Electron-Beam Modification of Nitrile Rubber in the Presence of Polyfunctional Monomers

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ABSTRACT: The structural changes of nitrile rubber in both the presence and the absence of polyfunctional monomers, such as trimethylolpropane triacrylate (TMPTA), tripropyleneglycol diacrylate (TPGDA), and trimethylolmethane tetraacrylate (TMMT), at different doses of electron beam irradiations, were investigated with the help of FTIR spectroscopy (in the ATR mode), solid-state NMR, dynamic mechanical thermal analysis, and sol–gel analysis. There was a significant decrease in the concentration of olefinic groups for modified system with 3% TMPTA compared to that of the unmodified nitrile rubber on irradiation. This was also confirmed by the increase in the carbon resonances attributed to C—C linkages from solid-state NMR for the modified system, indicating more crosslinkages. The increase in crosslinking was also revealed by the increase in % gel content and dynamic storage moduli with radiation dose. The lifetime of spurs formed and the critical dose, an important criterion for overlapping of spurs, were determined for both grafted and ungrafted nitrile rubber using a mathematical model. The ratio of scissioning to crosslinking for nitrile rubber was determined using the Charlesby–Pinner equation. Mechanical properties were studied for the modified and the unmodified systems and the tensile strength was found to increase with grafting of polyfunctional monomers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 435–447, 2005

Key words: electron-beam irradiation; nitrile rubber; mechanical properties; Charlesby–Pinner plot; infrared spectroscopy

INTRODUCTION

Electron-beam (EB) modification of polymers results in formation of a three-dimensional network structure through union of macroradicals generated. This 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 other thermochemical means.[1,2] Compared to the conventional chemical processes, radiation crosslinking has advantages because it is faster, more versatile, brings about uniform crosslinking, consumes less energy, and generates inherently waste free products.[3] These advantages have led to its commercial applications involving the curing of extruded articles such as wire and cable insulants, molded goods, tire components, heat shrinkable tubes, and so on. Harmon[4] carried out a comparative study on radiation-cured and chemically vulcanized natural rubber. Pearson and Böhm[5] investigated the improvement in physical properties of polybutadiene rubber and its copolymers with EB irradiation. Ostwald and Zapp[6] reported that the physical properties of radiation crosslinked chlorobutyl compounds, containing thioether or polythiols as crosslink promoters, were comparable to those imparted by conventional curing systems. The effect of acid on radiation grafting of functional monomer onto silicone rubber was discussed by Hongfei et al.[7]

Usually, some monomers are used as radiation sensitizers to reduce the dose of irradiation, which may affect the polymer chain. Datta et al.[8] carried out a structural modification of ethylene–vinyl acetate copolymer in the presence of trimethylol–propane trimethacrylate (TMPTMA) and triallyl cyanurate (TAC). The effect of monomers on electron-beam crosslinking of synthetic elastomers was also investigated by Bhowmick et al.[9,10]

Nitrile rubbers are synthetic and noncrystalline polymers that exhibit elastomeric properties when vulcanized. They are widely used to meet the industrial requirements of oil and heat resistance. Modification and curing of nitrile rubber by EB irradiation has not been investigated so far, although a large number of applications is possible using this technology. The present article deals with the influence of radiation dose, and nature and level of different polyfunctional monomers on chemical structure and the mechanical and dynamic mechanical properties of nitrile rubber. The lifetime of spurs[11] formed has been determined for both unmodified and trimethylol propane triacrylate (TMPTA)–modified nitrile rubbers.

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Energy range	0.5–2.0 MeV
Beam power through the whole energy range	20 KW
Beam energy speed	±10%
Average current	15 mA
Adjusting limits of 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	$3 \times 380/220$ V
Power supply voltage frequency	50 Hz
Consumption of power (total)	150 kW

EXPERIMENTAL

Materials

Nitrile rubber (ACN content 34% ML_{1+4} at 100°C, 46) was supplied by JSR Industries (Osaka, Japan). Tripropylene glycol diacrylate (TPGDA, density 1050 kg m^{-3}) and trimethylolpropane triacrylate (TMPTA, density 1110 kg m^{-3}) were obtained from the UCB Chemicals (Brussels, Belgium). Tetramethylolmethane tetraacrylate (TMMT, density 1110 kg m^{-3}) was procured from the Shin-Nakamura Co. (Tokyo, Japan).

Preparation of samples

The nitrile rubber was mixed with one of the acrylates—TPGDA, TMPTA, or TMMT—in a Brabender plasticorder (PLE-330; Brabender OHG, Duisburg, Germany) at 120°C for 3 min at 60 rpm rotor speed. These mixes were then formed into sheets using a 6 $\times$ 13-in. open mill (Schwabenthan, Berlin, Germany). The sheets were compression molded between Teflon sheets at a temperature of 105°C and at a pressure of 5 MPa in an electrically heated press for 3 min to obtain sheets of dimension 11.5 $\times$11.5 $\times$ 0.1 cm.

Irradiation of samples

The molded nitrile rubber samples were irradiated in air at room temperature of 25 $\pm$ 2°C by an electron-beam accelerator at the NICCO Corp. (Shyamnagar, West Bengal, India). The specifications of the electron-beam accelerator are given in Table I.

Sample designations

The samples were designated as $M_{x/y/z}$. Here, x indicates the level of polyfunctional monomer (in %); y indicates the nature of polyfunctional monomers that is, TPGDA(TG), TMPTA(TP), and TMMT(TT), respec-

tively; and z indicates the irradiation dose (in kGy). For example, $M_{0/0/100}$ and $M_{3/TP/100}$ represent neat nitrile rubber irradiated at 100 kGy and nitrile rubber containing three parts of TMPTA irradiated at 100 kGy, respectively.

Characterization of samples

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

ATR spectra of the blends of nitrile rubber, with various polyfunctional monomers at different concentrations, were taken on smooth, thin irradiated films by use of a Nicolet Nexus Fourier infrared spectrophotometer (Nicolet Analytical Instruments, Madison, WI) operating in horizontal attenuated total reflectance (HATR) mode. All the results given herein are the averages of two measurements, with 32 scans for each measurement at a resolution of 4 cm^{-1}.

Solid-state NMR spectroscopy

The solid-state ^{13}C-NMR experiments were performed at 75.5 MHz on a Bruker 300 MSL spectrometer (Bruker, Darmstadt, Germany). Magic angle spinning (MAS) and high-power proton decoupling were used with cross polarization (CP) to obtain the spectra. The spinning speeds ranged from 1.0 to 3.0 kHz and the sample temperature was 27°C. The spectral width was 29,240 Hz and 512 data points, with acquisition time of 0.014 s, were collected for each spectrum.

Gel fraction studies

Gel fraction of the irradiated polymers 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 samples before and after swelling, as follows:

$$\text{Gel fraction} = W_2/W_1 \qquad (1)$$

where W_1 is the initial weight of the polymer and W_2 is the weight of the insoluble portion of the polymer in the gel. The results reported are the averages of three samples.

