

## A Comparison of the Physical Properties of Radiation and Sulfur-Cured Poly(Butadiene-co-Styrene)

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### Synopsis

The physical properties of radiation- and sulfur-cured poly(butadiene-co-styrene)-based stocks were compared. It was found that the measured lower ultimate strength of radiation-cured stocks is in part attributable to the difference in the glass transition temperatures of the stocks cured by the two methods (an increase in  $T_g$  is caused by sulfur curing). Another factor contributing to the difference in performance is the apparent nonuniform crosslink density distribution in radiation-cured stocks containing carbon black filler. A higher crosslink density in the immediate vicinity of carbon black particles was postulated based on a to-be-expected distribution of secondary electron energy at interfaces with an appreciable change in density between neighboring phases. The invoked difference in network topology, supported by solvent swelling measurements on sulfur- and radiation-crosslinked vulcanizates can explain not only the slightly lower ultimate strength of radiation-cured stocks but also the superior fatigue and crack propagation performance measured for these vulcanizates. Finally, theoretical arguments were presented to explain the inferred large strength deficiency of radiation-cured rubbers reported by other investigators on the basis of chain scissions encountered during radiation crosslinking.

### INTRODUCTION

The voluminous literature on the irradiation of rubbers which has been published over the last 30 years has made little mention of the physical properties of vulcanizates cured by this method. The data reported infer that the strength of radiation-cured rubbers, and particularly of natural rubber, is appreciably lower than that of rubber stocks cured with sulfur-accelerator curing systems. The ability of polysulfide linkages to dissipate localized stresses was invoked to rationalize these findings. However, recently published data on polybutadiene, poly(butadiene-co-styrene), poly(butadiene-co-acrylonitrile), and ethylene-propylene copolymers<sup>1</sup> have shown that the tensile strength of radiation-cured gum and carbon black-filled vulcanizates is about equal to that of their conventionally cured counterparts. It is believed that the earlier observed findings can be attributed to cure-retarding impurities or compound ingredients present in the rubber or added to the stock during compounding. Such chemicals increase the dose requirement for cure and consequently result in the occurrence of a greater number of unavoidable side reactions such as scissions. Moreover, degradation of the rubber by ozone generated by the radiation source may have been a contributing factor, particularly since many of the earlier experiments were carried out with gamma rays, in which case a prolonged exposure of the

sample in the ozone-rich environment was required. The results of these earlier investigations have recently been summarized in a review article.<sup>2</sup>

It is the objective of this work to expand on the most recent studies by a more detailed investigation of the dynamic physical properties of poly(butadiene-co-styrene) rubber.

## EXPERIMENTAL

### Sample Preparation

Solution-polymerized poly(butadiene-co-styrene), made and sold by Firestone under the trade name Stereon 700 ( $M_n = 1.2 \times 10^5$ ,  $M_w/M_n = 2$ ), was used throughout this study. The compositions of the compounds prepared from it are listed in Table I. The stocks were made by blending the elastomer, filler, and curatives in a Brabender Plasticorder, followed by additional mixing on a two-roll mill. The samples were subsequently molded and heat cured at 418°K for 30 min in an electric press. To facilitate the removal of the rubber samples from the mold, they were sandwiched between two  $1.25 \times 10^{-2}$ -cm-thick Mylar sheets.

Radiation vulcanization was effected by passing the Mylar-covered samples, placed on a horizontal conveyor belt, through a scanned electron beam 61 cm. wide and oscillating at 60 Hz. In those cases where irradiation was to be carried out at elevated temperatures, a special environmental cell was used which permitted exposure of the samples in an inert gas atmosphere. The energy of the electrons produced by a Dynamitron accelerator and the sample thickness were chosen in such a way that only the initial, almost linear part of the depth-dose distribution function was utilized in the irradiation of the samples. By a two-side exposure of the samples under these conditions, it was possible to achieve an almost uniform dose distribution throughout the plaques. This was confirmed by dose measurements on a multilayer composite phantom comprised of alternating layers of rubber stock and dosimeter tapes. Dosimetry measurements were performed using the bleaching of blue cellophane, the rate of which had been previously calibrated by calorimetry. The average dose rate used in the experiments was 1 Mrad/sec.

### Physical Measurements

Stress-strain properties were measured in triplicate on an Instron tester using ring samples with an inside diameter of 1.57 cm which were cut from slabs approximately 0.2 cm thick. A testing speed of 5 cm/min was employed.

The dependence of the torsion modulus on temperature was determined with the help of a Tinius Olson tester using samples  $0.63 \times 5.0 \times 0.2$  cm in size. The entire probe assembly was dipped into a liquid nitrogen-ethanol mixture which permitted cooling of the rubber samples to temperatures well below the glass transition temperature  $T_g$ . Raising the temperature with the aid of an electric heater, measurements were then made at intervals of 3°K. A stirrer was used to ensure a uniform temperature profile across the rubber sample.

Flex life and crack propagation measurements were carried out with a Monsanto fatigue-to-failure tester in constant strain mode. Dumbbell-shaped

TABLE I  
Compound Recipes for Sulfur- and Radiation-Cured Stocks

	S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>	R <sub>1</sub> -R <sub>6</sub>
Masterbatch <sup>a</sup>	156	156	156	156	156
Sulfur	1.4	1.6	1.75	1.9	—
Santocure NS	0.8	0.9	1.0	1.1	—
<i>p</i> -Dichlorobenzene	—	—	—	—	2

<sup>a</sup> Masterbatch: Stereon 700, 100 phr; ISAF, 50 phr; ZnO, 3 phr; stearic acid, 2 phr; Santoflex 13, 1 phr.

samples (7.6 cm long, 0.15 cm thick), with a beaded edge for slip-free clamping, were used for the flexing experiments. After mounting, the samples were precycled to 10<sup>4</sup> cycles using the strain amplitude selected for the experiment. The permanent set developed was subsequently taken up by an adjustment of the sample holder position. A similar correction was performed every 10<sup>5</sup> cycles. During the test, the probe was subjected for a quarter of each cycle to an increasing strain at constant acceleration which was released during the second quarter cycle. The sample was then held at zero strain for half a cycle to allow recovery to the original unstrained length. The number of cycles to failure were recorded automatically.

