

Dynamic Mechanical Properties of Electron Beam Modified Fluorocarbon Rubber

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ABSTRACT: The dynamic mechanical properties of electron beam modified fluorocarbon rubbers (terpolymer: F content, 68% and H, 1.4%; copolymer: F content, 65% and H, 1.9%) were studied. With an increase in the radiation dose, the loss tangent maximum decreases and the glass transition temperature increases. The influence of the polyfunctional vinyl monomer, trimethylolpropane triacrylate (TMPTA), is to decrease the loss tangent value, especially at higher doses. At a particular level of the multifunctional monomers tripropylene glycol diacrylate (TPGDA), TMPTA, and tetramethylmethane tetracrylate, the dynamic mechanical thermal analysis indicated the lowest degree of crosslinking for the system based on TPGDA. MgO-based systems register a decrease of the loss tangent peak height and an increase in the storage moduli compared to the control rubber. The results are explained on the basis of gel fraction, scission reactions, and structural changes as measured with the help of IR-attenuated total reflectance spectroscopy. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2079–2087, 1998

Key words: dynamic mechanical properties; electron beam irradiation; fluorocarbon rubber

INTRODUCTION

In recent years, there has been increasing demand for fluorocarbon elastomers in the aircraft and automotive industries. Typical applications for aircraft include O rings for sealing hydraulic, fuel, and engine lubricating systems; those for automobiles are crankshaft and pinion seals, carburetor check valves and valve tips, shock absorber seals, check valves on emission control systems, and so on.¹ Chemical industries use fluororubber in pipe expansion joints, oil and chemical discharge hoses, electrical sleeves, and connectors. Stability at very high temperatures, toughness and flexibility at low temperatures, and resistance to many corrosive chemicals are some of the

properties that are not covered by the conventional polymers and are achieved with fluorocarbon rubbers. These materials have also been gaining importance in the cable industries recently. Most of the above commercial applications are based on the copolymers (of vinylidene fluoride and hexafluoropropylene) and terpolymers (of vinylidene fluoride, hexafluoropropylene, and tetrafluoroethylene). Recently we demonstrated electron beam (EB) curing and modification of fluorocarbon elastomers in the presence and absence of polyfunctional monomers.² EB curing of elastomers has become popular in many applications, because it has certain advantages over conventional curing processes, such as curing at room temperature, the absence of catalyst residue, and as a source of an enormous amount of radicals and ions.³ Dynamic mechanical properties are important in the applications of the elastomers mentioned. The investigation of dynamic mechanical properties has proved to be very useful in determining the glass transition region, relaxation

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spectra, and crosslinking of polymers.⁴ The dynamic loss modulus or internal friction is sensitive to many kinds of molecular motion, relaxation processes, and structural heterogeneities.⁵ With the help of these data, the behavior of fluorocarbon elastomers in actual practical applications can be predicted. EB irradiation of polymeric material like fluorocarbon rubber causes crosslinking (involving C—C bonds) and scission which causes segmentation of the polymeric chain, thus introducing heterogeneity into the system.⁶

Traeger and Castonguay studied the effect of radiation on the dynamic mechanical properties of styrene-butadiene rubber (SBR).⁷ Chaki et al. reported the dynamic mechanical relaxation of EB crosslinked polyethylene grafted with methyl methacrylate.⁸ Kwei and Kwei observed that molecular polydispersity tends to lower the modulus of irradiated polyvinyl chloride (PVC).⁹ Datta et al. reported the dynamic mechanical thermal analysis of EB initiated grafting and crosslinking of ethylene vinyl acetate in the presence and absence of a polyfunctional vinyl monomer like trimethylolpropane trimethacrylate.¹⁰ Thavamani and Bhowmick discussed the effect of crosslink density and resin on the dynamic mechanical properties of hydrogenated nitrile rubber (HNBR).¹¹ However, studies on the dynamic mechanical properties of EB modified fluorocarbon rubber have not been taken up so far, although most of the applications mentioned above require these data. The present article embodies the effect of radiation dose; the level of multifunctional monomer (TMPTA); the nature of functional monomers like tripropylene glycol diacrylate (TPGDA), TMPTA, and tetramethylolmethane tetracrylate (TMMT); magnesium oxide; and the nature of rubber (both the copolymer and terpolymer) on the dynamic mechanical properties of EB modified polymers. IR spectroscopy and gel content were used to understand the nature and level of structural modification in the presence of EB and polyfunctional monomer.

