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Electron beam induced structural modification of a fluorocarbon elastomer in the presence of polyfunctional monomers

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Abstract

The influence of polyfunctional monomers—tripropyleneglycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), tetramethylolmethane tetracrylate (TMMT) and triallyl cyanurate (TAC)—on the structural changes of fluorocarbon terpolymer (F content 68%, H 1.4%) in the presence of an electron beam has been investigated with the help of IR spectroscopy (in the ATR mode) and sol-gel analysis. The absorbances at 1397, 1021, 672 and 504 cm^{-1}, due to the C–F group, decrease on irradiation of the mixtures of fluoroelastomer and TMPTA, indicating dehydrofluorination and scission. The concentration of the double bond decreases both in the polyfunctional monomer and its blends with the polymer as a result of grafting and crosslinking. The concentration of the carbonyl group increases with radiation dose in the fluoroelastomer due to aerial oxidation. The effect of trimethylolpropane triacrylate (TMPTA) is to lower the amount of oxidation, especially at relatively higher levels. At a particular radiation dose, the behaviours of TPGDA, TMPTMA, TMMT and TAC based systems are similar to that of the TMPTA based one. The gel content increases with radiation dose. The influence of polyfunctional monomer on gel fraction is more prominent at higher concentrations, where distinct changes are observed at lower doses. At a particular level of multifunctional monomer, the gel fraction is lower for systems based on TPGDA. The ratio of chain scission to crosslinks calculated using the Charlesby–Pinner equation indicates a much higher crosslinking efficiency with polyfunctional monomer–fluorocarbon rubber matrix as compared to the control rubber. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorocarbon rubber; Electron beam curing; Polyfunctional monomer

1. Introduction

Modification of thermoplastics and rubbery materials by electron beam (EB) radiation is a potential method for the development of new polymers and composites. Irradiation of polymeric materials results in grafting and subsequently the 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 the formation of crosslinks 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 crosslinking at much reduced radiation dose levels to meet the optimum properties without much deterioration of the base polymers [7,8].

Harmon [9] carried out a comparative study between radiation cured and chemically vulcanized natural rubber. Pearson and Bohm [10] investigated the physical properties of polybutadiene and its copolymers. Radiation curing results in tensile strengths almost equal to that obtained by conventional curing methods. Loan [11] found that for poly(isobutylene-isoprene) the rate of net degradation decreases with increasing isoprene content in the polymer. The temperature dependence of scission yield for poly(isobutylene) was measured by Wundrich [12], and Zapp and Oswald [13] have reported that the physical properties of radiation crosslinked chlorobutyl compounds, containing thioether polythiols as crosslinking promoters, are comparable to those imparted by conventional curing systems. Arakawa et al. [14] discussed radiation-induced oxidation of polyethylene, ethylene–butene-copolymers and ethylene propylene copolymer rubber. The effect of acid on radiation grafting of functional monomer onto silicone rubber has been discussed by Hongfei [15]. Dutta et al. [16] have

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previously carried out a structural modification of ethylene–vinyl acetate copolymer in the presence of trimethylolpropane trimethacrylate (TMPTMA) and triallyl cyanurate (TAC). The influence of electron beam irradiation on plastics has also been reported by various authors [17–20]. The effect of γ-radiation on synthetic elastomers has also been investigated by a few workers [21–23].

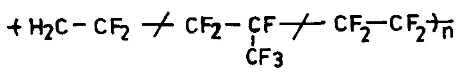
Fluorocarbon elastomers are synthetic, non-crystalline polymers that exhibit elastomeric properties when vulcanized. They are designed for demanding service applications characterized by a broad temperature range and contact with chemicals, oils and fuels. In the majority of applications like engine oil seals, hoses, O-rings, cables etc., copolymers of vinylidenefluoride (VF), hexafluoropropylene (HFP) and optionally tetrafluoroethylene (TFE) are used as fluorocarbon rubbers.

However, modification and curing of a fluorocarbon terpolymer (of VF, HFP and TFE) by electron beam (EB) irradiation has not been investigated so far. The present paper is a report of the studies of the effect of radiation dose and nature and level of polyfunctional monomer on chemical structures of fluorocarbon rubbers. Basic investigations have been carried out with the fluorocarbon terpolymer (DuPont Grade) and trimethylolpropane triacrylate (TMPTA). Di-acrylate (tripropyleneglycol diacrylate, TPGDA) and tetracrylate (tetramethylolmethane tetracrylate, TMMT), trimethacrylate (TMPTMA) and triallyl cyanurate (TAC) have also been used for the purpose of comparison. The acrylates and the cyanurate are polyfunctional monomers that produce a large number of free radicals on irradiation and promote crosslinking reactions by free-radical mechanisms [6,16,17].

2. Experimental

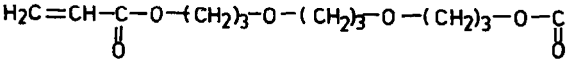
2.1. Materials

Fluorocarbon terpolymer (Viton B-50, 68%F, 1.4%H, density, 1850 kg m^{-3}) was supplied by E.I. duPont de Nemours and Co., USA. Tripropyleneglycol diacrylate (TPGDA, density 1050 kg m^{-3}) and trimethylolpropane



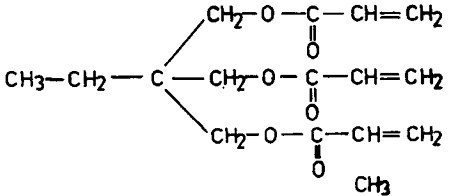
$$\left[H_2C-CF_2\right]\left[CF_2-\underset{\displaystyle CF_3}{CF}\right]\left[CF_2-CF_2\right]_n$$

(Flurocarbon terpolymer)

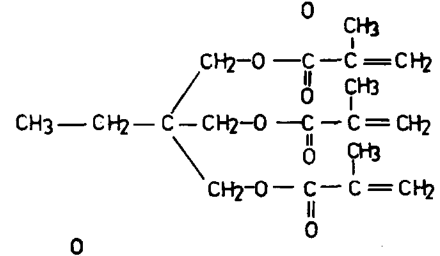


$$H_2C=CH-\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}-O-(CH_2)_3-O-(CH_2)_3-O-(CH_2)_3-O-\underset{\displaystyle O}{\underset{\|}{C}}-CH=CH_2$$