Determination of crosslink density

Crosslink density, which is the number of network chains per unit volume, was determined from initial weight, swollen weight, and final deswollen weight of the samples. The samples were swollen in methyl ethyl ketone. The number of crosslink points (includ-

ing chemical and physical interactions), v_{phys} per unit volume, was calculated using the following relation[12]:

$$v_{\text{phys}} = \frac{-1}{2^{-}V} \left[\frac{\ln(1 - v_r) + v_r + \chi_1 v_r^2}{v_r^{1/3}} \right] \quad (2)$$

where χ_1 is the polymer–solvent interaction parameter; V is the molar volume of the solvent; v_r is the volume fraction of the rubber in the swollen gel, and was calculated using the following relation[13]:

$$v_r = \frac{(D_s - F_f A_w)\rho_r^{-1}}{(D_s - F_f A_w)\rho_r^{-1} + A_s\rho_s^{-1}} \quad (3)$$

where v_r, D_s, F_f, A_w, A_s, ρ_r, and ρ_s are, respectively, volume fraction of rubber, deswollen weight of the sample, fraction insoluble, sample weight, weight of the absorbed solvent corrected for swelling increment, density of rubber, and density of solvent, respectively.

Mechanical properties

Tensile specimens were punched out from the molded sheets using ASTM Die C. The tests were carried out according to the ASTM D 412-98 method in a universal testing machine (Zwick 1445; Zwick GmbH, Ulm, Germany) at a crosshead speed of 500 mm/min at 25°C. The average of three tests are reported here.

Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical thermal characteristics of the rubber samples were evaluated in a DMTA IV (Rheometric Scientific, Piscataway, NJ) under tension mode. The experiments were carried out at a frequency of 1 Hz. The measurements were taken from −80 to 100°C, at a heating rate of 2°C/min. The data were analyzed using RSI Orchestrator application software (Rheometric Scientific) on an Acer computer attached to the machine. The storage modulus and loss tangent (tan δ) were measured for all the samples under identical conditions.

RESULTS AND DISCUSSION

IR studies

Effect of radiation dose and level of TMPTA on structural changes of nitrile rubber

Figure 1(a) shows the IR spectra in the region of 4000–600 cm^{-1} of neat nitrile rubber. The various peak positions and their assignments are summarized in Table II. Figure 1(b), which shows the spectra of the irradiated nitrile rubber at different doses in the region of 1700–1600 cm^{-1}, reveals a decrease in the concentration of the unsaturation group on the backbone of nitrile rubber chain, compared to that of the unirradiated system. This

is attributed to self-crosslinking of the samples during irradiation under normal atmosphere [Scheme 1(a)]. This is also supported by gel fraction studies, discussed later. Similarly, nitrile rubber containing 3 phr of TMPTA was irradiated at different doses and the variation in the unsaturation group is also shown in the same figure. The possible reactions of grafting and crosslinking of nitrile rubber with TMPTA are shown in Scheme 1(b). A decrease in the peak height in the region of 1700–1600 cm^{-1} is also observed here. The absorbance value attributed to >C=C< group for $M_{0/0/0-500}$ and $M_{3/TP/0-500}$ decreases sharply in the initial stage [Fig. 1(c)]. The changes are marginal after 150 kGy. The reasons, discussed in the next sections, are predominantly attributable to crosslinking. However, the chain scission, as shown in Scheme 2, at higher doses cannot be ruled out.

The chain scission is also confirmed from the occurrence of peaks at 1962 and 1675 cm^{-1}, which are attributed to the asymmetric stretching vibrations of the C=C=C groups and vinyl groups, respectively. The bond energy of labile hydrogens in the methylene linkage is about 377 kJ mol^{-1}. On irradiation, these hydrogens are split off, generating macroradicals on the carbon atoms of the diene unit. On the other hand, these macroradicals either react with oxygen in air, resulting in formation of carbonyl groups, or lead to formation of double bonds. Various reactions such as aerial oxidation, ether formation, and recombination [Scheme 2(b)–(d)] compete with an increase in pulsed electron-beam irradiation in $M_{0/0/0-500}$ and $M_{3/TP/0-500}$. Figure 1(d) shows an increase in >C=O stretching values at 1735 cm^{-1}, up to a certain dose, for the unmodified and the modified systems. The absorbance value passes through a maximum up to 150 kGy in grafted and ungrafted rubbers and then decreases marginally at higher irradiation doses. There is also an increase in C—O—C stretching frequencies attributed to the formation of ether linkages at different doses for the modified and the unmodified systems [Fig. 1(e)]. These plots [Fig. 1(d) and (e)] have the same trend. From these plots it may be concluded that carbonyl groups and ether linkages are formed as a result of aerial oxidation [Scheme 2(b)–(c)], which increases with radiation dose up to 150 kGy, and then there may be a greater occurrence of chain scissioning and breakdown of network structure at higher doses because of availability of large numbers of free radicals.

NMR analysis

Solid-state ^{13}C-NMR spectroscopy has proved to be very useful for analysis of chemical structure, particularly in polymeric systems. This has prompted, for the first time, the use of NMR technique for characterization and quantification of the changes in nitrile rubber with and without 3 phr of TMPTA irradiated with 100 kGy. Figure 2 shows the NMR spectra of
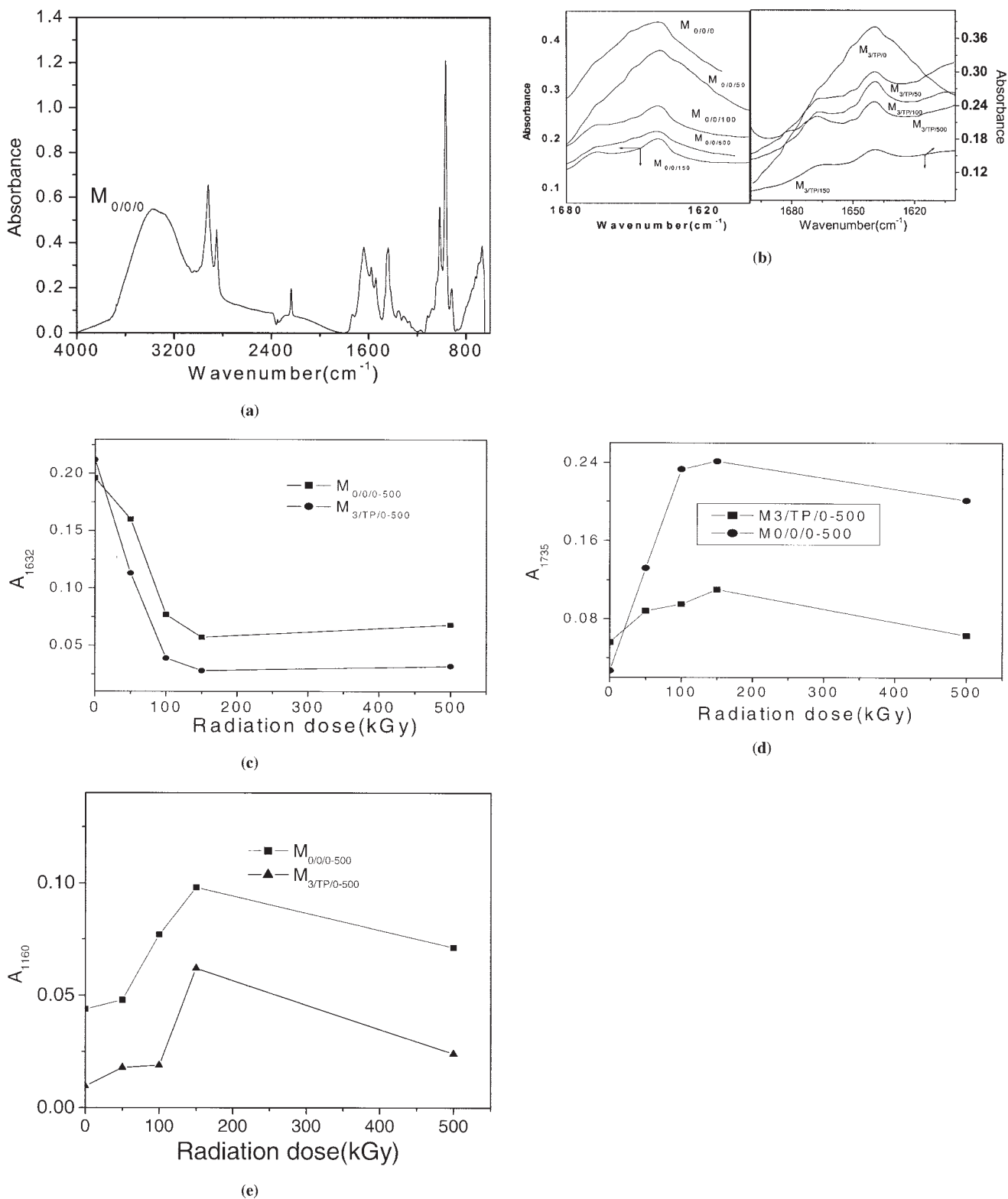
Figure 1 (a) IR spectra of neat nitrile rubber in the region 4000–400 cm^{-1}. (b) IR spectra of >C=C< stretching vibrations for $M_{0/0/0-500}$ and $M_{3/TP/0-500}$ with doses of 50, 100, 150, and 500 kGy. (c) Variation of the absorbance of >C=C< at 1632 cm^{-1} for $M_{0/0/0-500}$ and $M_{3/TP/0-500}$ with doses of 50, 100, 150, and 500 kGy. (d) Variation of the absorbance of >C=O at 1735 cm^{-1} for $M_{0/0/0-500}$ and $M_{3/TP/0-500}$ with doses of 50, 100, 150, and 500 kGy. (e) Changes in the absorbance value of C—O—C at 1160 cm^{-1} for $M_{0/0/0-500}$ and $M_{3/TP/0-500}$ with doses of 50, 100, 150, and 500 kGy.

