

Oxidative Aging of Natural Rubber Vulcanizates. Part I. The Scission of Peroxide Vulcanizates

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Synopsis

A new method has been developed for measuring the number of molecules of oxygen required (ϵ) to cause a main chain scission in peroxide vulcanizates of natural rubber. This method is based on experimentally derived relationships and is not dependent on statistical theories of rubber elasticity. The value ϵ is only slightly temperature dependent, ranging from 28 at 65°C. to 22 at 100°C. The effects of several types of antioxidant have been examined, in all cases ϵ was greatly reduced. The effect of antioxidant 2246 has been studied in more detail and the results indicate that there is a high probability of scission occurring at the termination step in the oxidation chain.

During the oxidation of natural rubber, the polyisoprene chain undergoes scission and numerous attempts have been made to explain the mechanism of this process.¹⁻⁴ An essential concept in such explanations is the number of molecules of oxygen absorbed per scission event (ϵ).*

For unvulcanized rubber such measurements are, in principle, quite straightforward. All that is required is a correlation between oxygen absorbed and the change in molecular weight, since for 1 g. of polymer, if ${}_0M_n$ and ${}_1M_n$ are the initial and final number-average molecular weights then the number of cuts q (expressed as moles of isoprene units cut) is given by

$$q = (1/{}_1M_n) - (1/{}_0M_n) \quad (1)$$

The values of M_n are usually obtained from viscosity data and several workers^{1,3,5} have used this method.

In a vulcanizate this method is not possible and recourse has to be made to less rigid methods. Up to the present most of these methods have been based more or less on the statistical theories of rubber elasticity, and have not been capable of direct experimental verification. Owing to these deficiencies the following method has been developed.

* Some confusion has arisen in the past from the use of the term scission efficiency which, although usually defined as number of cuts per molecule of oxygen absorbed, has also been defined as the reciprocal of this.^{5,6} To avoid further confusion the term scission efficiency is not used at all.

EXPERIMENTAL

Vulcanizates were prepared from acetone-extracted purified natural rubber (United States Rubber Co.) and vulcanized with 2% recrystallized dicumyl peroxide for 10 min. at 100°C. followed by 50 min. at 150°C. A chromium-plated mold was used producing sheets $10 \times 10 \times 0.03$ cm. Under these conditions there was negligible anisotropy in the vulcanized sheets. These were extracted for 48 hr. in cold methanol/chloroform/acetone azeotrope, in a Soxhlet apparatus, and stored *in vacuo*. Antioxidants, after recrystallization, were swollen overnight from ethyl acetate solution. Samples were oxidized under oxygen at atmospheric pressure in a simple apparatus consisting of a reaction tube immersed in a thermostated oil bath connected by capillary tubing to a simple gas buret. The rubber sheets (usually 10×5 cm.) were placed on smoothed aluminum foil which was then inserted into 1-in. diameter specimen tubes before placing in the reaction vessel; this prevented the latter from becoming contaminated with sticky rubber in the event of excessive degradation. Although oxygen has access from only one side of the sheet, at temperatures of 100°C. and below there was no evidence of diffusion control nor of any effect of the aluminum itself.

Stress-strain measurements were carried out on the machine developed in these laboratories by Greensmith⁷ using strips 10×0.5 cm., which were stamped out from the sheets with a special cutter made from razor blades.⁸ The C_1 values were obtained by plotting stress/ $[\alpha - (1/\alpha^2)]$ against $1/\alpha$ and extrapolating to $1/\alpha = 0$.

Results and Discussion

In simple extension natural rubber vulcanizates obey the Mooney-Rivlin relationship⁹

$$f = 2A_0[C_1 + (C_2/\alpha)] [\alpha - (1/\alpha^2)] \quad (2)$$

where A_0 is the initial cross-sectional area, α the extension ratio, f the stress, and C_1 and C_2 are constants depending on the vulcanizate. Mullins¹⁰ has shown experimentally that C_1 is related to the number-average molecular weight M_n of the rubber chains prior to crosslinking and the number-average molecular weight between crosslinks M_c by:

$$C_1 = [(1/2) \rho RT/M_c] + 0.78 \times 10^6 [1 - (2.3 M_c/M_n)] \text{ dyne/cm.}^2 \quad (3)$$

where ρ is the density, R the gas constant, and T the absolute temperature.