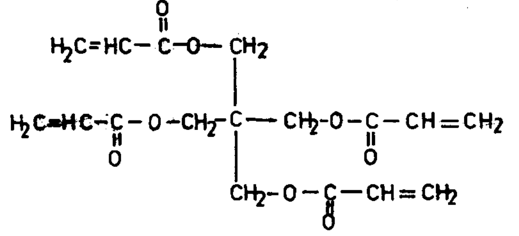
(TPGDA)



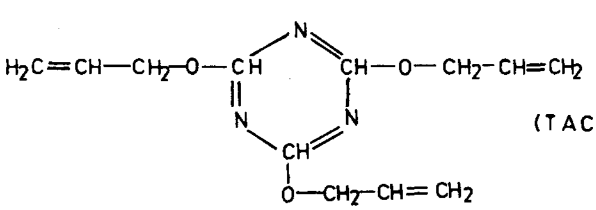
(TMPTA)



(TMPTMA)



(TMMT)



(TAC)

Table 1
Specification of the electron beam accelerator (ILU-6)

Energy range	0.5–2.0 MeV
Beam power through the 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 s
Repetition rate	2–50 Hz
Pulse current:	
Maximum	900 mA
Minimum	400 mA
Power supply voltage	3 × 380/220 V
P.S. voltage frequency	50 Hz
Consumption of power (total)	150 kW

triacrylate (TMPTA, density 1110 kg m^{-3}) were obtained from UCB Chemical, Belgium. Trimethylolpropane trimethacrylate (TMPTMA, density 1110 kg m^{-3}) and tetramethylolmethane tetracrylate (TMMT, density 1110 kg m^{-3}) were procured from the Shin-Nakamura Company, Japan. Triallylcyanurate (TAC, density 1110 kg m^{-3}) was provided by NICCO India Ltd, Calcutta. The probable structures of the rubber and radiochemicals are given on the previous page.

2.2. Preparation of samples

The fluorocarbon rubber was mixed with TPGDA, TMPTA, TMPTMA, TMMT or TAC in a Brabender Plasticorder PLE-330 at room temperature (25°C) for 3 min and 60 rpm rotor speed. The mixes were formed into sheets using a 6″ × 13″ open mill (Schwabenthon, Berlin). The sheets were compression moulded between Teflon sheets at a temperature of 105°C and a pressure of 5 MPa in an electrically heated press for 3 min to obtain sheets of dimension 11.5 cm × 11.5 cm × 0.1 cm.

2.3. Irradiation of samples

The moulded Viton B-50 samples were irradiated in air at room temperature of 25 ± 2°C by an electron beam accelerator (model ILU-6) at the Bhabha Atomic Research Centre (BARC), Bombay. Irradiation doses of 20, 50, 100, 200 and 500 kGy (1 kGy = 0.1 Mrad) were used. The specifications of the electron beam accelerator are given in Table 1.

The samples were designated as $\mathrm{TG}_{x/y}$, $\mathrm{TP}_{x/y}$, $\mathrm{TM}_{x/y}$, $\mathrm{TT}_{x/y}$ and $\mathrm{TC}_{x/y}$; TG, TP, TM, TT and TC stand for systems based on TPGDA, TMPTA, TMPTMA, TMMT and TAC, respectively; x indicates the level of polyfunctional monomer in percent and y indicates the irradiation dose in kGy.

2.4. Characterization of samples

2.4.1. Attenuated total reflectance (ATR)/infrared (IR) spectroscopy

ATR spectra of the blends of fluorocarbon rubber with various polyfunctional monomers at different concentrations were taken on smooth thin (~0.4 mm) irradiated films using a Perkin-Elmer (model 837) spectrophotometer. IR spectra of the multifunctional monomers were also taken on KBr (potassium bromide) pellets. All the results given in this paper are the averages of two measurements, with three scans for each measurement at a resolution of 1 cm^{-1}.

2.4.2. Gel fraction

Gel fraction was measured by immersing the samples in methyl ethyl ketone at room temperature (25°C) for 48 h (equilibrium swelling time was determined from the experiments) and calculated from the weight of the sample before and after swelling as follows:

$$\text{Gel fraction} = W_2/W_1$$

where W_1 = initial weight of the polymer and W_2 = weight of the insoluble portion of the polymer. The results reported here are the averages of three samples.

3. Results and discussion

3.1. Irradiation of the monomers

The IR spectra of unirradiated and irradiated tripropyleneglycol diacrylate (TPGDA), trimethylolpropane triacrylate (TMPTA) and tetramethylolmethane tetracrylate (TMMT) in the region 4000–400 cm^{-1} have been taken. Fig. 1a describes the spectra of representative TMMT. The peak positions and their assignments are given in Table 2. They agree well with the values given in the literature [24]. The spectra of other monomers are also in line with the literature. The peaks can be explained from the structures of the multifunctional monomers as shown before.

Table 2
Peak position and assignment of peaks in the IR spectra of multifunctional monomers

Wave number (cm^{-1})	Functional group
2970	=CH stretching vibration of vinylidene hydrocarbon
1740	> C=O stretching vibration
1632	> C=C < stretching for vinylidene group
1470	> CH_2 scissor vibration
1410	> CH_2 in-place deformation of vinylidene hydrocarbon
1378, 1346	–CH symmetric deformation of ester
1294	Assymmetric C–O–C stretching vibration of acrylates
1274, 1065	Symmetric C–O–C stretching vibration of acrylates
1157	Assymmetric C–O stretching vibration of saturated aliphatic ether
985	–CH out of plane deformation
814	–CH_2 out of plane deformation

The inset of Fig. 1a shows the IR spectra in the region 1700–1500 cm^{-1} of the irradiated TMMT with radiation doses of 20, 50, 100 and 200 kGY. A decrease in the absorbance ratio of 1632 cm^{-1} with respect to 1470 cm^{-1} (Fig. 1b) is observed with an increase in the radiation dose. The reduction of double bonds is also corroborated from the absorbance ratio of 2970 cm^{-1} over 1470 cm^{-1}, shown in the same figure (Fig. 1c). The decrease is sharp up to 50 kGy, beyond which the change is marginal. All the monomers behave similarly. The results can be explained as follows.

The monomer TMMT polymerizes through its double bonds (Scheme 1) in the presence of high energy electron beam irradiation and forms three-dimensional network structures. As a result, it transforms from the liquid to the solid state. The residual unsaturation observed in the cross-linked material must be due to unreacted double bonds and this may be due to the bulky structure of the monomer which shields double bonds from further reaction in the cross-linked structure [16,17]. The mechanism of crosslinking of TPGDA and TMPTA is similar to that of TMMT. It is interesting to note that the absorbance ratio A_{1740}/A_{1470} of the multifunctional monomers shown in Fig. 1d is constant throughout the entire range of radiation dose studied, supporting the absence of oxidation of the monomers under the influence of the electron beam.