Similarly shaped but 20-cm-wide samples were used for crack propagation measurements. Special holders were fabricated for the mounting of these wide samples in the Monsanto tester. Following precycling and permanent set adjustment in the manner described above, a 5-cm-long horizontal cut starting from one side was introduced along an imaginary center line of the sample. The position of the crack tip was marked and the increasing cut length was measured as a function of the number of cycles.

### Solvent Swelling Measurements

The volume fraction of rubber in swollen gum or carbon black-filled rubber,  $V_r$ , was determined by swelling the cured samples in the solvent of choice at room temperature for approximately 70 hr. During this time period, the solvent was changed after the first day. The samples were then weighed and subsequently dried in vacuo until a constant weight was achieved. Finally,  $V_r$  data were calculated using the dry weight to correct for the loss of sol.

A differential thermal analyzer made by du Pont, Model #900, was employed for the determination of glass transition temperatures.

## RESULTS

### Physical Strength

The stress at break of radiation- and sulfur-cured carbon black-reinforced poly(butadiene-co-styrene) vulcanizates is compared in Figure 1. Here as well as in many of the other graphs, the 300% modulus was selected as a measure of crosslink density since an almost linear relationship between it and dose has been noted for the carbon black-filled rubber compounds of this study. Aside from

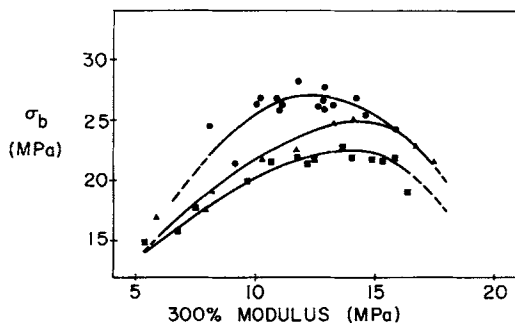


Fig. 1. Stress at break measured at test temperatures indicated in parenthesis: (■) radiation (297°K); (▲) radiation (292°K); (●) sulfur (297°K).

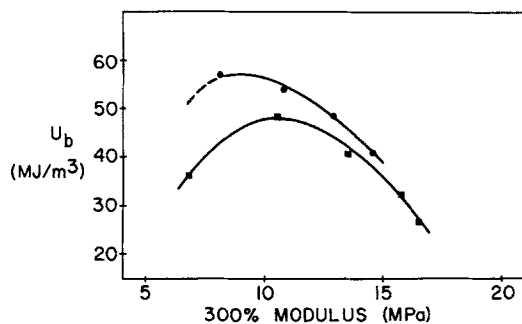


Fig. 2. Energy at break measured at 292°K: (■) radiation; (●) sulfur.

the curves representing measurements carried out at 297°K, data are shown for radiation-cured samples tested at 292°K. This seemed important since an about 5°K higher glass transition temperature has been measured for the sulfur-cured vulcanizates. This additional curve thus allows strength comparisons to be made at equal  $T - T_g$ . The graph shows a similar dependence of the stress at break on crosslink density for both types of networks; however, a shift of the tensile strength maximum toward higher moduli values can be noted for the radiation-cured rubbers. This shift is not observed when the stress-at-break data are plotted against  $V_r$ , the volume fraction of rubber in the toluene-swollen vulcanizate. The maxima then occur at  $V_r = 0.215$ .

A 16% lower tensile strength maximum is observed for the radiation-cured samples, which is reduced to 8% when the testing is done at equal  $T - T_g$ . This somewhat reduced tensile strength should also manifest itself in a lower energy to break,  $U_b$ , and hysteresis at break,  $H_b$ , which is shown in Figures 2 and 3.  $U_b$  was determined by measuring the area under the stress-strain curve. To measure  $H_b$ , a sample was extended to within a few per cent of the breaking stress and then retracted to zero stress at the same strain rate. Graphic integration of the area bounded by the extension and retraction curve yielded the hysteresis at break. As anticipated, we notice a lower energy to break for the radiation-cured samples. It is interesting to note, however, that the interdependence of hysteresis and energy to break first noted by Harwood and Payne<sup>3</sup> is preserved in this case with the data for both types of networks lying on the same curve. The fact that this relationship holds not only for a vulcanizate of given crosslink

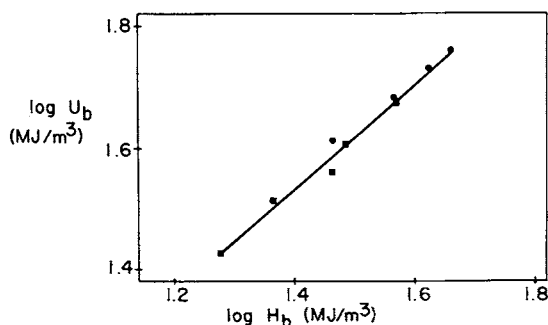


Fig. 3. Energy at break vs hysteresis at break for BD/S copolymers of different crosslink densities measured at 292°K: (■) radiation; (●) sulfur.

