

## Bond Rupture During Ozone Cracking of Torsional Loaded Styrene-Butadiene

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### Synopsis

The molecular bond rupture rate during ozone attack of torsionally loaded rubber was determined from electron paramagnetic resonance (EPR) measurements. The rupture rate was successfully correlated by a Griffith-type energy balance to the strain-energy release rate in the samples. These observations substantiate the results from a similar study on tensile loading previously reported. In both cases there is a one-to-one correspondence between the rate of bond rupture (or crack growth) and the rate of energy release from the strain field and external work. A fracture energy,  $\gamma_n$ , of approximately  $5 \times 10^{-12}$  ( $\pm 20\%$ ) ergs per free radical formed during the cracking was experimentally determined.

### INTRODUCTION

It is a common experience that rubbers crack and deteriorate when held for long periods under stress. Ozone is recognized as a primary cause of this degrading.<sup>1</sup> Such environmental cracking has been studied by many investigators in the past.<sup>2,3</sup> One of the earliest successful approaches to explain certain types of fracture was by Griffith.<sup>4</sup> He concluded that an infinitesimal increase in crack length could occur only if sufficient (strain) energy was present or work was done to provide the energy input necessary to create the new surface. The analysis of a small crack in a large, thin elastic plate resulted in

$$\sigma_c = \left[ \frac{2\gamma_c E}{\pi a} \right]^{1/2} \quad (1)$$

where  $E$  is Young's modulus,  $2a$  is the crack length, and  $\gamma_c$  is the specific fracture energy (in.-lb per square in. projected new fracture surface).

Other investigators have generalized the Griffith approach to include in the specific fracture energy the effect of plastic dissipation, viscoelastic effects, etc.<sup>5-6</sup> These results have been expressed as

$$\sigma_c = K \sqrt{E/a} \Sigma \gamma_t \quad (2)$$

where  $K$  is a constant dependence on sample crack and loading geometry,  $a$

is the crack half-length, and  $\Sigma\gamma_t$  is the summation of all the dissipative effects during crack extension. That is,

$$\Sigma\gamma_t = \gamma_v + \gamma_b + \gamma_d + \gamma_{KE} + \dots \quad (3)$$

where the subscripts *v*, *b*, *d*, and *KE* refer to viscoelastic, brittle, ductile, and kinetic energy, respectively. In a brittle material,  $\gamma_b$  dominates the summation from which we recover Eq. (1).

A reactive atmosphere can aid crack propagation and in this way effectively lower the specific fracture energy.<sup>7</sup> Solomon and Van Bloois,<sup>8,9</sup> in a study of partly unsaturated rubber hydrochloride films, compared ozone-induced stress cracking to brittle fracture where the ozone greatly reduced the energy for crack growth from that for tearing in the absence of ozone. Similarly, Braden and Gent<sup>3,10,11</sup> concluded that the appropriate criterion for ozone-induced crack growth was the elastic stored energy. This concept has been extended by Simonson et al.<sup>7</sup> in a correlation of bond rupture during ozone cracking with the strain-energy release rate. Through the use of electron paramagnetic resonance, an empirical relationship was established between the free radicals generated, i.e., bonds ruptured, by the combined effects of stress and ozone and the stretch ratio  $\lambda$ . This result was combined with rubber elasticity in a Griffith-type formulation. For the various tensile loadings of the *cis*-polybutadiene rubber studied, a very good correlation was found between the Griffith formulation and experiment.<sup>15</sup> Assuming each bond ruptured results in  $0.5 \times 10^{-14}$  sq cm of new fracture surface,<sup>12</sup>  $\gamma$  was found to be equal to  $\sim 425$  ergs/cm<sup>2</sup>. A pleasing aspect of the study was the very small variation in  $\gamma$  that was required to fit all the experimental data. All the stress relaxation, creep, and cyclic strain tests could be fit by the above value plus or minus 15%, a very small variation when compared with most fracture studies. It should be noted that this value of  $\gamma$  is somewhat higher than determined from observations of macroscopic cracks ( $\gamma = 50$  to 120 ergs/cm<sup>2</sup>) by Braden and Gent<sup>10,11</sup> and Andrews.<sup>13,14</sup> This difference was attributed to the assumption of the area created per bond rupture. It was concluded that cracks are apparently able to seek out paths where fewer chains per sq cm of surface need be broken than were the crack to proceed through an average section of the material. In order to extend these previous investigations to loadings other than tension, studies of torsional loading of rubber in ozone environment were performed and will now be summarized.

