

# Electron Beam Modification of *Filled* Fluorocarbon Rubber

INDRANIL BANIK, ANIL K. BHOWMICK

Rubber Technology Centre, Indian Institute of Technology, Kharagpur—721302, India

Received 12 March 1999; accepted 19 May 1999

**ABSTRACT:** The effect of electron beam irradiation on the properties of carbon black-, silica-, and clay-filled fluorocarbon rubber has been studied over a range of radiation doses, loadings, and nature of the fillers. Compared to the unfilled irradiated rubber, the tensile strength and modulus improve with a decrease in the particle size of the carbon black filler. Similar improvement in these properties is observed with an increase in both the radiation dose and the amount of the filler upto a certain level. The dynamic mechanical analysis reveal an increased glass transition temperature ( $T_g$ ), a reduced value of the mechanical loss factor at  $T_g$ , and an enhanced dynamic storage modulus for the filled samples. The results are explained with the help of sol-gel analysis and volume fraction of rubber. It is observed that higher reinforcement in the case of the filled vulcanizate is obtained by electron beam modification, as compared to that using the conventional curing system. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 2016–2025, 2000

**Key words:** electron beam modification; filled fluorocarbon rubber

## INTRODUCTION

The concept of reinforcement is basically related to composites built from two or more structural elements or components of different mechanical characteristics, whereby the properties of one of these elements are combined with the set of favorable properties of the other components. Fillers improve the properties of an elastomer and reduce cost. A reinforced elastomer shows an increase in modulus, hardness, tensile strength, failure, and other properties related to the performance of the vulcanizate. Formation of a carbon gel, an “infinite” carbon elastomer network is a prerequisite for reinforcement.<sup>1</sup> In the glassy state, below  $T_g$ , a carbon gel does not function, thus eliminating reinforcement. Strength of elastomer–filler bond is the determining factor for a

reinforced vulcanizate. Strong adherence of the elastomer to the filler surface is required for the reinforcement of an elastomer. In the conventional thermochemically cured rubber vulcanizates, the nature of chemical functional groups on the filler surface can influence the course/rate of crosslinking reactions. In the radiation curing of filled vulcanizates, surface groups on the filler are expected not to affect the rate of crosslinking. Also, most of the studies on fluorocarbon rubber demonstrate the effect of MT carbon black on the properties of rubber, as this filler is used mostly with conventional vulcanization system. There is no systematic investigation on the nature and level of filler on the mechanical and especially dynamic mechanical properties of the fluorocarbon rubber. Because the predominant intermediate in radiation chemistry is the free radical and the amount of radicals<sup>2</sup> generated in a polymer system is a function of the absorbed irradiation dose,<sup>3</sup> it is chiefly the dosage of radiation that is expected to govern the nature of the networking reaction in a filled polymer system. Premature vulcanization, prevalent in the conventional cur-

Correspondence to: A. K. Bhowmick.

Contract grant sponsor: Board of Research in Nuclear Sciences, Department of Atomic Energy, Mumbai.

*Journal of Applied Polymer Science*, Vol. 76, 2016–2025 (2000)  
© 2000 John Wiley & Sons, Inc.

**Table I** Formulation of the Mixes

Sample Designation	FKM Rubber, phr	Filler, phr	Radiation Dose, kGy	Diak#1, phr	MgO, phr
T <sub>0/50</sub>	100	—	50	—	—
T <sub>0/100</sub>	100	—	100	—	—
T <sub>0/200</sub>	100	—	200	—	—
T <sub>0/500</sub>	100	—	500	—	—
H <sub>30/50</sub>	100	HAF,30	50	—	—
S <sub>30/50</sub>	100	SRF,30	50	—	—
L <sub>30/50</sub>	100	Silica,30	50	—	—
Y <sub>30/50</sub>	100	Clay,30	50	—	—
S <sub>10/50</sub>	100	SRF,10	50	—	—
S <sub>20/50</sub>	100	SRF,20	50	—	—
S <sub>30/50</sub>	100	SRF,30	50	—	—
S <sub>50/50</sub>	100	SRF,50	50	—	—
S <sub>30/100</sub>	100	SRF,30	100	—	—
S <sub>30/200</sub>	100	SRF,30	200	—	—
S <sub>30/500</sub>	100	SRF,30	500	—	—
CH <sub>30</sub>	100	HAF,30	—	0.4	5
CS <sub>30</sub>	100	SRF,30	—	0.4	5
CL <sub>30</sub>	100	Silica,30	—	0.4	5
CY <sub>30</sub>	100	Clay,30	—	0.4	5

ing process due to unavoidable or excessive mixing, hinders smooth mold flow during processing, and often leads to inferior vulcanizate properties. This can also be avoided in the radiation vulcanization method. Hence, electron beam processing, like the other radiation processing techniques, generates less scrap. The effects of filler on the physicomechanical properties of both natural and synthetic rubbers under the influence of  $\gamma$ -radiation are reported in the literature.<sup>4</sup> However, there is no study on the electron beam crosslinking of rubber in presence of fillers. The present article embodies the effect of nature and loading of fillers and radiation dose on the physicomechanical properties of the electron beam cured terpolymeric fluorocarbon rubber. The fluoroelastomers are superior to other synthetic rubbers due to their service life extending over broad temperature ranges and in terms of excellent resistance to heat, fluids, and outdoor weather.<sup>5,6</sup>

## EXPERIMENTAL

### Materials

The fluorocarbon rubber FKM (vinylidene fluoride-co-hexafluoropropylene-co-tetrafluoroethylene, F content 68%, H, 1.4%) and the curative, hexamethylene diamine carbamate (Diak#1),

were obtained from E.I. duPont de Nemours & Co., USA. The fillers HAF (particle size 29 nm) and SRF (60 nm) carbon black, silica (precipitated, 30 nm) and clay (soft, 1500 nm) were obtained from standard sources. The formulation of the mixes is given in Table I.

