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Bulk and Surface Modification of Elastomers by Electron Beam Irradation: Structure-property Relationship

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SUMMARY : Bulk and surface modification of ethylene propylene diene monomer (EPDM) and fluoroelastomer by electron beam irradiation was investigated. The structure of the modified elastomers was analysed with the help of Infrared (IR) spectroscopy, Electron Spectroscopy for Chemical Analysis (ESCA) and gel content. Mechanical and dynamic mechanical properties of bulk modified fluoroelastomers and surface energy and frictional coefficient of the surface modified EPDMs were measured. The properties were correlated with the structure developed.

Introduction

Modification of thermoplastic and rubbery materials by electron beam irradiation is a potential method for the development of new polymers and composites. Irradiation of polymeric materials results in grafting and subsequent formation of a three dimensional network through the union of macroradicals generated[1-4]. The process is very clean, requires less energy, permits greater processing speed and operates at ambient temperature. Such consequences are rarely possible in the case of crosslinking induced by thermochemical means[5,6]. Other advantages include formation of crosslinking in the solid state, no heat treatment and the ability to crosslink polymers which are largely resistant to chemical treatments. The use of polyfunctional monomers, such as multifunctional acrylates and allylic reactive molecules, in blends with the base polymer, is very effective in achieving the crosslinking at a reduced radiation dose level to meet the optimum properties without much deterioration of the base polymers.[7,8]

Pearson and Bohm[9] investigated the physical properties of radiation cured polybutadiene and its copolymers. Loan[10] found that the rate of net degradation decreased with increasing isoprene content in the poly (isobutylene isoprene) polymer. Zapp and Oswald[11] reported the physical properties of radiation crosslinked chlorobutyl compounds. Harman[12] carried out a comparative study between radiation cured and chemically vulcanised natural rubber. Arakawa et al[13] discussed radiation induced modification of

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polyethylene, ethylene-butene copolymers and ethylene propylene copolymer rubber. Bhowmick et al[14] carried out structural modification of ethylene vinyl acetate copolymer in the presence of trimethylol propane trimethacrylate and triallyl cyanurate. The influence of electron beam radiation on polymers was reported recently by several authors[15-18]. The effect of gamma radiation on synthetic elastomers was also investigated by a few workers[19-20].

The surface modification of polymers has attracted considerable interest in recent years. Techniques such as chemical reaction[21], graft copolymerization[22], physical blending[23], oxidation[24], plasma, corona discharge and laser modification[25-26] and treatment with ozone [27] were used for this purpose. Photo-chemically induced grafting of vinylic monomers such as acrylic acid and acrylamide was shown to give materials that exhibited increased surface wettability[28]. The electron beam initiated surface modification of polymers is a relatively modern technique because of the advantages described before. The effect of triallyl cyanurate in the presence of electron beam on the structure and surface properties of polyethylene was described[29]. Modification of isotactic polypropylene by a cold plasma or an electron beam was also discussed[30]. Sen Majumder and Bhowmick[31,32] reported on electron beam irradiated ethylene propylene diene rubber (EPDM).

The present paper will highlight bulk and surface modification of EPDM and fluorocarbon rubber by electron beam irradiation. The structure developed on irradiation has been analysed by infrared (IR) spectrophotometer and electron spectroscopy for chemical analysis (ESCA), and gel content. Surface energy and frictional properties of the modified surfaces has been reported here. Mechanical and dynamic mechanical properties of the bulk modified samples have been investigated. Finally, the properties have been correlated with the structure developed.

Experimental

Materials :

Keltan 520-DCPD containing rubber of density 860 kg/m^3, diene content = 4.5 mol%, viscosity average molecular weight = 1.93x10^5 g/g mol and ethylene propylene ratio = 58/42 mol/mol was obtained from DSM Chemicals, Holland.

Fluorocarbon rubber (Viton B-50, 68% Fluorine, 1.4% Hydrogen, density = 1850 kg/m^3) was supplied by EI dupont de Nemours and Company, USA.

Trimethylol propane triacrylate (TMPTA, flash point >100°C, boiling point >100°C , specific density 1110 kg/m^3) was obtained from UCB Chemicals, Belgium. Methyl Ethyl Ketone (MEK) and Acetone used were of chemically pure grade and obtained from E. Merck Ltd., Mumbai and Ranbaxy Laboratories, Punjab, India respectively. For contact angle measurements, doubly distilled water, analytical grade formamide and diiodomethane were used.

Preparation of the samples :

Bulk Modification[16] :

Fluorocarbon rubber was mixed with TMPTA in the Brabender Plasticorder PLE 330 at room temperature for 3 minutes at 60 rpm rotor speed. EPDM was mixed with DCP (0.2 phr) and then further compounded with TMPTA in the Plasticorder at 25°C for 2 minutes at the same rotor speed. The mixes were then sheeted out on an open roll mill followed by compression molding at a temperature of 105°C for 3 minutes for fluorocarbon rubber and at a temperature of 150°C for 45 minutes for EPDM rubber at a pressure of 5 MPa to obtain rectangular sheets.

Surface Modification [31] :

EPDM was mixed with 0.2 phr DCP on an open roll mill at 25°C. The mix was then compression molded between Teflon sheets at a temperature of 150 °C and at a pressure of 5 MPa for 45 minutes optimum cure time to obtain rectangular sheets of 150x120x2 mm in dimension. The sheets were then washed with acetone to remove any trace of residual peroxide on the surfaces and air dried at room temperature. They were then vertically immersed completely in a solution of MEK for 30 minutes. The time and the concentration were optimised by infrared spectroscopic studies. The sheets were then air dried at 25 °C for 30 minutes. Only EPDM was used in this investigation.

Irradiation of the samples :

The molded rectangular rubber sheets, both surface and bulk modified, were irradiated in an electron beam accelerator (Model ILU-6) in the presence of air at Bhabha Atomic Research Centre, Mumbai. Irradiation doses from 0-500 kGy were used. Specifications of the electron beam accelerator were reported earlier[14]. The bulk and surface modified samples were designated as $TP_{x/y}$ (for fluorocarbon rubber) or $EB_{x/y}$ (for EPDM) and $E_{x/y}$ respectively where, x = TMPTA concentration in percent, y = irradiation dose in kGy.

Structure Determination :

Attenuated Total Reflectance (ATR) Spectroscopy/Infrared (IR) spectroscopy :

ATR spectra of the fluorocarbon rubber and EPDM rubber samples modified with TMPTA at different concentrations were taken on smooth thin irradiated films using KRS-5 crystal in a Perkin Elmer Model 837 spectrophotometer. IR spectra of TMPTA were taken on KBr pellets.