3.2. *Effect of radiation dose and TMPTA level on structural changes of the fluorocarbon elastomer*

Fig. 2a displays the IR spectra (in ATR mode) in the region 2000–400 cm^{-1} of the unirradiated rubber, while the insets of Fig. 2a and Fig. 2b record the spectra in the regions 1900–1500, 1500–1350 and 700–600 cm^{-1} for the rubbers irradiated with 20, 50, 100, 200 and 500 kGy dose. The peak intensities and their assignments for the fluoroelastomer are given in Table 3. These are in accordance with the values mentioned in the literature [24]. On irradiation, the peaks at 1397 and 672 cm^{-1} due to the C–F functional group gradually decrease (Fig. 2b) and the bands at 1740 and 1632 cm^{-1} due to carbonyl groups and double bonds, respectively, appear (inset of Fig. 2a). The absorbance of the 1740 cm^{-1} peak increases with the increase in radiation dose. Fig. 2c and d shows the variations of absorbances at 1740, 1632, 1397, 1021, 672 and 504 cm^{-1} with radiation dose. All the absorbances due to the C–F group show a similar trend, i.e. they decrease sharply with radiation dose in the initial stage. Due to this dehydrofluorination,

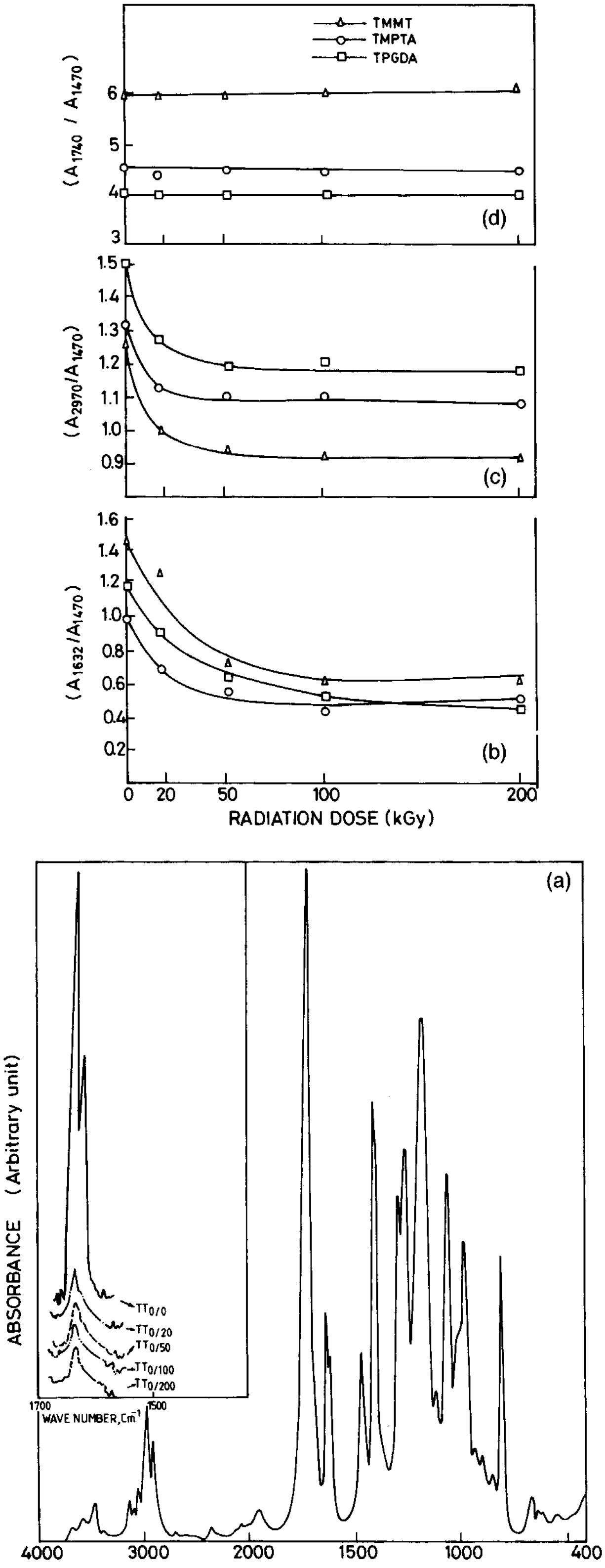
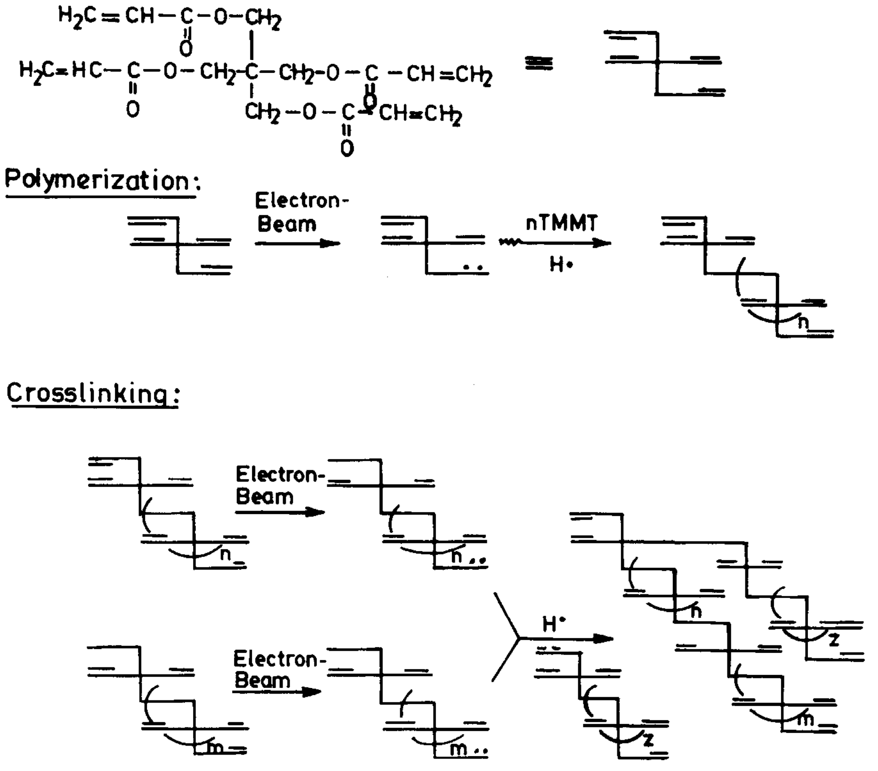