EXPERIMENTAL

Materials

Copolymer (F, 65%; H, 1.9%) and terpolymer (F, 68% and H, 1.4%) fluorocarbon rubbers were supplied by E. I. du Pont de Nemours & Co. TPGDA and TMPTA were obtained from UCB Chemicals (Belgium); TMMT was procured from Shin-Naka-

Table I Specification of Electron Beam Accelerator (ILU-6)

Energy range	0.5–2.0 MeV
Beam power through whole energy range	20 kW
Beam energy spread	10%
Average current (E-1.5 MeV)	15 mA
Adjusting limits for current	0–30 mA
Accelerating voltage frequency	100–120 MHz
Duration of pulse	400–700 μ s
Repetition rate	1–50 Hz
Pulse current	
Maximum	900 mA
Minimum	400 mA
Power supply	
Voltage	3 \times 380/220 V
Voltage frequency	50 Hz
Consumption of power (total)	150 kW

mura Chemical Co. (Japan). Rubber grade magnesium oxide was used.

Preparation and Irradiation of Samples

The rubbers were mixed with polyfunctional monomers in a Brabender Plasticorder PLE-330 at room temperature ($25 \pm 2^\circ\text{C}$) and 60 rpm rotor speed. The mixes were then sheeted out from an open mill. The sheets were compression molded between Teflon sheets at 105°C and 5 MPa pressure in an electrically heated press for 3 min to obtain $11.5 \times 11.5 \times 1$ mm rectangular sheets. The molded samples were irradiated in air at room temperature by an EB accelerator (model ILU-6) at Bhabha Atomic Research Centre (BARC), Mumbai. Irradiation doses of 20, 50, 100, and 200 kGy were used. The specifications of the EB accelerator are given in Table I.

The samples were designated as $\text{BD}_{x/y}$, $\text{BT}_{x/y}$, $\text{BTM}_{x/y}$, $\text{AT}_{x/y}$, and $\text{BT}_{x/y}\text{M}_Z$, where B is the terpolymer, A is the copolymer, x is the level of multifunctional vinyl monomer in percent, y is the radiation dose in kilograys (kGy), D is the TPGDA, T is the TMPTA, TM is the TMMT, M is the magnesium oxide (MgO), and Z is the amount of the MgO used per hundred parts of rubber (phr).

Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic mechanical spectra of various irradiated samples were obtained using a DMT analyzer (DMTA, MK II) from Polymer Laboratory Ltd., U.K. All the samples ($43.5 \times 12.5 \times 1$ mm)

were analyzed in dual cantilever bending mode at a constant frequency of 10 Hz, a strain of 64 μm (peak to peak displacement), and a temperature range from -50 to 150°C . The heating rate was $2^\circ\text{C}/\text{min}$. DMTA MK II software (version 1.2) was used for data acquisition and analysis. The data were analyzed using a Compaq computer.

IR Spectroscopy in Attenuated Total Reflectance (ATR) Mode

IR spectra (in ATR mode) of the control samples and the blends of fluorocarbon rubbers with the polyfunctional monomer were taken on smooth thin (≈ 0.4 mm) irradiated films using a Perkin-Elmer (model 843) spectrophotometer. All the results given are the average of two measurements with three scans for each measurement.

Gel Content

The gel fraction was measured gravimetrically by immersing the samples in methyl ethyl ketone at room temperature (25°C) for 48 h. The equilibrium swelling time was determined from swelling studies at different times. The gel fraction was calculated from the weight of the samples before and after swelling as follows:

$$\text{gel fraction} = w_2/w_1$$

where w_1 is the initial weight of the polymer and w_2 is the weight of the insoluble portion of the polymer. The results reported here are the average of three measurements.

RESULTS AND DISCUSSION

Effect of Radiation Dose

Figure 1(a) shows the damping behavior (as the loss tangent) of the control rubber treated with different irradiation doses against testing temperatures at a frequency of 10 Hz. As the temperature is increased, the damping goes through the maximum in the transition region and then decreases in the rubbery region. Such behavior is typical of all linear amorphous polymers.⁵ The damping is low below the glass transition temperature (T_g) as the chain segments in that region are frozen in. Below the T_g , the deformations are thus primarily elastic, and the molecular slip resulting in viscous flow is low. Also, above the T_g in the rubbery region the damping is low be-