X-ray Photoelectron spectroscopy:

X-ray photoelectron spectroscopy of the surface modified samples was taken using a VG Scientific ESCA Lab MKII Spectrophotometer employing an exciting radiation of 1250 electron volt (MgK_α). The working pressure in the instrument was $2x10^{-9}$ torr. C1s and O1s spectra were deconvoluted with the help of a standard Gaussian programme on a computer.

Gel Fraction :

Previously weighed samples were allowed to swell in a solvent for equilibrium time after which the test pieces were taken out and dried to a constant weight in a vacuum oven at 70°C. Gel content was calculated using the relation

$$\text{Gel content (\%)} = (W_2/W_1)x100 \qquad \ldots (1)$$

where, W_1 = Initial weight of the polymer

W_2 = Weight of the insoluble portion

The conditions for swelling were as follows :

For fluorocarbon rubber, the solvent was methyl ethyl ketone, and the equillibirum time was 48 hours at 25°C. For EPDM, the solvent was n-heptane and swelling time was 12 hours at 40 °C.

Measurement of Properties :

Contact Angle Measurement :

The contact angles were determined using a Kernco model G-II contact angle meter. The sessile drop method of measurement of the contact angle was employed using 4 μl drops of bidistilled water, formamide and diiodomethane as the probe liquid. The equilibrium time was 10 minutes in each case and maximum error in θ was ± 1° on the average of at least six measurements. All *investigations* were carried out at 20 ± 2°C in a closed sample box . The parameters of the test liquid used were taken from earlier paper[32]. The values of θ were used to calculate the work of adhesion, W_A and the total surface energy of the surface. Three liquids were used in the measurement of contact angle, two of which were polar. From the contact angles of apolar liquid 1 and polar liquids 2 and 3, a set of three equations was constructed [33-34].

$$\gamma_1 \left(1 + \cos \theta_1\right) = 2\sqrt{\gamma_s^{LW} \gamma_1^{LW}} \qquad \ldots (2a)$$

$$\gamma_2 \left(1 + \cos \theta_2\right) = 2\sqrt{\gamma_s^{LW} \gamma_2^{LW}} + 2\sqrt{\gamma_s^{(+)} \gamma_2^{(-)}} + 2\sqrt{\gamma_s^{(-)} \gamma_2^{(+)}} \qquad \ldots (2b)$$

$$\gamma_3 \left(1 + \cos \theta_3\right) = 2\sqrt{\gamma_s^{LW} \gamma_3^{LW}} + 2\sqrt{\gamma_s^{(+)} \gamma_3^{(-)}} + 2\sqrt{\gamma_s^{(-)} \gamma_3^{(+)}} \qquad \ldots (2c)$$

With the parameters γ_l and γ^{lw}, $\gamma^{(+)}$ and $\gamma^{(-)}$ for a number of useful liquids — water, formamide and diiodomethane, equations 2(a)-2(c) were solved for the three parameters of the solid.

The thermodynamic work of adhesion was determined from the equilibrium contact angle θ and the surface tension of the liquid as follows :

$$W_A = \gamma_l \,(1 + \text{Cos}\,\theta) \qquad \ldots (2d)$$

Friction properties :

The friction measurement was performed on a Zwick UTM machine. Normally all the tests were carried out at 25°C on an aluminium friction table of roughness 0.72 μm. The sliding speed was $8.3\text{x}10^{-4}$ m/s. The average steady state value of the kinetic force of friction, F, was noted on the $1.8\text{x}10^{-1}$ m path travelled by the sample. The coefficient of the kinetic friction μ was calculated as follows :

$$\mu = F/F_n \qquad \ldots (3)$$

where, F_n is the normal force due to the applied load. Estimates of the layer moduli of the samples were made by the bending of the treated and untreated sample strips[35]. The equation used was

$$d_2/d_1 = 1 + 6E_1 t_1/E_2 t_2 \qquad \ldots (4)$$

where d, t, E terms refer to the deflection, thickness and modulus respectively of treated and untreated samples. Approximate thickness, t, of the modified layer of the surface treated samples was measured from crosssections of the sample using an optical microscope at 200 magnification. Young's Modulus, E was determined on tensile dumbell at a rate of 8.3×10^{-3} m/s at 27°C according to ASTM D412-92 method. These were reported in an earlier paper[36].

Dynamic Mechanical Properties :

The dynamic mechanical spectra of various irradiated samples were obtained using a dynamic mechanical thermal analyser (DMTA MKII) from POLYMER Laboratory Ltd., UK. All the samples (43.5x12.5x1 mm) were analysed in dual cantilever bending mode at a constant frequency of 10 Hz and a strain of 64 μm (peak to peak displacement) and a temperature range from -50 to 150°C. Heating rate was 2°C per minute. DMTA MKII software was used for data acquisition and analysis. The data were analysed using a COMPAQ computer.

Mechanical properties :

Tensile strength, elongation at break, 300% modulus and tensile set at 100% elongation were measured on dumbell specimens according to ASTM D412-93 specification in a Zwick 1445 Universal Testing Machine at a strain rate at 8.3×10^{-3} m/s at a room temperature of 25±2°C. Hysteresis loss was also measured at the same temperature.

Results & Discussion

IR spectra of unirradiated TMPTA and TMPTA radiated to various irradiation doses were taken. The peak at 1630 cm^{-1} due to C=C stretching vibration of the control TMPTA decreases with radiation dose upto 100 kGy. Liquid TMPTA becomes solid on irradiation. The peak absorbance at 1630 cm^{-1} normalized with respect to 1460 cm^{-1} due to CH_2 scissor vibration when plotted against the radiation dose indicates that the absorbance ratio decreases sharply with an increase in the irradiation dose in the initial stage before reaching an almost constant value (Figure 1a). Similar behaviour was observed also with other multifunctional acrylates[37]. During irradiation a large number of free radicals and radical cations is generated on the TMPTA molecule. As a result, TMPTA undergoes several reactions, i.e. polymerisation, cyclopolymerisation, crosslinking, cyclisation etc. as shown in Scheme 1[31]. This explains the gradual decrease in absorbance ratio. The peak ratio of