Fig. 1. (a) IR spectra of pure multifunctional monomer, TMMT, in the region 4000–400 cm^{-1}. Inset: IR spectra of irradiated TMMT in the region 1700–1500 cm^{-1} showing variation of the peak at 1632 cm^{-1} with radiation doses of 20, 50, 100 and 200 kGy. (b) Plot showing the variation of the absorbance ratio A_{1632}/A_{1470} of TMMT irradiated with doses of 20, 50, 100 and 200 kGy. (c) Plot showing the variation of A_{2970}/A_{1470} of TMMT irradiated with doses of 20, 50, 100 and 200 kGy. (d) Variation of A_{1740}/A_{1470} of TMMT irradiated with dose of 20, 50, 100 and 200 kGy.

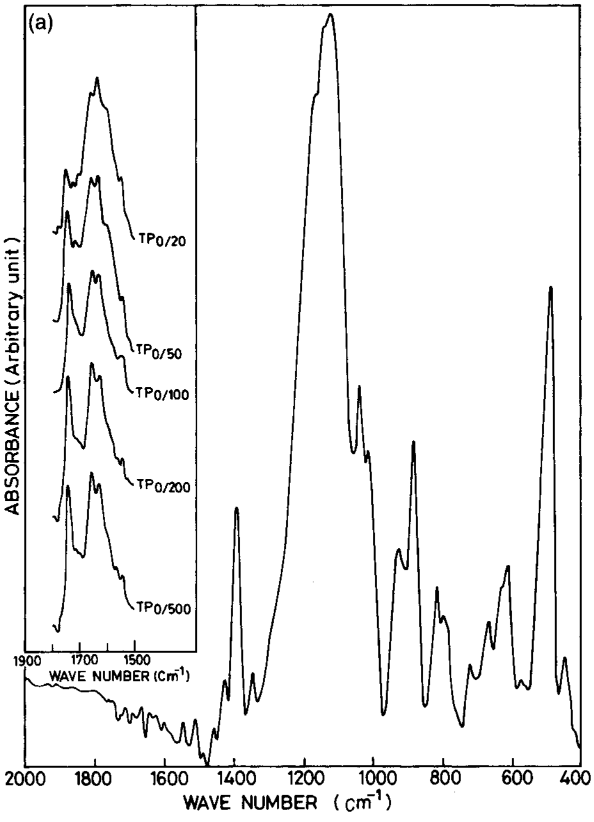


Scheme 1.

the double bonds, indicated by the 1632 cm^{-1} peak, are generated. Carbonyl groups are also 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 double bonds on the other hand shows a decreasing trend beyond 20 kGy after an initial rise. At very high radiation dose, there is again an increase. These observations can be explained as follows: the fluorocarbon rubber has labile hydrogens in its vinylidenefluoride unit (the bond energy of C–F is about 447 kJ mol^{-1}, while that of C–H is about 377 kJ mol^{-1}). On irradiation, these hydrogens are split off, generating macroradicals on the carbon atoms of the vinylidenefluoride (VF) unit. On the one hand, these macroradicals either react with oxygen in the air, resulting in the formation of carbonyl groups (Scheme 2A) or participate in dehydrofluorination resulting in the formation of double bonds (Scheme 2B). The resulting unsaturation can subsequently lead to the formation of crosslinks [6] through the addition of macroradicals across the double bonds so formed (Scheme 2C). On the other hand, macroradicals can recombine to form crosslinks (Scheme 2D). Again, due to the presence of the bulky groups F and CF_3 on the backbone of the polymer, radical recombination leading to the formation of crosslinks will be somewhat sterically hindered [4] and the chain molecule can then undergo scission (Scheme 3), involving network, backbone and side chains.

Both atmospheric oxidation and dehydrofluorination increase with radiation dose (up to a certain level), possibly due to the availability of a large number of radicals [16,19,20]. The fact that the change of absorbance due to C–F groups is not in line with the change in absorbance due to $>$C=C$<$ stretching can be accounted for by chain scission leading to a decrease in concentration of C–F groups as well as crosslink formation through double bonds.

The influence of 1, 2, 3 and 5% TMPTA on the structural changes of the fluorocarbon rubber has been investigated. Representative spectra in the region of 1800–1500 cm^{-1} for 1 and 5% TMPTA mixed with fluororubber and irradiated at 20, 50, 100, 200 and 500 kGy dose are shown in Fig. 2e. The variations of absorbances at 1740, 1632, 1397, 1021, 672 and 504 cm^{-1} are plotted against irradiation dose in Fig. 2c and d. It is observed that at low levels of TMPTA (1%) the variations of absorbances due to $>$C=C$<$ and $>$C=O stretching frequencies are almost similar to those of pure rubber. The oxidation steadily increases with radiation dose but shows marginal changes beyond 50 kGy. However, at a particular radiation dose, the concentration of C–F groups, indicated by absorbances at 1397, 1021, 672 and 504 cm^{-1}, is higher, which may be due to the fact that free radicals are generated on the multifunctional monomer at a much faster rate. These were also observed earlier with a few polymer systems [4,17,19]. However, at higher TMPTA concentrations, a slight change in the behaviour towards oxidation is observed. The absorbance due to carbonyl groups increases