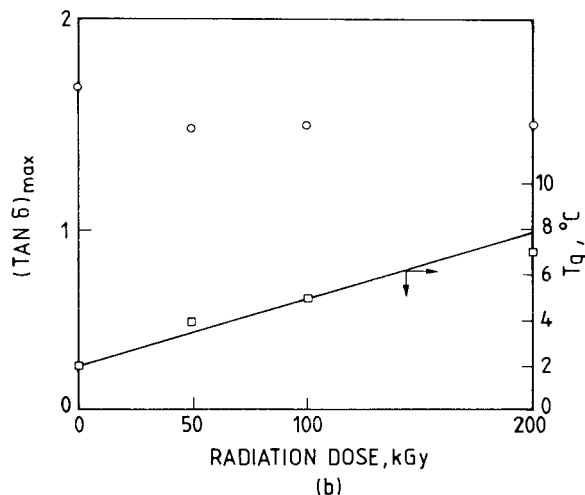
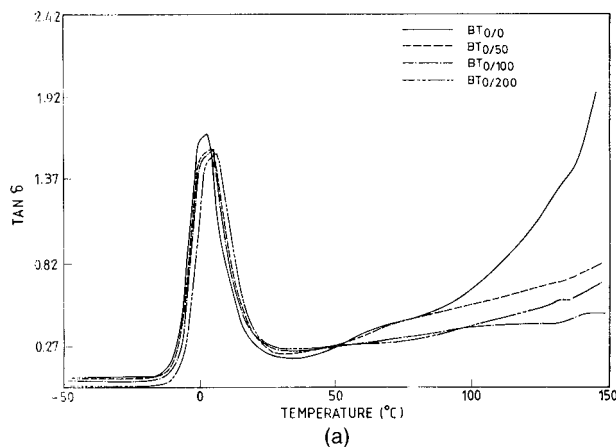


Figure 1 (a) Loss tangent of pure fluorocarbon rubber (terpolymer) irradiated to different radiation doses as a function of temperature. (b) Plot showing the variation of $(\tan \delta)_{\text{max}}$ and the glass transition temperature (T_g) of pure fluorocarbon rubber with radiation doses.

cause the molecular segments are free to move; consequently, there is little resistance to flow. Hence, when the segments are either completely frozen in or free to move, damping is low. In the transition region, on the other hand, the damping is high because of the initiation of micro-Brownian motion of the molecular chains.⁵ Some of the molecular chain segments are free to move; others are not. A frozen-in segment can store much more energy for a given deformation than a free to move rubbery segment. Thus, every time a stressed frozen-in segment becomes free to move, its excess energy is dissipated. Micro-Brownian motion is concerned with the cooperative diffusional motion of the main-chain segments. The position and the height of the loss tangent peak in the relaxation spectra of a poly-

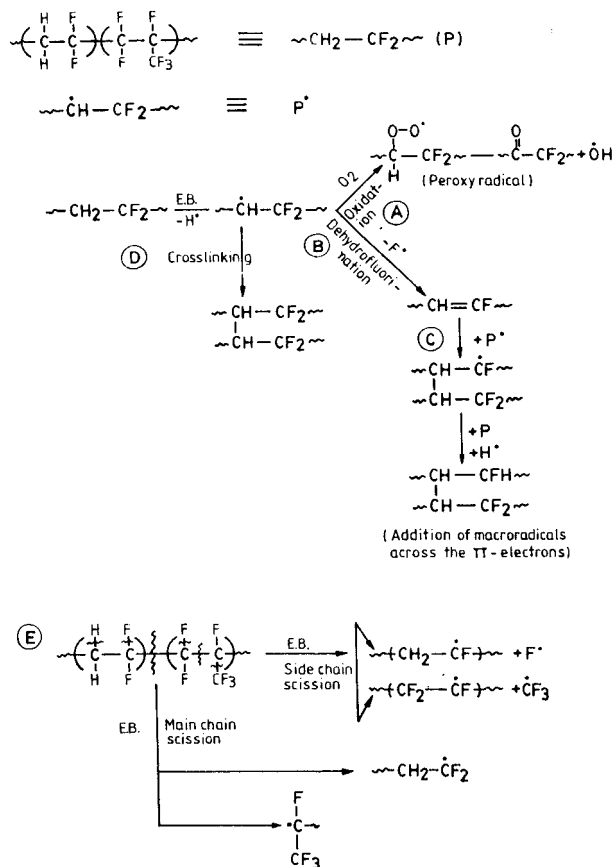
Table II Gel Fraction of Pure and Modified Fluorocarbon Rubbers