### Preparation and Irradiation of Samples

The rubber was mixed with the filler at  $25 \pm 2^\circ\text{C}$  in a Brabender Plasticorder PLE-330 at a rotor speed of 60 rpm for 3 min and sheeted out from a two-roll mill. These were then molded in an electrically heated Moore Press (UK) at a pressure of 5 MPa and temperature  $105^\circ\text{C}$ . The molded sheets of dimension  $11.5 \times 11.5 \times 0.1$  cm were irradiated at Bhabha Atomic Research Centre, Trombay (Mumbai) by an electron beam accelerator (model ILU-6) in air over the dose ranges of 0–500 kGy. The specifications of the electron beam accelerator were given in our earlier communications.<sup>7–10</sup> A dose of 50 kGy was chosen for most of this investigation, as many properties deteriorated beyond this dose.<sup>6–10</sup>

### Sample Designation

The samples were designated as  $F_{x/y}$ , where  $x$  denotes the level of the filler in phr,  $y$  the radiation dose in kGy. The systems based on HAF and SRF

carbon black, silica, and clay were specified as H, S, L, and Y, respectively, in place of F (Table I). The conventionally formulated analogues were specified as  $CF_x$ . The control rubber without any filler was designated by  $T_{o/y}$ .

### Mechanical Properties

The tensile properties, for example, tensile strength, elongation at break, and modulus at specified elongation were performed in a Zwick GmbH UTM (Model 1445) at a crosshead speed of 500 mm/min and at a temperature of  $25 \pm 2^\circ\text{C}$  as per the ASTM method D-412-93.

### Dynamic Mechanical Thermal Analysis (DMTA)

The DMTA analysis of filled irradiated rubbers were performed in a DMTA MK-II Thermal Analyzer (Polymer Laboratories, UK) at a frequency of 10 Hz and a strain amplitude of  $64 \mu\text{m}$  (peak-to-peak displacement) in the temperature range of  $-25$  to  $+100^\circ\text{C}$  using the samples of  $43.5 \times 12.5 \times 1$  mm dimensions.

### Sol-Gel Analysis

The gel fraction and  $v_r$ , volume fraction of rubber in the swollen gel, were measured gravimetrically using the solvent methyl-ethyl-ketone as reported in our earlier communication.<sup>7</sup> The volume fraction of the rubber was calculated using the equation reported in our earlier article.<sup>8</sup> The fraction of the filler was corrected in calculating the volume fraction of rubber for the filled vulcanizates.