TABLE II
Peak Position and Assignment of Peaks in the IR Spectra of Nitrile Rubber

Wavenumber (cm^{-1})	Functional group
3010	–CH stretching vibration of –CH groups
3080	–CH stretching vibration of olefinic group
2911, 2839	–CH stretching vibration of methylene groups
2223	Stretching vibration of aliphatic cyanides
1962, 1675	Asymmetric stretching vibrations of >C=C=C< group
1642, 1622	>C=C< stretching for aliphatic olefinic group
1421	H—C—H bending vibration of methylene group
975	–C=C—H deformation for aliphatic unsaturation

these samples. The assignment of resonances was done with reference to Sadtler's guide to ^{13}C-NMR.[14] ^{13}C-NMR assignments for the olefinic region of polybutadiene were previously reported by several investigators.[16–21] A strong peak with high intensity at 34.6 ppm is assigned to the >CH$_2$ group, which is at the alpha position to the double bond in nitrile rubber. A peak at 118 ppm is assigned to nitrile carbon resonance. The olefinic regions of the spectrum appear in the regions of 125–135 ppm. Two resonances, with chemical shifts at 133 and 128 ppm of the control, are compared with those of the irradiated samples in the inset of Figure 2. The decrease in intensity of olefinic resonances on irradiation is attributed to the formation of an allylic radical from the butadiene part of the copolymer followed by addition of the radical to the olefinic linkage of the other chain, which lead to high network chain density. Formation of the allylic radical is favored because of low bond energy and also because the radicals can be stabilized by delocalization.[15]

The spectra also contain two regions, as shown in Figure 2. The 70–80 ppm region consists mainly of a peak at 76 ppm in the case of M$_{3/TP/150}$ and at 78 ppm in the case of M$_{0/0/150}$. These peaks arise as a result of C—O—C linkages, which may result by oxidation on irradiation. The intensity of C—O—C linkage was found to be less for M$_{3/TP/150}$ than for the other sample. The 40–60 ppm region consists of several peaks with chemical shifts of 42.3, 45.1, and 46.2 ppm, except that the peaks at 46.2 ppm in both cases are of very low intensity. The peak at 46.2 ppm arises as a result of carbon–carbon crosslinking. The peaks in the 50–60 ppm range with higher intensities are observed with M$_{3/TP/150}$ but not with M$_{0/0/150}$. This may be attributable to grafting of TMPTA on to the nitrile rubber matrix. Thus, additional peaks appear in the deshielded region. Apart from this, two weak resonances at 111 and 138 ppm in the spectra of M$_{0/0/150}$ and M$_{3/TP/150}$, corroborating the FTIR results, are observed. These are attributed to vinyl end groups, which are possibly byproducts of main chain scission caused by disproportionation of the allylic radical. The carbonyl frequency was observed at 192 and 193 ppm

for nitrile rubber irradiated at 150 kGy. In addition, ester carbonyl in the crosslinked structure was observed at 160 ppm.

Gel fraction

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

Less attention has been paid to the interaction between intermediates, despite its potential importance. Herein, an attempt has been made to study the possibility of overlapping of spurs or intermediates in nitrile rubber. The mode of spur formation and its overlapping, leading to crosslinked networks, depend on the energy deposition per unit ion length or linear energy transfer (LET) in radiation technology.

According to Kudoh et al.,[22] concentration of spurs (c) is related to radiation dose by the following equation:

$$c = kR\tau(1 - e^{-D/R\tau}) \qquad (4)$$

where k is the yield of spur formation (spurs cm^{-3} Gy^{-1}), R is the dose rate, τ is the lifetime of the spurs, and D is the radiation dose (kGy).

The variation of % gel content with radiation dose was mathematically interpreted and reported in our previous communication[11]:

$$G = a(1 - e^{-bD}) \qquad (5)$$

where G is the percentage of gel formed as the result of radiation and a and b are constants.

