JOURNAL OF MATERIALS SCIENCE **40** (2005) 2823–2831

Dynamic mechanical analysis of electron beam irradiated sulphur vulcanized nitrile rubber network—some unique features

V. VIJAYABASKAR, A. K. BHOWMICK*
Rubber Technology Centre, Indian Institute of Technology, Kharagpur 721302, India
E-mail: anilkb@rtc.iitkgp.ernet.in

Mixed crosslinking system with electron beam irradiation as one of the crosslinkers in rubber has been developed for the first time. This paper describes some unique features of dynamic mechanical properties of the electron beam irradiated nitrile rubber vulcanizates at varying levels of sulphur in the network. Dynamic mechanical thermal analysis (DMTA) was performed on these vulcanizates over a range of temperatures (−80°C to +80°C), frequencies (0.032 to 32 Hz) and strains (0.001 to 10%). The results showed that there were significant changes in tan delta peak temperature and storage modulus on irradiation of these vulcanizates. The vulcanizates containing higher amount of sulphur formed intense crosslinked networks and crosslink rearrangements, which were supported by the increase in the storage modulus and shift in tan delta towards higher temperature as compared to their control counterpart. There is also an increase in the peak height due to chain scission and subsequent plasticization. A concept of network distribution using the plots of the storage modulus ratio divided by frequency against inverse of frequency was introduced. This contravening nature was also affirmed with the help of these curves showing broader network distribution for irradiated samples having lower amount of sulphur. This was also supported from the crossover frequency values estimated from the plot of storage and loss modulii against frequencies observed. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Modification of thermoplastic and rubbery materials by electron beam radiation takes an important position in the present scenario to implement a pollution free technology. Irradiation of polymeric materials by electron beam leads to superior properties to those by other radiation induced modifications like gamma rays which have low achievable dose rate than the former. This process is so rapid that there is insufficient time for significant amount of oxygen to diffuse in to the polymer matrix and impart aerial oxidation. Also, it is safe, as there is no radioactivity. Electron beam (EB) irradiation of polymeric material like nitrile rubber causes not only crosslinking (involving C—C bonds), but also scissioning which causes segmentation of the polymeric chain. This introduces heterogeneity in to the system. It has also been demonstrated that apart from crosslinking, oxidation and degradation of network structure take place during EB radiation. The above structural changes lead to drastic change of mechanical, dynamic mechanical, elastic property and thermal stability of the materials [1]. On the other hand, though conventional curing agents are used to improve the physical properties of rubbers, their dispersion in the polymer matrix is the limiting factor. To overcome some of the demerits of crosslinking and vulcanization by conventional curing agents, the concept of "mixed crosslinking" system using EB irradiation was introduced in nitrile rubber for the first time. Also, it is known from the literature survey that the effects of irradiation on sulphur vulcanized rubber network is yet to be reported. Several references of mixed crosslinking system namely sulphur and peroxides, sulphur and zinc oxides etc. including those from this laboratory have been found in the literature [2–9]. The structural changes due to the action of electron beam on sulphur crosslinked nitrile rubber and the mechanical properties of the vulcanizates have been reported in our earlier communications [10, 11]. The dynamic mechanical method assesses structure and properties of solids and viscoelastic liquids via their dynamic moduli and damping. In particular, changes in these parameters are studied as a function of measurement temperature, frequency and strain in Dynamic Mechanical Thermal Analysis (DMTA). The term, dynamic properties refer to the response to periodic or transient forces which do not cause failure or appreciable fatigue (permanent change of properties) during the investigation. Several efforts have been made in this field to show this dynamic mechanical approach to be a very useful tool in delineating glass transition region,

---

*Author to whom all correspondence should be addressed.

0022–2461 © *2005 Springer Science + Business Media, Inc.*

relaxation spectra, degree of crystallinity, phase separation, chemical composition of polymer blends, grafting of polymers and copolymers, and crosslinking of polymers [12–15]. The dynamic loss modulus or internal friction is sensitive to many kinds of molecular motion, transitions, relaxation processes and structural heterogeneities [16]. The behavior of any elastomer for any practical application can be predicted with the help of these data.

A few workers have studied the effect of radiation on dynamic mechanical properties of different polymers. Traeger and Castonguay have studied the effect of γ-irradiation on the dynamic mechanical properties of styrene-butadiene rubber (SBR) [17]. Chaki *et al.* have reported the dynamic- mechanical relaxation of EB crosslinked polyethylene grafted with methyl methacrylate [18] . Kwei and Kwei have observed that molecular polydispersity tends to lower the modulus of irradiated polyvinyl chloride PVC [19]. Datta *et al.* have reported the dynamic mechanical thermal analysis of electron beam initiated grafting and crosslinking of ethylene- vinyl acetate copolymer in the presence and absence of polyfunctional vinyl monomer like trimethylolpropane trimethacrylate (TMPTMA) [20]. Banik *et al.* have studied the effect of radiation dose in presence of various monomers on the influence of dynamic mechanical properties of fluorocarbon elastomer [21]. Thavamani and Bhowmick have discussed the effect of crosslink density and resin on the dynamic mechanical properties of hydrogenated nitrile rubber (HNBR) [22]. However, studies on the dynamic mechanical properties of nitrile rubber having mixed crosslinking system with electron beam as one of the crosslinkers have not been taken up so far, although a few novel applications have been developed for such system in the author's laboratory.

In our investigation of the effect of radiation dose and level of sulphur on the dynamic mechanical properties of EB modified nitrile rubber, we observed some unique behaviour, which is the subject of this paper. Also, we are reporting for the first time an analysis of network distribution using dynamic mechanical method.