Sample	Gel Fraction	Sample	Gel Fraction
BT _{0/0}	—	BT _{5/0}	—
BT _{0/20}	0.56	BT _{5/20}	0.75
BT _{0/50}	0.65	BT _{5/50}	0.83
BT _{0/100}	0.77	BT _{5/100}	0.89
BT _{0/200}	0.87	BT _{5/200}	0.94
BT _{1/0}	—	BD _{3/50}	0.56
BT _{1/20}	0.60	BT _{3/50}	0.77
BT _{1/50}	0.76	BTM _{3/50}	0.78
BT _{1/100}	0.84	BT _{3/50} M ₀	0.82
BT _{1/200}	0.89	BT _{3/50} M ₅	0.85
		BT _{3/50} M ₁₀	0.87
		AT _{0/50}	0.63
		AT _{1/50}	0.72

mer are indicative of the structure and the extent to which a polymer is crosslinked. Figure 1(a) depicts the variation of loss tangent with temperature; the damping peak temperature of the pure fluorocarbon rubber is found to be at 2°C. With an increase in radiation dose, the transition temperature shifts by about 4–6°C. This is accompanied by a decrease in the $(\tan \delta)_{\max}$ value. These are displayed in Figure 1(b). The shifts in either direction are in accordance with the increasing degree of crosslinking and structural changes due to modification. The gel content (shown in Table II) increases with increasing doses of irradiation. Crosslinking hinders the segmental motion, and this then requires a higher temperature for the inception of rotation. However, the peak temperature does not show any significant shift at higher radiation doses; this is probably due to the combined effect of crosslinking (involving shorter and longer chains) and scission reactions prevailing in the presence of the EB. The decrease of the loss tangent peak height of the irradiated samples is possibly due to either crosslinking of the macromolecular chain or perturbed relaxation of the chain molecules as a result of structural changes. The loss tangent data at a higher temperature (125°C) indicate that the same is decreased with irradiation dose up to a level of 100 kGy. Beyond this, $\tan \delta$ values are higher than those of the sample irradiated at the 100-kGy dose predominantly due to the scission reaction. However, the sample displays lower values than the control.

Irradiation of the fluorocarbon polymer in the presence of air initiates aerial oxidation that gen-

erates carbonyl groups on the backbone [Scheme 1(A)]. Arakawa et al.¹² reported the oxidation of polyethylene and ethylene propylene copolymer. These structural changes can be better monitored through IR spectroscopic studies (ATR mode) of the irradiated rubber. The IR spectra of the unirradiated rubber in the 2000–400 cm^{-1} region reveals absorption peaks at 1455 cm^{-1} due to $\backslash \text{CH}_2$ scissor vibration of the vinylidene fluoride unit; at 1397 and 1354 cm^{-1} due to C—F and —CF₃ stretching vibration, respectively; at 1021 cm^{-1} due to C—F and —CF₃ stretching; at 803 cm^{-1} due to C—F deformation vibration; at 727 cm^{-1} characteristic of C—F deformation vibration and —CF₃ asymmetric deformation; at 672 cm^{-1} specific to C—F deformation vibration and asymmetric —CF₃ deformation; at 504 cm^{-1} due to both C—F deformation and asymmetric —CF₃ deformation vibrations; and at 461 cm^{-1} due to asymmetric rocking vibration of the —CF₃ group, which agree with the literature values.¹³ On irradiation, all the bands due to C—F and —CF₃

