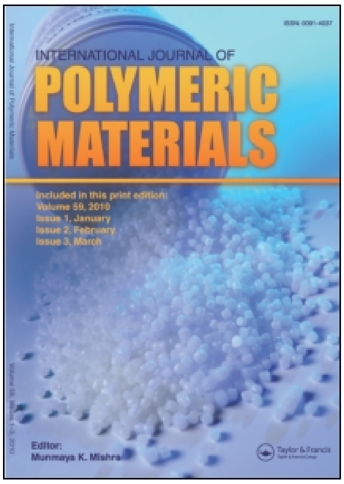

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Tanny, G. B. and Pierre, L. E. St.(1972) 'Radiation Induced Stress Relaxation of Silica-Polydimethylsiloxane Composites', International Journal of Polymeric Materials, 1: 3, 237 — 250
To link to this Article: DOI: 10.1080/00914037208075287
URL: http://dx.doi.org/10.1080/00914037208075287

Intern. J. Polymeric Mater., 1972, Vol. 1, pp. 237–250

Printed in Great Britain

Radiation Induced Stress Relaxation of Silica-Polydimethylsiloxane Composites

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(*Received January* 10, 1972)

A study of G (scission) for silica filled dimethylsiloxane composites has been carried out by measurement of stress relaxation in a γ-ray flux. The results show the same trend as those derived from a combination of sol-dose and swelling experiments.

G (scission) is found to be strongly dependent on the weight fraction of filler in the composite, as well as on the particle size. A model involving reaction of physisorbed polymer chains with electrons and/or positive holes, generated within the silica by γ-radiation, is proposed to explain the increase in the scission yield. The model also explains the observation of a large negative activation energy on the basis of an increase in the rate of annihilation of the holes and electrons within the silica particles.

INTRODUCTION

A topic of increasing attention in radiation chemistry is the enhancement of radiation yields for molecules adsorbed on a microporous support. The generality of this effect is revealed by the fact that small molecules as chemically diverse as hexamethyldisiloxane,[1,2] water,[3] cyclohexane,[4] azoethane,[5] ethanol[6] and nitrous oxide,[7] all demonstrate marked increases in their product yields when irradiated on silica. However, relatively few investigations have concerned the irradiation of large molecules intimately mixed with filler particles.

Fock[8] found that polytetrafluoroethylene, PTFE, filled with carbon black was more crystalline after irradiation and showed a greater loss of modulus

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compared to pure PTFE. He suggested that the presence of carbon black caused increased backbone scission.

In studies on silica-silicone systems, several authors[9-11] claimed that irradiation of a filled PDMS elastomer did not lead to any enhancement of G (crosslinks)† over that for the pure siloxane gum. However, more comprehensive results,[12] obtained recently, contradict the earlier observations and G (crosslinks) is indeed found to increase in proportion to the volume fraction of silica filler.

Since the technique of stress relaxation successfully measured G (scission) in a study of filler free siloxane networks,[13] it was utilized in the present investigation as a means of examining the cleavage of polymer chains during irradiation of silica-silicone composites.

THEORY OF STRESS RELAXATION OF FILLED ELASTOMERS

The theory of stress relaxation has been described in detail by Berry and Watson,[14] and its application to irradiated siloxane networks has already been demonstrated.[13] Although the inclusion of filler particles does not appear to change the theory, it is advisable to re-examine the basic assumptions of the theory to elucidate any effect of the filler on stress relaxation.

The fundamental requirement of all theories of stress relaxation is that, at a given extension ratio and constant temperature, the stress per unit original cross-section, f, is directly proportional to the network density (the number of elastically active chains/gm), N, i.e.

$$f = k\,N \tag{1}$$

Chahal[15] has shown that the modulus (at 100–300% extensions) of PDMS samples, filled with 30 parts silica/100 parts polymer and cured with γ-rays, was linearly dependent on the network density as measured by swelling. Brender[12] has recently shown that this behaviour is maintained over a wide range of silicon concentrations and particle size. Thus any PDMS network having a silica concentration of up to 30 phr, and whose network density is within the range studied,[15] appears to obey Eq. (1). Therefore, one would expect to obtain linear plots of the Berry and Watson function,[14] $[f_0/f_t]$,‡ versus time for any of the composites mentioned. The slope of such plots yields α, the number of cuts per original network chain per unit time, from which one computes G (scission).

$$G\,(\text{scission}) = \alpha \cdot N_0 \cdot \Phi^{-1} \cdot 10^2 \tag{2}$$

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† The number of events per 100 e.v. of γ energy are expressed as G values.