2. Experimental

2.1. Preparation of the samples, materials, experimental setup and sample designation

The list of chemicals, nature and grade of the rubber and their suppliers are listed in Table I. The whole experimental plan was divided in two categories to study the effects of mixed crosslinking system on the structure and the final properties of the vulcanizates, and also to find out the interaction between the radiation and the sulfur/accelerator cure system. The samples are designated as $M_{\mathrm{a/b/c}}$ where 'M' stands for nitrile rubber, 'a' for amount of sulphur (phr), 'b' for accelerator (phr) and 'c' for radiation dose in kGy. For example, $M_{1.5/0.5/150}$ indicates sample containing 1.5 phr of sulphur, 0.5 phr of accelerator (MBTS) and a irradiation dose of 150 kGy. Compound formulations were made based on the following variation of sulphur and accelerator levels: High sulfur-low accelerator ($M_{1.5/0.5/0\text{-}300}$) and low sulfur-high accelerator ($M_{0.5/1.5/0\text{-}300}$) (Table II). Both $M_{1.5/0.5/0\text{-}300}$ and $M_{0.5/1.5/0\text{-}300}$ were irradiated at different doses of 50 150 and 300 kGy. The nitrile rubber was mixed with sulphur, MBTS and other ingredients using conventional mixing procedure in an open two-roll mill (Schwabenthan, Berlin, Germany). The optimum cure time of all the compounds in the above two sets was determined from the rheometric study of the corresponding compounds in an Oscillating Disk Rheometer (ODR, 100S Monsanto) at 150°C.The sheets were compression molded between Teflon sheets at a temperature of 150°C and at a pressure of 5 MPa in an electrically heated Moore press for optimum cure time to obtain sheets of dimension 115 mm × 115 mm × 1 mm.

TABLE I Details of the Materials and their suppliers

Material	Supplier/manufacturer
NBR (ACN content: 33%)	JSR Industries Ltd., Osaka, Japan.
Zinc Oxide	E-Merck, Mumbai, India
Stearic acid [a]	Local supplier
Dioctyl phthalate	Ranbaxy Ltd., Mumbai, India
MBTS[b]	ICI Ltd., Rishra, India
Sulphur	Qualigens, Mumbai, India
Methyl ethyl ketone	E-Merck, Mumbai, India

[a] Rubber grade.

[b] Mercapto benzothiazole disulphide (accelerator).

TABLE II Formulation of various compounds

Ingredients	M1	M2
NBR	100	100
Sulfur	1.5	0.5
Stearic acid	1.0	1.0
ZnO	5.0	5.0
DOP	4.0	4.0
Accelerator (MBTS)	0.5	1.5
Radiation dose (kGy)	50, 150 and 300	50, 150 and 300

In order to study the effects of electron beam radiation dose on the vulcanizate properties, the molded sheets were irradiated at three different doses: 50, 150 and 300 kGy.

2.2. Irradiation of the samples

The molded nitrile rubber samples were irradiated in air at room temperature of 25 ± 2°C by an electron beam accelerator at the NICCO Corporation Ltd, Shyamnagar in West Bengal, India. The specifications of the electron beam accelerator are given in Table III.

2.3. Dynamic mechanical properties

The dynamic mechanical properties of the vulcanizates were measured by means of a dynamic mechanical thermal analyzer (DMTA IV, Rheometric Scientific Inc., NJ) using rectangular specimen of dimensions of 30 × 10 × 1.5 mm, in a tensile mode. Data acquisition was done using RSI Orchestrator software through Acer computer. Three types of tests, namely, temperature sweep (−80 to +80°C), strain sweep (0.001 to

TABLE III Specification of the electron beam accelerator at NICCO Corporation Ltd., Shyamnagar, West Bengal, India

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 × 380/220 V
P.S. voltage frequency	50 Hz
Consumption of power (total)	150 kW

10%) and frequency sweep (0.032 to 32 Hz) were performed.

2.3.1. Temperature sweep measurement

The measurement was carried out in the temperature range of −80 to 80°C with intervals of 2°C/ min. The test frequency was fixed at 1 Hz and strain amplitude was set at 0.01% double strain amplitude (DSA).

2.3.2. Strain sweep measurement

In this case, double strain amplitude ranging from 0.001 to 10% was applied with a frequency of 10 Hz at constant temperature of 25°C. The data were taken with 5 points per decade and the full curves were recorded.

2.3.3. Frequency sweep measurement

Frequency sweep was carried out in the temperature range of −80 to 150°C and data were taken at every 5°C. A ramp and soak program was used to control the temperature profile. At each temperature, the specimen was soaked for 5 min before testing. Storage modulus, E', loss modulus, E'' and tan δ were measured in the frequency range of 0.032 to 32 Hz. 1% strain amplitude was used in all the measurements.