**Scheme 1**

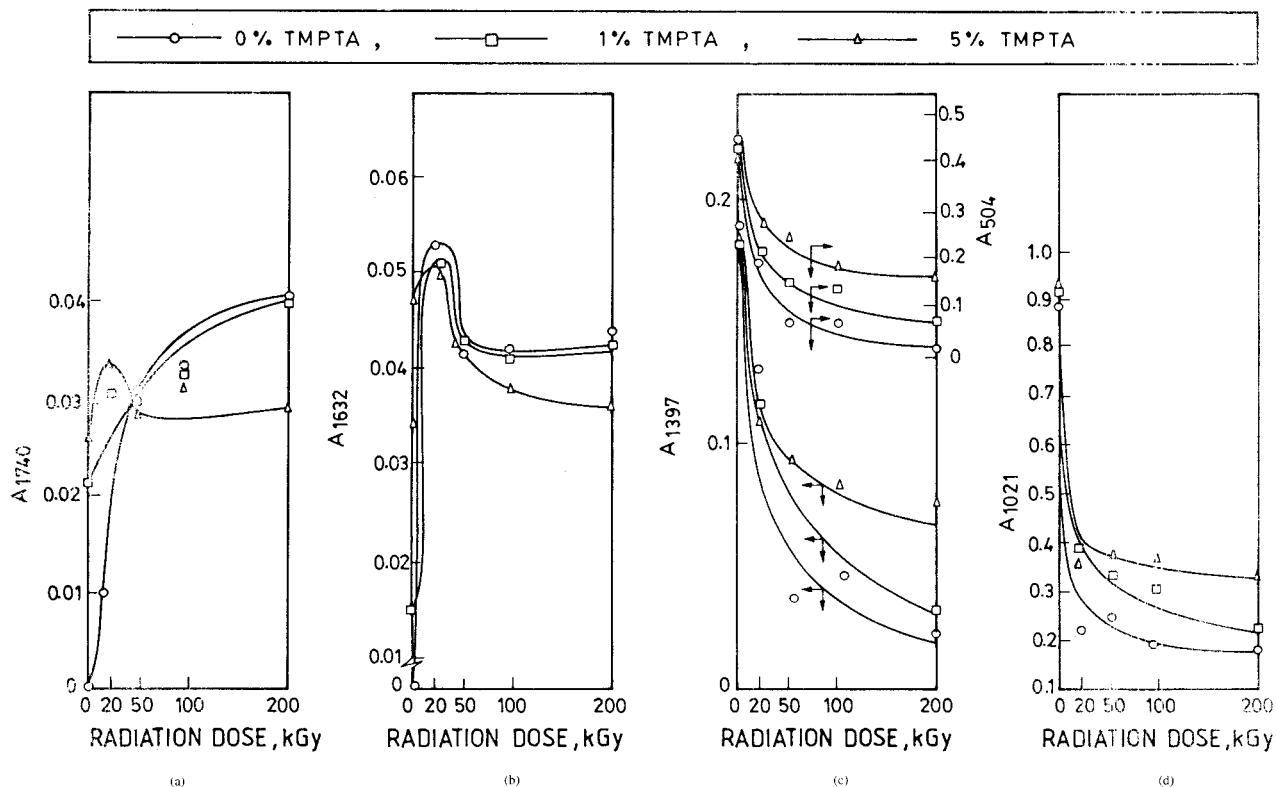


Figure 2 Plots showing the variation of absorbances at (a) 1740, (b) 1632, (c) 1397, (d) 1021, and (c) 504 cm^{-1} of pure and TMPTA mixed fluorocarbon rubbers (terpolymer) with radiation doses.

groups are changed and new peaks at 1740 and 1632 cm^{-1} appear. These are shown in Figure 2(a-d) against irradiation dose. The band at 1740 cm^{-1} corresponds to $\text{C}=\text{O}$ (carbonyl) stretching frequency, and the peak at 1632 cm^{-1} is characteristic of the $\text{C}=\text{C}$ (double bonds).

Double bonds are generated owing to dehydrofluorination [Scheme 1(B)], the latter also being measured from the absorbances due to C—F functional groups at 1397, 1021, 672, and 504 cm^{-1} . Figure 2(a-d) also displays the variation of peak intensities at 1740, 1632, 1397, 1021, and 504 cm^{-1} . It is observed that the concentration of carbonyl group increases with radiation dose but shows marginal variations beyond 50 kGy, while the absorbances due to $\text{C}=\text{C}$ stretching show a decreasing trend beyond 20 kGy after an initial rise. Frequencies due to C—F functional groups decrease with irradiation dose and are then found

to vary marginally beyond 50 kGy. Dehydrofluorination can subsequently lead to the formation of crosslinks through the addition of macroradicals across the π bonds generated on irradiation.¹⁴ Again irradiation of the fluorocarbon rubber initiates both crosslinking through the union of macroradicals generated through the splitting-off of labile hydrogens in its vinylidene fluoride unit [Scheme 1(D)] and scission [Scheme 1(E)] due to the presence of bulky groups like CF_3 and F on its backbone.^{3,15} The results beyond 50 kGy indicate the interplay of various factors as stated above. Any irregularity observed between variations of $\text{C}=\text{C}$ and C—F frequencies are per-

haps due to reactions of scission involving C—C and C—F bonds, as well as formation of crosslinks through double bonds [Scheme 1(C)]. So the increase of the gel fraction with an increase in radiation dose is due to the formation of a network structure, which again involves radical-radical recombination and macroradical addition across double bonds.

