases from 1.15 to 0.90. The maximum shift of the T_g can be seen at 20% TMPTA concentration, which also corresponds to the minimum $\tan \delta_{\max}$ value. The influence of the TMPTA concentration on the damping behavior of EPDM is, again, corroborated by the IR studies and crosslinking density [Figs. 3 and 4(a)]. The dynamic storage moduli of the EPDM/TMPTA mixed systems (Fig. 9), conse-

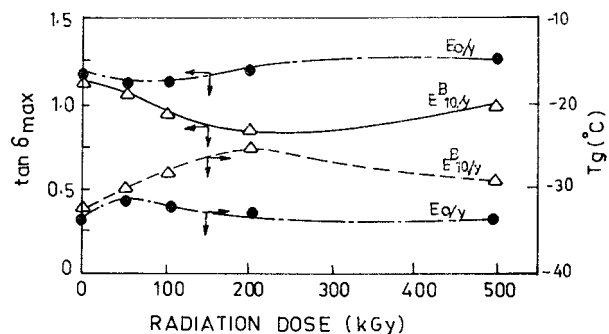


Figure 8 Change of T_g and $\tan \delta_{\max}$ with irradiation dose for the control and the modified EPDMs.

quently, are higher than those of the control irradiated rubber at any temperature of testing. It is also observed that the $EB_{5/100}$ sample shows higher losses than those of the $EB_{10/100}$ sample when subjected to periodically varying stresses at temperatures higher than 50°C . Increase of temperature perhaps randomizes the motion of the free chain ends and molecular chain segments of $EB_{5/100}$ due to lower crosslinking density. As a result, an increased slippage between the free-chain moieties causes the $\tan \delta$ to increase with temperature, as compared to the blends having relatively higher levels.

Effect of the Nature of Monomer

Multifunctional vinyl unsaturated monomers are used in radiation-crosslinked rubber formulations

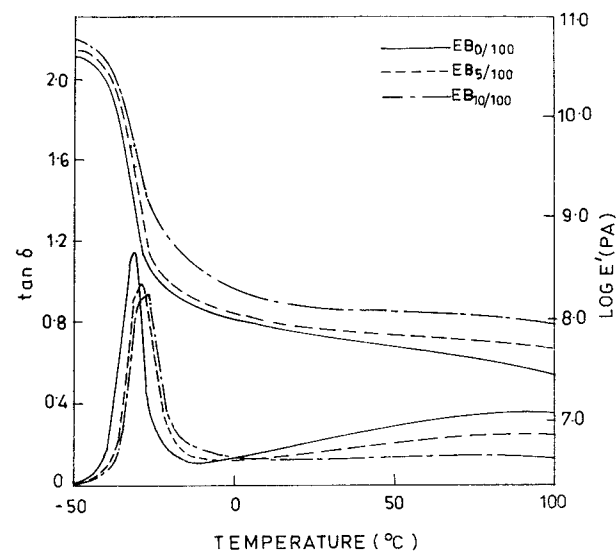


Figure 9 Representative plot of $\tan \delta$ and $\log E'$ versus temperature for EPDM modified with different concentrations of TMPTA at a fixed irradiation dose of 100 kGy.

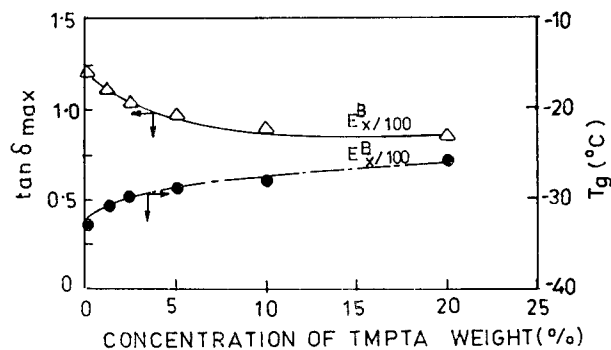


Figure 10 Change of T_g and $\tan \delta_{\max}$ with concentration of TMPTA.