‡ Subscripts refer to time, e.g. f_0 is the stress per original cross-section at time zero.

where G (scission) is the number of elastically active chains lost per 100 e.v. of γ energy, N_0 is the original network density, and Φ is the dose rate (e.v./gm-unit time).

In filler free siloxane networks, it has already been established[13] that G (scission) calculated from Eq. (2) is equivalent to an absolute number of chemical cleavages. However, a question arises in this regard for the case of filled rubbers.

The network density, N_0, as measured by swelling, represents an "effective" network density in the sense that one assumes that the presence of the filler particles may be ignored and treats the system as though it was homogeneous. Mullins and Tobin[16] showed that for certain reinforcing carbon blacks dispersed in rubber, the same value of the network density was obtained from swelling and modulus measurements if the measured strain was corrected through the use of a "strain amplification factor", which is dependent on both the shape and concentration of the filler. This implies that some composites can indeed be considered simply as uniform rubber networks which are in a state of strain larger than that actually measured, due to the presence of the filler particles.

Other workers[16,18,19] have suggested that the situation may be more complex in that the filler particles could cause stress concentration in the network. According to this view, the stress born by chains near the particle surface is considerably different from that in the bulk. Hence the cleavage of some chains would result in a different change in the overall stress than the cleavage of others. One would thus obtain a G (scission) which was an average value of the loss of elastically active chains but the relation of this average to the actual number of chemical scissions which occurred would be unknown.

The overall conclusion to be drawn is that, for composite rubber, the G (scission) determined by stress relaxation reflects the number of chemical cleavages occurring, but is probably not an absolute measure. Qualitatively, however, one would hope to use it in examining the effect of silica on radiolytic scission.

EXPERIMENTAL

Stress Relaxation Apparatus and Procedure

Both the apparatus and procedures are identical to those given in previous work.[13] The range of sample extensions was 3-15%. All experiments were performed in an N_2 atmosphere.

Sample Preparation

Polymer The polymer used was identical to that described in Ref. 13, namely, a 5×10^5 $\overline{M}_n$ PDMS gum.

Silica The silicas used in this work were commercially available Cab-O-Sil, grades L-5, M-5, and EH-5, the properties of which are given below. This data is taken from Ref. 2.

	L-5	*M*-5	*EH*-5
Surface area, m^2/gm (BET)	50±3	200±25	390±40
Particle diameter, angstroms	500	120	70

Preparation of Composites[15]

The composites were prepared by mixing known quantities of silica, which had been dried at 130°C and 1μ pressure, into a 20% solution of PDMS in n-hexane. The mixture was "thoroughly agitated with a stainless steel spatula" until the solvent evaporated. When the sample was "practically dry and had become granular in form", it was dried "at room temperature under vacuum for 6–8 hours". This material was then "worked with a stainless steel rolling pin until the air pockets were removed and the sample appeared homogeneous", after which it was pressed in a die between aluminium foil sheets and cross-linked by γ-radiation.

Except for the 35/100 L-5 and the EH-5 samples, the composites were prepared by Dr. R.S. Chahal of this laboratory.

Swelling Measurements

The method of swelling the samples was identical to that reported earlier.[13]

Correction for the presence of silica was made on the basis of its known weight fraction and the original weight of the sample before swelling. No correction for solvent adsorbed on the silica was necessary, since the quantity was too small to cause a significant change in the volume fraction of polymer, even at the highest concentration of silica.

Dose Rate

All of the stress relaxation experiments were carried out at a dose rate of 0.37 M rads/hr in the source described previously.[13]

Sol-Dose Experiments

Samples of gum filled with M-5 silica were prepared in a manner similar to that for the composites. The aluminium foil-composite sandwich was cut into strips approximately 1 in wide, which were then wrapped individually in more aluminium foil and irradiated in a source having a dose rate of 7.5×10^5 rads/hr.

Duplicate samples (0.5–1.5 gm in weight) were placed in weighed Whatman seamless extraction thimbles (a blank sample set was carried along with the irradiated samples for each silica concentration). The samples were then extracted with toluene for a minimum of 120 hours. (The effect of a longer extraction time, 240 hours, was checked, but no significant difference in the final weight was observed.) After extraction, the samples were dried in a vacuum oven at 80–100°C for 24 hours and weighed.