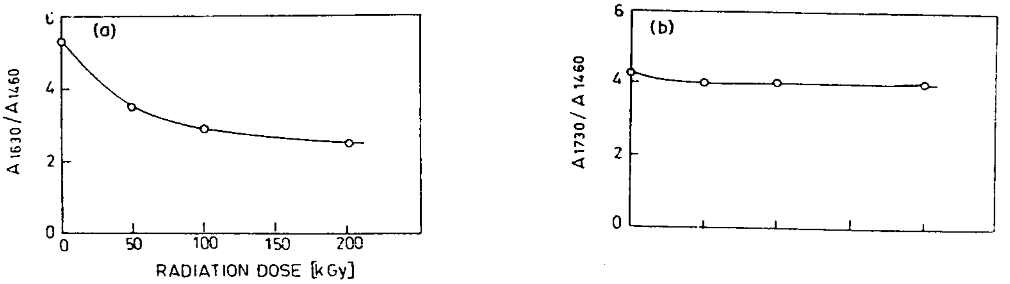
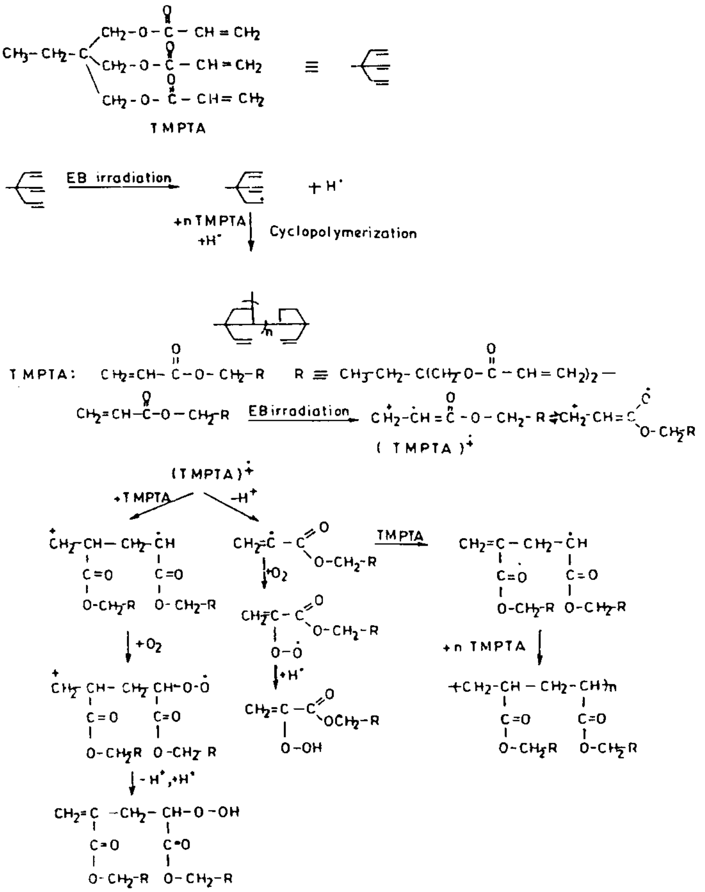


Fig. 1 Change of absorbance ratio of A_{1630}/A_{1460} and A_{1730}/A_{1460} with irradiation dose for TMPTA



SCHEME 1. REACTION SCHEME SHOWING PLAUSIBLE MECHANISM OF POLYMERIZATION OF TMPTA BY FREE RADICAL AND IONIC MODES

absorbances at 1730 cm^{-1} and 1460 cm^{-1} does not change with irradiation dose (Figure 1b), as the carbonyl groups as such have no active role to play in the polymerisation or crosslinking of the TMPTA molecules.

From the IR-ATR spectra of the control EPDM rubber, the main peaks are observed at 1730, 1630, 1460, 1375, 1260, 1120 and 1019 cm^{-1}. On irradiation at 50, 100 and 200 kGy irradiation doses, the peak absorbances at 1730, 1260, 1120 and 1019 cm^{-1} initially increase. On the other hand, the absorbances at 1460 cm^{-1} and 1375 cm^{-1} decrease. Absorbance at 1630 cm^{-1} remains almost constant. These are shown in Figure 2. The increase in absorbances at 1260, 1120, 1019 and 1730 cm^{-1} is due to the oxidation of EPDM. The decrease in absorbance at 1460 and 1375 cm^{-1} is due to the chain scission and disproportionation. The constant absobance values at 1630 cm^{-1} are due to self-crosslinking through the double bonds as well as generation of double bonds. Thus, an equilibrium is struck between crosslinking, grafting, scission and disproportionation at the above irradiation doses[31]. Although ions and excited state molecules can give rise directly to chemical reactions, evidence indicates that in most cases, specially for organic polymers, the predominant intermediate in radiation chemistry is the free radical[4]. At higher doses, the scission reactions predominate making the C-O-C absorbance almost constant. Figure 2 also shows the changes in absorbance at 1730, 1630, 1460, 1375, 1260, 1120 and 1019 cm^{-1} at various irradiation doses in presence of TMPTA for bulk and surface modified samples. The trends in the values of absorbance at 1730, 1019, 1120 and 1260 are same as the control sample due to the reasons given above. The higher concentration of C-O-C in the case of treated sample is due to the presence of C-O-C group of TMPTA, which is grafted onto EPDM. The absorbances at both 1460 cm^{-1} and 1375 cm^{-1} due to $> CH_2$ scissor vibration and CH_3 stretching vibration respectively exhibit an upward trend upto 50 kGy irradiation dose due to enhancement of grafting and crosslinking of EPDM by TMPTA with irradiation. These are well supported by the increase in gel content with irradiation dose. A representative figure is shown in Figure 3. After 50 kGy dose the increase is marginal, as other reactions such as chains scission, disproportionation etc. predominate at higher radiation doses in the presence of electron beam. The results are further corroborated from the XPS analysis. Table 1 shows the detailed results of the representative samples of EPDM. C1s peak for the control EPDM, $E_{0/0}$, appears at 284.9 ev binding energy. The additional peaks observed due to curve fitting of C1s are at 286.2 ev (a shift of 1.3 ev) and 287.7 ev (a shift of 2.7 ev) which may be ascribed to C - O and C = O groups respectively.