3. Results and discussion

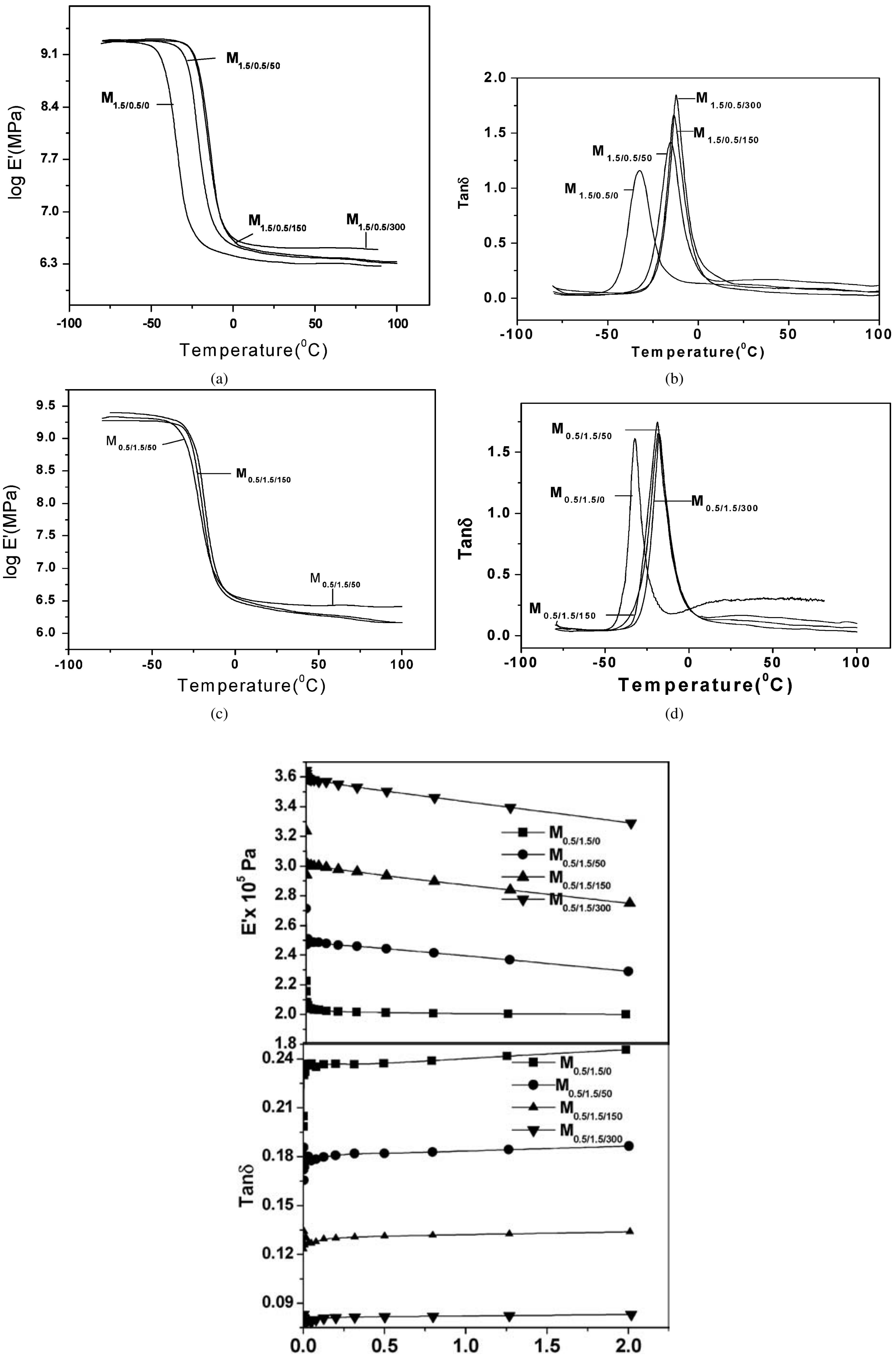
3.1. Effect of variation of temperature

The dynamic mechanical spectrum of nitrile rubber vulcanizates with 1.5 and 0.5 parts of sulphur irradiated at different irradiation doses over a range of temperatures is shown in Fig. 1a–d. The typical behaviour of all amorphous polymers is reflected in the tanδ-temperature curve with a continuous rise in damping, reaching a maximum in the transition region and a subsequent fall in the rubbery region, and also in the storage modulus temperature curve, exhibiting a drastic fall in modulus at a particular temperature. The values of storage modulus at three different arbitrarily chosen temperatures are reported in Table IV. The storage modulus increases with the increase in radiation dose in the whole temperature range (Fig. 1a). In Fig. 1b the damping peak temperature of the nitrile rubber vulcanizates with 1.5 parts of sulphur, without any radiation dose is found to be-33°C. With an increase in radiation dose, the transition temperature shifts to −13°C for M 1.5/0.5/150 (Table IV). This is further increased although marginally, when the sample is irradiated at 300 kGy. The shift is due to the increasing degree of crosslinking which is revealed from the increase in their volume fraction of rubber, V_r at higher doses (Table IV), which can also explain the changes in the storage modulus. There is not much shift in the peak temperature at higher radiation doses beyond 50 kGy. This may be due to the combined effect of crosslinking (involving both shorter and longer chains), scission reactions prevailing in the presence of electron beam and also modification in the crosslink structure. The tanδ peak height also increases with radiation dose (Fig. 1b), which may be attributed to scission reactions, generating more mobile molecules. This is unique in the sense that Tg is shifted towards higher temperature and the storage modulus is increased over the whole range of temperature, yet the tanδ at the peak height maximum increases. The behaviour of the system with lower amount of sulphur (0.5 phr) is similar, when the samples are irradiated, although the difference is lower. The interaction between sulphur crosslinks and highly energized electrons could be very complex with large number of possible outcomes. For example, a polysulphidic linkage can break at any point leading to new crosslinks having various sulphur ranks, all of which are smaller in length as compared to the original crosslinks. The S—S bond energy having the lowest energy is more prone to get ruptured at the first instance, in such interaction. This is reflected in the increment of V_r due to monosulphides only (Table IV) as determined by various chemical probe treatments and NMR studies and reported in our earlier paper [10]. Irradiation of the samples also lead to scissioning as well as crosslinking. More monosulphidic linkages are formed on irradiation in the system having higher amount of sulphur (scheme-1). This scheme was ascertained by a kinetic model, chemical probe treatment and NMR techniques The Charlesby-Pinner plot of $S + S^{1/2}$ (where $S =$ the sol fraction) versus 1/radiation dose as per Equation 1 [23] was applied for the mixed crosslinking systems.

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

where, $u_1 =$ number average degree of polymerization, $p_0 =$ fracture density per unit dose in Mrad, $q_0 =$ density of crosslinked units per unit dose in Mrad and $R =$ radiation dose in kGy. The intercept of this plot 'p_0/q_0' gives an idea of the ratio of chain scission to crosslinking. A scission to crosslink ratio of 0.17 for $M_{0.5/1.5/0\text{-}300}$, as compared to 0.14 in $M_{1.5/0.5/0\text{-}300}$ system is observed. This implicates the occurrence of chain scissioning to crosslinking comparatively higher in the former.