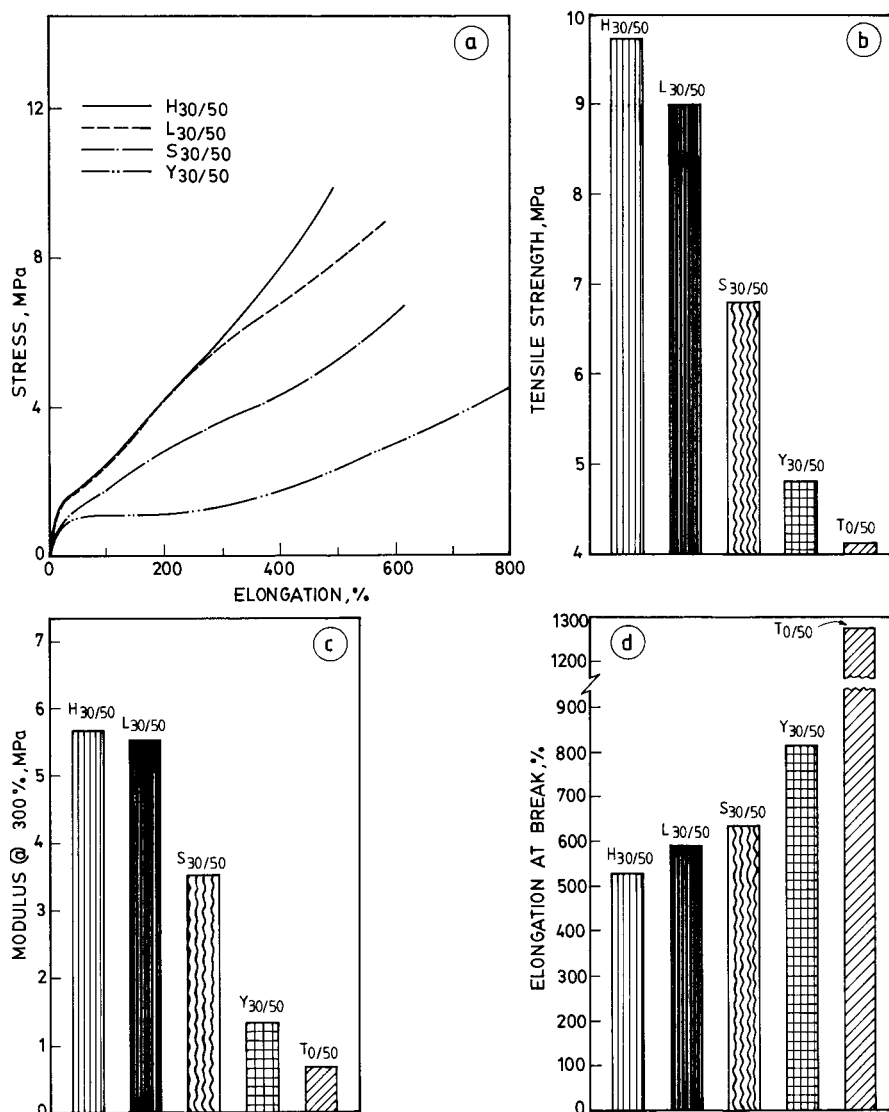
## RESULTS AND DISCUSSION

### Effect of the Nature of Fillers

The stress-strain properties of the fluorocarbon elastomer mixed with 30 phr of HAF, SRF, silica, and clay at a fixed radiation dose of 50 kGy are shown in Figure 1(a). Figure 1(b)–(d) displays the variation of tensile properties (tensile strength, modulus, and elongation at break) of the fluorocarbon rubber, calculated from Figure 1(a). It is observed that the modulus of the filled fluorocarbon rubber vulcanizate increases with a corresponding increase in the tensile strength, and decrease in the elongation at break as the particle size of the carbon black filler is decreased. As expected, the reinforcement follows the following order: HAF > silica > SRF > clay. As this rubber

could not be cured with peroxide (an equivalent free radical system), we have cured the rubber with hexamethylenediamine carbamate to the same value of the modulus (0.65 MPa) and volume fraction of rubber (0.06) as the gum system. The effect of filler on this conventional system has been studied. It is noted that all the fillers interfere with the diamine crosslinking reaction of the fluorocarbon rubber. As shown in the rheometer curve (Fig. 2), only the SRF shows a slight increase in torque. This sample,  $CS_{30}$ , when vulcanized for 8 min at  $150^\circ\text{C}$  and then postcured, does not show any significant reinforcing effect. For example, the tensile strength of the conventionally cured SRF carbon black-filled system increases from 1.4 to 4.2 MPa, and the modulus at 300% elongation from 0.66 to 4.18 MPa upon postcuring; the corresponding figures for the electron beam cured analogues are 10.6 MPa from 6.6 MPa for the tensile strength and 6.32 MPa from 3.53 MPa for the modulus. It is apparent that all the surface active fillers absorb diamine, which is not released even during the postcuring reaction. This simply demonstrates the superior vulcanizate properties of the electron beam-cured filled fluorocarbon elastomers, and in that sense, the above results are of paramount importance. Both the gel fraction and the volume fraction of rubber,  $v_r$ , shown in Figure 3(a)–(b), are found to increase with the incorporation of carbon black and silica. The data on failure properties and  $v_r$  suggest an increase in the reinforcing effect of carbon black and silica filler on the rubber matrix. The interaction of particulate fillers with an elastomer is dependent on a number of factors such as extensivity and intensity factor along with the geometric one.<sup>11</sup> The extensivity factor is the total amount of surface area of filler per cubic centimeter of the compound, in contact with the elastomer. The intensity factor is the specific activity of this solid surface per square centimeter of interface, determined by the physical and the chemical nature of the filler surface and, to some extent, of that of the elastomer. The geometric factor is related to structure and porosity of the filler. Reinforcement factor can be obtained from the total surface area and its specific activity:<sup>11</sup> total area  $\times$  specific surface activity = reinforcement factor.

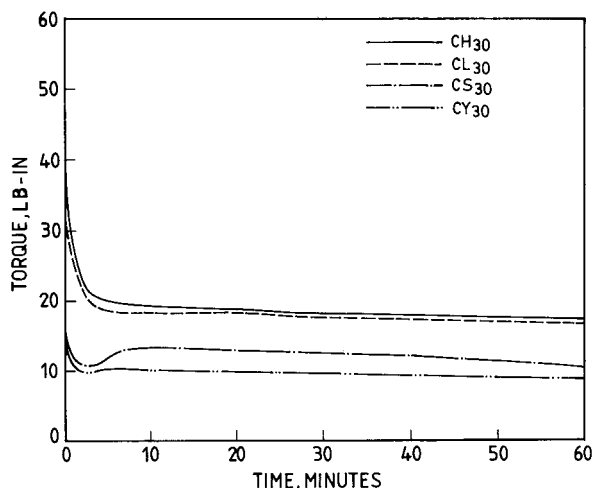
The nature of the solid surface may be varying in a chemical sense, having different chemical groups: hydroxyl or metaloxide in white fillers, organic carboxyl, quinone, or lactone groups in carbon black, etc. In a physical sense, they may be different in adsorptive capacity (centered on sur-



**Figure 1** (a) Stress–strain plot of HAF-, SRF-, silica-, and clay-filled fluorocarbon rubber samples at a fixed radiation dose of 50 kGy and at a constant filler loading of 30 phr. (b–d) Variation of tensile strength, modulus, and elongation at break of fluorocarbon rubber samples with different fillers at a constant radiation dose of 50 kGy and loading of 30 phr.