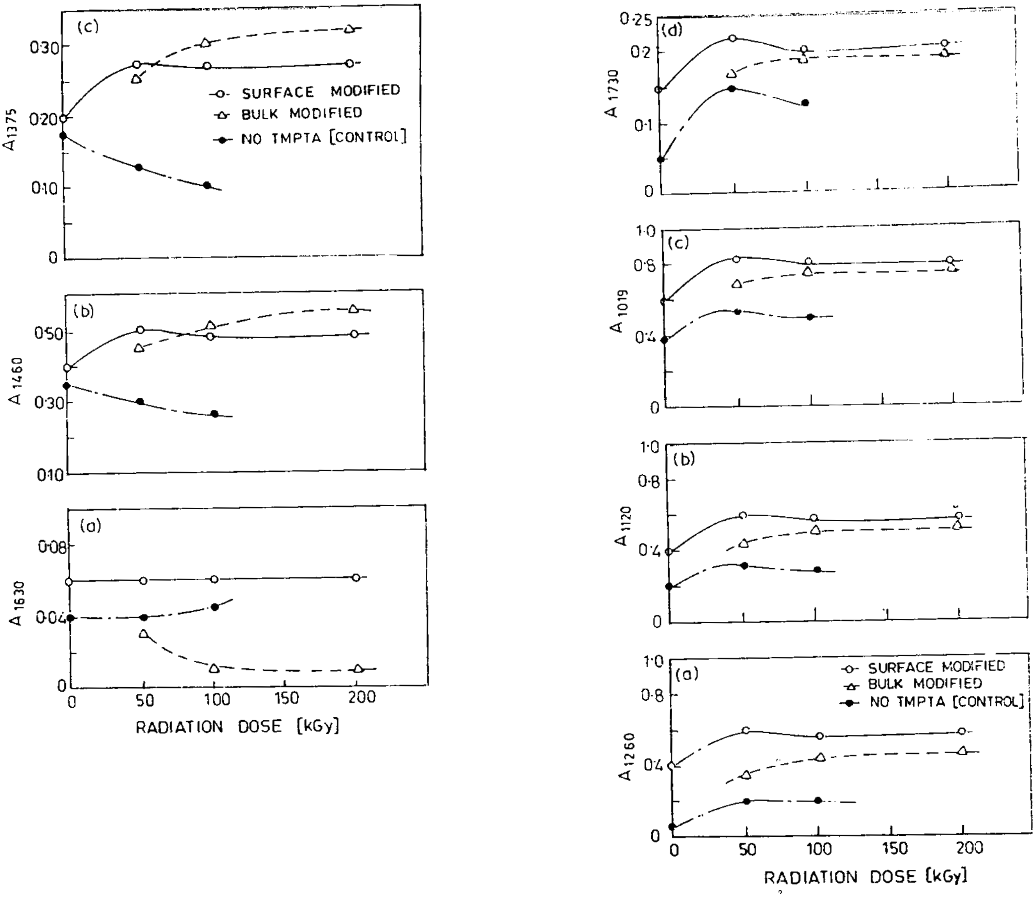


Fig. 2 Change of absorbances of surface modified, bulk modified and control EPDM samples with irradiation dose.

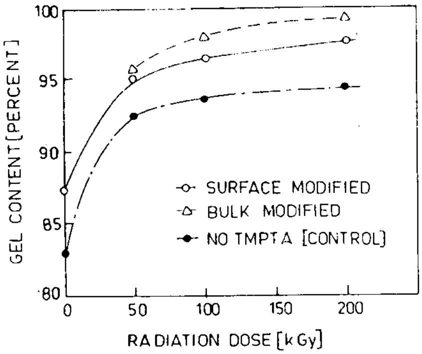


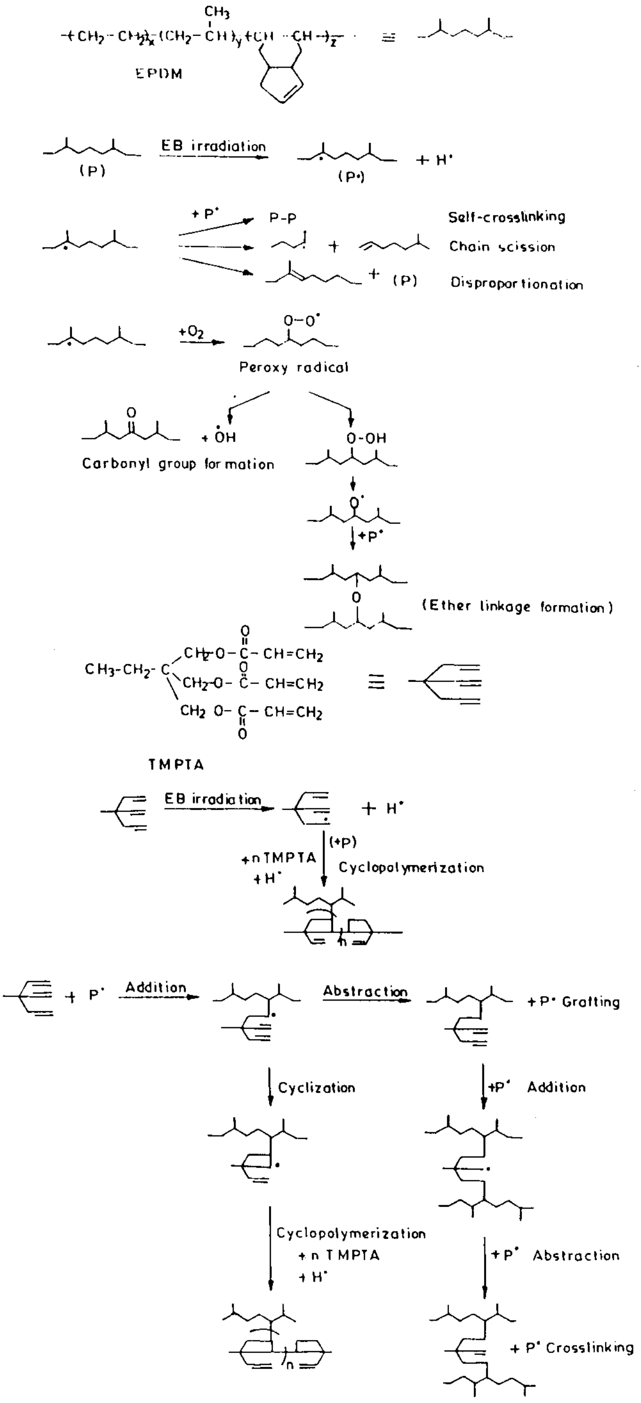
Fig. 3 Plot of gel content of EPDM against irradiation dose.