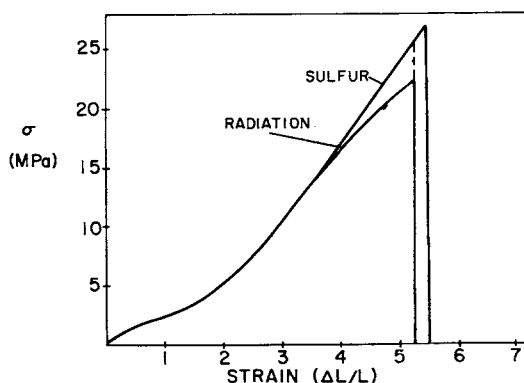


Fig. 4. Stress-strain curves of radiation- and sulfur-cured BD/S copolymers with identical 300% modulus.

density tested at different temperatures and strain rates as reported in the literature but also for rubbers with different types and distributions of crosslinks defines the broad universality of this concept. The equation might thus also apply to composites, heterogeneous in crosslink density, carbon-black concentration, or type, etc.

The lower energy to break of radiation-cured samples is, however, only partially attributable to a lower ultimate tensile strength. This can be gleaned from Figure 4, which compares the general shape of the stress-strain curves for the two types of vulcanizates cured to the same 300% modulus value. The curves are about identical up to  $\lambda = 3$ , above which a gradual divergence is notable. The sulfur-cured vulcanizate shows continued strain hardening which has often been ascribed to a nonaffine deformation of the network. In contrast, the stress-strain curve of the rubber cured by radiation exhibits a gradually decreasing slope followed by a break of the sample at a lower strain level. For the case depicted in Figure 4, it can be calculated that approximately 30% of the higher  $E_B$  measured for sulfur-cured vulcanizates is attributable to the divergence in the stress-strain curves, the remaining 70% is due to higher elongation-at-break values. While the actual difference in  $E_B$  varies with the degree of cure obtained in the rubbers (Fig. 2), the contribution of these two factors remains about the same.

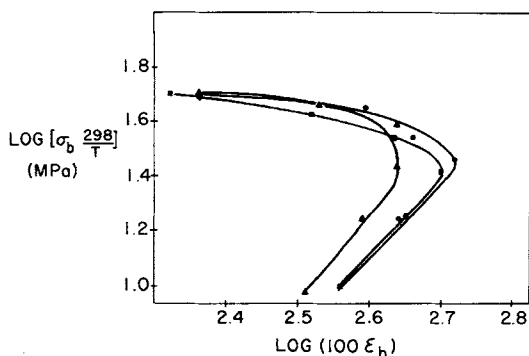


Fig. 5. Rupture data (failure envelopes) for radiation- and sulfur-cured BD/S copolymers: (●) sulfur; (▲) radiation [ $V_r(\text{rad}) = V_r(\text{sulfur})$ ]; (■) radiation [ $300\% M(\text{rad}) = 300\% M(\text{sulfur})$ ].

The above referred-to divergence of the stress-strain curves at high extensions does not occur with gum vulcanizates. There, the characteristic sharp upturn of the curves on approach of the extensibility limit is noted for both radiation as well as sulfur-cured rubbers, suggesting that the phenomenon is associated with the presence during radiation cure of carbon black filler.

A more general dependence of ultimate tensile properties on crosslink density and other network characteristics can be gleaned from an examination of the failure envelopes. Provided time-temperature superposition is applicable, it has been shown by Smith<sup>4</sup> that failure data obtained at different temperatures and strain rates superimpose on a plot of  $\log \sigma_b (T_0/T)$  versus  $\log \epsilon_b$  ( $\epsilon_b = \lambda_b - 1$ ) and yield a master curve called the failure envelope. Figure 5 shows such a plot for a sulfur-cured sample and two radiation-cured rubber vulcanizates, one having an equal 300% modulus, the other showing an equal volume fraction of rubber (swollen in toluene at 292°K) compared to the sulfur-cured stock. As will be shown later, the expected equal correlation of modulus and volume swelling of the vulcanizate in a solvent does not hold true for these two vulcanizates, and, consequently, both conditions (300% modulus = const.,  $V_r = \text{const.}$ ) are used as somewhat arbitrary points of reference. The points on the failure envelope were determined by measuring the ultimate strength  $\sigma_b$  and strain at break  $\epsilon_b$  for the polymers in a stress-strain experiment at a constant strain rate of 5 cm/min but at different temperatures. As can be seen, a considerable lower maximum extensibility is observed for the radiation-cured rubbers when compared at  $V_r = 0.232$ . This trend holds true for a broad range of  $V_r$  values (Fig. 6). A lower maximum extensibility of radiation-cured rubbers is also noted for vulcanizates of equal modulus, yet the difference in  $(\lambda_b)_{\text{max}}$  values is much smaller than in the case of  $V_r = \text{const.}$

### Fatigue Failure

The results of flex life measurements carried out at 292°K in the constant strain mode are shown in Figure 7. There, the number of cycles to failure are plotted as a function of the energy of deformation expended during each flex cycle. The results of measurements carried out at different strain amplitudes as well as with compounds cured to different crosslink densities are all included in this graph.

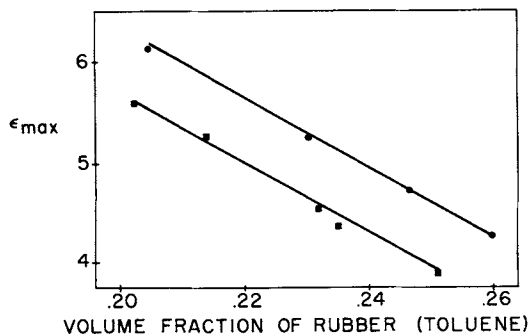


Fig. 6. Maximum extensibility for radiation- and sulfur-cured BD/S copolymers: (●) sulfur; (■) radiation.