These are also further reflected in the V_r values due to carbon–carbon linkages for $M_{1.5/0.5/150}$ vs. $M_{0.5/1.5/150}$ determined by the chemical probe treatment [10]. These changes in the structure might result in the variation of network distribution, on irradiation of the vulcanizates.



(a)

(b)

(c)

(d)

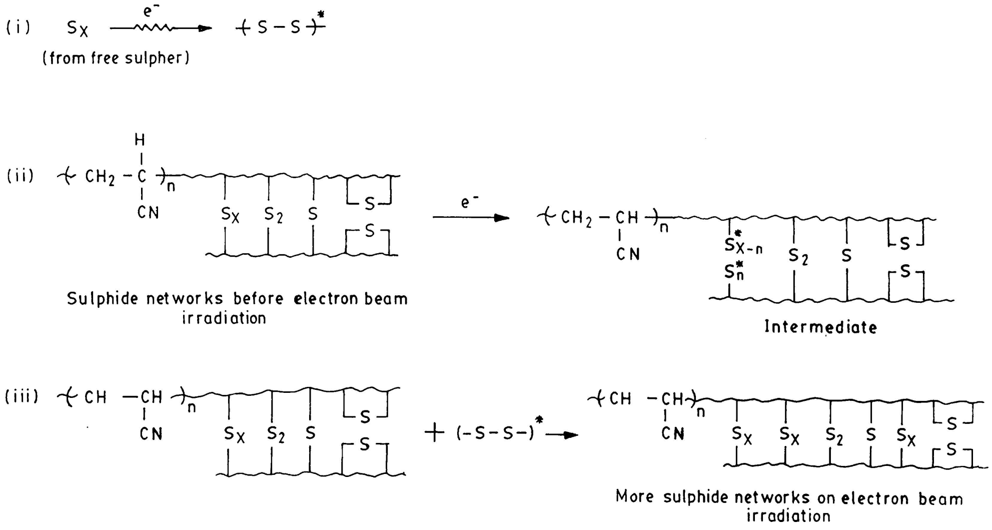
(e and f)

Figure 1 (a, b) Storage moduli and loss tangent of M 1.5/0.5/0-300 at different radiation doses as a function of temperature. (c, d) Storage moduli and loss tangent of $M_{0.5/1.5/0\text{-}300}$ at different radiation doses as a function of temperature. (e, f) Variation of Storage moduli and loss tangent of $M_{0.5/1.5/0\text{-}300}$ at different radiation doses as a function of double strain amplitude.

TABLE IV Dynamic storage modulus at three different temperatures and T_g for modified and unmodified nitrile rubber on irradiation with different doses

System	Dynamic storage modulus at three different temperatures (Pa) −70°C	25°C	70°C	T_g(°C)	Volume fractions due to different linkages (V_r)[a] Both C—C and sulphur links	C—C Crosslinks	Total sulphur crosslinks	Mono sulphidic crosslinks
$M_{1.5/0.5/0}$	1.81×10^9	2.1×10^6	1.59×10^6	−33.0	0.017	0.0	0.017	0.003
$M_{1.5/0.5/50}$	1.96×10^9	2.46×10^6	2.31×10^6	−15.0	0.149	0.104	0.045	0.029
$M_{1.5/0.5/150}$	1.99×10^9	2.81×10^6	2.38×10^6	−13.0	0.181	0.121	0.060	0.042
$M_{1.5/0.5/300}$	2.49×10^9	3.34×10^6	3.27×10^6	−12.0	0.211	0.148	0.063	0.050
$M_{0.5/1.5/0}$	1.86×10^9	2.27×10^6	1.66×10^6	−32.0	0.009	0.0	0.009	0.0006
$M_{0.5/1.5/50}$	1.94×10^9	2.36×10^6	1.77×10^6	−19.0	0.116	0.088	0.028	0.006
$M_{0.5/1.5/150}$	1.98×10^9	2.65×10^6	1.95×10^6	−18.0	0.161	0.111	0.050	0.025
$M_{0.5/1.5/300}$	2.11×10^9	2.90×10^6	2.58×10^6	−17.0	0.196	0.143	0.053	0.034

[a] The volume fractions mentioned above are reported by V. Vijayabaskar, Francis Rene Costa and Anil K. Bhowmick, in *Rubber Chem. Technol* **77** (2004) 624.



Scheme 1 On irradiation (carbon-sulphur crosslinks).

The unexpected variation in the dynamic mechanical properties is due to the above factors.

Effect of strain

The behaviour of $M_{0.5/1.5/50\text{-}300}$ and $M_{1.5/0.5/50\text{-}300}$ networks is further exemplified from the measurement of these dynamic mechanical properties in varying double strain amplitudes at room temperature (Fig. 1e and f). The plots for the representative systems $M_{0.5/1.5/0\text{-}300}$ are given. A similar trend is observed for the other system. On application of strain, the storage moduli decrease and tanδ values marginally increase. As reported in earlier section, the samples $M_{1.5/0.5/0\text{-}300}$ have higher initial storage moduli, over its counterpart with low sulphur system at the same strain.