Because the gel formation is ascribed to the overlapping of active free radicals, which are otherwise called spurs, concentration of spurs can be directly related to the concentration of gel formed because of irradiation. This physical model describes the expected dependency of spur formation with radiation dose. Here, we have assumed that spurs have a constant size throughout life, although it is more natural to assume that a spur expands with time.
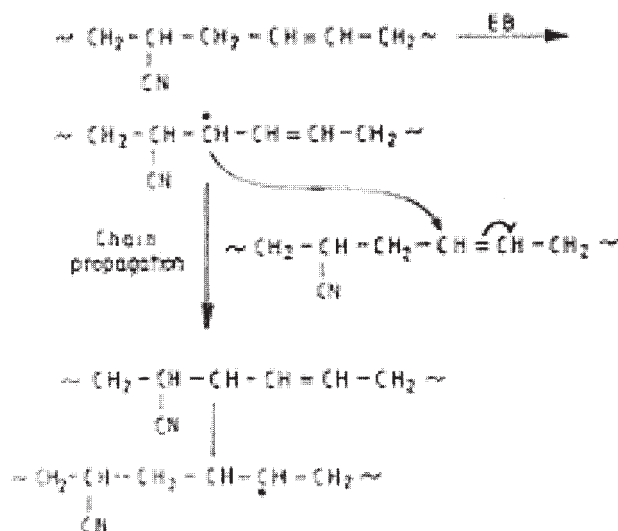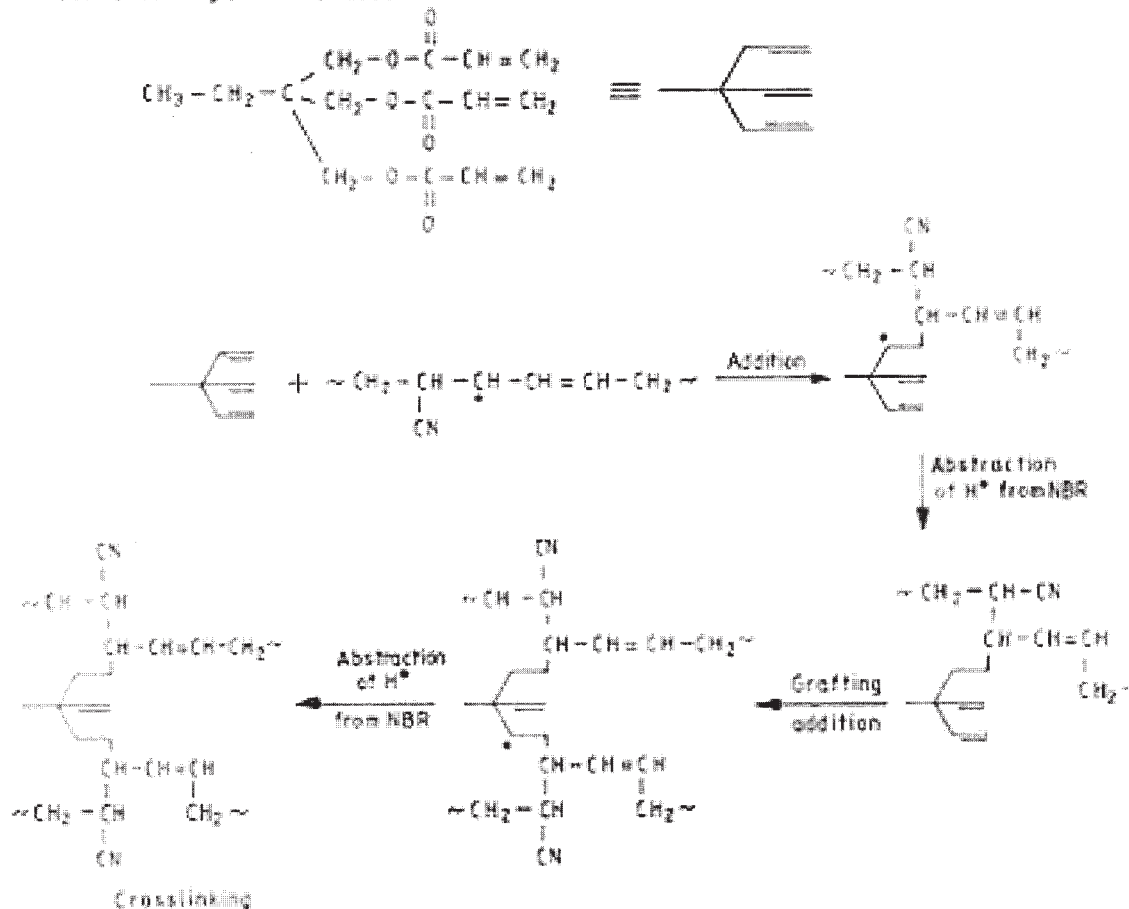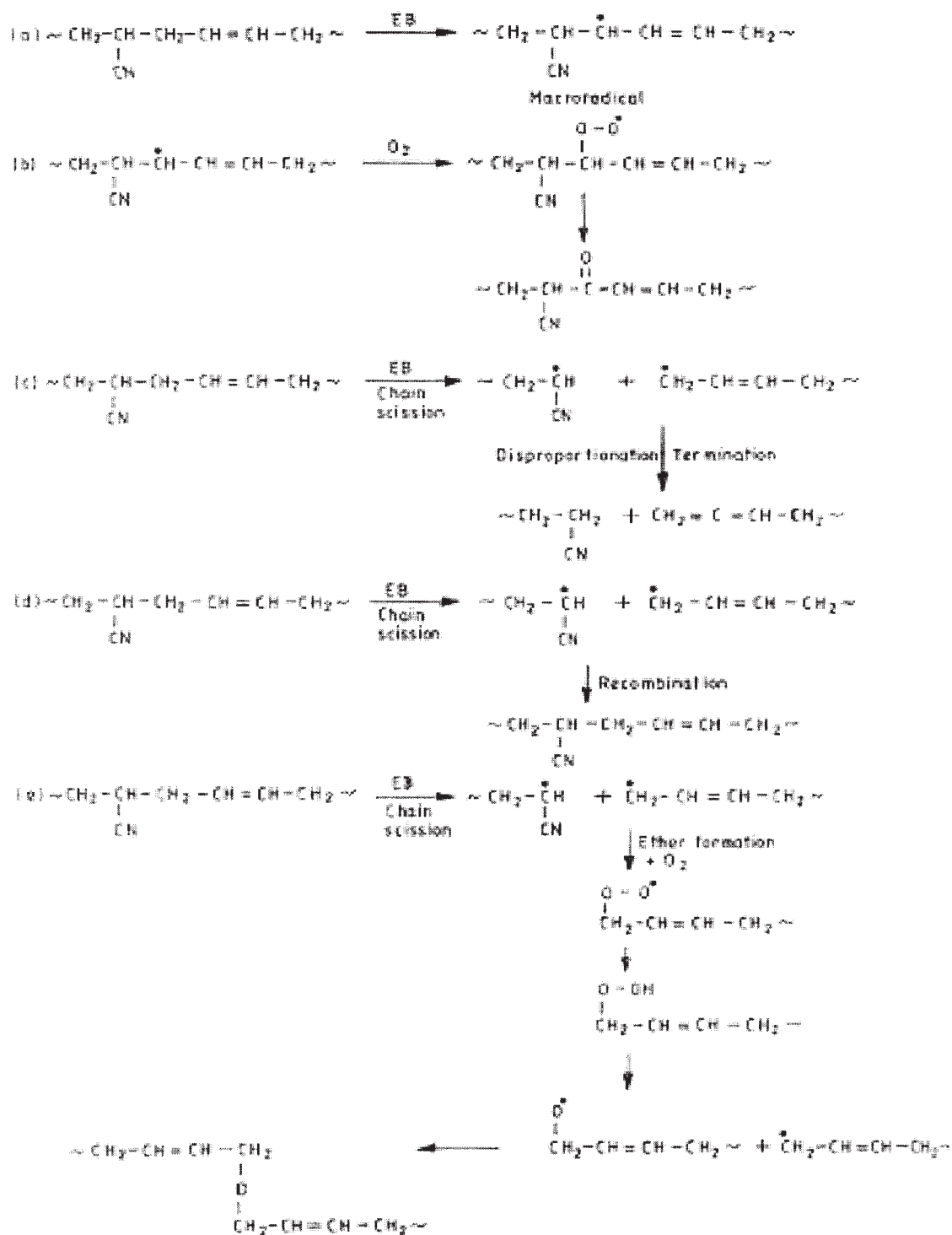
Scheme 1

By comparing eqs. (4) and (5), the constants a and b can be obtained as

$$a = kR\tau \tag{6}$$

$$b = 1/R\tau \tag{7}$$

The value of b indirectly correlates the lifetime of spurs with radiation dose (R), which remains constant throughout the experiment.