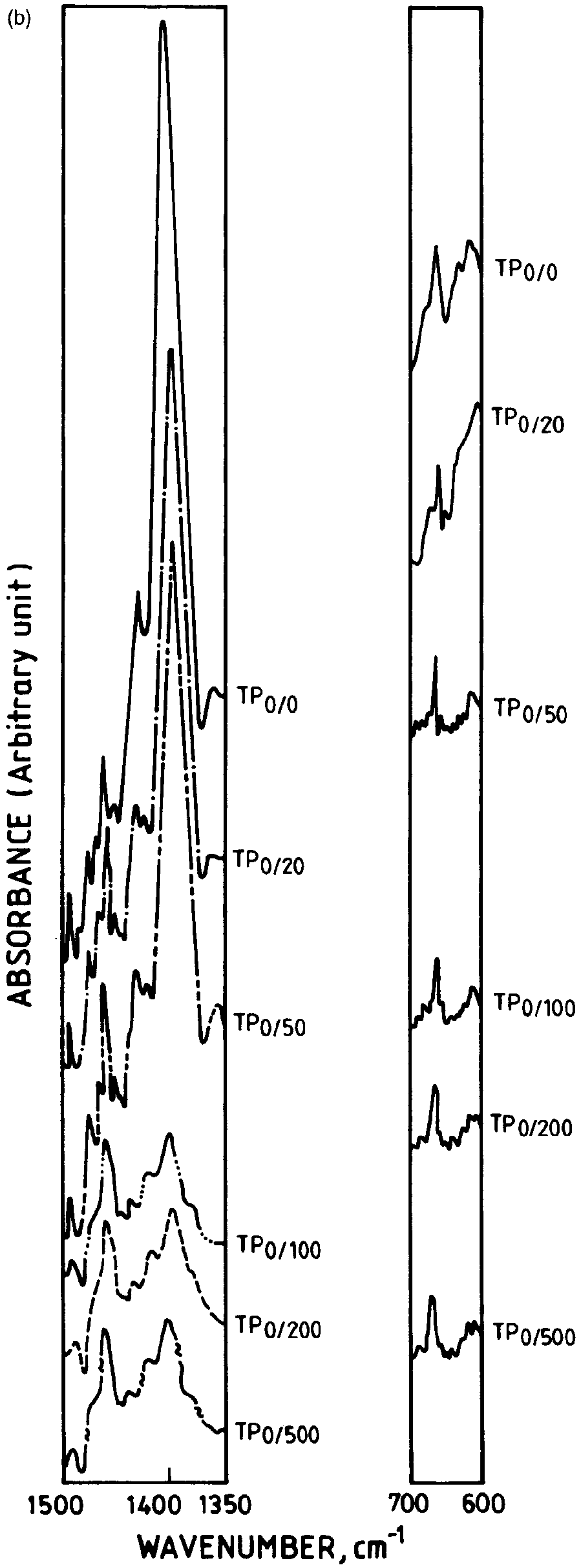


Fig. 2. (a) IR spectra of pure fluorocarbon rubber in the region 2000–400 cm^{-1}. Inset: IR spectra of pure fluorocarbon rubber irradiated with doses of 20, 50, 100, 200 and 500 kGy in the region 1900–1500 cm^{-1} showing the variation of absorbance at 1740 and 1632 cm^{-1}. (b) IR spectra of pure and irradiated fluoropolymer showing variation of absorbance at 1397 and 672 cm^{-1} in the regions 1500–1350 and 700–600 cm^{-1}. (c) Plot showing the variation of absorbances at 1740 and 1632 cm^{-1} of the control and the TMPTA mixed rubber irradiated with 20, 50, 100, 200 and 500 kGy. (d) Plot showing the variation of absorbances at 1397, 1021, 672 and 504 cm^{-1} of the control and the blends of fluororubber with TMPTA irradiated with doses of 20, 50, 100, 200 and 500 kGy. (e) Variation of absorbances at 1740 and 1632 cm^{-1} of the control and the irradiated blends of fluorocarbon rubber with TMPTA in the region 1800–1500 cm^{-1}. (f) and (g) Plots showing the variation of absorbances at 1740 and 1632 cm^{-1} of irradiated blends of TPGDA, TMPTA, TMPTMA, TMMT and TAC at monomer levels of 1, 3 and 5% (irradiation dose = 50 kGy)

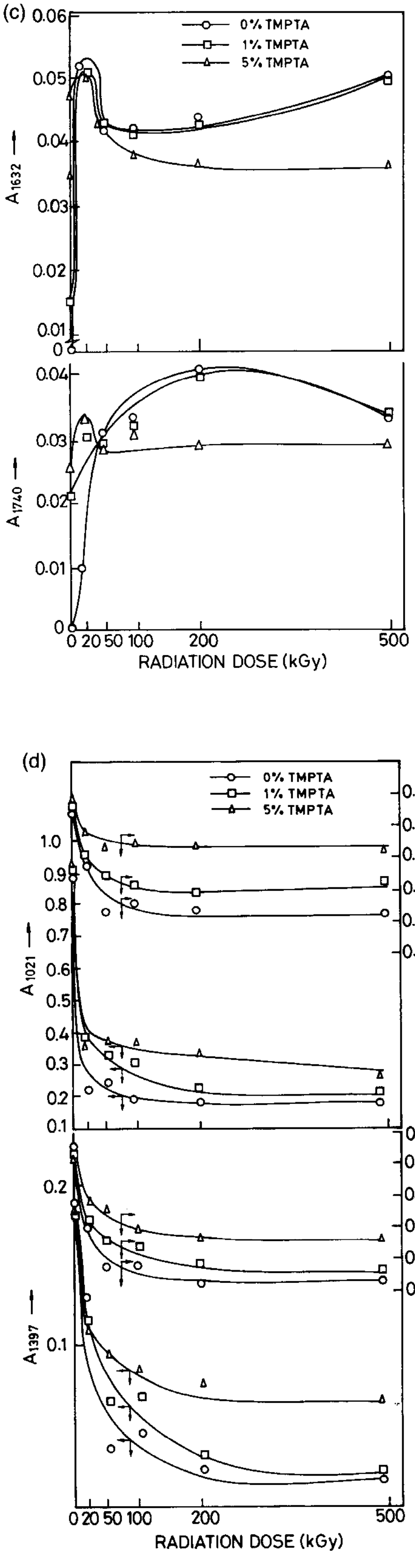


Fig. 2. (*continued*).