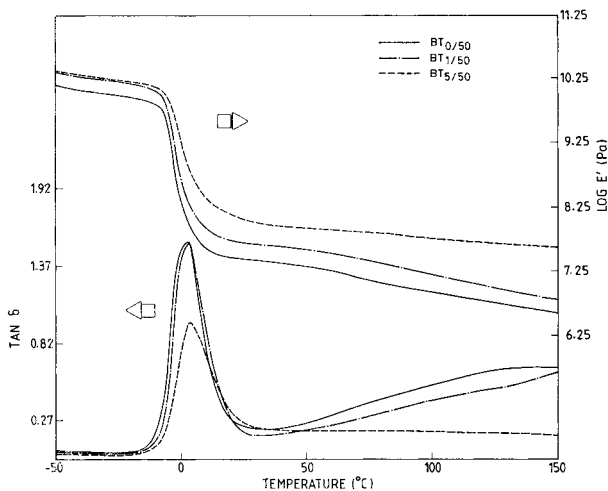


Figure 3 Loss tangent and the dynamic storage moduli of TMPTA blended fluorocarbon rubbers (terpolymer) irradiated with a constant dose of 50 kGy as a function of monomer level.

Effect of Monomer Level

Figure 3 shows the variation of loss tangent and storage moduli against testing temperature of the terpolymeric fluorocarbon rubber blended with TMPTA at levels of 0, 1, and 5 parts and irradiated with a 50-kGy dose. It is clear that at low levels of TMPTA the behavior of the fluororubber TMPTA blends is nearly the same as that of the control rubber; a marked change in behavior is observed only at relatively high levels of TMPTA (5 parts). The dynamic storage moduli of TMPTA mixed systems are higher than the control (irradiated) rubber at any temperature of testing; it is proportional to the amount of radiation dose. The much lower intensity of the loss tangent peak at higher levels of TMPTA reflects the increased degree of crosslinking at the 50-kGy radiation dose. The gel fraction of the blends at higher levels of TMPTA (Table II) is also higher than either the control or 1 part TMPTA mixed system, and the results support the above-mentioned observations. A multifunctional vinyl monomer like TMPTA promotes rapid free-radical induced propagation reactions,⁵ leading to network (cross-linked) polymer structures through grafting via their double bonds^{6,16} (Scheme 2). Grafting of TMPTA is also supported by the absence of any characteristic IR peak in the chloroform extract in the blends.

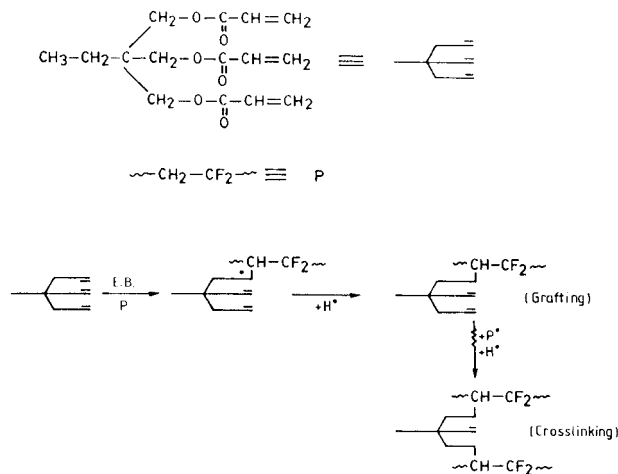
A mobilizer like TMPTA increases the radical-radical terminations and hence decreases the extent of scission reactions and oxidation.¹⁵

IR spectroscopic studies [Fig. 2(a-d)] reveal reduced concentration of $\text{C}=\text{O}$ and $\text{C}=\text{C}$ groups and increased $\text{C}-\text{F}$ intensities, particularly at higher levels (5 parts) and doses beyond 50 kGy.

It was also observed that low TMPTA mixed systems show higher losses when subjected to periodically varying stresses at temperatures higher than 50°C. An increase of temperature perhaps randomizes the motion of free chain ends and molecular chain segments of low TMPTA blended systems. As a result, an increased slippage between free chain moieties causes the $\tan \delta$ of the low TMPTA mixed systems to rise with temperature, as compared to blends of rubber with TMPTA at relatively higher levels.

Influence of Monomer Nature

Multifunctional vinyl unsaturated monomers are used in radiation crosslinked rubber formulations to reduce the dose level to obtain optimum properties or to achieve an increased state of cure at the same dose.⁶ Their reactivity is governed by various factors like the number of double bonds,¹⁷ shape and size,¹⁸ and so on. Figure 4 displays the plot of loss tangent and the dynamic storage moduli of TPGDA, TMPTA, and TMMT mixed fluorocarbon rubber (terpolymer) against testing temperature at a frequency of 10 Hz. An irradiation dose of 50 kGy was used. It is observed that the height of the $\tan \delta$ peak decreases as the number of double bonds in the polyfunctional monomer is increased. The storage modulus of the