Table 1 : XPS Details of C1s and O1s spectra from the control and the grafted EPDMs

SAMPLE CODE	C1s		O1s	
	PEAK POSITION (eV)	RELATIVE AREA (%)	PEAK POSITION (eV)	RELATIVE AREA (%)
$E_{0/0}$	284.9	80.5	532.4	78.8
	286.2	14.2	533.2	21.2
	287.6	5.3		
$E_{10/50}$	286.3	69.7	534.6	80.4
	288.6	24.4	536.9	19.6
	290.9	3.9		
	293.5	2.1		
$E_{10/100}$	285.7	75.4	533.6	77.0
	288.1	19.6	535.7	23.0
	290.5	3.5		
	293.0	1.5		
$E_{10/200}$	285.4	78.0	533.0	75.5
	287.5	19.0	535.2	24.5
	288.9	3.0		

There is a distinct shift of the peaks to higher binding energy on irradiation of the samples. A marked decrease in the relative area concentration of the C1s core peak and a corresponding increase in the concentration of the other constituent peaks are also observed. These changes are largest in the case of $E_{10/50}$ sample. The same effect is also prominent in the appearance of the peaks in the O1s region. The oxygen concentration is highest with $E_{10/50}$ sample. The results are in accordance with those of IR-ATR measurements, where the absorbance at 1730 cm^{-1} due to C = O and at 1260, 1120 and 1019 cm^{-1} due to C-O-C exhibit maximum values at 50 kGy irradiation dose. As the concentration of TMPTA is increased, the absorbance values at 1730, 1630, 1460, 1375, 1260, 1120 and 1019 cm^{-1} increase in the lower concentration range & then decrease, yielding an optimum value at 10% concentration for the surface modified samples. All the reactions could be explained with help of Scheme 2[31].

The results of Fluorocarbon elastomer are very similar, expecting that there is considerable dehydrofluorination upto a certain irradiation dose[37]. The characteristics peaks of fluorocarbon rubber are observed at 1455 (> CH_2 scissor vibration of vinylidene fluoride unit), 1397 (CF stretching vibration), 1354 (-CF_3 stretching vibration), 1021 (C-F and CF_3 stretching), 803 (C-F deformation), 727 (C-F deformation, -CF_3 stretching), 672 (C-F deformation vibration, asymetric-CF_3 deformation) and 504 (C-F deformation asymetric-CF_3 deformation vibration) cm^{-1}. The effects of irradiation on the absorbances at 1397, 1021, 504, 672, 1740 and 1632 cm^{-1} are shown in Figure 4. On irradiation, the peaks at 1397, 1021, 672, 504 cm^{-1} due to C - F functional groups gradually decrease. The absorbances at 1740 and 1632 cm^{-1} due to carbonyl groups and double bonds appear[37]. Due to dehydrofluorination, the double bonds indicated by 1632 cm^{-1} peak are generated. Carbonyl groups are formed owing to the atmospheric oxidation. The concentration of carbonyl group increases sharply with radiation dose in the initial stage, but changes only marginally beyond 50 kGy. A slight decrease is observed beyond 200 kGy. The concentration of the double bonds on the other hand shows a decreasing trend beyond 20 kGy after an initial rise. At high irradiation dose, there is again an increase. These observations are explained with the help of the following scheme (Scheme 3)[37]. Macroradicals are first generated which either react with oxygen in the air or participate in the dehydrofluorination. The resulting unsaturation can subsequently lead to the formation of crosslinks through the addition of macroradicals across the double bonds. Macroradicals can recombine also to form crosslinks. Due to the bulky groups of CF_3 on the backbone of



SCHEME 2. REACTION SCHEME SHOWING ELECTRON BEAM IRRADIATION OF EPDM AND PLAUSIBLE MECHANISM OF INTERACTION OF TMPTA WITH EPDM

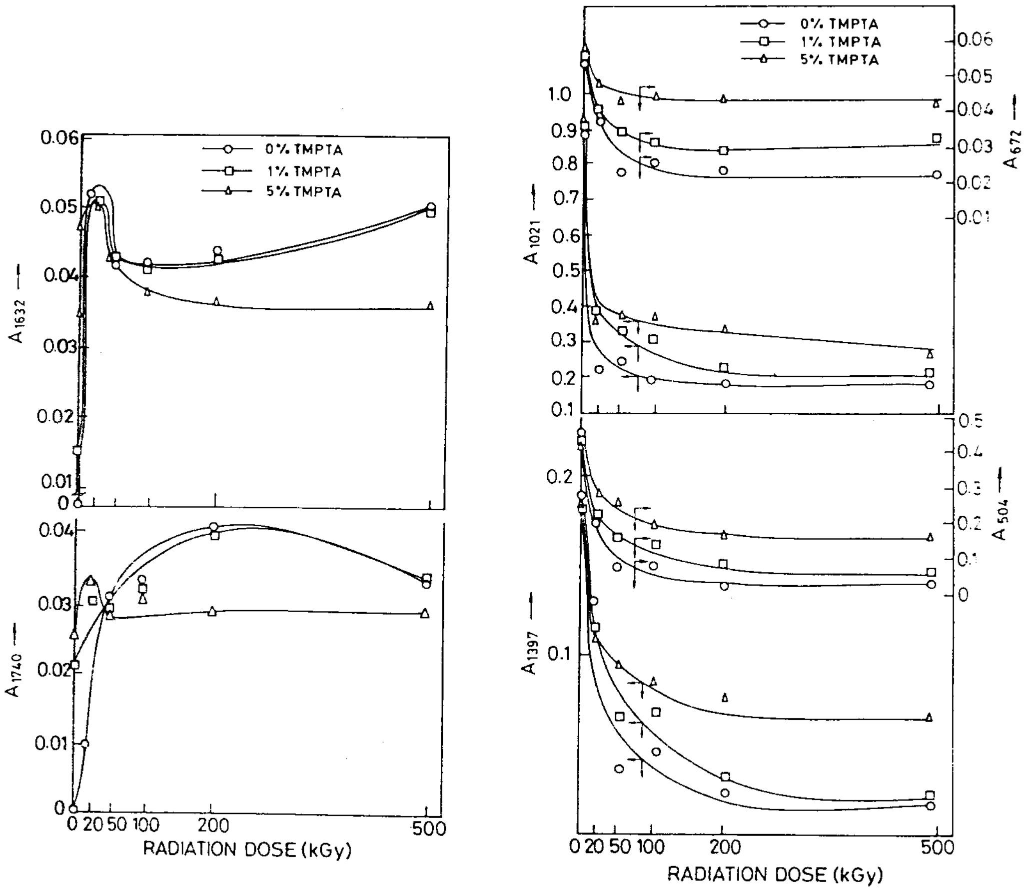
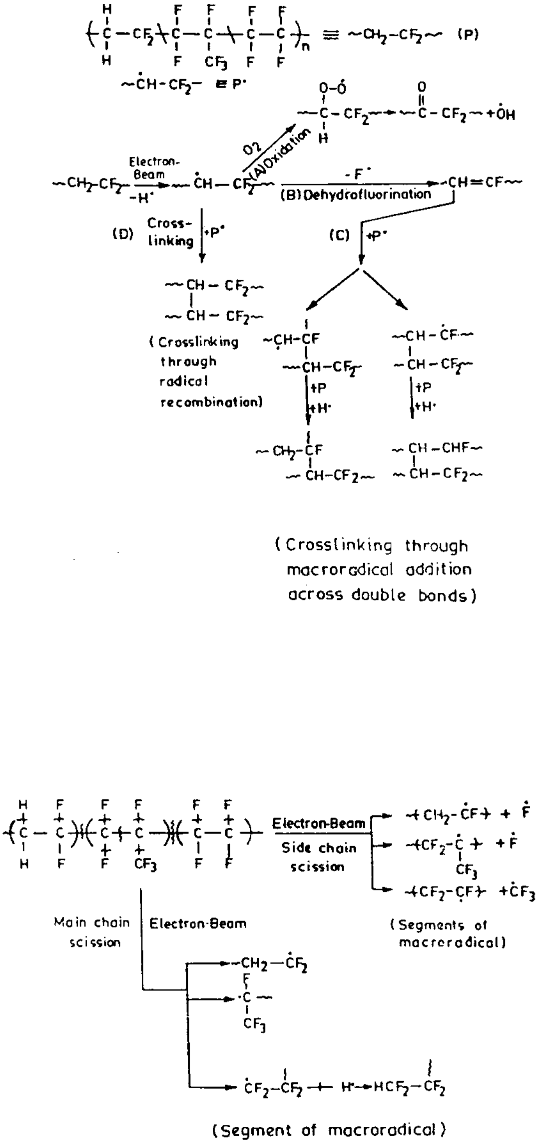