face flaws in the lattice) and in energy of adsorption. The formation of chemical bonds between filler surface and polymer also imparts high modulus to a filled vulcanizate. The filler-to-rubber linkages are proportional to the surface area of the black being loaded into the matrix, and evidence suggests that filler-to-rubber linkages are formed by interaction of polymeric free radicals with black either during milling<sup>12</sup> or in vulcanization.<sup>13</sup> In both the cases, the number of free radicals generated will be higher for a black with low particle size, and is expected to decrease with

an increase in particle diameter. Because active sites are reportedly the one containing hydrogen, small particle-sized HAF will perhaps generate greater amount of radicals on the surface and reinforce a rubber matrix more through establishment of more effective rubber-filler covalent linkages. With silica and clay, there are secondary bonds between the silanol groups and fluorine. These bonds may be of hydrogen bonding type or dipole–dipole interaction type. It is observed from Figure 1(b)–(d) that on the whole, the modulus, and the tensile strength increase with a corre-

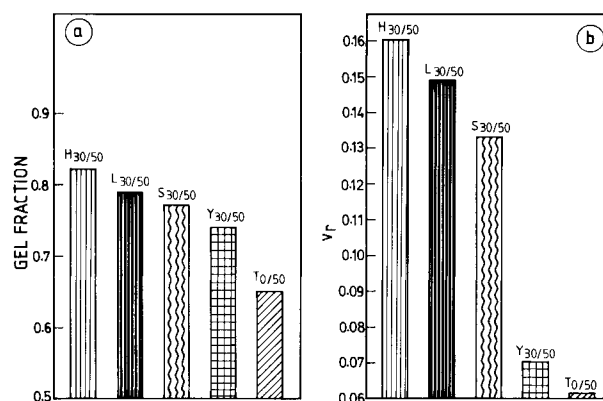


**Figure 2** Rheographs of conventionally formulated fluorocarbon elastomer with different fillers (HAF, SRF, silica, and clay) at a particular loading of 30 phr of the fillers.

sponding increase in  $v_r$  (the volume fraction of rubber). There is also a decrease in elongation at break. The increase in modulus with reduced particle size can also be explained in terms of hydrodynamic effect. The hard filler particles embedded in the rubber matrix resists the orientation of the matrix molecules in the direction of flow lines during deformation.<sup>12,14,15</sup> The stronger the resistance, the more intense the interaction between rubber and filler surface. It has also been postulated<sup>16</sup> that the rigid dispersed filler phase increases the local strain of the rubber matrix leading to the amplification of the overall strain.

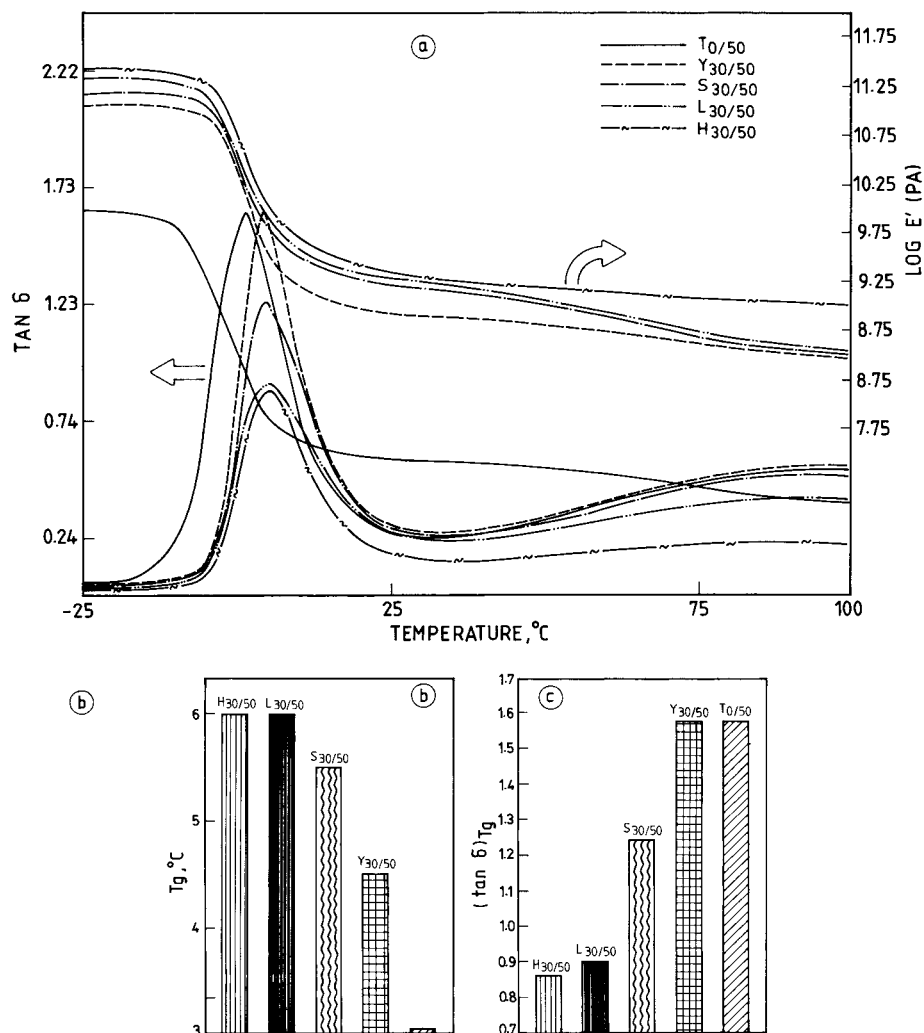
Dynamic mechanical properties of the sample have been measured [Fig. 4(a)–(c)]. Figure 4(a) shows the variation of  $\tan \delta$  and  $\log E'$  against temperature.  $(\tan \delta)_{T_g}$ , i.e., the maximum value of  $\tan \delta$ , which is due to the glass transition of the filled rubber, and the temperature at which the transition takes place, i.e.,  $T_g$ , have been calculated from these curves, and are shown in Figure 4(a). The increase in  $T_g$  and the dynamic storage modulus and reduction of loss tangent peak maximum, with diminishing particle size of the carbon black, silica, and clay filler, indicates the restricted mobility of the molecular segments. This results from strong surface adsorption forces arising out of the fluoroelastomer chain molecules, with the filler interstices and the establishment of covalent bonds between the macroradicals formed on irradiation and those generated on the filler surfaces.<sup>17</sup> There is, thus, an increased possibility