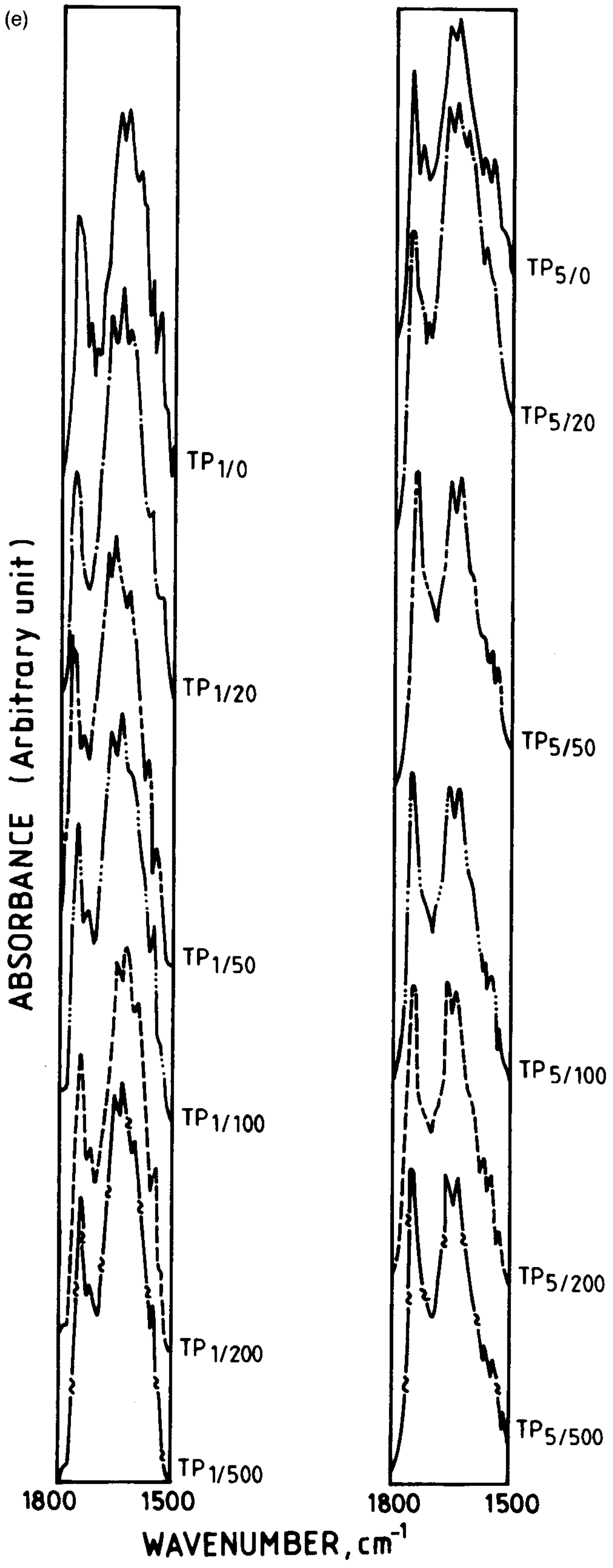


Fig. 2. (*continued*).

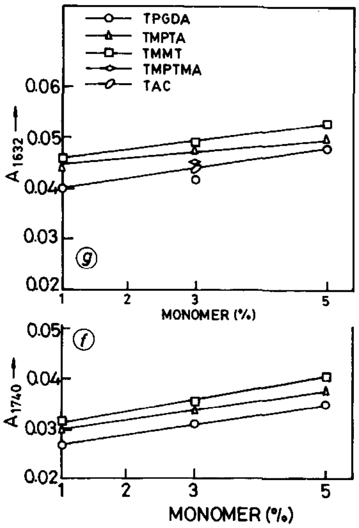
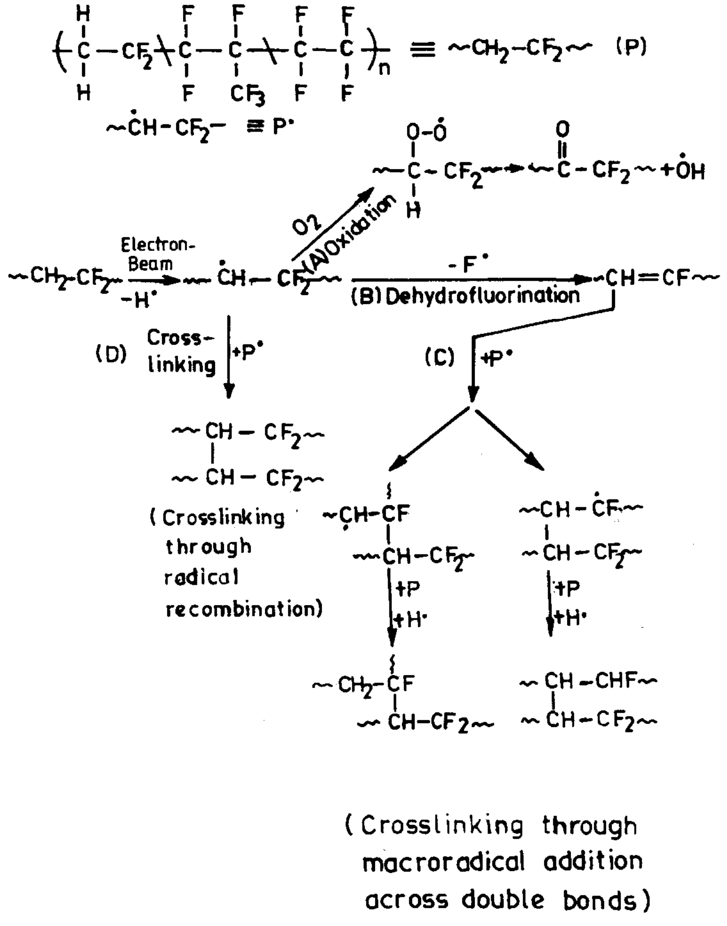


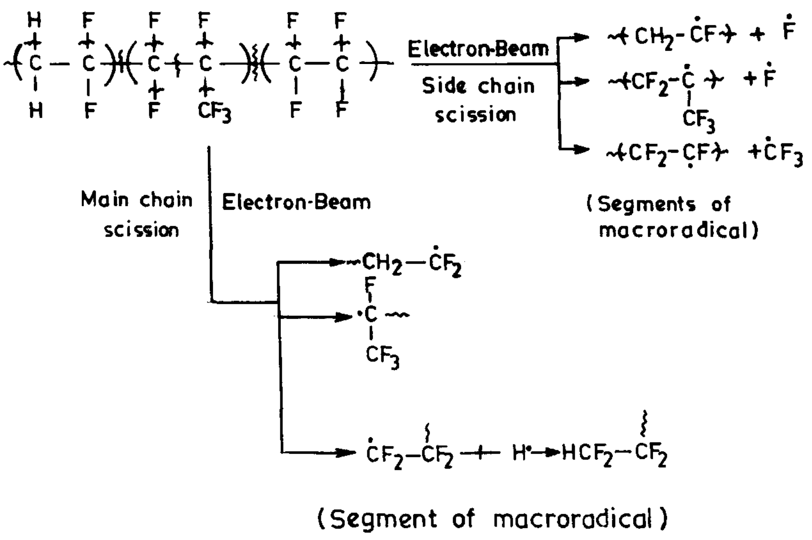
Fig. 2. (*continued*).

gradually with radiation dose, but the change is marginal beyond 20 kGy. The variation in the concentration of double bonds follows a similar trend for all the rubbers up to 50 kGy, although the concentration of the double bonds is lower at higher TMPTA levels. For example, at 200 kGy, the peak intensity of 1632 cm^{-1} is 0.044 and 0.037 for 1 and 5% TMPTA. The breakdown of C–F bonds, as recorded by the peaks at 1397, 1021, 672 and 504 cm^{-1}, is also much lower in the presence of high concentrations of TMPTA (Fig. 2c).