If during aging, scission occurs only in the main chains M_c will remain constant. Under these conditions changes in M_n will be reflected as changes in C_1 and measurements of the latter before and after aging will enable the number of cuts to be calculated. Remembering that $q = [O_2]/\epsilon$ eq. (3) becomes

$$C_1 = C_1^0 - \frac{[O_2]}{\epsilon} \left(1.13 \rho RT + \frac{1.79 \times 10^6}{M_c} \right) \quad (4)$$

where C_1^0 is the initial value of C_1 and $[O_2]$ is the number of moles of oxygen absorbed per gram of rubber. This equation indicates that provided ϵ remains constant during ageing and no net change in crosslink density occurs, then a plot of C_1 vs. oxygen absorbed should be linear with a slope inversely proportional to ϵ .

Figure 1 shows plots of C_1 vs. wt.-% of oxygen absorbed for various temperatures. Although these plots show excellent linearity, the initial C_1 does not always lie on this straight line, the reason for this is not understood.

The initial number-average molecular weights of the rubbers were calculated from the intrinsic viscosities in toluene using the calibration of Angier et al.¹¹ [this relationship was used rather than the more recent relationship of Bristow¹² since the earlier one was used by Mullins in

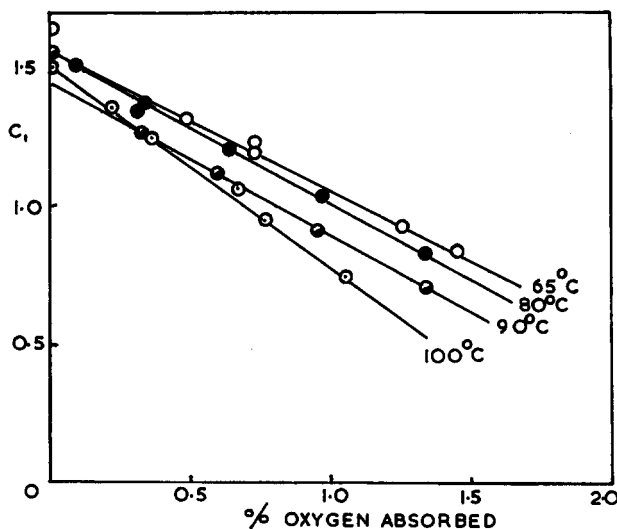


Fig. 1. C_1 vs. wt.-% of oxygen absorbed.

deriving eq. (3)]. Using the measured initial value of C_1 and the value of \bar{M}_n obtained as above, the value of M_c was calculated from eq. (3). Insertion of the value of M_c obtained into eq. (4) enables values of ϵ to be calculated from the slopes in Figure 1. If this technique is valid the value of ϵ obtained should be independent of the degree of crosslinking of the vulcanizate. Measurements on a vulcanizate with $C_1 = 3.4$ where the degree of crosslinking is approximately twice that of the vulcanizates in Figure 1 gives a linear C_1 /oxygen plot and, within experimental error, the same value of ϵ . This result would seem to rule out the possibility that the linearity of the plots arises from a fortuitous combination of changes in M_c and ϵ during aging.

Table I summarizes the data obtained at various temperatures.

TABLE I
Effect of Temperature on ϵ

Crosslinks (moles/g. $\times 10^4$)	Temperature, °C.	ϵ
4.7	65	28.0
4.7	80	24.2
4.6	90	23.3
4.1	100	22.0
8.0	80	24.8

The probable error in these results is ± 0.5 . Figure 2 shows a plot of ϵ vs. $1/T$ giving an activation energy of ca. 2 kcal./mole which is the difference between the activation energies of scission and oxidation.