RESULTS AND DISCUSSION

A. General Behaviour of Filled Gums

In order to examine the effect of a large concentration of filler on radiation-induced stress relaxation, experiments were performed on two samples, each containing 30 parts M-5 silica per hundred parts of PDMS, and which had been crosslinked with two different network densities. The stress relaxation results are shown in Figure 1, plotted as $[f_0/f_t - 1]$ versus time. As in the pure gum,[13] the plots are linear and the slopes of the plots decrease inversely with an increase in the network density. Once again, stress relaxation was observed only within the γ source.

It was found that in the pure gum,[13] although the slope of the plot varied inversely with network density, the overall extent of scission remained constant. This pattern is only partially true of the results from Figure 1, calculated as G (scission) values in Table I. As can be seen, a further experiment at a higher network density revealed an apparent increase in G (scission). Although this effect is most interesting, its detailed investigation was considered beyond the scope of the present study. To avoid any dependence of G (scission) on network density, all samples used in subsequent work had network densities between 3 and 6×10^{19} chains/gm. (cf. Table I).

Comparison of the values of G (scission) in the pure PDMS, (0.7), and that of 30 phr, M-5, silica filled, (10.6), reveals an apparent enhancement of the radiation yield which parallels the behaviour observed in the model compound studies.[1,2] In order to further elucidate this effect, experiments were performed on samples possessing a number of different filler concentrations and network densities within the range already mentioned.

These results are summarized in Figure 2, in which G (scission) has been plotted as a function of the concentration of M-5 silica. The data falls on a smooth curve in which G (scission) increases slowly at first, and then enters a "critical concentration" region after which it increases dramatically.

TABLE I

G (scission) as a function of network density for a 30 phr M-5 composite

Network density × 10^{-19} (chains/gm)	G (scission)
4.64	10.6 ± 1.0
6.40	10.8 ± 1.0
9.80	15.0 ± 1.5

This behaviour is interesting because it bears at least a superficial resemblance to the trend observed in the yield enhancement of the model compound study.[2] However, prior to entering a discussion of the full meaning of the data, it was thought to be valuable to check the results through the alternate technique of sol-dose measurements.

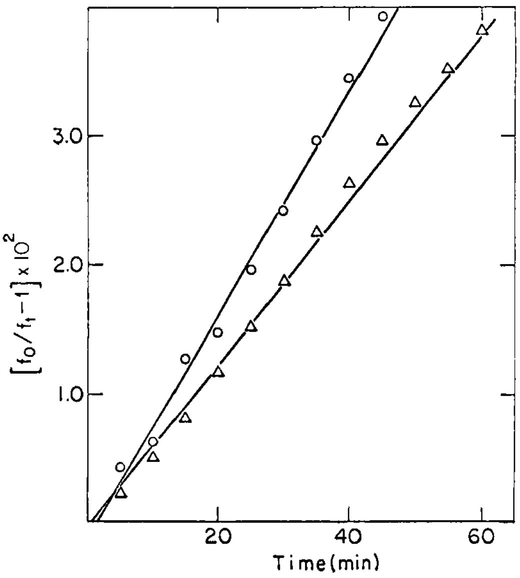


FIGURE 1 γ-ray induced stress relaxation of 30 phr M-5 filled PDMS in N_2, 0.4 Mr/hr at 34°C. Network densities,

(○) $N_o = 4.6 \times 10^{19}$ chains/gm
(△) $N_o = 6.4 \times 10^{19}$ chains/gm

Charlesby and Pinner[20] derived the expression

$$S + S^{1/2} = X_o/Y_o + 1/\mu Y_o D \qquad (3)$$

where S is the soluble fraction, D is the dose, μ is the initial M_n (where

$M_n = M_w/2$), X_o is the number of scissions per gram per unit dose, and Y_o is the number of crosslinks per gram per unit dose. The results of sol-dose experiments at four different filler concentrations, examples of which are shown in Figure 3, revealed that the presence of the filler did not change the linear relation predicted by Eq. (3). However, an increase in the scission to crosslink ratio, the intercept X_o/Y_o, is observed as the filler concentration increases (Table II).

Since the intercept represents an absolute ratio of chemical events, i.e. the ratio of bond cleavage to the introduction of covalent crosslinks, one may conclude that the trend displayed by *G* (scission) (Figure 2) is primarily due to the effect of silica on the radiation chemistry of the polymer.