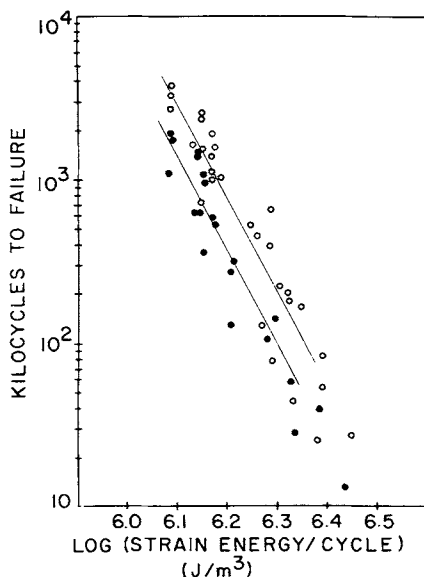


Fig. 7. Fatigue failure data obtained under cyclic test conditions at 292°K: (●) sulfur; (○) radiation.

A considerable degree of scatter of the data points can be observed, which is to be expected from such a measurement. It was determined, however, that considerable separation of the 95% confidence domains determined for the two sets of data points exists. The two straight lines fitted through the data points below  $W = 2.2 \times 10^6 \text{ Jm}^{-3}$  using the least-squares method indicate that the radiation-cured stocks have an about two times greater flex life. At high energies per cycle, the data fall below the straight-line approximation of the low energy-per-cycle data. This trend has been observed before<sup>5</sup> and has been interpreted by a gradual transition from rough to smooth cut growth as  $W_0$  approaches a value at which tearing occurs catastrophically. The observed greater flex life of radiation vulcanizates could be due to either a smaller rate of crack initiation or to a slower crack propagation. The former might not be totally unexpected since different molding and curing conditions were used. The sulfur-cured stocks were vulcanized under pressure at 418°K, whereas only atmospheric pressure

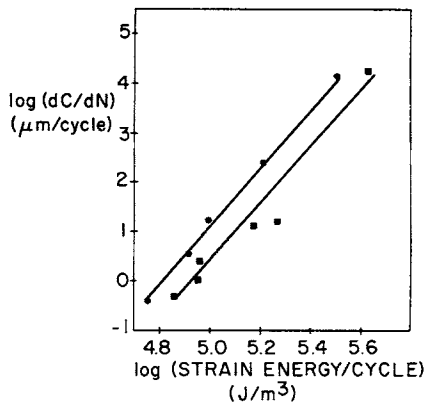


Fig. 8. Cut growth data obtained in pure shear under cyclic test conditions at 292°K. The 300% modulus of the samples was 9.5 MPa: (●) sulfur; (■) radiation.

was acting on the molded samples during radiation cure at 292°K. Density measurements carried out on both types of compounds prior to and after vulcanization did not reveal any porosity in the cured samples and only a minor densification was noted, such as would be expected by the crosslinking.

To clarify the contribution of the two mechanisms to the observed flex life differences, crack propagation measurements were performed at 292°K in the constant strain mode on samples cured to a 300% modulus of 9.3 MPa. The results are shown in Figure 8. A reduced crack propagation rate is noted for the radiation-cured stocks, the magnitude of which is somewhat larger than what would be anticipated from the flex-life data of Figure 7. Theory predicts that the slope of the fatigue-to-failure and crack propagation curves (Figs. 7 and 8) be equal. Our data yield values of 5.8 and 6.0, respectively.

### Glass Transition Temperature

Changes in glass transition temperature are associated with a vulcanization of rubber compounds. Figure 9 shows data obtained on three carbon-black-filled stocks: one cured with sulfur, the other two, by irradiation at 292° and 418°K, respectively. Doses and sulfur levels were adjusted such that an equal modulus of 7.6 MPa was obtained for the three samples. The inflection points on the torsion modulus-temperature curves were taken as a measure of the glass transition temperature. Figure 9 reveals a 6°K higher glass transition temperature for the sulfur-cured stock when compared to the sample which was radiation crosslinked at 292°K. In the case of irradiation at 418°K, the temperature used for sulfur curing, an about 1°K lower  $T_g$  was noted. No attempt was made to interpret this small difference as it might be within the error of the experiment. DTA data of gum and filled compounds (Table II) show a similar trend. Here again, we find an increase in  $T_g$  of 4°K on sulfur curing, in contrast to no  $T_g$  change associated with a radiation cure. The latter observation is in line with theoretical predictions one can make assuming a chemical crosslink density in the irradiated sample of  $M_c \geq 5000$ . The fact that somewhat different  $\Delta T_g$  values were determined from DTA and torsion modulus data is not surprising, since the measurement of the glass transition temperature is sensitively de-



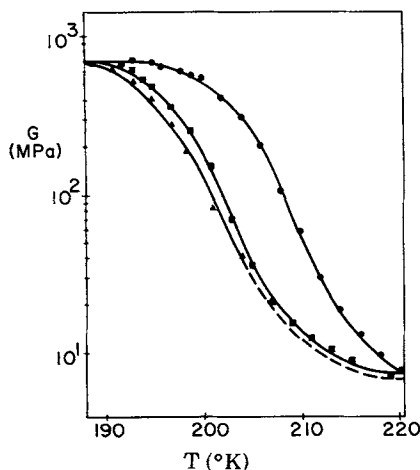


Fig. 9. Shear modulus measured in torsion for samples cured at temperatures indicated in parenthesis: (■) radiation (292°K); (▲) radiation (418°K); (●) sulfur (418°K).