On application of high strain, the polysulphidic linkages in $M_{1.5/0.5/0\text{-}300}$ (Table V) may reorganize due to their less bond dissociation energy (262 kJ mol^{-1}). In order to understand the effects quantitatively the values of E_0 ($M_{0.5,1.5/1.5,0.5/150}$) and E_∞ ($M_{0.5,15/1.5,0.5/150}$) have been noted and the difference E_0-E_∞ has been calculated. These values are shown in Table V. It is observed that these values in general are higher for $M_{1.5/0.5/150}$ at all irradiation doses. As the dose increases, $\Delta E'$ also increases. Probably, irradiation induces scission of the main chain and crosslinks which rearrange during strains. As the sulphur level is higher there is more rearrangement and hence a higher value of $\Delta E'$ is obtained. It is also interesting to note that even though the crosslink density (proportional to V_r) is higher in the $M_{1.5/0.5/0\text{-}300}$, the drop in E' with strain is also higher.

3.2. Frequency dependence of storage modulus, loss modulus and tanδ

Even though the above observations are useful to predict the influence of electron beam on the vulcanizates

TABLE V E_0, E_∞ and ($E_0 - E_\infty$,) values of NBR with different radiation doses at 1.5 and 0.5 phr of sulphur

SI.no.	Samples	$E_0 \times 10^6$ pa	$E_\infty \times 10^6$ pa	($E_0 - E_\infty$) $\times 10^6$ pa
1	$M_{1.5/0.5/0}$	2.53	2.17	0.36
2	$M_{1.5/0.5/50}$	2.89	2.42	0.47
3	$M_{1.5/0.5/150}$	3.57	2.88	0.69
4	$M_{1.5/0.5/300}$	3.92	3.41	0.51
5	$M_{0.5/1.5/0}$	2.24	2.01	0.23
6	$M_{0.5/1.5/50}$	2.71	2.29	0.42
7	$M_{0.5/1.5/150}$	3.24	2.74	0.50
8	$M_{0.5/1.5/300}$	3.64	3.29	0.35

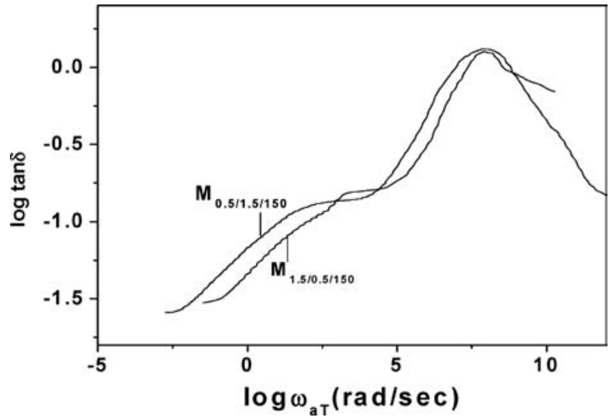
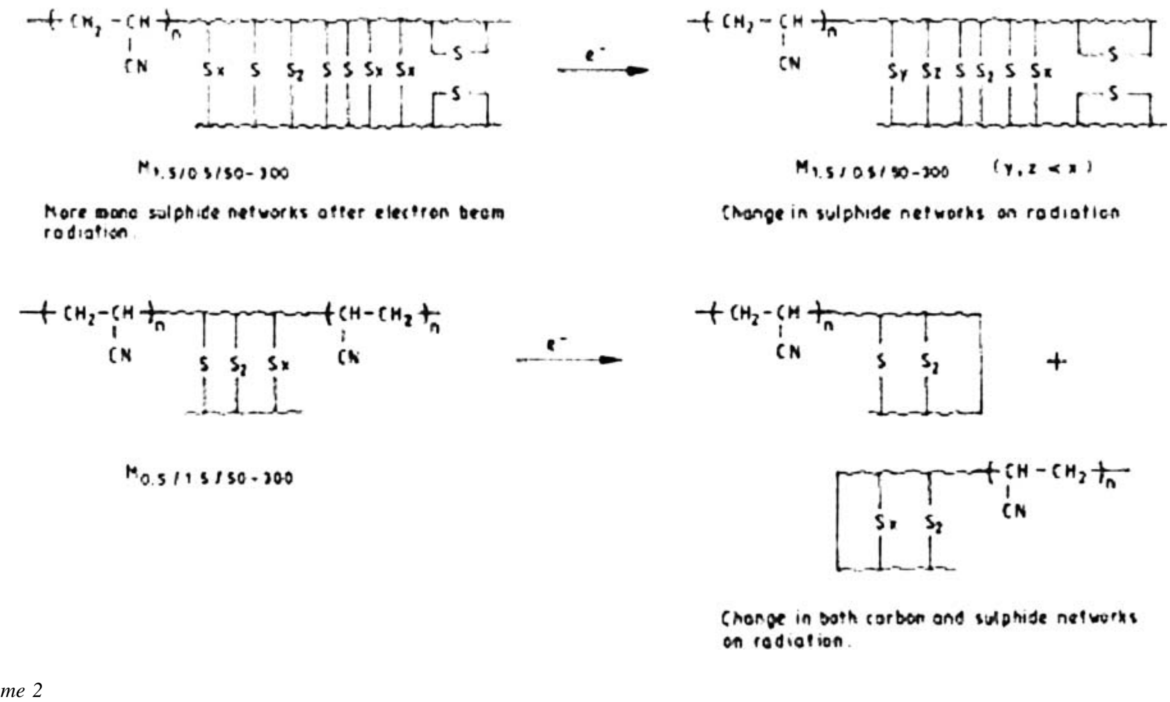


Figure 2 Master curves for $M_{1.5/0.5/150}$ and $M_{0.5/1.5/150}$ showing the variation of loss tangent at different frequencies and temperatures.