A shortcoming in using the intercept of Eq. (3) is that it yields only the ratio of scissions to crosslinks but gives the absolute value of neither. However, if the value of either can be independently calculated, then, obviously, both quantities are known. The absolute value of *G* (crosslinks) may be calculated

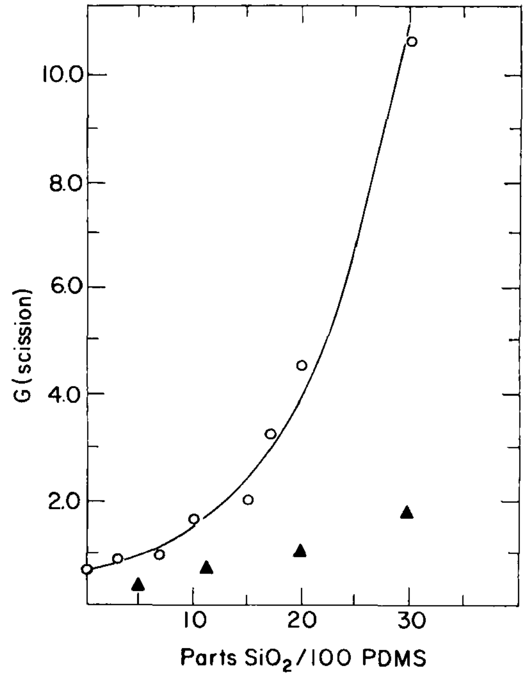


FIGURE 2 Variation of *G* (scisson) with M-5 SiO_2 concentration; 34°C, N_2 atmosphere, 0.4 Mr/hr.

(○) Obtained from Stress Relaxation
(▲) Computed from sol-dose (Table II)

TABLE II

G (scission) and *G* (crossslinks) as a function of filler concentration from sol-dose measurements

Filler Concentration (wt. % SiO_2)	*G* (scission)/*G* (crosslinks)	*G* (crosslinks)	*G* (scission)
5.0	0.24	1.63	0.39
10.0	0.30	2.20	0.66
16.7	0.47	2.40	1.00
22.3	0.54	3.40	1.90

from the slope of the plots in Figure 3 if the initial number average molecular weight, μ, is known.

Since the composites are prepared by mixing a solution of the polymer with the silica filler, adsorption from solution of the larger molecular weights will occur preferentially, thus shifting the bulk number average molecular weight to lower values. One cannot, therefore, rely upon the value of μ determined for the pure polymer. Nonetheless, the values of *G* (crosslinks)

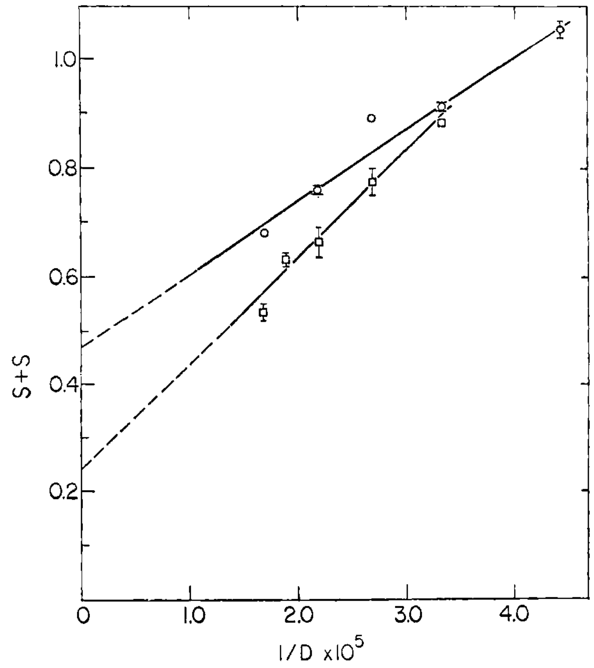


FIGURE 3 Sol-dose experiments for 5.0 wt. % (□) and 16.7 wt. % (○) M-5 silica in PDMS. Points with bars represent duplicates.

and *G* (scission), assuming a μ equal to that of the pure gum are useful indicators of a trend. In Figure 2, the results of such calculations for *G* (scission), (Table II), have been plotted together with those derived from stress relaxation, and the general direction of both results is clearly the same. Extrapolation of the data for *G* (scission) derived from sol-dose, to zero filler concentration yields *G* (scission, pure gum) = 0.3, a value approximately one half that already established.[13] In addition, the result of a similar extrapolation of *G* (crosslinks) from Table II is the same factor smaller than that generally accepted.[21] Clearly, the use of the μ of the pure gum in the calculation of *G* (crosslinks) from Eq. (3) has resulted in an underestimate of the true values of both *G* (crosslinks) and *G* (scission).