pendent on the tool and on sulfur curing thus suggests that aside from the formation of C—S<sub>n</sub>—C crosslinks, other products such as vicinal polysulfide crosslinks, cyclic sulfides, and pendent sulfur-containing groups are generated which represent a considerable modification of the polymer backbone and thus cause an increase in the glass transition temperature. Such reactions have already been reported in the literature.<sup>6</sup>

### Network Topology

In an effort to discover any differences which might exist in network topology between radiation- and sulfur-crosslinked rubbers, swelling experiments were conducted on both gum- as well as carbon black-filled vulcanizates. The work of Flory<sup>7</sup> suggests a simple relationship between crosslink density or the elastic modulus of a given polymer and equilibrium swelling, with the polymer solvent interaction coefficient as the only adjustable parameter. One would expect, therefore, the data points for the radiation and sulfur-cured stocks to fall on a single curve. This, however, has not been found in our experiments. The results obtained, illustrated in form of the dependence of  $V_r$ , the volume fraction of rubber in the solvent-swollen vulcanizate on the 300% modulus, are shown in Figures 10 and 11. A similar plot is obtained if the force of retraction at  $\lambda = 3$  (equilibrium modulus) is used instead of the dynamic 300% modulus. For any given  $V_r$  value, one observes a higher 300% modulus for radiation-cured, filled samples (Fig. 10) regardless of whether they were irradiated at 292° or at 418°K.

TABLE II  
 $T_g$  (DTA) Changes in BD/S Copolymers (Streon 700) on Curing

Gum and compound (50 phr ISAF)	$T_g$ , °K
Uncured	195
Radiation (cured at 292°K)	195
Radiation (cured at 418°K)	194
Sulfur (1.4 phr S, cured at 418°K)	199

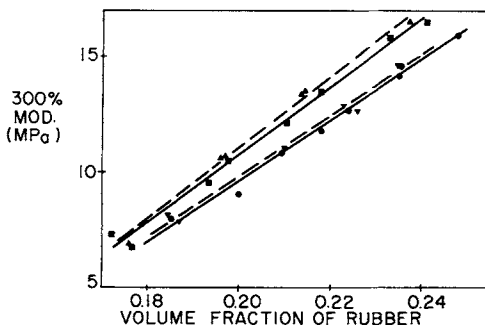


Fig. 10. Swelling of carbon-black-filled vulcanizates in toluene and tetrahydrofuran (THF) at 292°K: (■) radiation (toluene); (▲) radiation (THF); (●) sulfur (toluene); (▼) sulfur (THF).

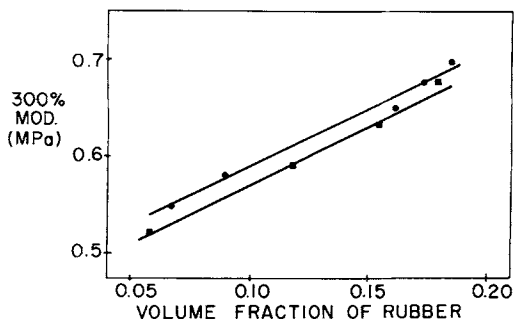


Fig. 11. Swelling of gum vulcanizates in toluene at 292°K: (■) radiation; (●) sulfur.

This difference in strength, which varied somewhat with the degree of cross-linking (12% at  $V_r = 0.235$  for toluene), was noted in samples swollen either with toluene or with tetrahydrofuran (THF). The latter polar solvent was used to elucidate the possible contribution of the relatively polar sulfur, present only in the heat-cured sample, to the observed differences in swelling behavior. As can be gathered from Figure 10, the curves for THF and toluene can be superimposed by a parallel shift as would be expected from the difference in polymer-solvent interaction parameters. The difference in modulus at any  $V_r$  value, however, has not diminished with the use of THF.

Identical measurements carried out on gum rubbers yield quite different results (Fig. 11). Here, the moduli values ( $V_r = \text{const.}$ ) of the radiation- and sulfur-cured samples are identical within the error of the experiment. This finding is in line with the predictions of the Flory-Rehner equation and eliminates the possibility that the modulus difference seen in Figure 10 is attributable to a change in solvent-polymer interaction coefficient caused by the presence of sulfur in one sample. The evidence rather suggests that in contrast to gum vulcanizates, radiation- and sulfur-cured stocks containing carbon black filler have a different network topology.

## DISCUSSION

The findings of earlier investigations (summarized in ref. 2) all indicate a considerably lower ultimate strength for radiation-cured poly(butadiene-co-styrene). The reported strength deficiency relative to their sulfur-cured

counterparts of 30% and more, we believe, can in part be attributed to main chain scissions generated simultaneously with crosslinking. The total number of scissions induced during radiation vulcanization,  $[S]$ , depends on their yield per unit dose,  $G(S)$ , and on the total dose  $R$  required for cure:  $[S] = G(S)R$ . Irradiation of the BD/styrene rubbers in air, the presence of certain chemicals, and higher irradiation temperature all raise  $G(S)$ . The cure dose, in turn, that is, the dose required to obtain a certain modulus in the vulcanizate, is increased by a number of crosslink-retarding chemicals present, particularly in emulsion-polymerized rubbers, and by additives such as antioxidants, processing aids, oil, etc., added to the stock during compounding.

The effect of main chain scissions on the physical properties of cured vulcanizates can be understood in terms of the reduction in molecular weight of the elastomer and the associated increase in the chain end contribution. If a certain modulus is to be achieved in a vulcanizate regardless of whether or not scission is occurring during crosslinking, the increase in chain ends (chains which have no load-bearing capability) has to be compensated by an increase in the number of chemical crosslinks. The associated decrease in the average molecular weight of an elastically active strand and its effect on failure properties such as energy to break can be estimated as follows.