Fig. 4 Plot of A_{1740}, A_{1632}, A_{1397}, A_{1021}, A_{672} and A_{504} against irradiation dose for fluorocrbon elastomer.



Scheme 3 : Reaction scheme showing electron beam initiated reactions of fluoroelastomer.

the polymer, the chain molecules can undergo scission involving network, backbone and side chains.

As the concentration of TMPTA is increased, the concentration of C - F groups indicated by the absorbances at 1397, 1021, 672 and 504 cm^{-1} is higher. This is due to the fact that the free radicals are generated on TMPTA at a much faster rate. These then participate in the reactions shown in Scheme 3. The trends of the results are similar. The gel content of the elastomer increases with irradiation dose to a constant value at higher dose, as shown in Figure 5. It was reported by using the Charlesby-Pinner Equation[6] that the scission reactions are suppressed in presence of the trimethylol propane triacrylate[37].

Properties

Surface Properties :

Surface Energy :

The values of the contact angles of water, formamide and diiodomethane were determined. Representative values using water as the probe liquid are reported in Table 2. It is observed that the contact angle of water in the control EPDM surface is lowered from 84° to 70° with 50 kGy irradiation dose. With further irradiation the same increases. The work of adhesion is maximum for $E_{0/50}$ samples in the series. At a constant irradiation dose, the contact angle decreases with increasing TMPTA concentration, giving rise to enhanced values of the work of adhesion.

The total surface energy γ_s and its components γ_s^{LW}, $\gamma_s^{(+)}$,$\gamma_s^{(-)}$ and γ_s^{AB} were determined for the control and the modified surfaces using Equations 2(a) - 2(c). These values are plotted against irradiation dose and TMPTA concentrations. A representative plot is shown in Figure 6. The total surface energy increases with irradiation dose for the control and the modified surface upto a certain irradiation dose at a constant TMPTA level. While the maximum increase is 8% for the control EPDM, there is an increase of 31% for the $E_{10/50}$ sample. At higher irradiation doses, the total surface energy, γ_s, is lowered. The increase in γ_s is due to the increase in $\gamma_s^{(-)}$ as shown in the same Figure. The changes in γ_s^{LW} and $\gamma_s^{(+)}$ are marginal. $\gamma_s^{AB}/\gamma_s^{LW}$ accordingly increases. Similarly, the total surface energy displays a maximum value at 10% TMPTA concentration at 100 kGy irradiation dose[32]. As the concentration is further increased to 20%, there is a drop in the surface energy, the energy again increasing marginally at 50% TMPTA level. The changes in $\gamma_s^{(-)}$ can explain such variation. It is interesting to note that IR & XPS results are in line with

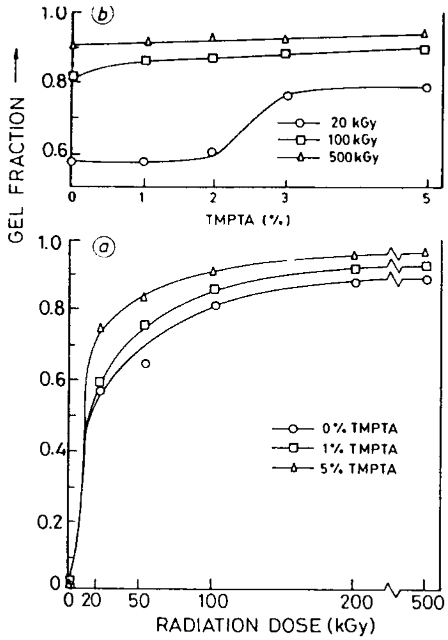


Fig. 5 Plot of gel content against irradiation dose for fluorocarbon elastomer.

Table 2 : Contact Angle and Work of Adhesion of the Control and the Modified EPDM Surfaces

SAMPLE CODE	θ_{WATER} (DEGREE)	W_A (mJ/m^2)
$E_{0/0}$	84	80.4
$E_{0/50}$	70	97.7
$E_{0/100}$	88	75.3
$E_{0/500}$	92	70.3
$E_{10/0}$	88	75.3
$E_{10/50}$	69	98.9
$E_{10/100}$	76	90.4
$E_{10/200}$	83	81.7
$E_{10/500}$	82	82.9
$EB_{10/50}$	90	72.8
$EB_{10/100}$	84	80.4
$EB_{10/200}$	86	77.9