### EXPERIMENTAL AND ANALYTICAL PROCEDURES AND RESULTS

Circular cross-sectional rods (0.25 in. diameter  $\times$  1.5 in. length) of styrene-butadiene (SBR 1710) (provided by A. G. Veith of B. F. Goodrich, Akron, Ohio) were placed in a quartz environmental chamber within the cavity of the Varian E-3 spectrometer. EPR is a form of microwave absorption in which the presence of unpaired electrons (free radicals) can be

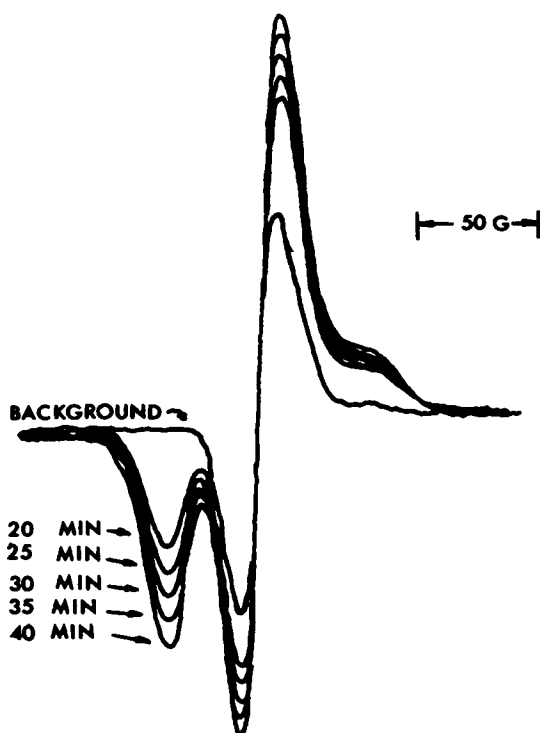


Fig. 1. Typical EPR spectra resulting from torsional loading of rubber in ozone after indicated periods of time.

detected if a sufficient number (threshold  $\cong 10^{12}$  free radicals in the cavity) is present. Experimentally, such free radicals were found in ozone-degraded styrene-butadiene (SBR 1710) as well as natural rubber (B. F. Goodrich), *cis*-polybutadiene (B. F. Goodrich) and every other rubber susceptible to ozone attack that was studied. During the cracking the ozone concentration was maintained at 2.8 mg/l. (the largest concentration the current generator could reliably maintain). The gas flow rate was thought sufficient to maintain an equilibrium concentration of near this value in the vicinity of the sample surface. Changes in the EPR spectra of SBR 1710 were monitored every 5 min during ozone attack. A typical family of spectra obtained in this manner is shown in Figure 1.

The tests conducted were for constant angle of twist (shear strain), with the resulting torque relaxation monitored as a function of time in the ozone environment. The rubbers studied had residual EPR signals that were very stable with time. Spectra taken before and after loading of the sample in the absence of ozone showed no noticeable change in this residual spectrum. However, when ozone was introduced, a change in the spectrum was observed within a few seconds (provided the twist angle was above a threshold twist of approximately  $15^\circ$ ).

Above this threshold, the rate of bond rupture increases rather rapidly, and for twist angles between approximately  $20^\circ$  and  $160^\circ$  it was empirically found that it could quite accurately be expressed by

$$\frac{dN}{dt} = (0.4\theta - 0.53) \times 10^{12} \frac{\text{spins}}{\text{min}} \quad (4)$$

where  $dN/dt$  is the rate of free-radical production and  $\theta$  is the angle of twist, expressed in degrees. This was for an ozone concentration of 2.8 mg/l. Earlier work<sup>1</sup> has demonstrated that the rate of bond rupture in tension is directly proportional to the ozone concentration. While it was not experimentally confirmed, the authors would suspect the same to hold true for torsion.

To keep the sample aligned in the cavity, each sample had less than 30 g/cm<sup>2</sup> of constant tensile longitudinal stress applied along with the induced torsional stress. This longitudinal stress is small in comparison to the applied torsional stresses and was neglected in the analysis. The torsional stresses produced stress concentrations at surface flaws in the specimens, which then acted as nucleation sites for cracks.<sup>8,9</sup> The resulting cracks were held "open" by the stress field during ozone attack on the unsaturated carbon bonds and the generation of free radicals with their associated EPR spectra. The experimentally obtained EPR spectra were numerically integrated twice, resulting in a measurement of the instantaneous number of free radicals present. Free radicals are inherently unstable entities and can vanish by combining with each other and/or reacting with impurities. The decay rate of the free radicals was carefully studied and used to calculate the net or total number of free radicals produced from the number measured. The total radical population as a function of time for different applied twist angles is shown by the solid lines in Figure 2. The slopes of these lines are shown in Figure 3 (these are also the basis of eq. (4) above).