The tensile modulus  $E$  can be calculated according to Langley<sup>8</sup>:

$$E = 3g\nu RT \quad (1)$$

where

$$\nu = (q\rho/M_0)W_g T_e^{1/2} + 2\epsilon T_e \quad (2)$$

where  $\nu$  is the concentration of elastically effective strands,  $q$  is the fraction of repeat units joined to another unit by an intermolecular crosslink,  $W_g$  is the gel weight fraction,  $\epsilon$  is the effective concentration of potential entanglements, and  $T_e$  is the entanglement trapping probability.

For crosslinking by radiation,  $q = q_0R$ , where  $q_0$  is the number of crosslinked units produced per unit dose. Moreover,  $T_e^{1/2} = (1 - W_s^{1/2})^2$  for  $M_w^0/M_n^0 = 2$ . Equation (2) can then be rewritten as follows:

$$\nu = \frac{(q_0R)}{(M_0)} (1 - W_s)(1 - W_s^{1/2})^2 + 2\epsilon(1 - W_s^{1/2})^4 \quad (3)$$

The sol weight fraction  $W_s$  remaining in a vulcanizate following simultaneous crosslinking and scission is, according to Saito,<sup>9</sup>

$$W_s + W_s^{1/2} = \frac{1}{q_0RP_n} + \frac{p_0}{q_0} \quad (4)$$

where

$$\frac{p_0}{q_0} = \frac{1G(S)}{2G(X)}$$

Equations (3) and (4) can be combined to eliminate  $q_0R$ :

$$p_0/q_0 = (W_s + W_s^{1/2}) - \frac{1}{M_0P_n} \frac{(1 - W_s) \cdot (1 - W_s^{1/2})^2}{[\nu - 2\epsilon(1 - W_s^{1/2})^4]} \quad (5)$$

If the vulcanizates are to be compared at equal modulus, then  $\nu = \text{const.}$   $W_s$

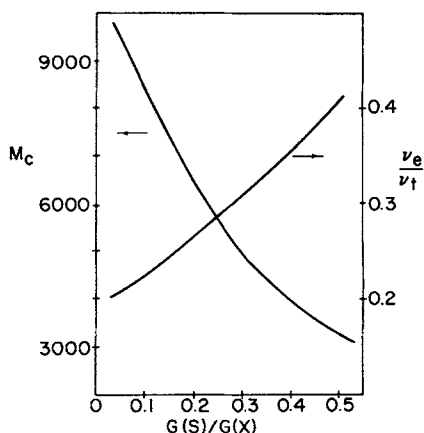


Fig. 12. Effect of  $G(S)/G(X)$  encountered during radiation vulcanization on the average molecular weight between elastically effective chemical crosslinks ( $M_c$ ) and on the chain-end contribution ( $\nu_{\text{end}}/\nu_{\text{tot}}$ ) for samples having identical tensile moduli;  $M_n^0 = 10^5$ ,  $M_w/M_n = 2$ ,  $\nu(\text{effective}) = 3 \times 10^{-4}$  moles/cm<sup>3</sup>.

can then be calculated as function of  $p_0/q_0$ . From this, we can determine the chain end contribution

$$V_e/V_t = 1 - (1 - W_s^{1/2})^2 \quad (6)$$

(the number of structural units in chain ends per total number of structural units) and the average molecular weight per elastically active strand

$$M_c = \frac{(1 - W_s^{1/2})^2}{\nu - 2\epsilon(1 - W_s^{1/2})^4} \quad (7)$$

$V_e/V_t$  and  $M_c$  were calculated for a polybutadiene of  $M_n = 10^5$  and  $M_w/M_n = 2$ . A density of elastically effective strands and entanglements of  $\nu = 3 \times 10^4$  and  $\epsilon = 1.7 \times 10^{-4}$  moles/cc, respectively, were chosen. The results shown in Figure 12 indicate a considerable effect of chain scissions on the chain-end contribution and on  $M_c$ , respectively. To estimate the effect of a reduction in  $M_c$  on failure properties, one can make use of the relationship between  $M_c$  and the maximum extensibility of a rubber network. Assuming an affine deformation of the network  $\lambda_m(\infty)$ , the maximum extension ratio that would be attainable if rupture did not occur should be proportional to  $M_c^{1/2}$ . However, experiments by Smith<sup>10</sup> have shown that the maximum observable extension ratio  $(\lambda_b)_{\text{max}} < \lambda_m(\infty)$  is proportional to  $M_c^{0.75}$ . This empirical relationship, together with the data of Figure 12, clearly illustrate that an increase in  $G(S)/G(X)$  encountered during vulcanization will result in a marked decrease in  $(\lambda_b)_{\text{max}}$  which, in turn, will cause lower failure properties such as tensile strength, energy to break, etc. The earlier reported low physical properties of radiation cured rubbers ( $G(S)/G(X)$  values of 0.15 were measured for irradiation *in vacuo* and much higher values must be anticipated for exposure in air) can thus be explained. A more detailed discussion of the effect of scission on the failure properties of vulcanizates is in preparation.<sup>11</sup>

Let us now return to the findings of this study. The results of our work indicate a difference in ultimate strength of 16% which reduces to 8% when the

samples are tested at equal  $T - T_g$ . In a separate experiment not reported here, we have found that only a negligible amount of scission occurred during the radiation curing of the samples used for this analysis. This was done by sol-gel analysis and subsequent interpretation of a Charlesby-Pinner plot<sup>12</sup> which yields  $G(S)/G(X)$ , the ratio of the  $G$  values for scission to crosslinking. Having excluded the possibility of degradation occurring on radiation curing, we conclude that the remaining 8% discrepancy in ultimate strength must relate to an inherent difference of the networks formed during vulcanization.