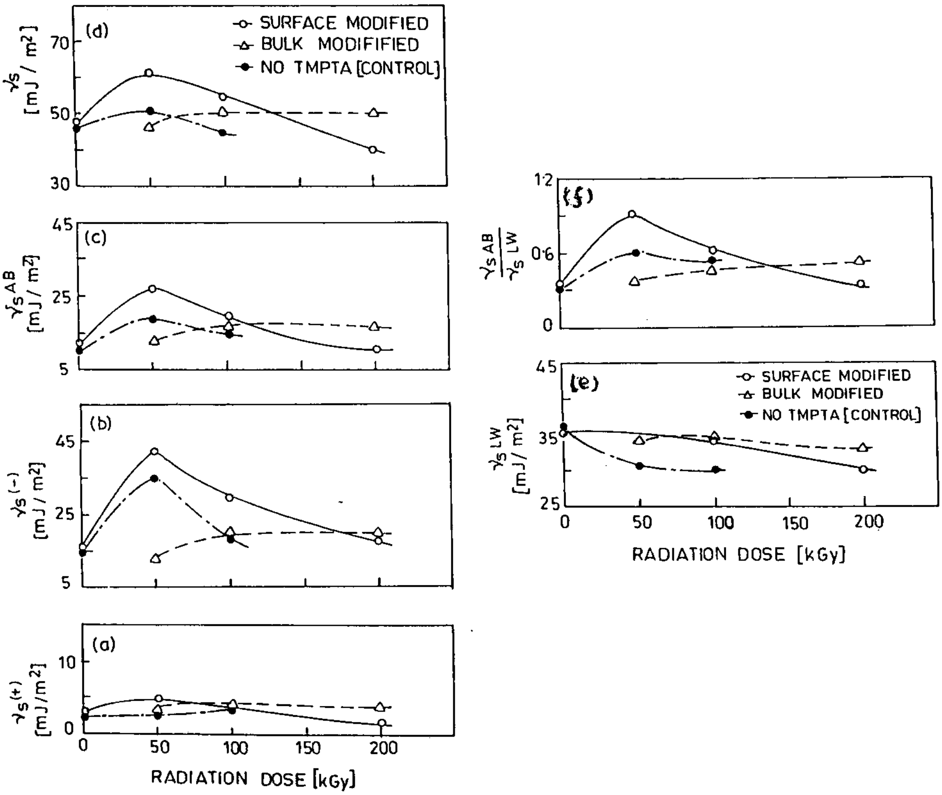


Fig. 6 Change of the surface energy parameters of control and modified EPDMs with irradiation dose.

these results. For example, it has been demonstrated earlier that A_{1730}, A_{1260}, A_{1120} and A_{1019} reach a maximum value at 50 kGy when the irradiation dose is varied at a constant 10% TMPTA level. Similarly, a maximum value of surface energy is obtained at 10% concentration at a constant value of irradiation dose (100 kGy), because the absorbances A_{1730}, A_{1630}, A_{1460}, A_{1375}, A_{1260}, A_{1120} and A_{1019} display maximum values at this concentration.

Frictional Properties of the Surface Modified Samples :

The influence of the concentration of TMPTA at a fixed irradiation dose of 100 kGy and of the irradiation dose at a constant level of TMPTA is shown in Figure 7. There is a marked decrease in μ on modification of the control unmodified sample, $E_{0/0}$, due to the increase in modulus of elasticity of the samples (E), causing a decrease in the contact area (A) ($E^{-2/3} \infty A$). In the plots μ passes through a maximum at 50 kGy irradiation dose when the TMPTA level is constant and through a maximum at 5% TMPTA concentration when the irradiation dose is 100 kGy. These could be explained by two mechanisms as follows : The first involves the shearing of the junctions formed as a result of adhesion at the regions of intimate contact. The second takes into account the dragging of the asperities on the harder body through the surface of the softer one. As the level of TMPTA is increased, the extent of grafting increases in the initial stage, which is also evident from Figure 2. The polarity would increase, causing the interfacial shear strength to increase. The surface changes may also contribute significantly to adhesion. The friction as a result increases. The factors responsible for increasing the interfacial shear strength and frictional coefficient are similar in this region. However, at a higher TMPTA level, the skin modulus and the Young's modulus increase and thereby reduce the friction coefficient. Also, at higher irradiation doses, scission of the rubber chains takes place; as reported earlier, thus breaking down the chains into small fragments and reducing the polar groups on the surface. With increasing irradiation dose, the surface hardness of the samples also increases. These factors contribute to the lowering of the frictional coefficient.

Bulk Properties :

Dynamic Mechanical Properties :

Figure 8 shows the damping behaviour, as the loss tangent, of the control & modified fluoroelastomers against testing temperatures at a frequency of 10 Hz. As the temperature is

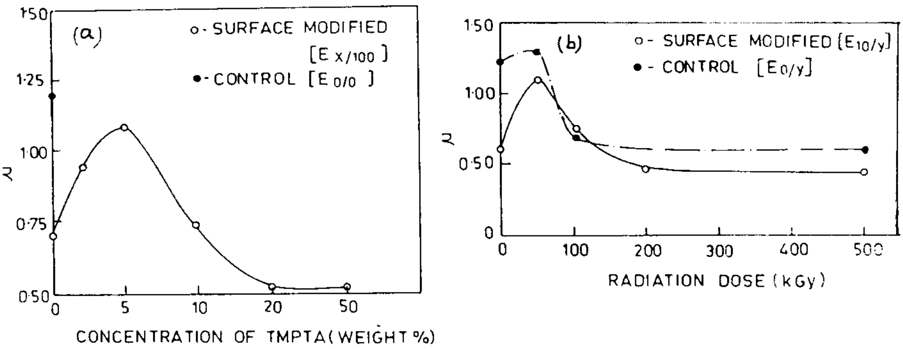


Fig. 7 Variation of the coefficient of friction :-

(a) with concentration of TMPTA

(b) with irradiation dose.

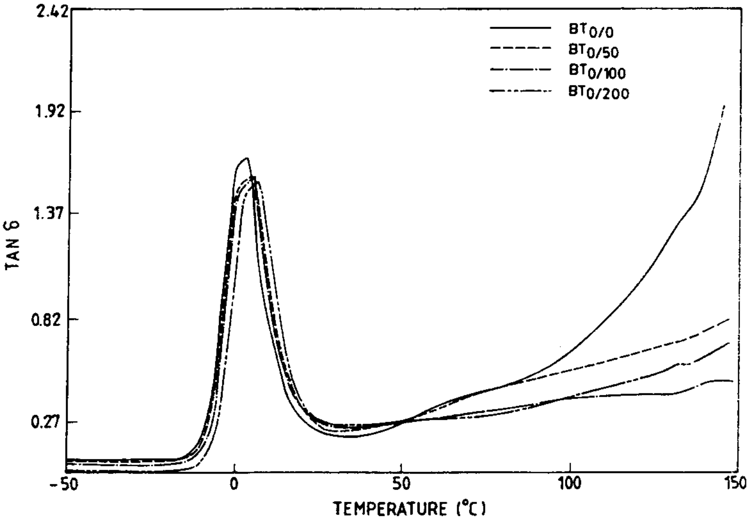


Fig. 8 Plot of tan δ of bulk modified fluorocarbon elastomers against temperature.

increased, the damping goes through a maximum in the transition region. When the segments are either completely frozen in or free to move, the damping is low. With increase in irradiation dose, the transition temperature shifts by 4-6°C accompanied by a decrease in the $(\tan \delta)_{max}$ value. These shifts are in accordance with the increasing degree of gel content (Figure 5) and structural modification (Figure 4). Gelling/crosslinking hinders the segmental motion and this requires a higher temperature for inception of rotation. The peak temperature does not show significant shift at higher irradiation dose probably due to the scission reactions alongwith crosslinking in the presence of electron beam (Scheme 3). The loss tangent data at higher temperature (145°C) indicate that the same is decreased with irradiation dose upto a level of 100 kGy. At higher level of TMPTA at a constant irradiation dose, the loss tangent decreases due to increased gel fraction, which has been reported earlier[37].