The important conclusion to be drawn from Figure 2 is that the stress relaxation technique yields values of *G* (scission) which show the correct effect of silica filler concentration and are of the correct order of magnitude.

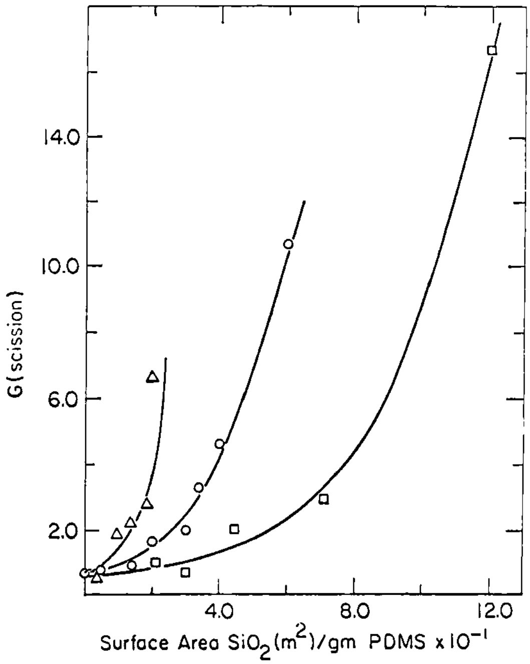


FIGURE 4 Variation of *G* (scission) with surface area of Filler for M-5, L-5, and EH-5 filled PDMS.

(□) 70 Å, EH-5 filler
(○) 120 Å, M-5 filler
(△) 500 Å, L-5 filler

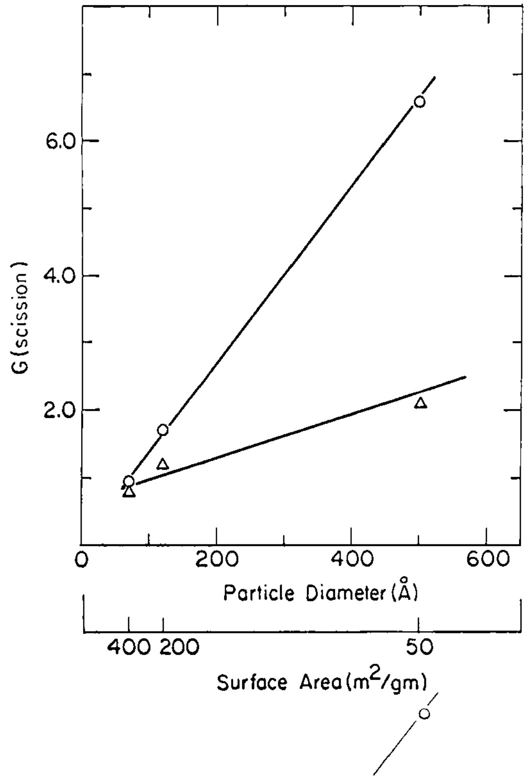


FIGURE 5 Variation of *G* (scission) with Particle Size at Constant Total Surface Area.
(○) = 2.3 × 10^3 (m^2/100 gm PDMS)
(△) = 1.5 × 10^3 (m^2/100 gm PDMS)

One can therefore apply the results obtained by this method to the further elucidation of the radiation chemistry.

B. The Effect of Filler Particle Size

In the study of the irradiation of hexamethyldisiloxane, MM, adsorbed on silica,[2] it was discovered that the size of the filler particle had an effect on the magnitude of the product yields obtained. The trend observed was an increase in the yield with increasing particle size. It was found that the calculated relative efficiency of energy transfer from the silica to the adsorbed species was highest for the smaller size particles and decreased with increasing particle size.