with high and low sulphur content, it is often necessary to understand the behaviour of these systems at high frequencies ranging from 10–100 Hz. Shown in Fig. 2 are the master curves of tanδ for $M_{1.5/0.5/150}$ and $M_{0.5/1.5/150}$ systems. Three temperature regions are identified from the master curves: high temperature (low frequency region), medium temperature (medium frequency region) and low temperature (high frequency region). At high temperature region or low frequency, tanδ of $M_{1.5/0.5/150}$ is less than that of $M_{0.5/1.5/150}$. In this region, the storage modulii of $M_{1.5/0.5/150}$ is comparatively higher than that of $M_{0.5/1.5/150}$ system. For example, at a frequency of 1.24 Hz the tanδ value of $M_{1.5/0.5/150}$ is 0.04 with a storage modulus of 2.7×10^6 Hz and $M_{0.5/1.5/150}$ shows a tanδ value of 0.07 and a storage modulus of 2.3×10^6 Hz at the same frequency. This clearly indicates that the higher crosslink density in $M_{1.5/0.5/150}$ increases the elasticity which results in their lower tanδ and higher storage modulus values. A similar phenomenon occurs at the high frequency region (9.1×10^7 Hz). In both these regions, higher chain scission to crosslink ratio in $M_{0.5/1.5/0\text{-}300}$ as observed from the scission to crosslink ratio from the Charlesby Pinner plot [10] results in plasticization of the network, which in turn causes an increase in tanδ values. In the medium frequency range for instance, a tanδ value of 0.14 occurs at a lower frequency of 1.3×10^3 Hz for $M_{1.5/0.5/150}$ as compared to 9.3×10^3 Hz for $M_{0.5/1.5/150}$. Chain scissioning as observed from the scission to crosslink ratio in the Charlesby Pinner plot is responsible for this behaviour.

3.3. Effect of radiation on network distribution of $M_{1.5/05/150,300}$ and $M_{0.5/1.5/150,300}$

On irradiation, both the systems containing chains of polysulphidic intermolecular crosslinks tend to break due to their low bond dissociation energies (262 kJ mole^{-1}) and form monosulphidic crosslinks (Table IV). Electron beam can also break C—C and C—S linkages due to their close proximity in their bond dissociation energies (376 kJ mole^{-1}). In addition, C—C crosslinks will be formed due to irradiation. This will result in a change in network chain distribution (Scheme-2) and can be visualized from their master curves. But the master curves relating E' and ω for $M_{1.5/0.5/150,300}$ and $M_{0.5/1.5/150,300}$ with different crosslink densities have close range of values and direct interpretation to their segmental motions is difficult. This critical problem has been resolved by resorting to the mathematical treatment by Tuminello [24] who developed a model for determining the molecular weight distribution (MWD) of a polymer melt. This is an improved method for predicting molecular weight distribution (MWD) from E' over Wu's method [25]. The behavior of E' against ω for a typical amorphous polymer is illustrated in Fig. 3.The glass transition temperature is a consequence of sub molecular units moving in the same time frame as the measurement frequency (ω). At higher frequencies, the apparatus views the material as a glass, since the sub molecular unit could not move as rapidly as ω. At lower frequencies still, a plateau region is observed due to the



Scheme 2

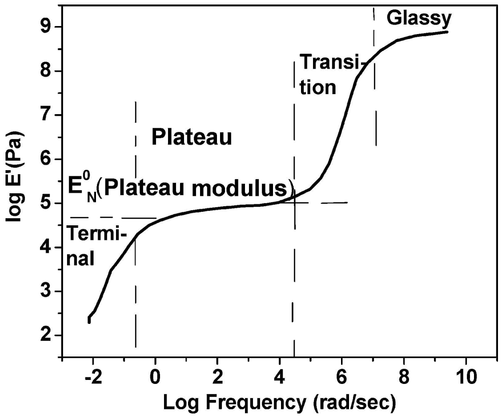


Figure 3 Typical E' master curve for a linear amorphous polymer.

presence of the transient entanglement network. The plateau modulus (E_N^0) has been defined as

$$E_N^0 = 2/\prod \int E'' d\ln\omega \tag{2}$$

The integration can be performed on the E'' curve resolved from the transition zone peak. The length of the plateau plus the breadth and shape of the terminal zone relaxation are strong functions of the MWD. Many examples of these observations are presented in the literature [14, 26, 27]. But terminal zone is absent in crosslinked elastomers due to the strong intermolecular linkages. Here, the network distribution is reflected from the plateau zone. So, the plateau zone extending to transition region has been taken in to considerations for the mathematical treatment. Work by Tuminello [24] had stated that the cumulative molecular weight distribution curve (CMWD) can be calculated from the plot of $(E'(\omega)/E_N^\circ)^{0.5}$ against log ω. The network distribution of crosslinked samples changes on irradiation and is shown in Scheme-2. It is difficult to determine the network distribution by GPC measurements. As a result this procedure is applied to $M_{1.5/0.5/150}$ and $M_{0.5/1.5/150}$ systems and the representative figures are shown in Fig. 4a.The onset of transition of $(E'(\omega)/E_N^0)^{0.5}$ for $M_{1.5/0.5/150}$ and $M_{1.5/0.5/300}$ occur at lower frequencies as compared to $M_{0.5/1.5/150}$ and $M_{0.5/1.5/300}$ systems (Table VI) .Increased scission which is comparatively more in nitrile rubber vulcanizates with lower amount of sulphur, will lead to both an increased scission to crosslink ratio in Charlesby Pinner plot [10] and also to an increased number of shorter chains. These chains relax faster and also plasticize the high molecular weight chains. The relaxation of shorter chains in $M_{0.5/1.5/150}$ and $M_{0.5/1.5/300}$ is further explained by plotting of $\frac{dE'/dE_N^0}{d\log\omega}$ against log $(1/\omega)$. Fig. 4b shows these curves. The broader differential curves in $M_{0.5/1.5/150}$ and $M_{0.5/1.5/300}$ reflect the occurrence of chain scissioning as compared to the narrower curves of $M_{1.5/0.5/150}$ and $M_{1.5/0.5/300}$. This is shown from the area under the curves for these systems in Table VI.The incidence of electron beam in the system having higher amount of sulphur results in more monosulphidic linkages. This is substantiated by the various instrumentation and modeling techniques, reported in our earlier communications [10]. But the same influence by the incidence of this energetic projectile on low sulphur system results in more scissioning as compared to high sulphur system and results in broader network distribution.