Comparison with Other Workers

These values of ϵ agree well with the findings of Barnard et al.¹³ who used a radio-tracer technique to count scission products and for end group analysis, but differ from the results of other published work. Thus using stress relaxation methods Tobolsky and co-workers² have found for peroxide vulcanizate values of ϵ of 15.5 at 50°C., 5.0 at 75°C., 2.0, at 100°C., and 1.0 at 120°C. Other workers^{14,15} have used vulcanizates containing sulfur crosslinks and their data cannot be compared. Bevilacqua³ has studied the scission of rubber in latex and obtained figures of 27 at 70°C.,

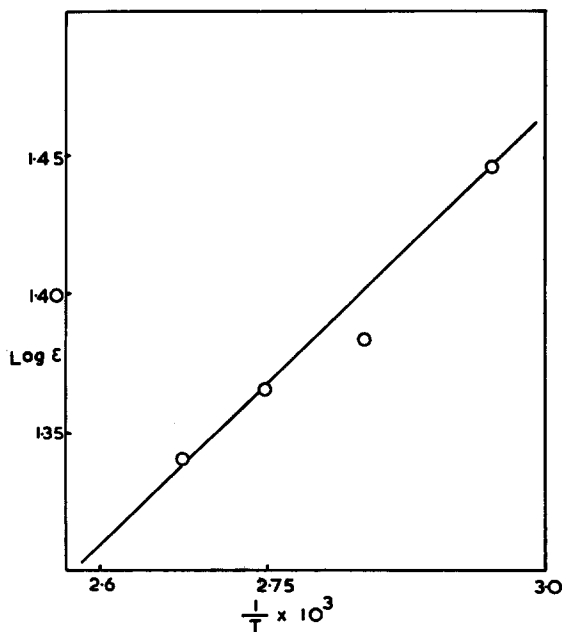


Fig. 2. Temperature variation of ϵ .

19 at 90°C., and 16 at 110°C. on using intrinsic viscosities to determine the extent of scission. He has also carried out similar measurements using rubber films produced from latex and obtained values of 10.5–11.4 at 130°C., 6.2 at 140°C., and 6.3 at 150°C. A later series of experiments gave an average figure of about 12 at 140°C., whereas measurements on a peroxide vulcanizate using sol gel analysis gave a figure of ca. 20 at 120°C.

With the exception of Barnard none of these workers used highly purified rubber, and as will be shown later the value of ϵ can depend markedly on the presence of small amounts of antioxidants. The values of Tobolsky are too low by a factor of at least 2 due to the neglect of entanglements¹⁶ in the stress-relaxation theory but the reason for the large temperature coefficient of ϵ is not certain. It is possible that the oxidative chain lengths were becoming very short at the higher temperatures when the scission at termination would become predominant (see pp. 1294, 1295). Bevilacqua's data suggest a greater temperature dependence of ϵ , but again latex contains many impurities which could affect ϵ and the data on dried films is too variable to reach any firm conclusion. It should be noted that the data of Morris¹ give an activation energy of approximately 3 kcal. for gutta-percha in solution.*

Effect of Antioxidants

A number of workers^{1,3,14,15} have investigated the effect of antioxidants and other additives on scission efficiency. Only Morris¹ used well-purified rubber and some workers^{14,15} used sulfur vulcanizates, the scission

TABLE II
Effect of Antioxidant on Rate of Oxidation and ϵ *

Antioxidant	Time to 0.39% w/w oxidation, hr.	ϵ
None	1	22
Agerite A.K. (2,2,4-trimethyl 1,2-dihydroquinoline)	5	5.0
2246 (2,2'-methylenebis- 4-methyl- <i>tert</i> -butyl phenol)	120	4.9
CdDBC (cadmium dibutyl dithiocarbamate)	167	14.4
Nonox ZA (<i>N</i> -phenyl <i>N'</i> -isopropyl diphenylenediamine)	410	4 → 11.9

* All antioxidants swollen into vulcanizates from 0.01M solutions in ethyl acetate.

behavior of which is likely to be more complex than carbon-carbon cross-linked vulcanizates. In this investigation the effect of a number of different types of antioxidant has been examined (Table II). All the anti-

* Since ϵ depends on the sum of two terms [(eq. (5))] each of which may be temperature dependent, the temperature dependence of ϵ will not in general be representable by a simple Arrhenius plot.