In order to determine if a similar behaviour occurred in stress relaxation, experiments were performed on samples containing various concentrations of L-5, 50 m^2/gm, and EH-5, 400 m^2/gm, silicas. The results of these experiments are shown in Figure 4, in which the abscissa has been plotted in units of "theoretical surface area/gm PDMS". This is simply the weight of silica per gm PDMS multiplied by the surface area per gram of silica, and it presents the data in a fashion analogous to the plots of yield versus surface coverage which were used in the model compound study.[2] It is apparent from Figure 4 that a family of relationships of *G* (scission) versus filler content exists, in which the variable is particle diameter. The relationship between *G* (scission) and the particle diameter may be obtained from Figure 4 by plotting "iso-surface area/gm PDMS" values of *G* (scission) versus particle diameter. From Figure 5 it appears that a linear relationship exists.

The pattern of Figures 4 and 5 is entirely analogous to that already observed with the gas yield from adsorbed MM. It may therefore be concluded that the effect of particle size has a basis in the radiation chemistry mechanism of energy transfer between filler and polymer. Thus, it is now appropriate to

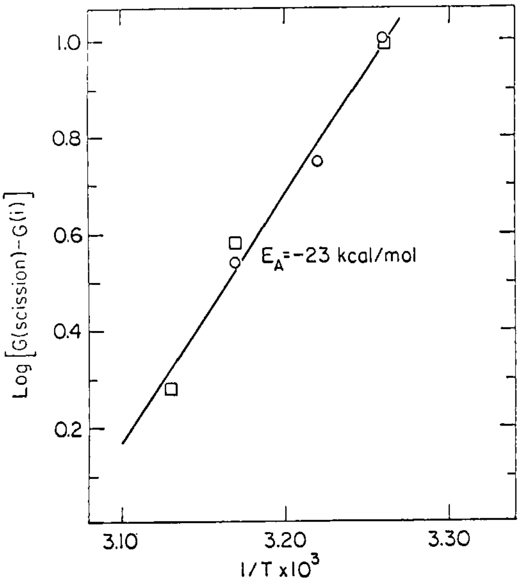


FIGURE 6 Arrhenius plot of *G* (scission) for 30 phr M-5 filled PDMS. Network density
(○) $N_o = 4.6 \times 10^{19}$ chains/gm.
(□) $N_o = 6.4 \times 10^{19}$ chains/gm.
N_2 atmosphere, 0.4 Mr/hr.

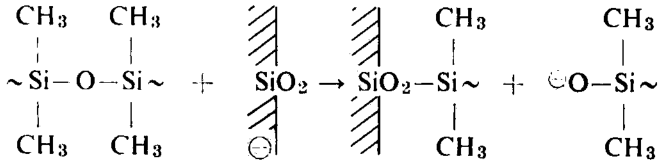
propose a mechanism for energy transfer which can predict the observed behaviour.

C. The Mechanism of Energy Transfer

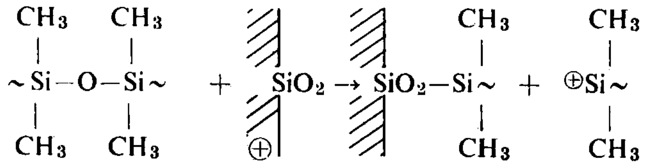
The two main features of silica-siloxane matrix irradiation, as studied by stress relaxation, are (i) an increase in the yield of polymer scissions as the number of silica particles increase, and (ii) a linear dependence of the yield on the size of the silica particle. These facts must therefore be predictable from any proposed mechanism.

A number of authors[4,6,7,22,23] have suggested from studies on the radiolysis of species adsorbed on silica, that energy transfer occurs via the generation and reaction of mobile species, such as electrons and positive holes.

Previous work[13] has demonstrated that SiO bonds may undergo rearrangement by a cationic mechanism, and nucleophilic attack on SiO bonds is already a well characterized part of siloxane chemistry.[24] Thus, scission mechanisms involving both electrons and positive centres can be pictured, as in Eqs. (4) and (5).



$$\sim Si(CH_3)_2-O-Si(CH_3)_2\sim + SiO_2^{\ominus} \rightarrow SiO_2-Si(CH_3)_2\sim + {}^{\ominus}O-Si(CH_3)_2\sim \qquad (4)$$



$$\sim Si(CH_3)_2-O-Si(CH_3)_2\sim + SiO_2^{\oplus} \rightarrow SiO_2-Si(CH_3)_2\sim + {}^{\oplus}Si(CH_3)_2\sim \qquad (5)$$

It should be noted that both of these mechanisms predict the phenomenon of radiation induced chemisorption, which was in fact observed in the studies[1,2] of hexamethyldisiloxane irradiated in the adsorbed state.