Both the grafted and the ungrafted nitrile rubbers show the same exponential behavior for the variation of gel content with radiation dose [Fig. 3(a)]. There is

Scheme 2

a considerable debate in the optical densification in the bombarded polymers. All the grafted rubbers show an increment in b value, as calculated from eq. (5).[11] For $M_{3/TP/0-500}$ and $M_{0/0/0-500}$, respectively, average b values of 0.11 and 0.08 are observed. The increase in b value for the modified rubber is correlated with the large concentration of radiation-induced intermediate species formed in a very short period of time. Enhanced interaction among these intermediates, attributed to overlapping between spurs, could tend to increase in the gel content.

A critical dose rate, at which the intermediate species begin to interact, and for which different systems can be compared, is also deduced from the
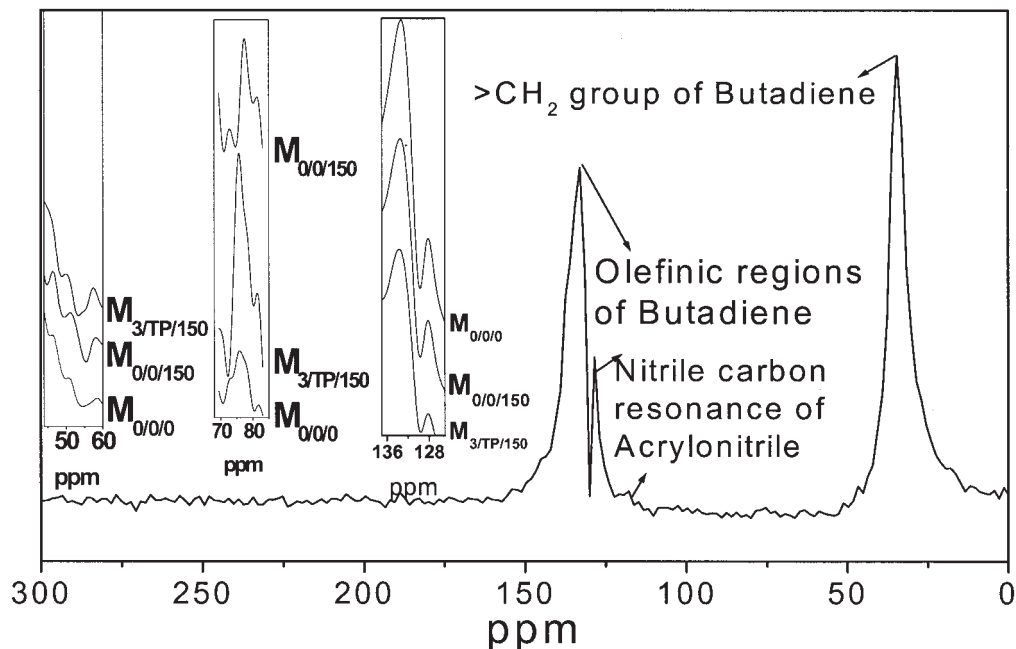
Figure 2 Solid-state NMR spectra of nitrile rubber in the region 300—0 ppm. Inset: NMR spectra of irradiated nitrile rubber in the regions of 40–50 and 70–80 ppm.

logarithmic expression of the mathematical model,[11] as follows:

$$\ln G = \ln a + \ln(1 - e^{-bD}) \qquad (8)$$

The straight-line plot of $\ln G$ versus $\ln(1 - e^{-bD})$ gives the value of critical dose on extrapolation to 1% gel formation. Figure 3(b) and (c) give the values of critical doses for 1% gel formation for neat nitrile rubber and modified nitrile rubber containing 3 parts of TMPTA. A minimum dose is required for the grafted rubbers to produce 1% gel; for instance, it requires a dose of 96.1 Gy for $M_{3/TP/0-500}$ compared to 134.8 Gy in $M_{0/0/0-500}$. This is explained by the fact that on grafting, a greater number of spurs is generated within a short time. This is further corroborated by use of a Charlesby–Pinner plot that relates sol fraction with radiation dose,[23] as follows:

$$S + S^{1/2} = p_0/q_0 + 10/q_0 R u_1 \qquad (9)$$

where u_1 is the number of average degree of polymerization, p_0 is the fracture density per unit dose (in kGy), q_0 is the density of crosslinked units per unit dose (in kGy), R is the radiation dose (in kGy); p_0/q_0 gives an idea of the ratio of chain scission to crosslinking. The much lower value of the ratio (0.29) for the 3% TMPTA system in $M_{3/TP/0-500}$, compared to that for the pure rubber $M_{0/0/0-500}$ (0.42), supports the increased crosslinking at 3% TMPTA system at the lower doses used [Fig. 3(d)].

Crosslink density was determined by using Flory's equation [eq. (2)][14] and also from the NMR measurements. The values are given in Table III. From the NMR spectroscopy, total crosslink density is given by

$$\mu = \frac{[0.5(\text{Sum of } I(\text{C–O–C}) \text{ resonances}) + \text{Sum of } I(\text{C–C}) \text{ resonances}] \times \rho/M_0}{I_0} \qquad (10)$$