to decrease the dose level required to obtain optimum properties or to achieve, at the same dose, an increased state of cure. Their reactivity is governed by various factors, namely, the number of double bonds, bulkiness, and so on. Figure 11 displays a plot of the loss tangent and the dynamic storage moduli of TPGDA-, TMPTA-, and TMMT-mixed EPDM rubber against the testing temperatures. The monomer level was kept constant at 10%, and the irradiation dose, at 100 kGy. It is observed that the height of the $\tan \delta$ peak decreases significantly as the number of double bonds in the polyfunctional monomer is increased. The storage modulus of the TMMT-based system is also the highest over the entire temperature range from -50 to 100°C . The T_g also exhibits the maximum value for this system, namely, at -25°C . Table IV reports the absorbance values and crosslinking density of the modified EPDMs. $\tan \delta$ decreases with increasing crosslink density as seen in the earlier section. It is observed that TMMT is more effective in producing a denser network (crosslinking density = 18.2) than is TPGDA, having the lowest unsaturation (crosslinking density = 10.0). It is also demonstrated that TMMT produces maximum structural changes in the EPDM among the three multifunctional monomers.

Tensile Properties

The effects of increasing concentration of TMPTA and irradiation dose on the tensile properties at room temperature of the bulk-modified and the control EPDM samples are given in Table V. At a fixed irradiation dose of 100 kGy, there is a significant change in the tensile strength of the samples with increasing TMPTA content up to 20% (from 1.3 MPa at 0% to 1.9 MPa at 20% TMPTA,

i.e., about a 46% rise). The same effect is observed with the moduli values. The moduli at 100 and 200% register a 50 and 63% increase, respectively. However, the elongation-at-break values decrease steadily.

The tensile strength of the control samples (without TMPTA) initially irradiated to 50 kGy shows a marginal increase from 1.2 to 1.5 MPa. The elongation-at-break, however, decreases while the moduli at 100 and 200% exhibit an appreciable increase of more than 50%.

For the 10% TMPTA-modified samples, an increasing irradiation dose brings about almost a 100% increment in the tensile strength. The moduli values show the same behavior as above, the increase, in this case, being almost 150 and 60%, respectively, at 100 and 200%. The elongation-at-break values, however, decrease.

With an increase in the unsaturation of the polyfunctional monomers, the tensile strength increases significantly (Table V). The moduli at 100 and 200% elongation display the same trend, while the elongation-at-break decreases steadily.

The tensile properties are a function of crosslinking density, molecular imperfection, reduced molecular weight due to degradation, etc. The results in Table V may indicate an interplay of the various factors. For example, an increase in the tensile strength and moduli of the samples on increasing both the concentration of TMPTA or the irradiation dose is probably due to the increase in the crosslinking density as depicted in Figure 4(a,b). However, this positive effect in the

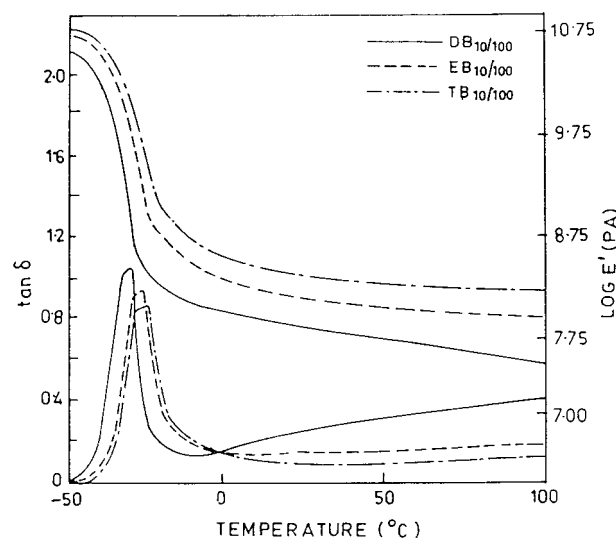


Figure 11 Plot of $\tan \delta$ and $\log E'$ against temperature for EPDM modified with different monomers.