Mechanical Properties :

The tensile strength, modulus and elongation at break are plotted against the irradiation dose at constant TMPTA level and against concentration of TMPTA at constant irradiation dose (Figure 9)[38]. The tensile strength increases with irradiation dose and reaches a maximum value at 50 kGy. This increases continuously with the monomer level. The elongation at break decreases with the irradiation dose and the monomer level, while the modulus increases continuously. The modulus of a vulcanizate is proportional to the number of crosslinks. As the gel fraction increases, with the irradiation dose or monomer level, the modulus also increases. Consequently the elongation at break decreases. The increase in tensile strength can also be explained with the help of gel fraction. The tensile strength of a rubber is a function of energy dissipation. As the gel fraction or crosslink density increases, the energy dissipation increases. However, at higher gel fraction the network is so dense that there is little energy dissipation in the matrix and the energy supplied is utilized in breaking the bond. The scission reactions at higher irradiation dose also cause lowering of the tensile strength.

Conclusions

Bulk modification of EPDM and fluorocarbon elastomers and surface modification of EPDM rubber by electron beam irradiation in presence of trimethylol propane triacrylate have been reported in this paper.

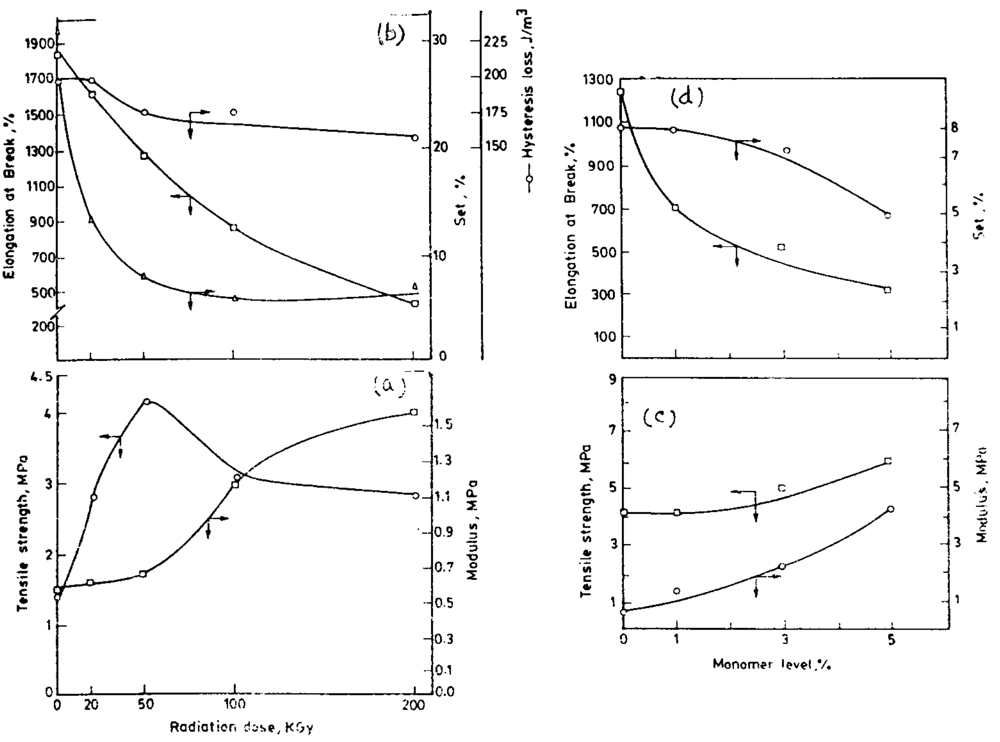


Fig. 9 Plots showing

(a) the variation of tensile strength and modulus of rubbers irradiated to different doses,

(b) the variation of hysteresis loss, set and elongation at break against irradiation dose,

(c) the variation of tensile strength and modulus with TMPTA levels, (d) the variation of elongation at break and set with monomer levels.

1. For the surface modified samples of EPDM rubber, the peaks at 1730, 1460, 1375, 1260, 1120, 1019 cm^{-1} show increased values, being maximum at 50 kGy irradiation dose. The relative concentration of the O1s peaks accordingly registers maximum value at the 50 kGy irradiation dose in the XPS analysis. In the case of the control sample, the absorbances at 1460 and 1375 cm^{-1} display gradual decrease with irradiation. The absorbances at 1260, 1120, 1019 and 1730 cm^{-1} for the bulk modified samples are in line with the results of surface modified samples. The above absorbance peaks increase with TMPTA concentration in the initial stage and record a maximum value at 10% TMPTA concentration at 100 kGy. The results are explained with the help of reaction schemes involving cyclopolymerization and grafting of TMPTA, crosslinking, oxidation, chain scission, and disproportionation of EPDM.
2. Fluorocarbon elastomer also undergo the above reactions in addition to dehydrofluorination which has been confirmed from the peak absorbances at 1397, 1021, 672 and 504 cm^{-1}.
3. The gel content in all the rubbers increase with irradiation dose or TMPTA level and finally levels off.
4. The total surface energy of the control and the surface modified EPDM samples increases from 46.1 to 49.7 mJ/m^2 and from 46.5 to 60.7 mJ/m^2 respectively, passing through an optimum value at 50 kGy irradiation dose. These values also show a maximum at 10% TMPTA concentration at 100 kGy irradiation dose where the structural changes are maximum.
5. The friction coefficient shows a rise upto 50 kGy irradiation dose at fixed 10% TMPTA concentration and upto 5% TMPTA at 100 kGy irradiation dose, and decrease at still higher doses or concentrations. The results are explained with the polarity of the surface groups in the initial stage and skin modulus, contact area and degradation at the later stage.
6. The tensile strength increases continuously with irradiation dose or TMPTA concentration upto a certain level after which there is a drop, while the modulus increases continuously with the above variables for fluorocarbon elastomer.
7. With the increase in radiation dose, the height of the damping peak decreases and the peak temperature of the irradiated fluorocarbon rubber shifts to higher values. This is more so with the mixes with higher concentration of TMPTA. The results are explained with the help of gel fraction, and the above chemical reactions.

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