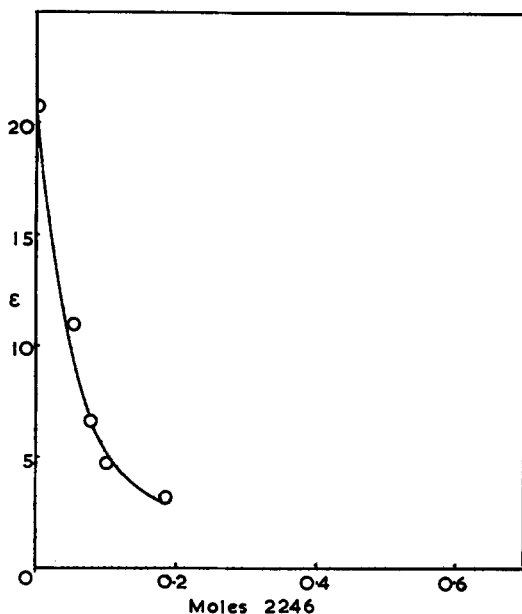


Fig. 3. Effect of 2246 concentration on ϵ at 100°C.

oxidants decrease ϵ markedly, and with the exception of Nonox ZA all give linear C_1 vs. oxygen uptake plots, suggesting that there is little if any crosslinking. Thus all these antioxidants, although reducing the rate of oxidation and consequent extent of degradation, considerably increase the relative ease of scission. This result is somewhat different from that obtained from other workers who found little or no change in ϵ , but in these cases the effect of additive on oxidation rate was small compared with those reported here. This suggests that their materials contained a considerable level of antioxidant initially, in the case of Morris¹ the additive was only a weak inhibitor.

The effect of antioxidants on ϵ was studied in greater detail using 2246, and Figure 3 shows how ϵ varies with antioxidant concentration. In a recent publication one of us⁵ has shown how, during the oxidation of natural rubber in solution, scission occurs during both the propagation and termination steps of the oxidative chain reaction. If the probabilities of scission at the propagation, termination, and initiation steps are W_p , W_t , and W_i then for a kinetic chain length of λ we can show⁵ that

$$\frac{1}{\epsilon} = W_p + \frac{W_t}{\lambda} + \frac{W_i}{\lambda} \quad (5)$$

The probability of scission on initiation W_i is very low since ϵ is unaffected by mode of initiation,^{1,5} nor is there any marked scission on heating oxidised rubber in the absence of oxygen^{1,17} thus (5) becomes

$$1/\epsilon = W_p + (W_t/\lambda) \quad (6)$$

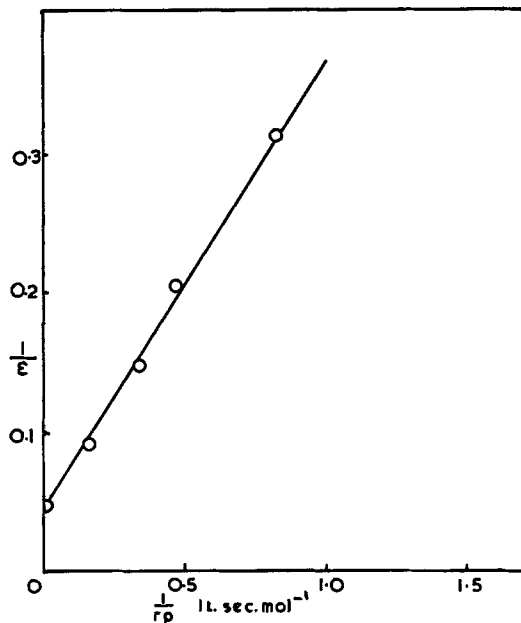


Fig. 4. Plot showing linear dependence of $1/\epsilon$ with the reciprocal of oxidation rate.