Table IV Absorbance Values and Crosslinking Density of the Modified EPDMs

Sample Code	A_{1730}	A_{1630}	A_{1460}	A_{1375}	A_{1260}	A_{1019}	Crosslinking Density (mmol/kg RH)
DB _{10/100}	0.19	0.10	0.27	0.19	0.24	0.20	10.0
EB _{10/100}	0.24	0.12	0.30	0.24	0.27	0.24	14.6
TB _{10/100}	0.29	0.15	0.34	0.27	0.30	0.30	18.2

case of the control samples without TMPTA is somewhat nullified by the reduction in molecular weight due to chain scission and imperfections created at higher radiation doses. The reduction in the elongation at break may be ascribed to the increasing crosslinking density and limited extensibility in the initial stage and increasing chain scission at higher radiation doses. The results of the nature of the monomer can also be explained by the same arguments as stated above.

Electrical Properties

Figure 12(a) shows the $\tan \delta$ versus temperature plot of three representative samples ($E_{0/0}$, $E_{0/50}$, and $EB_{10/50}$). The variation of the dielectric constant, ϵ' , with temperature is also illustrated [Fig. 12(b)]. A sharp peak is observed around -30°C for all the samples irrespective of the radiation dose or the concentration of TMPTA. On modification of the control unirradiated sample, $E_{0/0}$, by irradiation to 50 kGy or by 10% TMPTA at 50 kGy,

the samples become crosslinked, as can be seen from Figure 4(b). Moreover, due to aerial oxidation of the EPDM rubber, the dipoles (polar carbonyl groups) arise on the backbone of the macromolecular chains [Fig. 6(a–f)]. This dipolar concentration is further enhanced by the introduction of TMPTA into the rubber. The peak at -30°C for the samples is due to the movement of these polar groups. The increase in the loss tangent may be due to the formation of these carbonyl groups, which increase the dipolar concentration.^{18,19}

The dielectric constant, ϵ' , of the samples exhibits an exactly opposite trend [Fig. 12(b)]. The decrease of permittivity, on modification, indicates the restricted mobility of the dipoles ($\text{C}=\text{O}$ dipoles) as a result of crosslinking, which reduces the segmental mobility of the macromolecular chains. Thus, the above results simply indicate that crosslinking, on irradiation, inhibits the dielectric relaxation and orientation polarization.

Table V Tensile Properties of the Control and the Modified EPDMs

Samples EPDM	Tensile Strength (MPa)	Elongation at Break (%)	Modulus at 100% Elongation (MPa)	Modulus at 200% Elongation (MPa)
$E_{0/0}$	1.2	985	0.5	0.6
$E_{0/50}$	1.5	524	0.8	0.9
$E_{0/100}$	1.3	378	0.8	1.1
$E_{0/200}$	1.2	340	0.9	1.2
$E_{0/500}$	1.1	309	1.0	1.4
EB _{1/100}	1.4	360	0.9	1.2
EB _{2/100}	1.5	309	0.9	1.4
EB _{5/100}	1.8	293	1.0	1.5
EB _{10/100}	1.8	249	1.1	1.7
EB _{20/100}	1.9	230	1.2	1.8
EB _{10/0}	1.0	346	0.6	1.2
EB _{10/50}	1.4	261	0.9	1.4
EB _{10/100}	1.8	249	1.1	1.7
EB _{10/200}	2.0	229	1.4	1.8
EB _{10/500}	1.8	210	1.5	1.9
DB _{10/100}	1.4	309	0.8	1.4
TB _{10/100}	2.0	190	1.4	1.9