Scheme 2

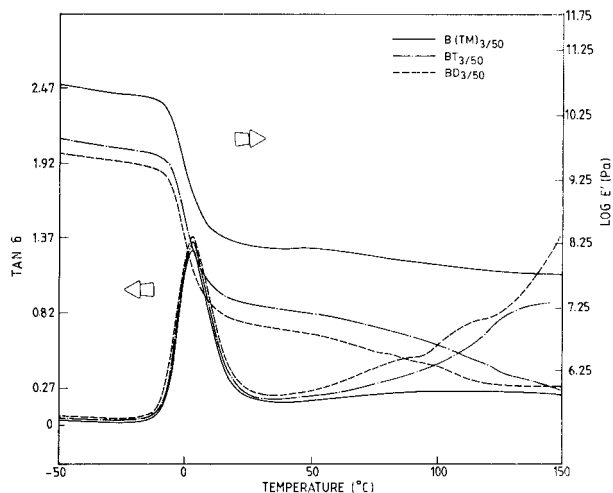


Figure 4 Relaxation spectra of systems based on various multifunctional monomers at a constant radiation dose of 50 kGy.

TMMT based system is also higher. Because the $\tan \delta$ decreases with increasing crosslink density,¹¹ it might be possible that TMMT is more effective in producing a slightly denser network than TPGDA having the lowest unsaturation. The gel fraction of the TPGDA mixed system (Table II) corroborates the above findings.

Effect of Magnesium Oxide

Magnesium oxide is used in the conventional formulations of fluorocarbon rubber to act as an acid (HF) acceptor. So it was of interest to see its role on the structural modification of fluorocarbon rubber in the presence of EB radiation. Figure 5 dis-

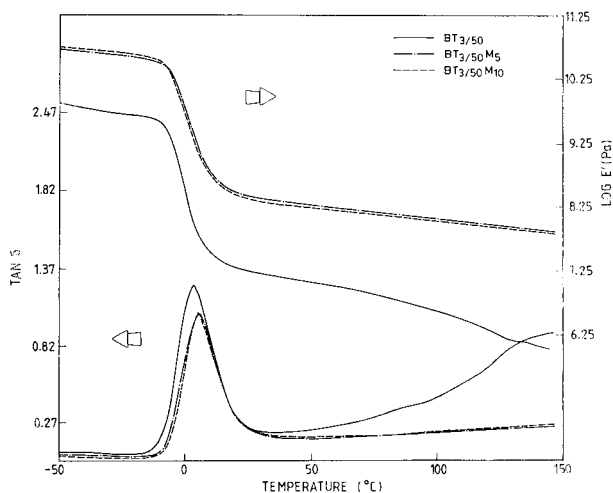


Figure 5 $\tan \delta$ and dynamic storage moduli of MgO mixed fluorocarbon rubbers (terpolymer) at a constant TMPTA level (3 parts) and an irradiation dose of 50 kGy.

Table III IR Spectroscopic Results of Systems Based on MgO and Various Polyfunctional Monomers

Sample	A_{1632}	A_{1021}	A_{1740}
BT _{3/50}	0.045	0.240	0.027
BT _{3/50} M ₅	0.048	0.100	0.025
BT _{3/50} M ₁₀	0.053	0.046	0.024
BT _{3/50} M ₁₅	0.055	0.025	0.023
BT _{1/50}	0.042	0.340	0.029
AT _{1/50}	0.049	0.370	0.032
B(TM) _{3/50}	0.047	0.380	0.034
BD _{3/50}	0.042	0.230	0.030

plays the variation of the loss tangent and the dynamic storage moduli of the terpolymeric fluorocarbon rubber against testing temperature in the absence and the presence of MgO at levels of 5 and 10 phr; each was irradiated with a dose of 50 kGy. TMPTA at a level of 3 parts was used. For clarity, the data of 15 and 20 phr MgO mixed systems are not shown. The relaxation spectra of the MgO mixed systems shows a shift of the damping peak temperature toward a higher temperature as compared to the system without magnesium oxide. Correspondingly, a higher storage modulus is obtained. The higher storage modulus for the MgO mixed system indicates a higher degree of crosslinking in the presence of MgO as supported by an increase in the gel fraction of magnesium oxide blended systems (Table II). IR studies register an increased concentration of double bonds (cf. A_{1632}) and a reduced concentration of C—F functional groups (cf. A_{1021}) as compared to the control rubber (Table III). Although the exact mechanism by which MgO functions is not clear, it may be explained on the basis of the fact that MgO (being basic in nature) probably increases the amount of unsaturation through dehydrofluorination by accepting the HF liberated in the presence of EB. Crosslink formation through the addition of macroradicals across the double bonds [Scheme 1(C)], and radical recombination may explain such observations.