where $I(\text{C—O—C})$ and $I(\text{C—C})$ are the intensities attributed to C—O—C and C—C crosslinks, respectively; I_0 is the reference intensity of the monomer unit chosen as the intensity of CH_2 group of butadiene part of the copolymer at 34.6 ppm; ρ is the density of the polymer; and M_0 is the molar mass of monomer unit. It is observed that the crosslink density of TMPTA-modified samples is much greater than that of the control samples. NMR data are in accordance with the swelling measurements. The assumption of no change in the molecular weight distribution in the Flory equation leads to the slightest changes between the spectroscopic crosslink density and the chemical crosslink density.[21] Also, the increase in resonances with crosslink density is attributed to the higher efficiency in the cross-polarization process. As the network structure increases, the mobility of the chain backbone decreases with the increased rigidity; thus, carbon–hydrogen distances become static and so cross-polarization can occur with greater efficiency.
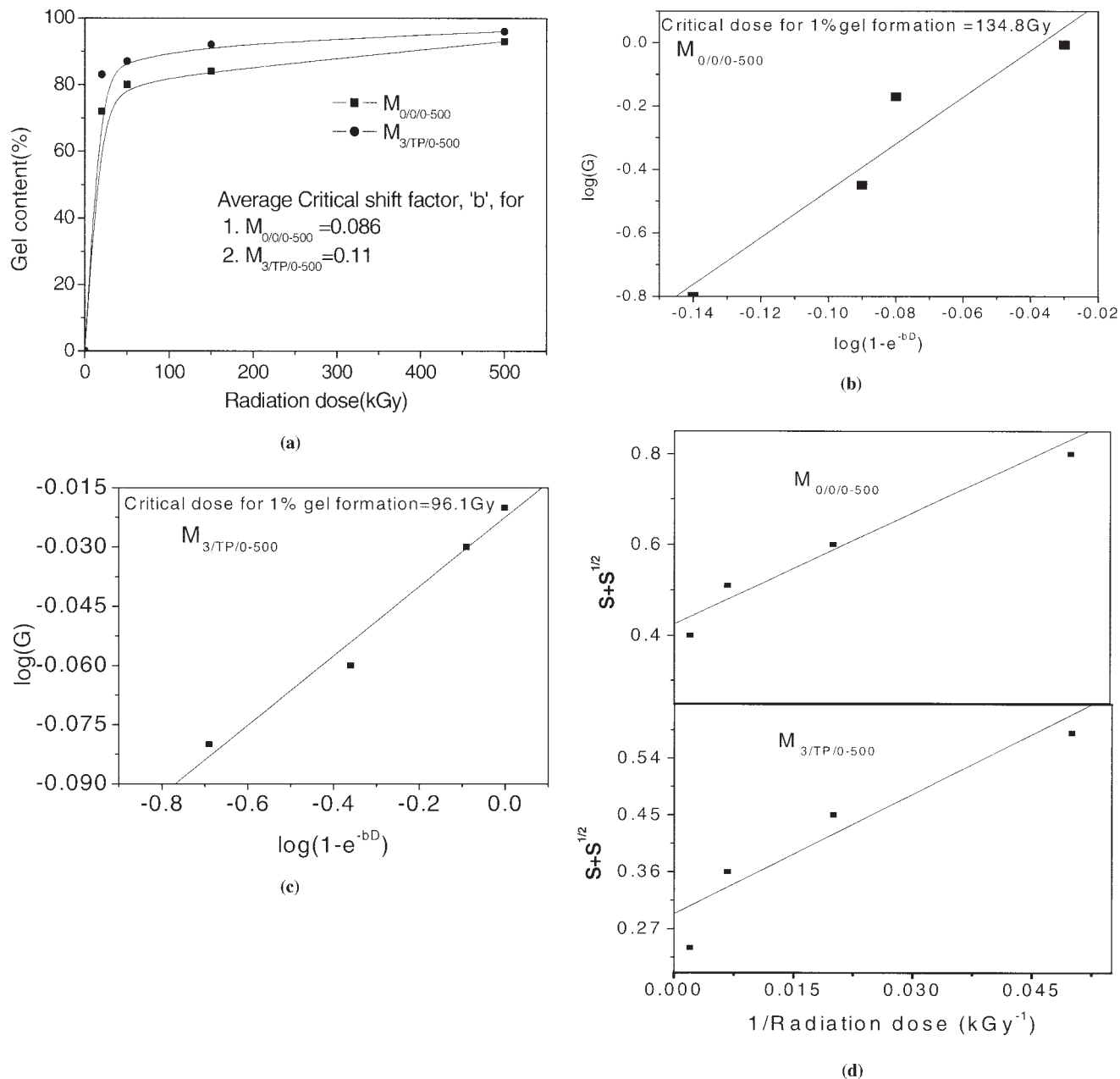
Figure 3 (a) Gel content values for the control and the grafted nitrile rubber irradiated at different doses of 20, 50, 150, and 500 kGy. (b–c) Determination of the critical dose for 1% gel formation for $M_{0/0/0-500}$ and $M_{3/TP/0-500}$, respectively. (d) Plots of $S + S^{1/2}$ versus $1/R$ for $M_{0/0/0-500}$ and $M_{3/TP/0-500}$ according to eq. (9).

Dynamic mechanical thermal analysis

The damping behavior of the control rubber, irradiated at different doses, is shown in Figure 4(a) over a

TABLE III
Comparison of Spectroscopic and Chemical Crosslink Density

Sample	Spectroscopic crosslink density (gmol/cm³)	Crosslink density from swelling measurements (gmol/cm³)
$M_{0/0/150}$	10.4 ± 10^{-4}	15.6 ± 10^{-4}
$M_{3/TP/150}$	11.5 ± 10^{-4}	19.2 ± 10^{-4}

range of temperatures. The damping goes through a maximum in the transition region and decreases in the rubbery region. Such behavior is typical of all linear amorphous polymers.[24] Damping is low below T_g as the chain segments are frozen in. Below T_g the deformations are primarily elastic and occurrence of molecular slip resulting in viscous flow is minimal. Also, above T_g the molecular segments are free to move and there is little resistance to flow, resulting in low damping. Thus, the damping is low when the chain segments are completely frozen in or free to move, although the damping is high in the transition region

(a)

(b)

(c)

(d)
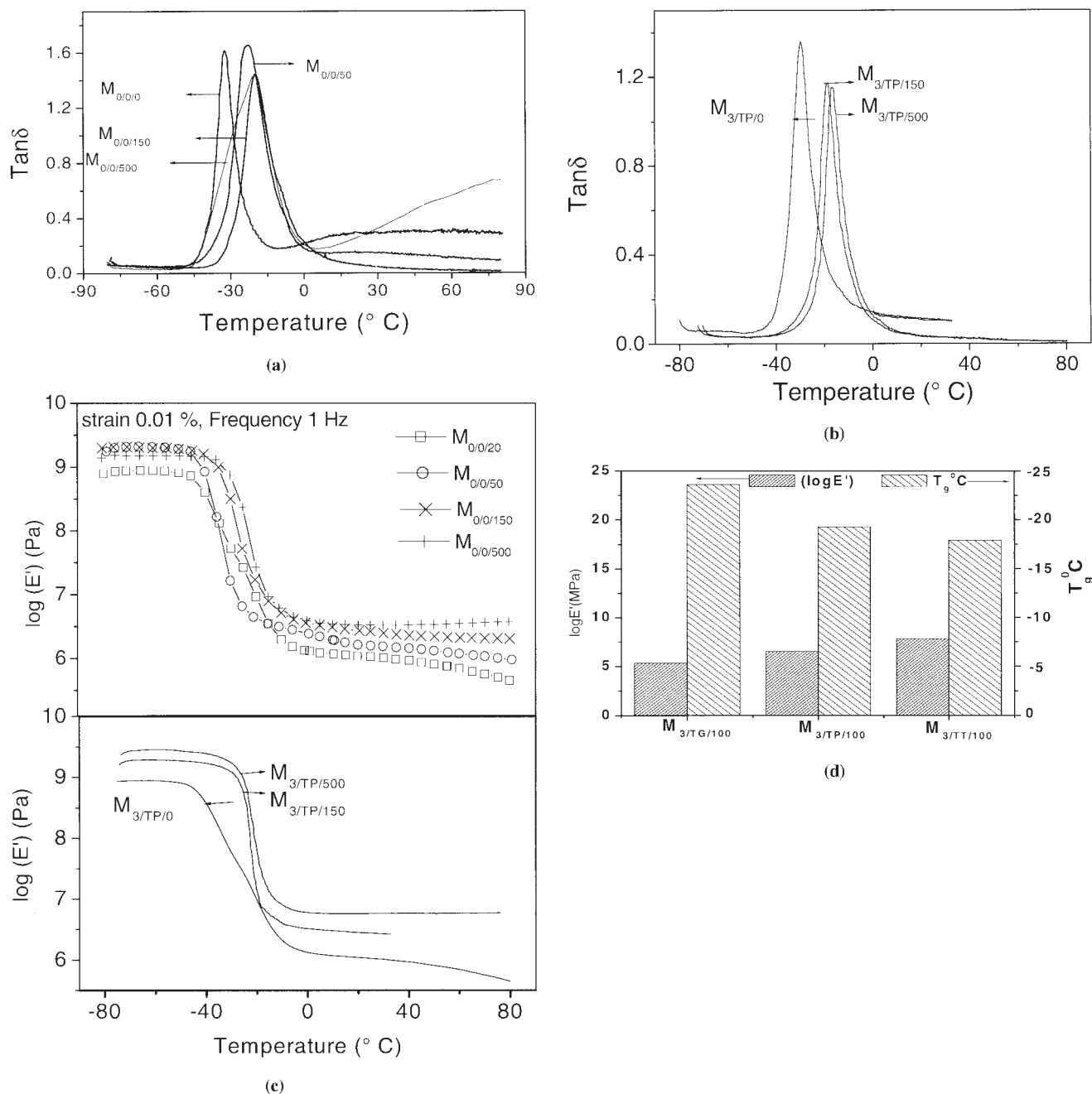
Figure 4 (a) Loss tangent of pure nitrile rubber irradiated at different radiation doses as a function of temperature. (b) Loss tangent of nitrile rubber blended with 3% TMPTA and irradiated at 150 and 500 kGy, as a function of temperature. (c) Dynamic storage moduli for the modified and the unmodified systems of $M_{0/0/0-500}$ and $M_{3/TP/0-500}$ as a function of temperature. (d) Plots of dynamic storage moduli, T_g for nitrile rubber blended with different polyfunctional monomers and irradiated at constant dose of 100 kGy.