of the formation of an encapsulating shell of higher rigidity. Smit<sup>18</sup> has demonstrated the existence of such a surface phase in carbon black-filled SBR vulcanizates with varying particle sizes of the black by dynamic measurements. Again, strong linkages between the rubber–filler surfaces have been reported to minimize energy losses by preventing the breakdown of the secondary structures of the filler.<sup>19</sup> These can explain the progressive decrease of the mechanical loss factor  $(\tan \delta)_{T_g}$  with the decrease in particle size of the filler. Because the value of  $v_r$  is increased with finer particles, the dynamic storage modulus is also enhanced. The formation of an immobilized surface layer has been found to increase the  $T_g$  of the filled SBR vulcanizates by several degrees with a corresponding decrease of  $\tan \delta$  at  $T_g$ .<sup>18</sup> The surface adsorbed layer also contributes to more gradual stress gradients and more uniform stress distribution across the solid–elastomer interface. This process first absorbs strain energy, and then dissipates it by slippage as frictional heat. The energy requirement for the rupture processes is thus increased by the dissipation of a portion of the strain energy as heat with diminishing filler sizes. Similar arguments can be given for reinforcing silica. In addition, strong interaction of the polar fluorocarbon rubber (due to the presence of C–F dipoles on the macromolecular chain backbone) with the polar silica surface (owing to the presence of OH dipoles) may also contribute to the reinforcement. Cases of such a reinforcement for polar poly(chloroprene) and poly(acrylonitrile-butadiene) rubber are reported in



**Figure 3** (a–b) Variation of gel fraction and volume fraction of rubber  $v_r$  of various filled FKM rubber at a fixed irradiation dose of 50 kGy.



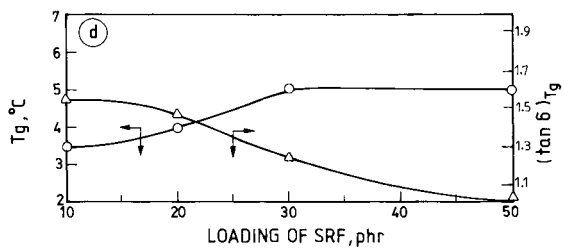
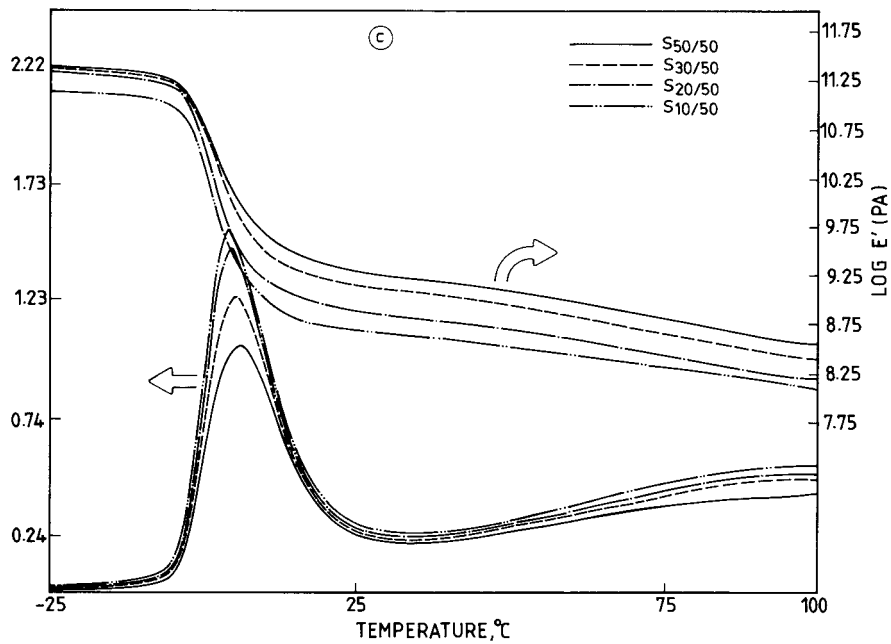
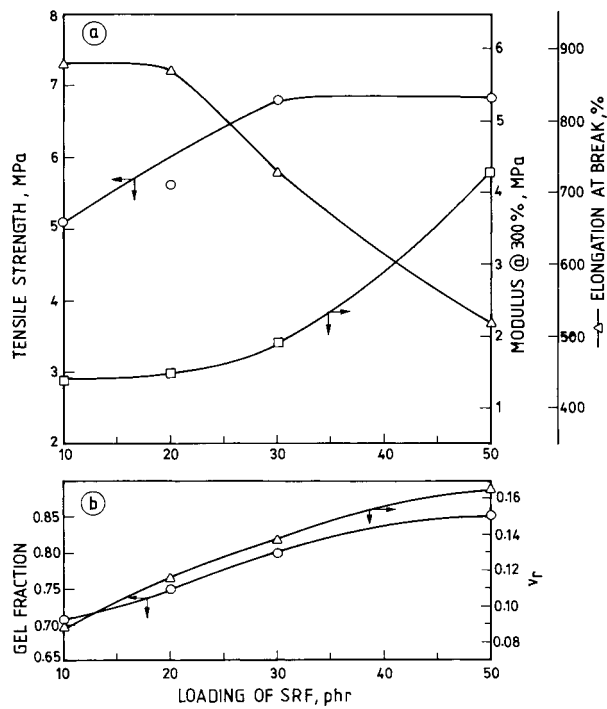