Influence of Rubber Nature

Figure 6 shows the variation of loss tangent against testing temperature of the blends of copolymeric and terpolymeric fluorocarbon rubber with TMPTA (1 part). An irradiation dose of 50 kGy was used. The $\tan \delta$ at a higher temperature (>25°C) of the system based on the terpolymer

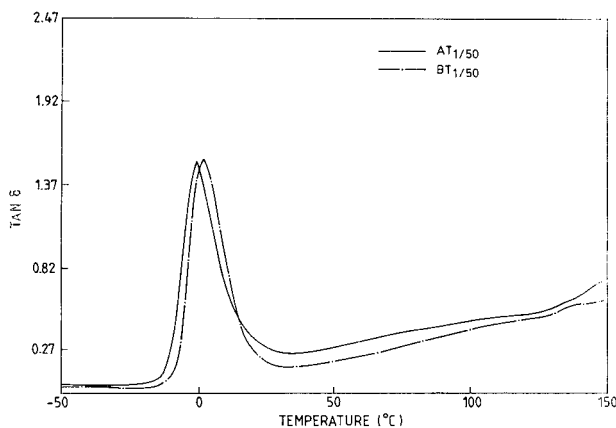


Figure 6 Plot showing the variation of loss tangent of the systems based on the copolymeric and terpolymeric fluorocarbon rubber at a TMPTA level of 1 part and a radiation dose of 50 kGy.

is much lower than that of the copolymer. The damping peak temperature of the blends of TMPTA with the terpolymer shows a higher shift compared to that of the copolymer.

All these observations point to the slightly higher degree of crosslinking of the system based on the terpolymer. The gel fraction of the TMPTA mixed terpolymer rubber is also slightly higher than the blends of TMPTA with the copolymer (Table II); this is in agreement with the relaxation spectra observed in the above two systems. This can be explained as follows: the hydrogen content of the copolymer (1.9%; F, 65%) is slightly higher than that of the terpolymer (1.4%; F, 68%); the macroradicals generated through splitting-off of the labile hydrogens of the copolymer react more with oxygen in air, leading to a slightly higher tendency toward oxidation (determined from the IR studies, Table III). Because oxygen stabilizes the radicals, chances that the macroradicals will unite to form crosslinks are reduced. As a result, the concentration of the free-chain ends is increased. This causes chain slippage under periodic stresses imposed on the macromolecular segments, thus giving rise to higher energy losses as shown by a higher value of the loss tangent of TMPTA mixed fluorocarbon (copolymer). A low state of cure of the copolymer as compared to the terpolymer has also been reported in the literature.¹⁹

CONCLUSIONS

The dynamic mechanical properties of EB modified fluorocarbon rubbers were investigated. With

an increase in radiation dose the height of the damping peak decreased and the peak temperature of the irradiated fluorocarbon rubber (terpolymer) shifted to higher values due to an increasing degree of crosslinking. A decrease of the maximum of the loss tangent peak was perhaps due to the combined effect of reduced segmental motion as a result of crosslinking and perturbed relaxation of molecules as a result of structural modification. The gel fraction increased with radiation dose but varied marginally at higher radiation doses. IR spectroscopic studies revealed that oxidation showed marginal changes beyond 50 kGy for pure rubber, while dehydrofluorination measured from the C—F stretching decreased with radiation dose.

In the blends of TMPTA with rubber, the grafting and crosslinking through double bonds of the monomer took place. The mixes of TMPTA and rubber with a higher level of the TMPTA (5 parts) showed an increased tendency toward crosslinking as compared to the blends at low levels of TMPTA (0 and 1 parts). The loss tangent maximum of fluorocarbon rubber mixed with TMPTA at low levels was higher and the corresponding storage moduli were lower as compared to a mix at higher levels of TMPTA. The gel fraction of the latter system was higher. IR spectroscopic studies indicated a decreased tendency toward reactions of scission at higher levels of the polyfunctional monomer. So the increased $\tan \delta$ at low levels of TMPTA was due to the relaxation of dangling free chain ends and entanglements.

The system based on TPGDA showed higher energy losses as compared to one based on TMMT or TMPTA, indicating reduced crosslink density of the former.

The loss tangent of the MgO mixed fluorocarbon rubbers was lower than that of the control rubber, and the storage modulus was higher, indicating an increase in the extent of crosslinking. IR spectroscopy (in ATR mode) showed a slightly higher tendency toward dehydrofluorination of MgO rubber mixtures.

The loss tangent of the system based on the copolymer was marginally higher than that of the terpolymer based one due to the lower gel fraction.

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