The accumulation of ruptured bonds with time resulted in a deterioration of the modulus and strength, and eventually, if loading and ozone conditions were maintained, wholesale macroscopic fracture of the sample would occur. The resulting torque relaxation during constant angle of twist tests was continually recorded. The relaxation curves were used to construct torque-angle of twist plots as shown in Figure 4. Associated with the torque relaxation is, of course, a change in stored strain energy. The torsional strain energy can be approximated by the area under the torque-versus-twist angle curves of Figure 4. Calculation of the torsional strain energy as a function of time might be accomplished by numerically calculating the area under the stress-strain curves at different exposure times, i.e., the area between the curves in Figure 4, or an empirical relationship between torque, twist angle, and time under stress and ozone might be developed. Both approaches were used in the study, but here we will concentrate largely on the latter. The following experimental observations were made on samples:

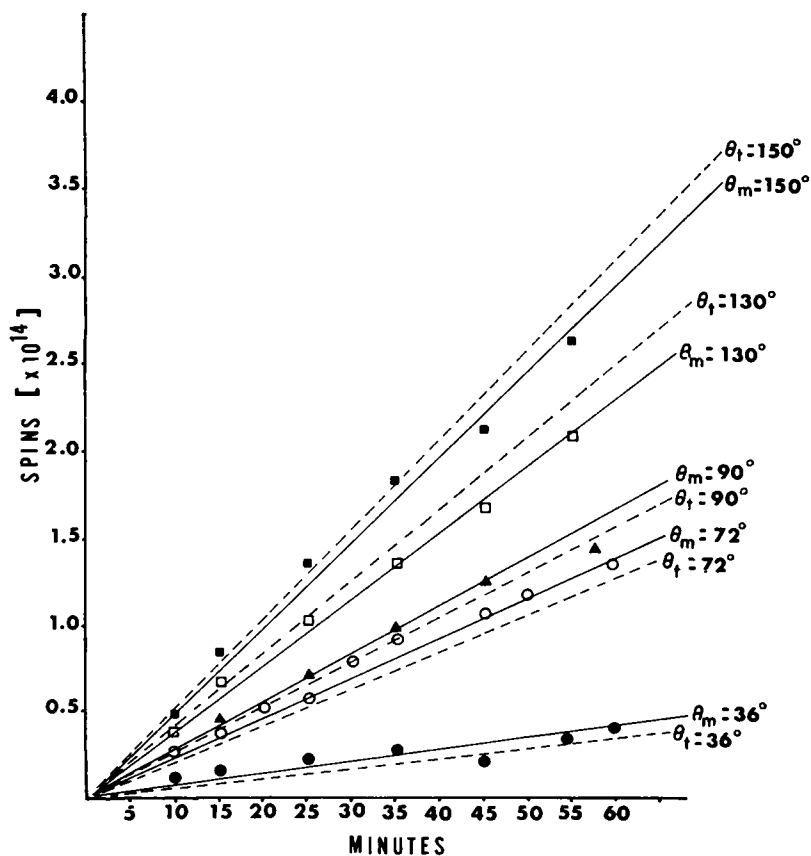


Fig. 2. Free radical concentration vs. time for various twist angles in an ozone concentration of 2.8 mg/l. Solid lines are experimental results, and dashed lines are the empirical representation of the data, eq. (4).

1. An approximately linear shear stress-strain (more properly torque-angle of twist) behavior was observed for the initial samples and those degraded under stress in ozone for various times over a range of twist angles between 0 and 180°.