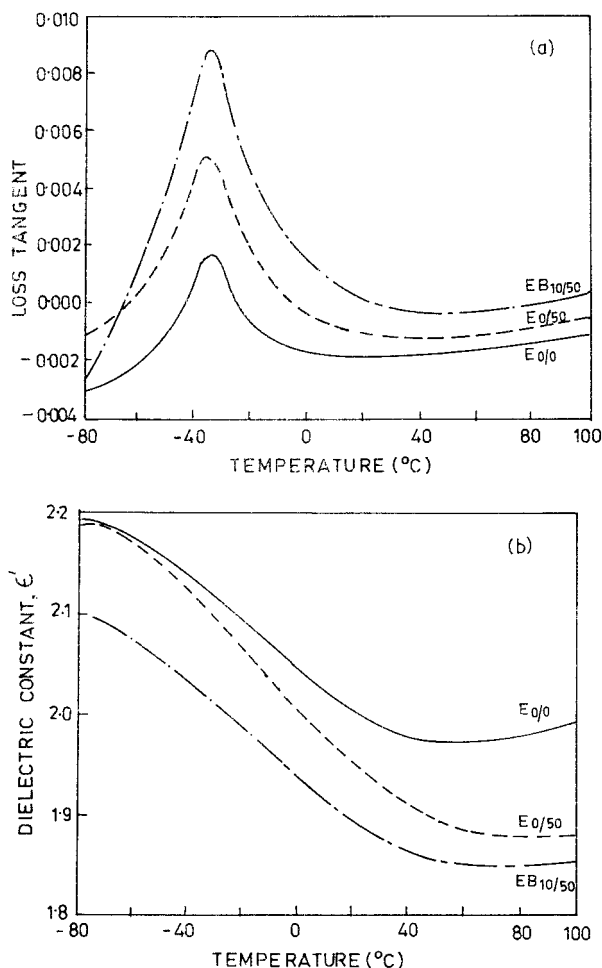


Figure 12 Representative figure showing the variation of (a) the dielectric loss tangent, $\tan \delta$ and (b) dielectric constant, ϵ' , with temperature for the control and the modified EPDMs.

CONCLUSIONS

EPDM rubber was bulk-modified using different concentrations of TMPTA (0–20%) at a constant electron-beam irradiation dose of 100 kGy and over a range of irradiation doses, that is, 0–500 kGy at a fixed TMPTA concentration of 10%. The nature of the monomer was also varied from diacrylate to tetraacrylate to study their effects on various properties. The results were correlated with the structural changes and crosslinking density of the EPDM modified by EB irradiation. The following conclusions may be drawn from this study:

- (i) With increase in the extent of modification of the rubber by TMPTA, the peak

absorbances measured by IR spectroscopy show definite changes. The peaks at 1730 cm^{-1} due to >C=O groups, at 1630 cm^{-1} due to the *trans*-vinylene bond stretching of TMPTA, at 1460 and 1375 cm^{-1} due to >CH_2 scissoring and —CH_3 vibrations, respectively, and at 1260 and 1019 cm^{-1} due to the C—O—C stretching vibration increase steadily, being optimum at 10% TMPTA concentration.

- (ii) With increase in the irradiation dose, the absorbances at 1730, 1460, 1375, 1260, and 1019 cm^{-1} increase sharply up to a level of 200 kGy for the bulk-modified samples, while that at 1630 cm^{-1} gradually decreases with irradiation. In the case of the control EPDM samples, the absorptions at 1460 and 1375 cm^{-1} show a gradual decrease with irradiation, while those at 1730 cm^{-1} increase up to 50 kGy dosage. The peak absorbances at 1260 and 1019 cm^{-1} also display maximum values at this stage. TMMT induces the maximum level of modification and, hence, maximum changes in the peak absorbances among the three monomers studied.
- (iii) The crosslinking density of the control as well as modified rubbers steadily increases with irradiation. A similar trend is shown by the samples modified with different concentrations of TMPTA.
- (iv) The modulus of the TMPTA-modified samples registers more than a 50% increase for the maximum TMPTA level (20%) as compared to the control irradiated rubber, however, at the cost of the elongation-at-break values. The tensile strength also increases. With increase in the radiation-dose level, the moduli of all the samples increase steadily, exhibiting more than a 100% increase, whereas the elongation-at-break values decrease. As the extent of modification increases with the number of double bonds in the monomers, the tensile strength and moduli also increase, while the elongation at break is lowered.
- (v) The DMTA results show an increased T_g and decreased $\tan \delta_{\text{max}}$ values on increasing both the TMPTA concentration and radiation doses, up to a certain level. The storage moduli of the samples in this region, however, exhibit a steady increase in both cases. As the nature of the monomers changes from di- to tetraacrylate,

the T_g is again increased and the $\tan \delta_{\max}$ lowered. Lowering of the $\tan \delta$ values and increase in the storage modulus of the modified samples are also observed in the glassy as well as in the rubbery regions.

- (vi) The permittivity of the samples decreases with an increased extent of modification (i.e., on increasing either the radiation dose or TMPTA concentration), while the dielectric loss tangent is increased.

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