This equation implies that as λ is decreased, which will occur as the antioxidant level is increased, the contribution of scission at termination will increase. Thus, provided W_i is sufficiently greater than W_p , scission at termination will predominate at the short chain lengths which prevail at the antioxidant levels usually used, and ϵ will be considerably reduced. This dependence of ϵ on chain length is further demonstrated if we replace λ in eq. (5) by r_p/r_i the ratio of the propagation and initiation rates, i.e.,

$$1/\epsilon = W_p + W_i (r_i/r_p) \quad (7)$$

Figure 4 shows the data of Figure 3 plotted as $1/\epsilon$ vs. $1/r_p$.

Since virtually all the termination steps involve antioxidant W_i remains constant, the linearity of the plot indicates that the rate of initiation remains constant also. This lack of dependence of rate of initiation with 2246 is surprising since Shelton and Cox¹⁸ have postulated that phenolic antioxidants can initiate oxidation, however we will not discuss the question further at this stage.

The data of Figure 4 enables us to obtain W_p and also an estimate of W_i . The intercept of Figure 4 at infinite oxidation rate is of course W_p and is indistinguishable from $1/\epsilon$ for the uninhibited material. Thus $W_p \approx 0.045$ and scission at termination is unimportant for uninhibited rubber under these conditions.

The minimum value of ϵ observed is ca. 3.3, thus from eq. (6) we have

$$W_i/\lambda < 1/3$$

Since the maximum value of W_t and the minimum likely value of λ are both unity we have

$$1 > W_t > 1/3 \text{ and } 1 < \lambda < 3$$

Thus at 100°C. the probability of scission occurring during termination with 2246 is at least 7 times as likely as scission during a propagation step, in other words at least 88% of the scission events occur during termination.

The actual mechanism of scission at termination is not known at present and until data on product analyses is available any discussion would merely be speculation.

To summarize, it is shown that in the absence of inhibitors the number of molecules of oxygen absorbed per main chain scission is only moderately affected by temperature. Inhibitors reduce this number quite considerably by shortening the kinetic chain length and thus increasing the importance of the highly probable scission at termination.

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Résumé

Une nouvelle méthode a été développée pour mesurer le nombre de molécules d'oxygène indispensables pour causer une scission de la chaîne principale dans la vulcanisation peroxydée du caoutchouc naturel. Cette méthode est basée sur les relations dérivées expérimentalement et n'est pas dépendante des théories statistiques de l'élasticité caoutchouteuse. ϵ varie faiblement avec la température passant de 28 à 65°C à 22 à 100°C. Les effets des divers types d'antioxydants ont été examinés et dans tous

les cas ϵ est fortement réduit. L'effet de l'antioxydant 2246 a été étudié plus en détail et les résultats indiquent qu'il a une forte probabilité de rupture se passant au cours de l'étape de terminaison de la chaîne d'oxydation.

Zusammenfassung

Eine neue Methode zur Messung der Anzahl (ϵ) der zur Herbeiführung einer Hauptkettenspaltung in Naturkautschuk-Peroxydvulkanisaten erforderlichen Sauerstoffmoleküle wurde entwickelt. Diese Methode beruht auf experimentell abgeleiteten Beziehungen und ist nicht von der statistischen Theorie der Kautschukelastizität abhängig zeigt nur eine geringe Temperaturabhängigkeit und beträgt 28 bei 65°C. und 22 bei 100°C. Der Einfluss mehrerer Antioxydanstypen wurde untersucht; in allen Fällen wurde ϵ stark herabgesetzt. Eingehender wurde die Wirkung des Antioxydants 2246 untersucht und die Ergebnisse zeigen, dass beim Abbruchschritt in der Oxydationskettenreaktion eine hohe Spaltungswahrscheinlichkeit besteht.

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