2. The decrease in torque with time (relaxation) was found to be very nearly linear until the cracks became relatively deep. For the twist angles and ozone concentration considered here, this was for a minimum of 1 hr. As a consequence, the torque  $T$  can be expressed as

$$T = \beta\theta [1 - \alpha t]$$

where  $\theta$  is the twist angle per unit sample length,  $t$  is the time, and  $\beta$  and  $\alpha$  are constants for a given material, sample size, and ozone concentration. For the styrene-butadiene samples and the conditions reported here,  $\beta$  and  $\alpha$  were determined from curve fitting to be 13.5 g-cm/radian and 0.151/

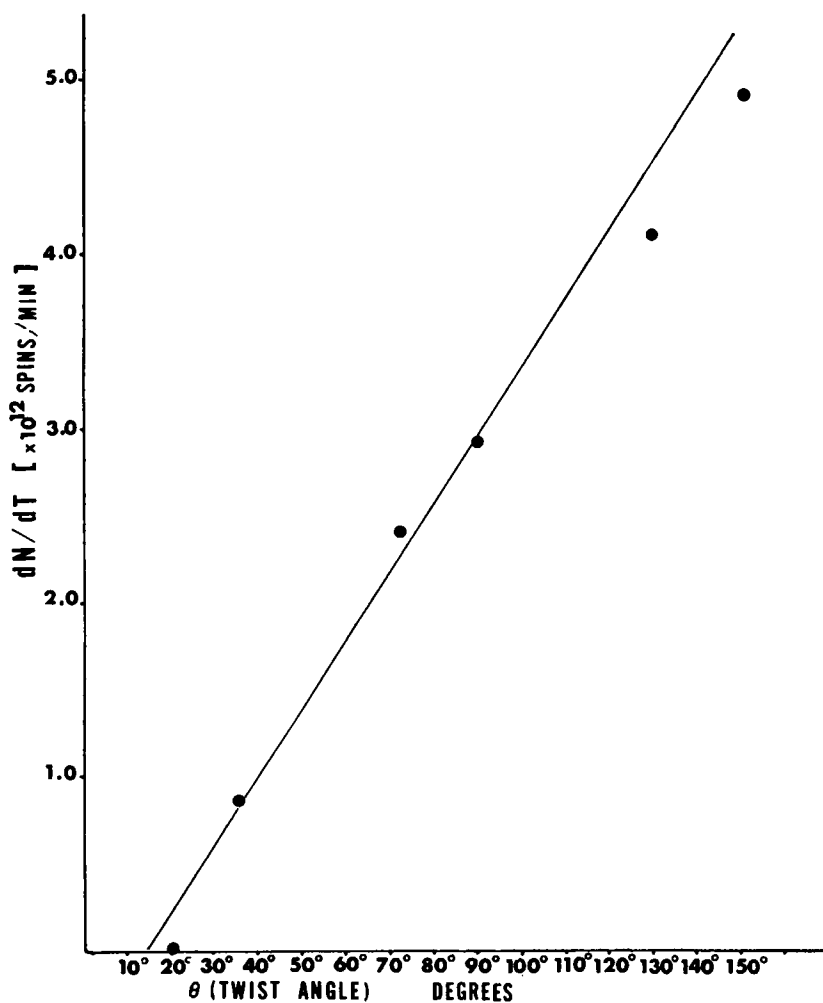


Fig. 3. Rate of free-radical production vs. twist angle in an ozone concentration of 2.8 mg/l.

min, respectively. The experimental scatter in both these parameters was less than 10%.

The stress relaxation, bond rupture, and other data were used in a Griffith-type energy balance. To account for the time dependence of the bond rupture, the general power equation<sup>5</sup> was used,

$$\dot{I} = \dot{F} + 2D + \dot{K} + \dot{\Gamma} \quad (6)$$

where  $\dot{I}$  is the rate of input work,  $\dot{F}$  is the rate of storing free energy,  $2D$  is the dissipation,  $\dot{K}$  is the rate of conversion to kinetic energy, and  $\dot{\Gamma}$  is the