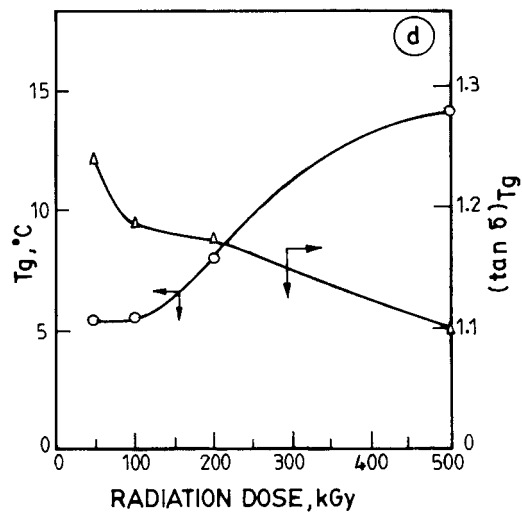
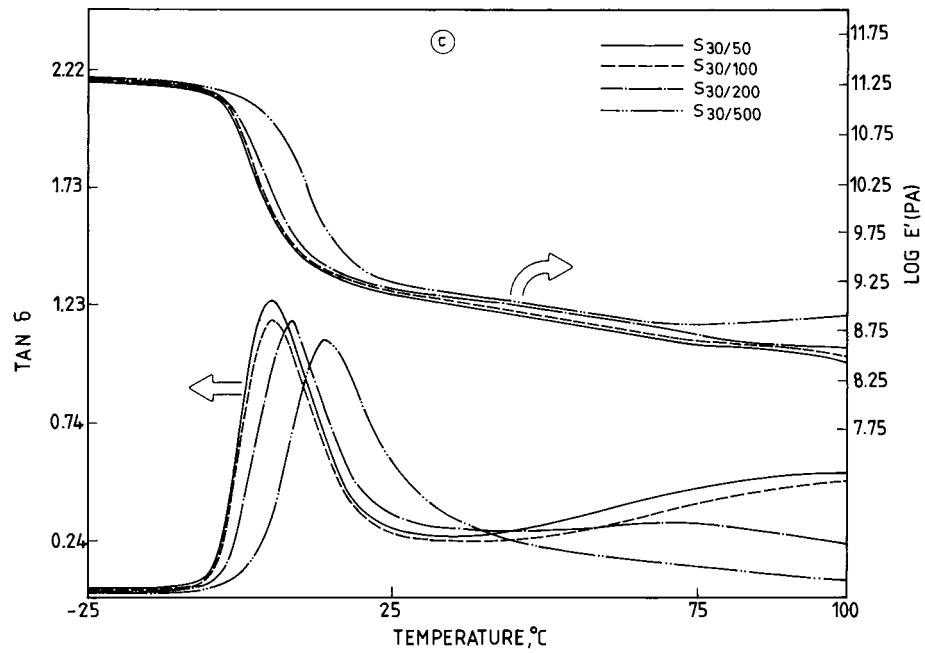
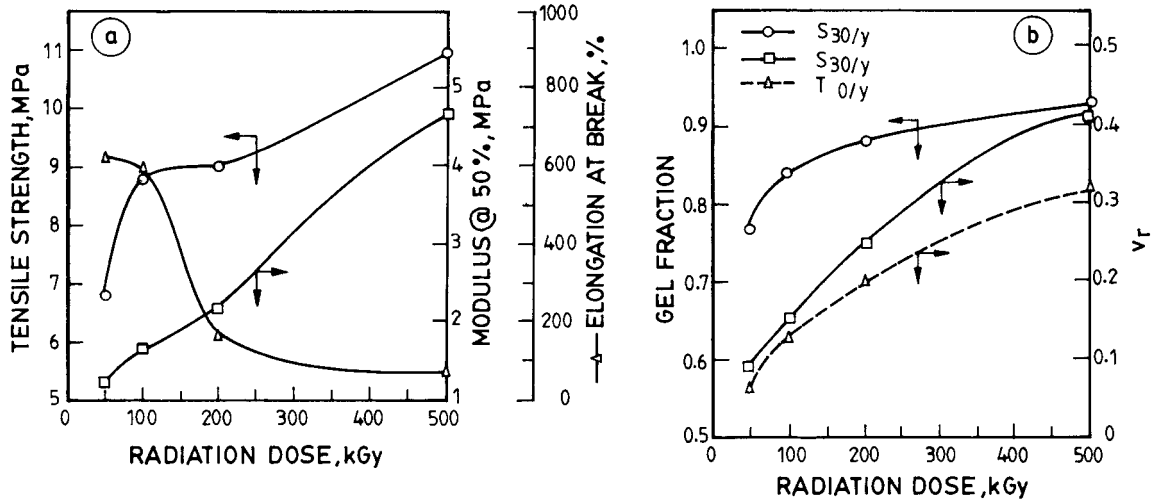
**Figure 4** (a) DMTA spectra (depicting  $\text{Log } E'$  and  $\tan \delta$ ) of the various filled FKM samples irradiated with a fixed dose of 50 kGy. (b–c) Variation of glass transition temperature  $T_g$  and peak value of  $\tan \delta$ ,  $(\tan \delta)_{T_g}$  of various filled FKM rubbers.