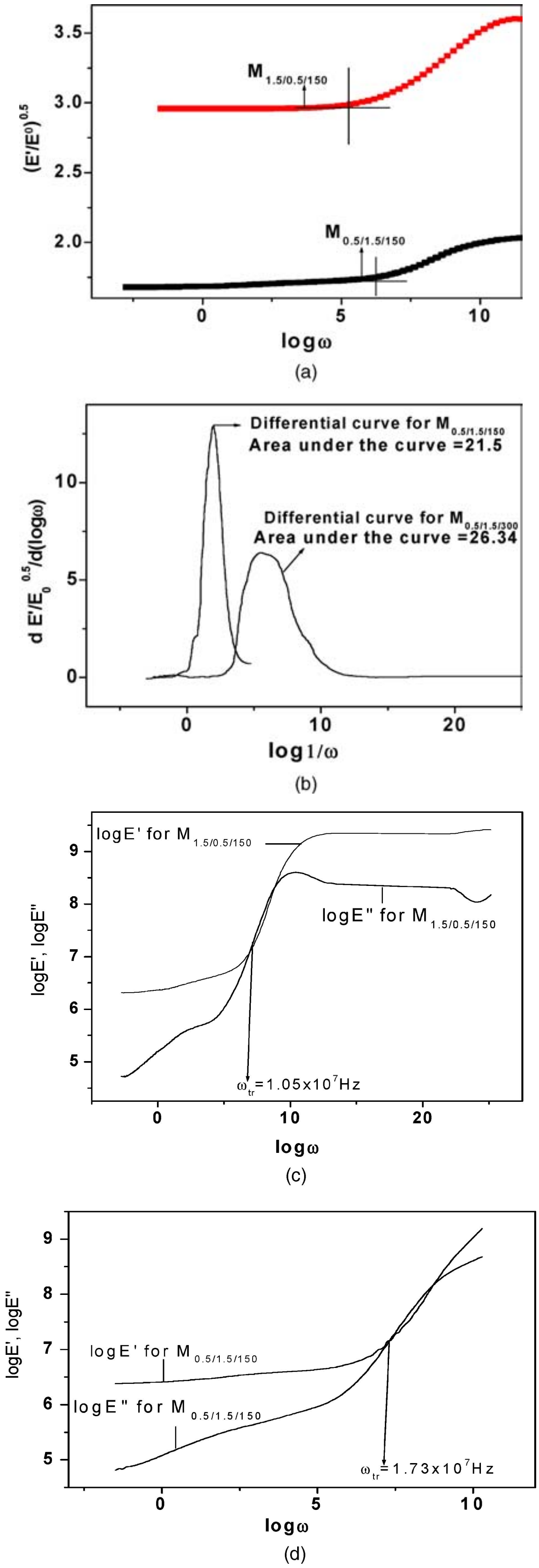


Figure 4 (a) Cumulative network chain distribution curves (CMWD) curves for $M_{0.5/1.5/150}$ and $M_{1.5/0.5/150}$, (b) Differential curves for $M_{0.5/1.5/150}$ and $M_{0.5/1.5/300}$ $(E'/E^\circ) \equiv E'(\omega)/E_N^\circ$ (c and d) Cross over frequencies for $M_{1.5/0.5/150}$ and $M_{0.5/1.5/150}$ from E' and E'' curve.

TABLE VI Logarithmic frequencies at the onset of transition of $(E'/E_N^0)^{0.5}$ curves, area under the curves for samples with different network distribution, Crossover frequency at various radiation doses and sulphur loadings by DMTA method

Samples	log ω in Hz at the onset of transition of $(E'/E_N^0)^{0.5}$ curves	Area under the curve (arbitrary units)	Crossover frequency, ω_{tr} Hz
$M_{1.5/0.5/150}$	5.26	4.53	1.05×10^7
$M_{1.5/0.5/300}$	1.52	8.37	7.72×10^7
$M_{0.5/1.5/150}$	6.24	21.50	1.73×10^7
$M_{0.5/1.5/300}$	3.31	26.34	9.09×10^7

3.4. Crossover frequency

Two characteristic zones of frequency scale are seen in Fig. 4c and d; At low frequencies, E' is nearly constant and E'' is smaller; At higher frequency range, they are similar in magnitude and increase with increase in frequency. The onset of the transition zone with increasing frequency might be specified by the intersection of two tangents drawn to E' and E'' curves. The intersection frequency 'ω_{tr}' is nearly the reciprocal of relaxation time τ_{tr} which is a measure of the time required for the complete configurational rearrangement, if a piece of macromolecule is caught between two crosslinks or two entanglements. The less frictional opposition, the higher the frequency to which oscillatory motions can go without getting in to the transition zone [28, 29]. From the above discussion, it is apparent that the intersection of E' and E'' curves to a higher frequency 'ω_{tr}' relates to the lower crosslink density in terms of viscoelastic measurements. This crossover is also related to the molecular weight distribution in the case of virgin polymer [30]. Measurement of this term gives insight of the structural changes in the sample on irradiation. The 'ω_{tr}' values for $M_{1.5/0.5/150}$, $M_{1.5/0.5/300}$, $M_{0.5/1.5/150}$ and $M_{0.5/1.5/300}$ are listed in Table VI. The higher value of ω_{tr} for $M_{0.5/1.5/150\text{-}300}$ indicates that the shorter chains formed due to chain scissioning shows a plasticizing effect These chains relax faster which is reflected in the onset of transition zone occurring at a higher frequency.