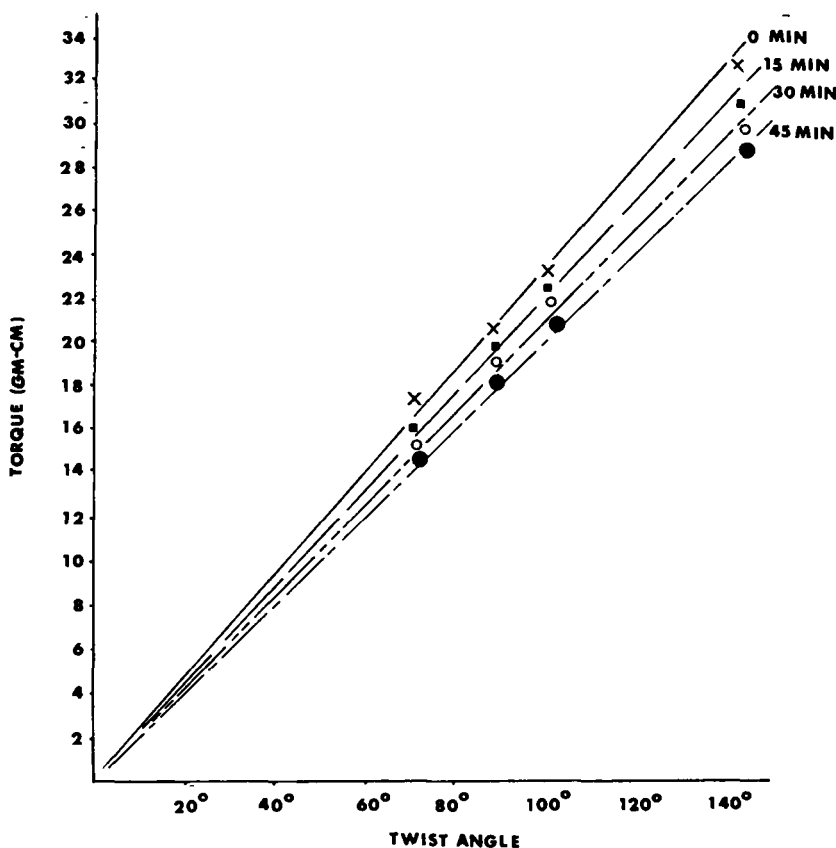


Fig. 4. Torque vs. angle of twist for samples subsequent to exposure to stress-ozone attack at indicated angle of twist.

rate at which energy is expended in crack formation. Using accepted notation,<sup>5,16</sup>

$$\dot{\Gamma} = \frac{d}{dt} \int_A \gamma(t) dA \tag{7}$$

$$2D + \dot{F} = \frac{d}{dt} \int_V \int_0^t \tau_{ij} \dot{\epsilon}_{ij} dt dV \quad i, j = 1, 2, 3 \tag{8}$$

where  $\tau$ ,  $\epsilon$ ,  $V$ , and  $A$  represent the stress, strain, volume, and fracture crack area, respectively.

For these constant angle of twist ("constant strain") tests, eq. (6) was simplified by the following approximations and assumptions:

1. Since the loaded boundaries do not move after achieving the constant step strain, the rate of input work,  $\dot{I}$ , would be zero.
2. Because the rate of crack growth was small, the kinetic energy  $\dot{K}$  was neglected.

With these approximations,

$$\dot{\Gamma} = -(\dot{F} + 2D). \quad (9)$$

The EPR spectrometer provides a means by which the number of bonds severed during ozone attack can be determined. These broken bonds accumulate to form the new fracture or crack area. This area has been reported to be approximately  $10^{-15}$  to  $10^{-14}$  cm<sup>2</sup>.<sup>12,15</sup> One might, therefore, convert the specific fracture energy  $\Gamma$  in eq. (7) to the average energy to rupture a bond by dividing by this area. The rate at which energy is "used" in the fracture process might, therefore, be expressed alternately as

$$\frac{d\Gamma}{dt} = \gamma_n \frac{dN}{dt} \quad (10a)$$

or

$$\frac{d\Gamma}{dt} = \gamma \frac{dA}{dt} \quad (10b)$$

where  $A$  is the fracture area and  $N$  is the number of bonds ruptured. Returning to eq. (9) and substituting the empirical results for the change in strain energy  $F$  and making use of eq. (10) for the surface free energy  $\Gamma$ , an ad hoc "Griffith"-type analysis can be accomplished directly. That is, the energy required to rupture a bond,  $\gamma_n$ , times the number of bonds ruptured determined from the solid lines of Figure 2 was equated to the released energy determined from Figure 4. If the proposed energy model is valid and the fracture energy  $\gamma_n$  is known, a knowledge of the stress relaxation allows calculation of the bond rupture rate (or vice versa). Alternately, these other two parameters can be used to calculate  $\gamma_n$ , and the consistency of  $\gamma_n$  would provide a check of the validity of the model. Empirically it was found that a  $\gamma_n$  of  $4.8 \times 10^{-12}$  ergs/spin ( $\pm 15\%$ ) satisfactorily fit the data. The dashed lines in Figure 2 are obtained from the relaxation data assuming  $4.8 \times 10^{-12}$  ergs/spin. This compares very favorably with the value of  $\gamma_n = 5 \times 10^{-12}$  ergs/spin obtained from studies on uniaxially loaded (creep, relaxation, cyclic) acrylonitrile-butadiene rubber (B. F. Goodrich Hycar 1043). (Hycar 1043 was not available to the authors in the correct form for the torsion and, hence, a direct comparison was unfortunately not possible.) These energies compare favorably with the dissociation energy of a carbon-carbon double bond normally assumed to be of the order of  $10 \times 10^{-12}$  ergs/bond.