From Fig. 1b and c for TMPTA irradiated with doses of 20, 50, 100 and 200 kGy, it is observed that the absorbance due to double bonds (at 1632 cm^{-1}) falls with irradiation dose, up to a dose of 50 kGy, beyond which it is almost constant. For the pure rubber, dehydrofluorination decreases from 20 kGy and shows marginal changes beyond 50 kGy. Since no trace of double bonds has been found in the chloroform extract of the irradiated blends of the rubber with TMPTA, it is probable that the decrease in the concentration of the double bond beyond 20 kGy is due to the double bonds of TMPTA being consumed in the process of grafting and crosslinking (Scheme 4). As with pure rubber, oxidation and dehydrofluorination increase with radiation dose for samples blended with low levels of TMPTA, due to the availability of a large number of radicals. Beyond 20 kGy, the tendency towards dehydrofluorination decreases, probably due to the participation of TMPTA in crosslink formation through its double bonds



Scheme 2.

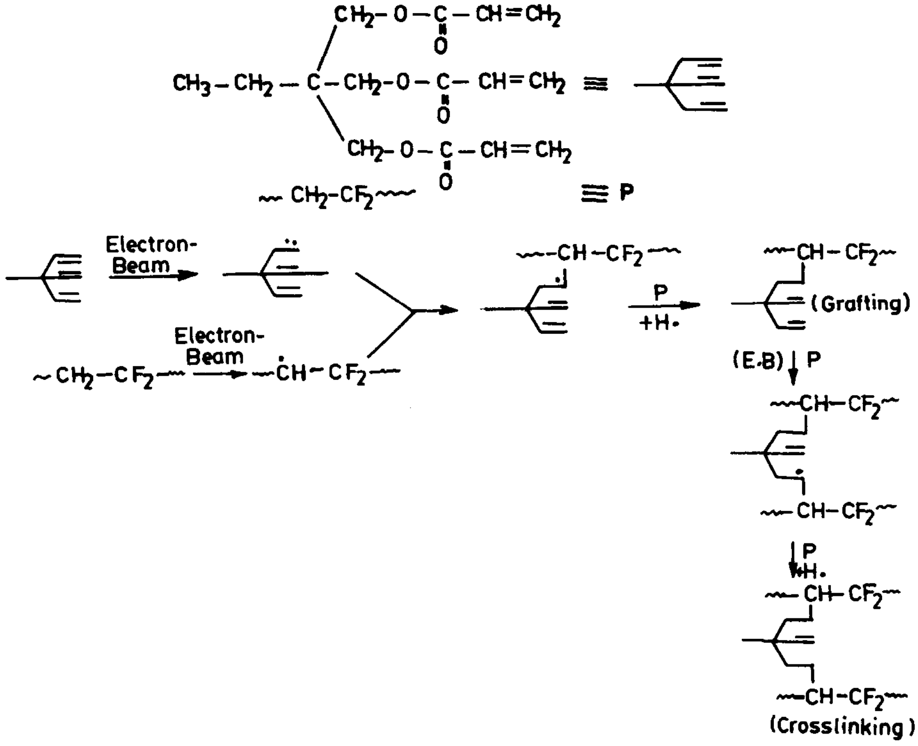


Scheme 3.

(Scheme 4), as supported by the sharp fall of the absorbance at 1632 cm^{-1} (due to vinylidene hydrocarbon) and peak intensities at 1397, 1021, 672 and 504 cm^{-1} (due to the C–F group). However, at high levels of TMPTA, the reactions of the mixture are controlled by the reactions of TMPTA [4]. As a result, more crosslinking and grafting and less atmospheric oxidation take place in the case of the mixtures. All the residual unsaturations observed in the blends of crosslinked material must either be due to unreacted double bonds of TMPTA, which are shielded from taking part in further reactions because of its bulky structure, or due to the double bonds generated by dehydrofluorination on irradiation.

As with pure rubber, the interplay of oxidation, dehydrofluorination, crosslinking and scission in the presence of a large number of radicals and the limited chain mobility of the network structure, are responsible for the constant concentrations of carbonyl group and double bonds beyond 50 kGy.

Fig. 2f and g displays the variations of the absorbances



Scheme 4.

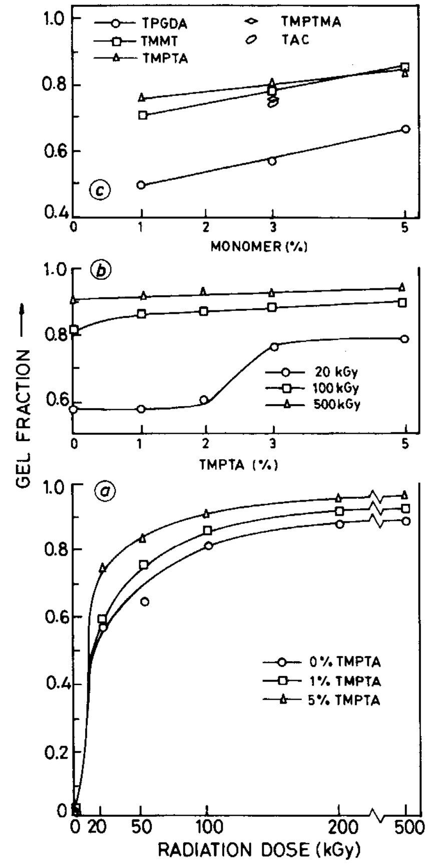


Fig. 3. (a) Plot of gel fraction of 0, 1 and 5% TMPTA systems with radiation doses of 20, 50, 100, 200 and 500 kGy. (b) Plot showing the variation of gel fraction at radiation doses of 20, 100 and 500 kGy of 0, 1 and 5% TMPTA systems. (c) Plot of gel fraction of TPGDA, TMPTA, TMPTMA, TMMT and TAC blended systems, against the level of monomer at constant radiation dose (50 kGy).

due to carbonyl groups and > C=C < stretching frequencies of the fluororubber blended with TPGDA, TMPTA, TMMT, TMPTMA or TAC at different levels of the monomers. The blends were irradiated with a constant radiation dose of 50 kGy. The concentrations of the double bonds and the carbonyl group increase with monomer level in a linear fashion. At a particular monomer level, their concentrations are different and dependent upon the structure of the monomer. TMMT and TMPTA are relatively more active than the others. The absorbances are again controlled by the number of initial double bonds, the stereochemistry of the monomers, and various competitive reactions, as stated earlier.