The greater strength of sulfur-cured samples has been often attributed to the invoked ability of polysulfide crosslinks to break and re-form under stress, a process which was neither anticipated to occur nor observed for carbon-carbon crosslinks generated by peroxide or radiation vulcanization. However, stress relaxation experiments performed by Tobolsky and Lyons<sup>13</sup> have shown no evidence for a mechanical lability of the weak  $S_n$  crosslinks at room temperature. In a more direct approach, Lal<sup>14</sup> was able to demonstrate that polysulfide crosslinks are not essential for attaining high tensile strength in natural rubber vulcanizates. This was accomplished by measurements on samples in which the polysulfide linkages were converted to mono- and disulfide crosslinks by reaction with triphenyl phosphine. This evidence placed considerable doubt on the validity of the crosslink slipping mechanism. The greater physical strength of sulfur-cured stocks may, in part, be attributable to an internally relaxed network formed by the thermal lability of the sulfur crosslinks at vulcanization temperatures. In line with this reasoning, C-C crosslinks formed by irradiation can permanently entrap stresses and strains introduced in the sample through prior molding, etc. These, one could argue, might result in a lower ultimate strength of the vulcanizate. An irradiation cure of the rubber stocks at a temperature such as is used for a sulfur cure would at least in part simulate the state of a stress-free vulcanizate. Experiments carried out under these conditions showed a considerable rate of scission occurring which itself caused a decrease in stress at break and thus interfered with the proving of the above hypothesis. Other factors, such as differences in the distribution of network chains, could also contribute to the measured lower physical strength of radiation-cured rubbers. This aspect will be discussed later in conjunction with solvent swelling data.

Contrary to the performance of the vulcanizates at strains near the maximum extensibility, the irradiated samples exhibit a greater fatigue life when undergoing cyclic deformation at small to moderate strains. The crack growth data of Figure 8 attribute the superior performance on flexing to a slower crack propagation rate. Andrews et al.<sup>15</sup> have shown that the number of stress cycles required for an original flaw to grow from a length  $C_0$  to  $C_1$  can be expressed as

$$\Delta N = ([n - 1]Bk^n W_0^n)^{-1} \{C_0^{1/n-1} - C_1^{1/n-1}\} \quad (8)$$

where  $W_0$  is the stored energy density at a distance away from the crack;  $k$  is a slowly varying function of the strain; and  $B$  and  $n$  are constants. The number of cycles to failure can then be calculated by assuming that  $C_1 \gg C_0$ :

$$N_f = A W_0^{-n} \quad \text{with} \quad A = ([n - 1]Bk^n C_0^{n-1})^{-1} \quad (9)$$

The data of Figure 7 conform to this relationship with  $n = 5.8$  and  $A$  (radia-

tion)/ $A(\text{sulfur}) = 2.05$ . Additional information can be gained from the cut growth data of Figure 8, which can be adequately represented by eq. (10):

$$dC/dN = BT^n \quad (10)$$

For the sample geometry chosen, the tearing energy  $T$  is equal to  $W_0l$ , where  $l$  is the height of the unstrained test piece. Our data yield  $n = 6$  and  $B(\text{sulfur})/B(\text{radiation}) \sim 4$ .

Since  $A(R)/A(S) < B(S)/B(R)$ , it must be concluded that the difference in flex life measured for the two vulcanizates can only in part be attributed to a difference in the dynamic cut growth constants  $B$ . Unfortunately, the data of this study cannot provide any further detail on possible variances of either  $C_0$  or  $k$  which one would have to assume in line with eqs. (9) and (10). However, an observation which might bear on this question is that the crack surface of the irradiated stock is somewhat rougher than that of the sulfur-cured vulcanizate which could imply a larger  $C_0$  for the former network.

The surprising and most informative result of this study is presented in the swelling data of Figures 10 and 11. They indicate a different modulus- $V_r$  relationship for radiation- and sulfur-cured vulcanizates and attribute these variances to the presence of carbon black. The latter observation, as well as the fact that similar data are obtained for stocks irradiated at 292° and 418°K (omitted in Figs. 10 and 11), eliminate the possibility that styrene-rich domains entrapped by room-temperature irradiation of the random copolymer are responsible for these findings.

Also ruled out can be the contribution of a slight crosslink density gradient one might expect in the sulfur-cured sample due to the heat conduction-controlled advance of the cure front. This can be concluded from Figure 10, which shows a linear dependence of modulus on  $V_r$  over a considerable crosslink density (modulus) range. A near independence of the  $M = f(V_r)$  relationship on crosslink density distribution was also confirmed experimentally using radiation-cured samples in which a crosslink density gradient across the sample thickness was introduced by variations in the energy of the electron beam used for the exposure.

An interpretation of the data is, however, possible if one considers the somewhat complex deposition of energy by ionizing radiation in a heterogeneous matrix such as is represented by the elastomer-carbon black dispersion. When a high-energy electron such as generated by the radiation source used in this study traverses a polymer, a large number of secondary electrons are produced along its track. These lower-energy electrons are responsible for essentially all the physical and chemical effects induced by the radiation act. They dissipate their energy of several hundred eV by interaction with the molecules of the surrounding matrix. Ions, excited species, and radicals are produced, some of which then cause the formation of a chemical crosslink.<sup>16</sup> The region of influence of a secondary electron approximated by a sphere with the point of its creation as center increases with the energy of the electrons and decreases with the density of the surrounding material. A range of 100 Å in water has been estimated<sup>17</sup> for an electron energy of 300 eV, and a similar travel distance should be encountered in polymers of unit density. The number of secondary electrons produced per volume element is proportional to the density of the polymer.