because of the initiation of micro-Brownian motion of the molecular chains.[25] A completely frozen-in segment can store in more energy for a given deformation than in a segment that is free to move. 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 polymer are indicative of the structure and the extent to which a polymer is crosslinked. In Figure 4(a) the damping peak temperature of the nitrile rubber is observed to be −32.4°C. With an increase in radiation dose, the transition temperature shifts to −20°C for $M_{0/0/150}$ (Table IV). The shift is attributed to the increasing degree of crosslinking and structural

TABLE IV
Dynamic Storage Modulli at Three Different Temperatures and T_g for Modified and Unmodified Nitrile Rubber on Irradiation with Different Doses

System	Dynamic storage modulli at three different temperatures (Pa)			T_g (°C)
	−70°C	25°C	70°C	
$M_{0/0/0}$	1.52×10^9	1.04×10^6	1.43×10^6	−32.4
$M_{0/0/50}$	1.93×10^9	1.54×10^6	1.89×10^6	−22.2
$M_{0/0/150}$	2.07×10^9	1.92×10^6	1.98×10^6	−20.0
$M_{0/0/500}$	2.44×10^9	2.65×10^6	2.07×10^6	−19.1
$M_{3/TP/150}$	2.63×10^9	3.31×10^6	2.28×10^6	−18.4
$M_{3/TP/500}$	2.80×10^9	5.73×10^6	3.64×10^6	−17.3

changes, which are revealed from the increase in the gel fraction values [Fig. 3(a)] and spectroscopic intensities.

Crosslinking hinders the segmental motion, which 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 a result of the combined effect of crosslinking (involving both shorter and longer chains) and scission reactions prevailing in the presence of the electron beam [Scheme 2(a)]. The decrease of the loss tangent–peak height of the irradiated samples is possibly attributable to either crosslinking of the macromolecular chain or perturbed relaxation of the chain molecules as a result of structural changes. Figure 4(b) shows the variation of tan δ against testing temperatures of the nitrile rubber blended with 3% TMPTA at two different radiation doses. The variation is similar to that of the unmodified rubber. $M_{3/TP/500}$ shows a T_g of −17.3°C compared to −18.4°C for $M_{3/TP/150}$. The dynamic storage moduli of the unmodified rubber at 25°C increase with increasing doses and the values for TMPTA mixed systems are also higher than that of the control rubber at ambient temperature of testing [Fig. 4(c), Table IV]. This reflects the increased degree of crosslinking for the modified rubber, which is also confirmed by the increase in their gel contents [Fig. 3(a)]. A multifunctional vinyl monomer like TMPTA promotes rapid free-radical–induced propagation reactions, leading to network (crosslinked) polymer structures through grafting by their double bonds [Scheme 2(a)]. It also acts as a plasticizer, giving efficient contact between the chains. A mobilizer like TMPTA increases the radical–radical termination and thus decreases the extent of scission reactions and oxidation.[26] IR spectroscopic studies and solid-state NMR analysis, as investigated, refer to reduced concentrations of >C=C< and >C=O groups for the TMPTA blended systems, which corroborate this observation [Figs. 1(c), (d), and 2].

Effect of nature of monomer

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.[27] Their reactivity is governed by various factors such as the number of double bonds and their nature. Figure 4(d) shows the plot of T_g and the dynamic storage moduli of TPGDA, TMPTA, and TMMT mixed nitrile rubbers against testing temperature at a frequency of 1 Hz. An irradiation dose of 100 kGy was used. It is observed that the T_g increases as the number of double bonds in the polyfunctional monomer is increased. The storage modulus of the TMMT-based system is also higher, thus supporting the inference that TMMT is more effective in producing a slightly denser network than TPGDA, which has the lowest unsaturation.

Mechanical properties

Figure 5(a) displays the stress–strain curves of various electron-beam–irradiated samples of nitrile rubbers ($M_{0/0/0–500}$). There is an upturn of tensile stress at certain elongation, as the radiation dose is increased from 0 to 500 kGy. The tensile strength, modulus, and elongation at break were calculated from these curves. Figure 5(b) and (c) show the variation of these values with radiation doses (0–500 kGy) for the unmodified and the grafted nitrile rubber. It is observed that in both the cases, the tensile strength increases in the initial stage, reaches a maximum at around 50 kGy, and then decreases with increasing radiation dose. The modulus at 100% elongation, however, increases continuously with radiation dose. The modulus of a vulcanizate is proportional to the number of crosslinks formed.[28] Because the degree of crosslinking, involving both shorter and longer macromolecular chains, is proportional to the integral radiation dose absorbed by the polymer, an increase in modulus is observed at higher radiation doses. The elongation at break decreases continuously at higher radiation doses. This ascertains the formation of network structure on irradiation.