It is not as yet clear whether one or two free radicals are formed per chain scission. Therefore, it cannot be resolved whether the ozone supplies (or otherwise lowers the energy) approximately 50% or only a small amount of the energy required to rupture the bond. In either case, the ozone does tend to initiate brittle fracture in the rubber.

An interesting observation during the investigation was the type and number of cracks produced. It has previously been noted<sup>10,15</sup> that on



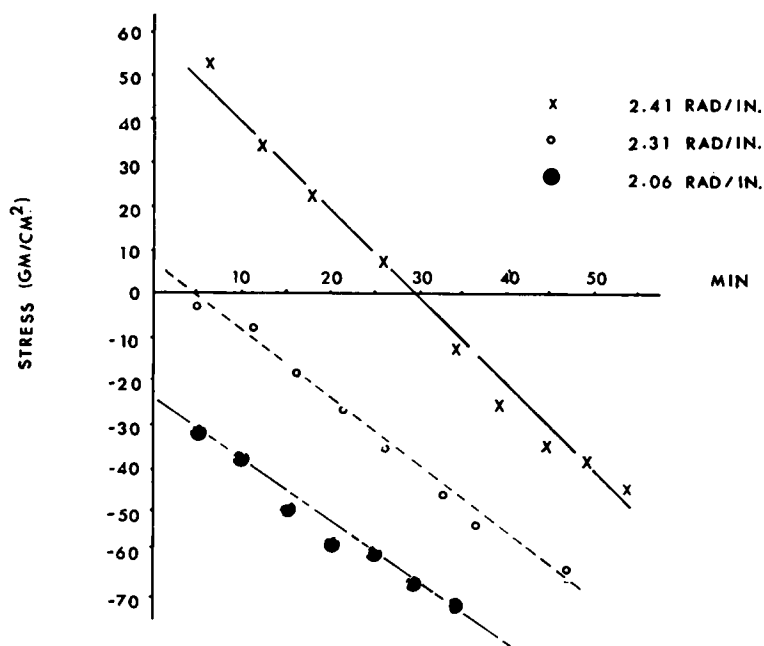


Fig. 5. Axial stress vs. time for samples loaded in combined tension-torsion in ozone.

tensile-loaded samples at low stress levels few cracks form, and these progress deep into the sample, while at progressively higher stress levels the number of cracks increased, and the depth of the crack penetration into the sample decreased. This has been attributed to mutual interference of the cracks with one another. Similar observations were made on the torsionally loaded samples. In tensile specimens most of the cracks are observed to form perpendicular to the axis of loading.<sup>15</sup> It was observed that for torsional loading the cracks were oriented along an approximately 45° plane to the longitudinal axis or once again perpendicular to the maximum tensile stress.

As a final note, a limited number of tests were conducted under combined axial and torsional loading. Figure 5 shows a plot of the longitudinal stress in these samples as a function of time for three different twist angles. As in the other tests the ozone concentration was maintained at 2.8 mg/l. (flow of ozone was sufficient to maintain equilibrium). For small torsional loads the coupling between the axial loading and the torsional load described by Rivlin<sup>17</sup> was apparent. Once again, as near as could be determined experimentally, the cracks produced were oriented perpendicular to the direction of maximum principal stress. The spectra produced were similar to those for pure torsion, with the usual slight variations in peak heights characteristic of changes in orientation of the chain segment associated with the radical in the microwave cavity of the EPR spectrometer. Instrumentation problems associated with the torsional transducer during large

changes in the axial load from tension through compression has as yet precluded making the Griffith energy balance for these combined loading tests.

## CONCLUSIONS

EPR techniques facilitate the monitoring of the production of free radicals resulting from polymeric bond rupture simultaneous with measurement of axial and torsional loads applied to a rubber sample in an ozone environment. A good correlation between atomic phenomena and macroscopic fracture mechanics was found. With a Griffith-type energy balance, it was determined that bonds rupture (cracks propagate) only if, and at rates dependent on, sufficient strain energy is present in the sample.

The observations reported here for torsional studies supplement those on tension reported earlier in lending credence to Griffith-type approaches to ozone attack in rubber. One might conjecture that similar approaches should be applicable to other types of environmental cracking in polymers.

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