4. Conclusions

The unique behaviour in dynamic mechanical properties of electron beam initiated crosslinking of nitrile rubber vulcanizate at varying temperatures, strains and frequencies has been addressed in this paper. The following observations have been made

1. The storage moduli are found to increase for both $M_{1.5/0.5/50\text{-}300}$ and $M_{0.5/1.5/50\text{-}300}$ and there is a shift in T_g towards higher temperature for these systems on irradiation.
2. The storage modulii of $M_{1.5/0.5/50\text{-}300}$ are comparatively higher than those of $M_{0.5/1.5/50\text{-}300}$ and accounted by the formation of monosulphidic linkages from the polysulphides by the incidence of electron beam.
3. This is also substantiated from the increase in E_0-E_∞ values for these systems.
4. Differential curves from the data obtained have been constructed for the irradiated samples and mathematically treated. $M_{0.5/1.5/150}$ is found to give a broader network chain distribution.
5. The formation of intense crosslinked network structures in $M_{1.5/0.5/50\text{-}300}$ is also inferred from their lower crossover frequency values.

Acknowledgement

The authors are grateful to NICCO Corporation Ltd., Shyamnagar, West Bengal (India) for funding this project particularly to Dr. V.K. Tikku, Sr. Vice President, (I.E. and T.Q.) for experimental assistance with radiation processing.

References

1. I. BANIK, T. K. CHAKI, V. K. TIKKU and A. K. BHOWMICK, *Angew. Makromol. Chem.* **263** (1999) 5.
2. H. P. BROWN, *Rubber Chem. Technol.* **36** (1963) 931.
3. N. D. ZAKHAROV and T. A. SHADRICHEVA, *ibid.* **36** (1961) 575.
4. A. K. BHOWMICK and S. K. DE, *ibid.* **53** (1980) 107.
5. N. D. ZAKHAROV and I. N. BEREZKIN, *Kauch. Rezina.* **20** (1961) 7.
6. R. A. ZINGARO and W. C. COOPER (Selenium, Van Nostrand Reinhold, New York, 1974) P. 728.
7. G. B. ABDULLAEV, T. K. ISMAILOV, S. A. ABASOV, G. G. AKHMEDEV, S. I. MAKHTIEVA, K. R. AKHMEDOV and T. A. PASHAEV, *Chem. Abstr.* **86** (1977) 19101u.
8. V. P. KVARDASHOV and A. E. KORNEV, *Khim. Khim. Technol.* **14**(11) (1971) 1757.
9. Y. MINORA, S. YAMASHITA, H. OKARNATO, N. MATSUO, M. IRAWA and S. I. KOTTMOTO, *Rubber Chem. Technol.* **52** (1979) 926.
10. V. VIJAYABASKAR, FRANCIS RENE COSTA and ANIL K. BHOWMICK. *ibid.* **77** (2004) 624.
11. V. VIJAYABASKAR, RAKESH GUPTA, P. P. CHAKRABARTI and ANIL K. BHOWMICK, *J. Appl. Polym. Sci.* 2004 (Communicated).
12. L. E. NIELSON, "Mechanical Properties of Polymers and Composites" (Marcel Dekker, New York, 1974).
13. N. G. MCCRUM, B. E. READ and G. WILLIAMS, "An elastic and Dielectric Effects in Polymer Solids" (Wiley, London, 1967).
14. J. D. FERRY, "Viscoelastic Properties of Polymers" (Wiley, New York, 1970).
15. V. D. MCGININSE, in "Crosslinking with Radiation Encyclopedia of Polymer Science and Engineering," edited by J. I. Kroschwitz (John Wiley and Sons 4, 1986) p. 418.
16. T. MURAYAMA, in "Dynamic Mechanical Properties, Encyclopedia of Polymer Science and Engineering," edited by J. I. Kroschwitz (John Wiley and Sons 5, 1986) p. 299.
17. R. K. TRAEGER and T. G. CASTONGUAY, *J. Appl. Polym. Sci.* **10** (1996) 491.
18. T. K. CHAKI, D. ROY, A. B. MAJALI and A. K. BHOWMICK, *J. Polym. Eng.* **13** (1994) 17.
19. K. P. S. KWEI and T. K. KWEI, *J. Appl. Polym. Sci.* **12** (1968) 1553.
20. S. K. DATTA, T. K. CHAKI, D. KHASTGIR and A. K. BHOWMICK, *Polym. and Polym. Comp.* **4** (1996) 419.
21. I. BANIK and A. K. BHOWMICK, *J. Appl. Polym. Sci.* **69** (1998) 2079.
22. P. THAVAMANI and A. K. BHOWMICK, *J. Mat. Sci.* **27** (1992) 32439.
23. A. CHARLESBY and S. H. PINNER, *Proc. Roy. Soc (London)* **A249** (1959) 367.

24. W. H. TUMINELLO, *Polym. Eng. Sci.* **26** (1986) 1339.
25. S. WU, *ibid.* **25** (1985) 122.
26. G. R. ZEICHNER and C. W. MACOSKO, "On-line Viscoelastic Measurements for Polymer Melt Processes" (SPEANTEC Tech.Conf., SanFrancisco, May, 1982).
27. T. MASUDA. K. KITAGAWA. T. LNOUE and S. ONOGI, *Macromolecules* **3** (1970) 116.
28. W. W. GRAESSLEY, "Viscoelasticity and Flow in Polymer Melts and Concentrated Solutions," in "Physical Properties of Polymers." edited by J. E. Mark (ACS, Washington, DC, 1984): *Faraday Symp. Chem. Soc.* **18** (1983) 7.
29. T. LIU, D. S. SOONG and M. C. WILLIAMS, *J. Rheology* **27** (1983) 7.
30. R. RAHALKAR and HENRY TANG, *Rubber Chem. Technol.* **61**(5) (1988) 812.

Received 19 November 2004
and accepted 5 January 2005