A final piece of evidence indicating the role of electrons and holes in the scission process can be inferred from the temperature dependence of G (scission). Figure 6 displays a large *negative* activation energy.

The observation of a negative activation energy can be understood in terms of a loss in the number of species in the silica. which are available to react with polymer chains, due to an increase in the rate of mutual annihilation.

Consider a spherical particle of radius r, volume V, in which y active species (holes and electrons) are generated per unit volume per unit time. Then, for a single particle, at a given dose rate, the total number of active species generated in the bulk of the particle per unit time is given by

$$\frac{d[a]_B}{dt} = Vy - k_{ann}[a]_B^2 \tag{6}$$

where $[a]_B$ is the total number of bulk active species per particle of radius r and k_{ann} is the rate constant for the reaction by which they are destroyed, i.e.

$$SiO_2^{\oplus} + e^{\ominus} \rightarrow SiO_2 \text{ (electron-hole combination)} \tag{7}$$

Considering the energies associate with the incident γ ray, it is obvious that temperature will play a negligible role in the ion generation rate, Vy, in Eq. (6). However, the rate of annihilation of ion centres, being diffusion dependent, will have a positive activation energy. Thus, the equilibrium concentration of active species, at any dose rate, will diminish with increasing temperature, hence, the overall negative energy of activation.

Finally, the dependence of the rate of scission on the particle diameter, rather than on the surface area (Figure 5), suggests that the availability of active sites at the particle surface is a function of the bulk diffusion of electrons within the solid. Measurements to elucidate the annihilation rate are presently under way.

Acknowledgements

One of the authors (G.B.T.) is indebted to the National Research Council of Canada for a Fellowship. The support of the Defence Research Board of Canada is also gratefully acknowledged.

The authors also wish to thank Dr. Chahal for his kind donation of composite samples.

References

1. R. S. Chahal and L. E. St. Pierre, *Can. J. Chem.* **47,** 2131 (1969).
2. K. S. Maeng, thesis, McGill University, Montreal, Canada (1969).
3. Z. I. Krylovia and P. I. Dolin, 2nd Taniba Conference, Budapest, Hungary (1966).
4. N. H. Sagert and P. J. Dyne, *Can. J. Chem.* **45,** 615 (1967).
5. J. G. Rabe, R. Rabe and A. O. Allen, *J. Am. Chem. Soc.* **86,** 3887 (1964).
6. L. Abrams and A. O. Allen, *J. Phys. Chem.* **73,** 2741 (1969).
7. J. W. Southerland and R. Goodrich, *J. Am. Chem. Soc.* **89,** 6779 (1967).
8. J. Fock, *Polymer Letters* **5,** 635 (1967).
9. E. L. Warrick, *Ind. Eng. Chem.* **47,** 2388 (1955).
10. R. K. Traeger and T. T. Castonguay, *J. Appl. Poly. Sci.* **10,** 535 (1966).
11. R. J. Jenkins, *J. Poly. Sci., Pt. A*-2 **4,** 41 (1966).
12. H. Brender and L. E. St. Pierre (in preparation).
13. G. Tanny and L. E. St. Pierre, submitted *J. Poly. Sci.*
14. J. P. Berry and W. F. Watson, *J. Poly. Sci.* **18,** 201 (1955).
15. R. S. Chahal, Thesis, McGill University, Montreal, Canada.
16. L. Mullins and N. Tobin, *J. Appl. Poly. Sci.* **9,** 2993 (1965).
17. E. Guth, *J. Appl. Phys.* **16,** 20 (1945).

18. H. M. Smallwood, *J. Appl. Phys.* **15**, 758 (1944).
19. R. Simha, *J. Phys. Chem.* **44**, 25 (1940).
20. A. Charlesby and S. H. Pinner, *Proc. Royal Soc.* (*London*), **A. 249**, 367 (1959).
21. *Polymer Handbook*, Ed. J. Brandrup and E. H. Immergut, Interscience, 1966.
22. P. J. Dyne and J. Denhartog, *Can. J. Chem.* **44**, 461 (1966).
23. G. Barter and P. Wagner, *J. Phys. Chem.* **68**, 2381 (1964).
    J. Phys. Chem. **69**, 491 (1965).
24. C. Eaborn, *Organosilicon Compounds*, Butterworths (London), 1960, Chapter 8, p. 257.