Table 3
Band position and their assignment in the IR spectra (in ATR mode) of pure fluorocarbon rubber

Wave number (cm^{-1})	Functional group
1455	> CH_2 scissor vibration of vinylidene-fluoride unit
1397	C–F 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; assymmetric –CF_3 deformation
504	C–F deformation; assymmetric –CF_3 deformation vibration
461	Assymmetric rocking vibration of –CF_3 group

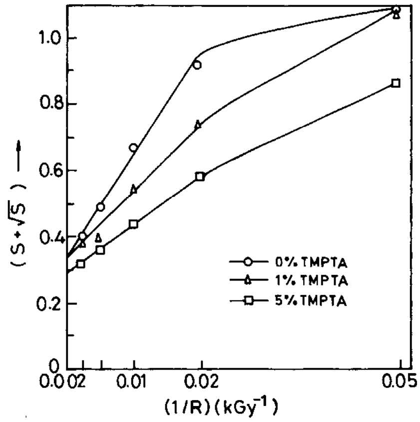


Fig. 4. Plot of $S+\sqrt{S}$ *versus* $1/R$ for 0, 1 and 5% TMPTA systems, according to Eq. (1).

3.3. Gel fraction

3.3.1. Effect of radiation dose, level and nature of polyfunctional monomers

Fig. 3a–c depicts the plots of gel fractions against radiation dose at 0, 1 and 5% TMPTA, against the level of TMPTA at constant radiation dose and against the level of monomer for three different types of monomer at 50 kGy radiation dose. It is observed that at a particular monomer level, the gel content increases with radiation dose up to 100 kGy and shows almost constant value with further increase in radiation dose. At a particular radiation dose (say 100 kGy), the gel content is higher at a higher monomer level, e.g. the gel fraction of pure rubber is 0.80, whereas those for 1 and 5% TMPTA are 0.83 and 0.89, respectively. At a radiation dose of 20 kGy, the gel content is highest for the 5% TMPTA system.

The increase of gel content with increase in radiation dose and monomer level is due to the formation of a three-dimensional network structure. On the other hand, beyond an optimum radiation dose (100 kGy), the increase is marginal due to the balance of various competitive reactions, as detailed in Schemes 2–4. An increased gel content at a higher level of TMPTA (5%) and a lower radiation dose (20 kGy) once again indicates the promotion of crosslinking.

It is also interesting to see (Fig. 3b) that at lower radiation dose (20 kGy) the gel content shows a sudden increase at 2% TMPTA before reaching a constant value. The level of monomer required for this sudden increase is much lower at a higher radiation dose. From Fig. 3c, it is observed that the gel content with TPGDA at any level of monomer is lower than with TMPTA, TMPTMA, TMMT and TAC. This probably indicates much higher efficiencies of the triacylates (TMPTA, TMPTMA), the cyanurate (TAC) and the tetracrylate (TMMT) in promoting the crosslinking due to their having more unsaturation in their structure than the multifunctional diacrylate (TPGDA).

A plot of $S+\sqrt{S}$ (where $S=$ the sol-fraction) versus 1/radiation dose (Fig. 4), from the Charlesby–Pinner equation [25]

$$S+\sqrt{S}=\frac{p_0}{q_0}+\frac{10}{q_0 R u_1} \quad (1)$$

(u_1 = number average degree of polymerisation, p_0 = fracture density per unit dose in kGy^{-1}, q_0 = density of crosslinked units per unit dose in kGy^{-1}, R = radiation dose in kGy), gives an idea of the ratio of chain scission to crosslinking. The much lower value of the ratio (0.29) for 5% TMPTA compared with those for pure rubber (0.35) and 1% TMPTA (0.34) supports the increased crosslinking with the 5% TMPTA system at the lower radiation doses used.

4. Conclusions

The structural features of electron-beam initiated grafting and crosslinking of a fluorocarbon rubber have been addressed in this paper. The following observations have been made.

1. Multifunctional monomers (TPGDA, TMPTA and TMMT) are polymerised and crosslinked during electron-beam irradiation by a free-radical mechanism. Residual unsaturations are found in the crosslinked material due to a shielding of double bonds.
2. For the pure fluorocarbon rubber, the amount of oxidation shows marginal changes beyond 50 kGy, while dehydrofluororination measured from the intensities of the C–F stretching frequency increases with radiation dose and then levels off.
3. In blends of TMPTA with rubber, grafting and crosslinking through the double bonds of the monomer take place. At low levels of TMPTA, the behaviour of the blends towards radiation-induced reaction is more-or-less similar to that of pure rubber. The concentration of carbonyl group changes marginally beyond 50 kGy, while dehydrofluorination shows an increasing trend beyond 20 kGy. However, at higher levels of TMPTA the tendency towards atmospheric oxidation and dehydrofluorination decreases in the early stages of the reactions. The residual unsaturations observed in the TMPTA rubbers are due to a mutual interplay of shielding of the double bonds of TMPTA and dehydrofluorination. At dose levels around 50 kGy and above, competitive reactions between oxidation, dehydrofluorination, grafting, crosslinking and scission are postulated.
4. The blends of rubber with TPGDA, TMPTMA, TMMT and TAC behave similarly to those with TMPTA, when these are irradiated with a radiation dose of 50 kGy.
5. The gel content increases with the radiation dose up to 100 kGy for fluorocarbon rubber mixed with low levels of TMPTA and then reaches a near limiting value. At higher levels, however, a marginal change is observed beyond 20 kGy. At a dose level of 50 kGy, the gel content is lower for systems based on TPGDA. The sol-gel analysis reveals that the probability of scission to crosslinking is lower for blends at higher levels of TMPTA as compared with that for pure rubber.

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