the literature.<sup>12</sup> What is most interesting from the studies of mechanical and dynamic mechanical properties is that reinforcement capacities of silica and HAF filler are comparable. This is important, in view of the recent impetus on utilizing green technology in the rubber industry. However, in the high-temperature range, the HAF

carbon black registers higher storage modulus values and lower  $\tan \delta$  values compared to silica. This is due to the fact that the electron beam crosslinking induces radicals on the carbon fillers, which can further interact with rubber, thus improving the adhesion between them. This is not possible in the case of silica.  $E''$  increases more

**Figure 5** (a) The tensile strength, modulus, and elongation at break of blends of fluorocarbon rubber with SRF at different loadings (10 to 50 phr) each irradiated with a constant dose of 50 kGy. (b) Variation of gel fraction and volume fraction of rubber  $v_r$  of FKM mixed with different levels of SRF and fixed dose of 50 kGy. (c) DMTA spectra of FKM rubber samples filled with various levels of SRF at a particular dose of 50 kGy. (d)  $T_g$  and  $(\tan \delta)_{T_g}$  of fluorocarbon elastomers at different loadings of SRF and irradiation dose of 50 kGy.







than the  $E'$  with the increase in temperature for the system.

### Effect of Filler Loading

Figures 5(a)–(d) shows the variation of mechanical (tensile strength, modulus, and elongation at break), dynamic mechanical properties, gel fraction, and volume fraction ( $v_r$ ) of rubber filled with different levels of SRF (10–50 phr) and irradiated with a constant dose of 50 kGy. Modulus is improved with the increase in filler loading. However, the elongation at break decreases and the tensile strength increases up to a certain level, for example, 30 phr loading. All these observations can be explained on the basis of an apparent increase in the degree of crosslinking measured by gel fraction and volume fraction,  $v_r$ , of rubber, as depicted in Figure 5(b). With an increase in loading of the filler, the number of particles, and hence, the amount of surface in contact with the rubber, is likely to increase. As explained earlier, the fraction of the surface-absorbed material increases, and this imposes more restriction on the mobility/rotation of fluorocarbon rubber chain segments. It is observed that both  $T_g$  and dynamic storage modulus increase, with a corresponding decrease in the loss tangent peak maximum ( $\tan \delta$ ) $_{T_g}$ , with an increase in the level of the filler. As explained above, ( $\tan \delta$ ) $_{T_g}$  of the filled vulcanizates is reduced, owing to the affinity of more filler to the rubber. The mechanical energy loss, as shown in Figure 5(c)–(d), is reduced with an increase in loading of the filler. Such physicochemical interactions (concentrated on specific adsorption sites) can also account for increased resistance to deformation of the fluorocarbon rubber matrix, resulting in increased modulus, tensile strength, and decreased elongation at break [Fig. 5(a)].

### Effect of Radiation Dose (at a Fixed Level of SRF)

Figure 6(a)–(d) shows the variation of mechanical, dynamic mechanical, and the gel fraction and the volume fraction of rubber ( $v_r$ ) of fluorocarbon

rubber blended with a constant loading of SRF carbon black and irradiated with various irradiation doses (50–500 kGy). It is observed that both the static and dynamic modulus [Fig. 6(a) and (c)] and  $T_g$  of the filled vulcanizate [Fig. 6(c) and (d)], increase with an accompanying decrease in ( $\tan \delta$ ) $_{T_g}$  [Fig. 6(c)] and the elongation at break [Fig. 6(a)]. Like the control rubber (i.e., one without any filler,  $T_{0/y}$ ) irradiated with different radiation doses, i.e., 50, 100, 200, and 500 kGy, there is an increase in  $v_r$  for the filled samples with irradiation dose, as shown in Figure 6(b). However, the increase of  $v_r$  of the filled system in the range of 200–500 kGy irradiation dose is much greater than that of the unfilled one, i.e., the difference of  $v_r$  between the filled and unfilled systems, ( $v_{r,\text{filled}} - v_{r,\text{unfilled}}$ ), in the higher radiation dose is much greater than that in the lower radiation dose. It is apparent that filler–rubber bonding increases the value of  $v_r$ . The results further indicate that at a higher radiation dose there is an additional bonding between the filler and rubber through the larger number of free radicals on the carbon black and rubber. Increased radical yields on the black–polymer interface, with an increase in the concentration of the curing agent, have been reported in the literature.<sup>15</sup> Because the radical yields in radiation-induced reactions are also proportional to the integral radiation dose<sup>3</sup> (curing agent) absorbed, an increased radical recombination reaction (between those on the carbon black and the fluorocarbon rubber) is likely to generate strong chemical linkages with an increase in the radiation dose. Various macromolecular relaxations, as explained in the previous section, are also minimized, leading to the reduction of ( $\tan \delta$ ) $_{T_g}$ . The progressive rise in properties with an increase in radiation dose is due to the increasing gel fraction and volume fraction of rubber. As explained in the preceding section, increased resistance to flow will give rise to the increase in modulus and reduced elongation at break. Such an increase in rubber–filler interaction due to the crosslinking agent is uncommon in conventional rubber vulca-