The tensile strength of a polymer is a function of crosslink density and energy dissipation. The tensile strength increases with crosslinks at lower crosslink density. This was previously reported for EB-modified fluorocarbon and EPDM rubbers.[9,10] There is an increment of 28.5% in 100% modulus and 21% in tensile strength for $M_{3/TP/150}$ compared to those of $M_{0/0/150}$ [Fig. 5(b) and (c)]. However, at higher crosslink density the network is so dense that there is little energy dissipation in the matrix and the energy supplied is used for breaking the bonds. At higher crosslink density, the segments of macromolecules become immobile, the system becomes stiffer, and the elasticity de-
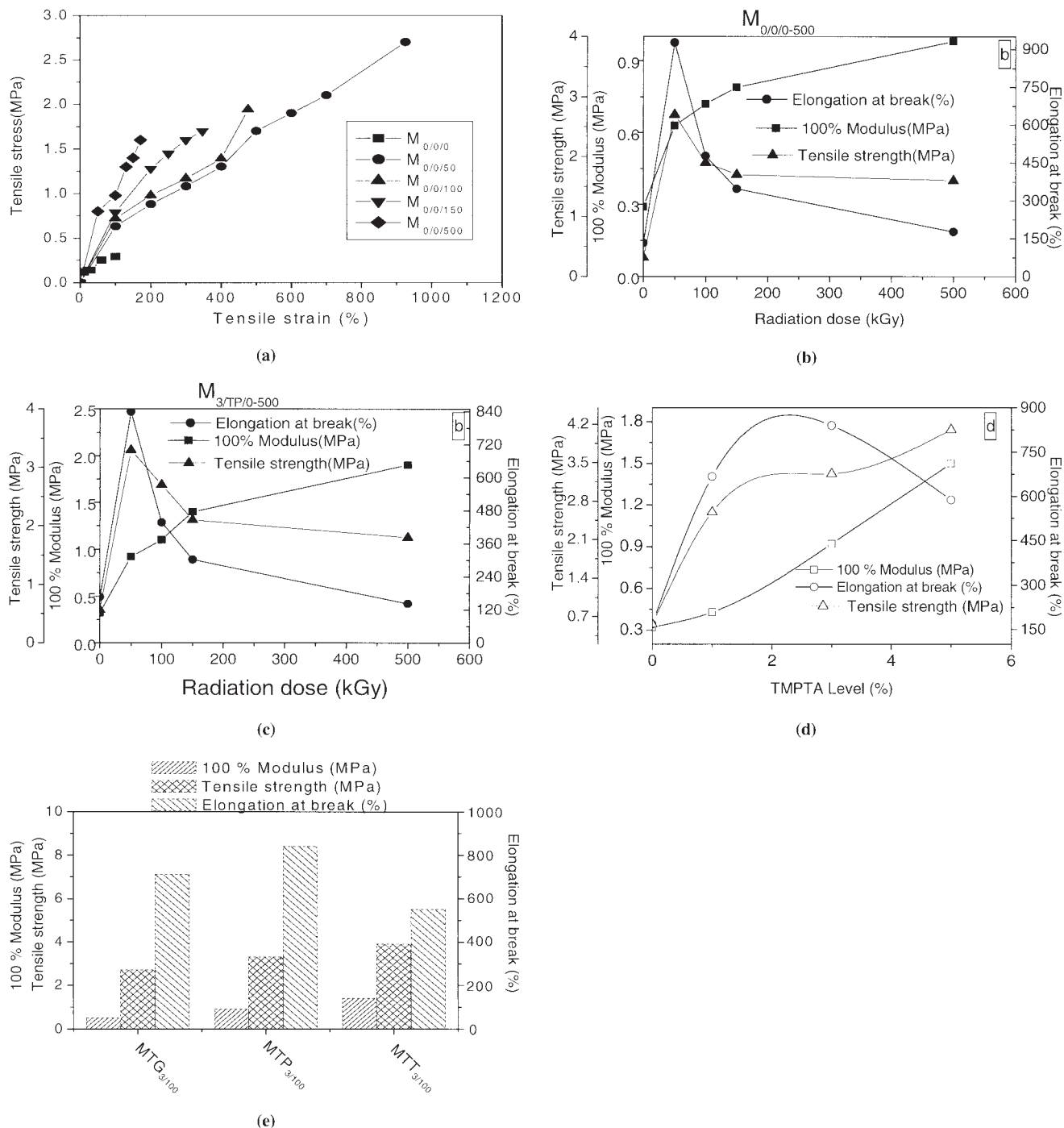
Figure 5 (a) Stress–strain plots of $M_{0/0/0-500}$ irradiated at 50, 100, 150, and 500 kGy. (b–c) Variation of tensile strength (MPa), elongation at break (%), and 100% modulus (MPa) for $M_{0/0/0-500}$ and $M_{3/TP/0-500}$, respectively. (d–e) Changes in tensile strength (MPa), elongation at break (%), and 100% modulus (MPa) for different levels of TMPTA and different polyfunctional monomers.

creases. However, the scission reactions at higher radiation dose, causing lowering of tensile strength values, also cannot be ruled out.

Effect of monomer level

Figure 5(d) shows the variation of tensile properties of nitrile rubber with TMPTA at 0, 1, 3, and 5 wt % at a

constant radiation dose of 50 kGy. It is observed that both the tensile strength and the modulus increase with increasing TMPTA level, whereas elongation at break show a decreasing trend at higher TMPTA level. As the amount of grafting of polyfunctional monomer increases in the rubber matrix, the end linking step increases, resulting in higher modulus and lower elongation at break values.

Effect of nature of monomer

Figure 5(e) shows the variation of tensile strength, modulus, and elongation at break of nitrile rubber with various polyfunctional monomers (such as TPGDA, TMPTA, and TMMT) at a constant level of 3 wt % and a radiation dose 100 kGy. It is observed that the tensile strength and the modulus of TMPTA and TMMT mixed rubbers are higher than those of TPGDA. The variation of the properties among the systems based on tri- and tetraacrylates are marginal. Because the modulus is proportional to the degree of crosslinking, it is probable that the difunctional TPGDA is less efficient than tri (TMPTA) and tetra (TMMT) functional acrylates as a crosslinking agent. The low crosslinking efficiency of the polyfunctional monomer with decrease in the number of unsaturation in the starting material was previously reported.[9]

CONCLUSIONS

The structural features of electron-beam–initiated grafting and crosslinking of nitrile rubber were addressed in this article. The following observations are made.

1. Nitrile rubber containing 3 phr of TMPTA leads to greater crosslinking on irradiation compared to that of the system without TMPTA. This is substantiated by the change in the following spectroscopic properties.

   - Decrease in $>C{=}C<$ concentration for the modified system with minimal aerial oxidation reactions showing low $>C{=}O$ concentration for $M_{3/TP/0-500}$ compared to that of $M_{0/0/0-500}$ by FTIR analysis.

   - Increase in carbon resonances with more C—C linkages for nitrile rubber with 3 phr of TMPTA on irradiation and increase in their spectroscopic crosslink density by solid-state NMR analysis.

2. The predominance of crosslinking for $M_{3/TP/0-500}$ is well understood by the increase in the average b value to 0.11 for $M_{3/TP/150}$ from 0.08 for $M_{0/0/150}$ and decrease in the critical dose to 96.1 from 134.8 Gy for the same two polymers.

3. There is an increase in storage moduli and a shift in T_g toward higher temperature on irradiation for both the modified and the unmodified systems on irradiation, indicating the occurrence of crosslinking.

4. The gel content increases with the radiation dose, up to 100 kGy, for both the ungrafted and the grafted nitrile rubber with 3% TMPTA and then reaches a near-limiting value. Sol–gel analysis re-veals that the probability of scission to crosslinking is lower for the grafted rubber (0.29) compared with that for the control rubber (0.42).

5. Tensile strength and elongation at break increase with the radiation dose, up to 50 kGy, and then decrease for the unmodified nitrile rubber. A similar trend is observed in the blend of 3% TMPTA and nitrile rubber. In both cases, the 100% modulus gradually increases with irradiation dose. Beyond a 50-kGy radiation dose, the tensile strength decreases as the result of high crosslink density and low energy dissipation.

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