We can now apply this information to describe the energy dissipation of

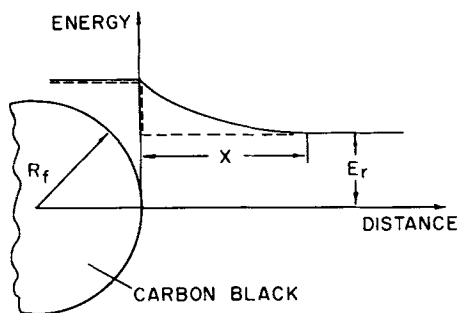


Fig. 13. Schematic of energy deposition near a carbon-black-rubber interface on irradiation of carbon-black-filled elastomer: (—) with energy transfer; (---) without energy transfer.

electrons for a carbon-black-filled elastomer. Figure 13 shows the energy deposited as a function of the distance away from the center of a carbon black particle schematically depicted as a sphere. The dotted line represents the situation in which either an equal or no energy exchange at all takes place across the carbon black (*cb*)-rubber (*r*) interface. The ratio of the energies deposited in the carbon black and the rubber matrix,  $E_{cb}/E_r = 1.8$ , is equal to the density ratio  $\rho_{cb}/\rho_r$  for the two materials. However, the greater number of electrons generated in the carbon black will cause more energy to be moved across the phase boundary into the rubber matrix than will be returned to the carbon black. This energy transfer across the phase boundary will, of course, only be effected by secondary electrons generated in the two materials near the interface. The thickness  $x$  of rubber around each carbon-black particle in which an energy  $E > E_r$  is deposited by energy transfer is governed by the maximum penetration into the rubber of electrons produced in the surface region of the carbon-black particle. Based on the estimated range of secondary electrons in polymeric materials, one can reason that  $x$  should be smaller than  $50 \text{ \AA}$ . The actual energy distribution is thus expected to follow the solid line. Moreover, since the number of crosslinks produced per volume element of rubber is proportional to the energy deposited in it, we must expect that an increased crosslink density will be encountered in the immediate vicinity of carbon black particles. The volume fraction  $\phi_r'$  of rubber affected by a higher crosslinking can be calculated using eq. (11):

$$\phi_r' = \frac{\phi_f}{\phi_r} \left\{ \frac{(R_f + x)^3}{R_f^3} - 1 \right\} \quad (11)$$

$$\phi_r = 1 - \phi_f \quad \phi_r = \phi_r' + \phi_r''$$

where  $R_f$  is the radius of the filler (carbon black) particle,  $\phi_f$  is the volume fraction of filler,  $\phi_r$  is the total volume fraction of rubber,  $\phi_r''$  is the volume fraction of rubber unaffected by this process, and  $x$  is the thickness of the above referred-to rubber layer surrounding the carbon black particle. The  $\phi_r'$  values calculated for rubber stocks containing filler particles of different size are listed in Table III. As can be gathered,  $\phi_r'$  is large for small particles and high filler levels such as are used in our study.

The effect of this nonuniform crosslink density in the rubber phase to be expected with radiation crosslinking on the physical properties of vulcanizates can only be qualitatively assessed. Let us for this purpose compare two hypothetical

TABLE III  
Volume Fraction of Rubber ( $\phi_r'$ ) Affected by Higher Crosslinking<sup>a</sup>

$R_f, \text{Å}$	$\phi_r'$
125	0.205
250	0.093
1250	0.017

<sup>a</sup> Assumption:  $X = 25 \text{ Å}$ ,  $\phi_f = 0.22$  (50 phr).

ISAF black-filled rubber vulcanizates having equal modulus: one, labeled A, with a uniform crosslink distribution throughout the rubber matrix, and another, B, possessing a distribution similar to the one described for radiation-cured vulcanizates. We would, first of all, expect that  $V_r(A)$  would be larger than  $V_r(B)$ . This should be the case since the modulus of ISAF-reinforced rubber exhibits a steep dependence on crosslink density. Moreover, the modulus increase should be particularly sensitive to crosslinks formed in the vicinity of carbon black particles as this region is mainly responsible for the reinforcement in strength of vulcanizates by carbon black fillers. Consequently, fewer crosslinks in the bulk of the rubber matrix should be required in case B to achieve a 300% modulus  $M(A) = M(B)$ , and hence sample B should swell more than sample A. It might be worth adding that one should not expect the swelling to be much affected by an increase in the density of crosslinks near the carbon-black surface. As shown by Kraus,<sup>18</sup> swelling of rubber in this region is already much restricted, and thus a further immobilization of the network there should be of little consequence. Secondly, the higher chemical crosslink density near the carbon-black particle should result in a lower hysteresis at break and a reduced  $(\lambda_b)_{\max}$  for case B. Both of the above predictions have been observed in our investigation. Finally, it is reasonable to assume that the cut growth rate encountered in sample B is smaller than in A because of the smaller crosslink density predicted for the bulk of the former sample. One would expect the tortuous path taken by a slowly growing crack around the filler particles to be mainly influenced by the viscoelastic response of the bulk of the rubber matrix and to a lesser degree by the regions around carbon black particles. A detailed assessment of the contribution that the more crosslinked regions of B make to the cut growth rate measured for the composite cannot be made at present. The greater flex life of radiation-cured stock is, however, worth noting. It suggests that composites of the type predicted to exist in radiation-cured, filled rubber vulcanizates be more extensively explored.

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