**Figure 6** (a) Mechanical properties of fluorocarbon rubber filled with SRF at a fixed loading of 30 phr and irradiated with different radiation doses (50, 100, 200, and 500 kGy). (b) Variation of gel fraction and volume fraction of the above SRF-filled FKM rubbers with radiation dose. Variation of  $v_r$  of the control rubber irradiated with same different radiation doses (i.e.,  $T_{0/y}$ ) is shown by the broken line. (c) DMTA spectra of the different SRF filled rubbers irradiated with various radiation doses. (d)  $T_g$  and ( $\tan \delta$ ) $_{T_g}$  of the above SRF-filled fluorocarbon elastomer at different radiation doses.

nizates. This is possible with high-energy irradiation like an electron beam.

## CONCLUSIONS

Among the various fillers HAF, SRF, silica, and clay, the improved mechanical properties, for example, tensile strength and modulus, are observed for HAF-, carbon black-, and silica-filled samples owing to increased rubber–filler interaction under the influence of radiation. The volume fraction of rubber,  $v_r$ , of the HAF- and silica-filled rubbers has been found to be greater than the SRF- and clay-filled rubber matrix. Dynamic mechanical properties display higher  $T_g$ , a lower  $\tan \delta$  peak value, and a higher storage modulus compared to SRF- and clay-filled samples.

The strength properties improve on increasing the level of filler at a particular radiation dose. These results are explained on the basis of sol-gel analysis.

A similar improvement in mechanical properties has been found to take place upon increasing the dosage of radiation at a particular level of the filler.

The authors are grateful to Dr. A. B. Majali and Dr. R. S. Deshpande of Bhabha Atomic Research Centre, Mumbai; Dr. V. K. Tikku, NICCO Corporation Limited, Calcutta, for experimental assistance with the work; and Board of Research in Nuclear Sciences, Department of Atomic Energy, Mumbai, for funding this project.

## REFERENCES

1. Donnet, J. B.; Voet, A. Carbon Black Physics, Chemistry and Elastomer Reinforcement; Marcel Dekker Inc.: New York, 1976.
2. Clough, R. L. Encyclopedia of Polymer Science and Engineering; John Wiley & Sons: New York, 1988, p. 666, vol. 13.
3. Charlesby, A. Nature 1953, 24, 167; Atomic Radiation and Polymers; Oxford: London, 1960.
4. Bohm, G. G. A.; Tveekrem, J. O. Rubber Chem Technol 1982, 55, 575.
5. Lynn, M. M.; Worm, A. T. Encyclopedia of Polymer Science and Engineering; John Wiley & Sons: New York, 1987, p. 267, vol. 7.
6. Banik, I.; Bhowmick, A. K.; Raghavan, S. V.; Majali, A. B.; Tikku, V. K. Polym Degrad Stabil 1999, 63, 413.
7. Banik, I.; Bhowmick, A. K.; Tikku, V. K.; Majali, A. B.; Deshpande, R. S. Radiat Phys Chem 1998, 51, 195.
8. Banik, I.; Bhowmick, A. K. Radiat Phys Chem 1999, 54, 135, and references therein.
9. Banik, I.; Dutta, S. K.; Chaki, T. K.; Bhowmick, A. K. Polymer 1999, 40, 447.
10. Banik, I.; Bhowmick, A. K.; J Appl Polym Sci 1998, 69, 2079.
11. Morton, M. Rubber Technology; Nostrand Reinhold: New York, 1987.
12. Blow, C. M.; Hepburn, C. Rubber Technology and Manufacture; Butterworths: London, 1982.
13. Medalia, A. I.; Kraus, G. In Mark, J. E.; Erman, B.; Eirich, F. R., Eds.; Science and Technology of Rubber; Academic Press: New York, 1994.
14. Medalia, A. I. J Colloid Interface Sci 1970, 32, 115.
15. Kraus, G. J Polym Sci 1970, B8, 601.
16. Rivlin, R. S.; Saunders, D. W. Philos Trans R Soc 1951, A253, 251.
17. Dogadkin, B. A.; Tarasava, Z. N.; Kaplunov, M. I.; Karpov, V. L.; Klawzen, N. A. Kolloidnyi Zhurnal 1958, 20, 260.
18. Smit, P. P. A. Rheol Acta 1966, 5, 20.
19. Medalia, A. I. Rubber Chem Technol 1978, 51, 437.