

Oxidative Stress Relaxation of Natural Rubber Vulcanizates at High Strains

C. L. M. BELL, *Natural Rubber Producers' Research Association, Welwyn
Garden City, Herts., England*

Synopsis

The effect of high strain on the oxidative stress relaxation of several natural rubber vulcanizates has been investigated. In the case of peroxide and CBS accelerated vulcanizates, the rate of stress relaxation increases with increasing strain, and this increase appears to be due to an increase in the rate of oxidation of the network. TMTD and MBT vulcanizates showed marked premature failure at high strains and no oxidative stress relaxation measurement could be made. It was found that the tensile strength of a TMTD vulcanizate was at least 20% higher in vacuum than in oxygen, due, it is believed, to stress-induced oxidative degradation at the tip of surface flaws in the rubber.

When a piece of rubber containing a small cut is repeatedly strained, the cut will not grow unless the strain energy exceeds a certain value. It has been observed¹ that this critical strain energy is dependent on oxygen pressure, being higher at low pressures. This suggests that some of the bonds in the rubber molecule are weakened in the presence of oxygen, in spite of observations to the contrary²⁻⁶ and that the rate of oxidative scission of the rubber chains might be stress-dependent.

Stress dependence of chemical reactions is well known in metal corrosion,⁷ in ozone attack on rubber,⁸ and in mastication-induced polymerizations in rubber.⁹ This investigation examines the stress dependence of the oxidative breakdown of vulcanized rubbers by stress relaxation, since this is a very sensitive measure of network destruction.

EXPERIMENTAL

In order to undertake stress-relaxation studies at comparatively high strains up to 500%, a completely new type of apparatus has been developed. This is to be described in detail elsewhere, but briefly the sample, in the form of a ring cut from 0.3-mm. thick sheet, is stretched between polytetrafluoroethylene pulleys by means of a small induction motor and the stress on the strip measured by a proof ring and transducer. The whole apparatus can be evacuated, and is immersed in a silicone oil bath thermostat.

The vulcanizates were all prepared from an acetone-extracted highly purified natural rubber (United States Rubber Co.) and were extracted after cure (with hot acetone-chloroform-methanol azeotrope) for 24 hr. and stored in sealed tubes *in vacuo* at -20°C . until required. The sheets ($10 \times 10 \times 0.03$ cm.) were cured in a chromium-plated mold with the minimum of milling before cure. Mix details are given in Table I for peroxide, *N*-cyclohexylbenzothiazole 2-sulfenamide (CBS), tetramethylthiuram disulfide (TMTD), and mercaptobenzthiazole (MBT) vulcanizates.

TABLE I

	Peroxide vulcani- zates	CBS accel- erated sulfur vulcani- zates	TMTD	vulcani- zates	MBT vulcan- izate (TMT type)
Acetone-extracted purified NR, parts	100	100	100	100	100
Recrystallized dicumyl per- oxide, phr	5	—	—	—	—
CBS, phr	—	2.37	—	—	—
Sulfur, phr	—	1.5	—	—	—
TMTD, phr	—	—	4.0	4.0	—
Sulfasan R, phr	—	—	—	—	1.7
MBT, phr	—	—	—	—	1.0
Zinc oxide, phr	—	5.0	5.0	5.0	2.0
Lauric acid, phr	—	10	—	1.5	1.0
Cure temperature, $^{\circ}\text{C}$.	130	140	140	140	140
Cure time, min.	40-100	20	120	420	240

The ring samples used in the relaxometer were stamped out from the extracted vulcanized sheets by using a special cutter; these were placed on the polytetrafluorethylene rollers of the relaxometer which, after being placed in the thermostat, was filled with nitrogen and allowed to attain thermal equilibrium. After equilibrium had been reached (the transducer, being temperature-sensitive, readily indicated this), the apparatus was evacuated and the samples stretched. The sample was maintained stretched *in vacuo* until the observed rate of "physical" relaxation had become negligible compared with the expected rate in the presence of oxygen. The time taken for this to occur varied with the type of vulcanizate and the extension ratio used and could be as long as 4 hr. at 65°C . After this physical relaxation had decreased to a negligible extent, oxygen at 760 mm. was admitted. (Due to the high thermal capacity of the apparatus, it was not found necessary to pre-heat the gas.) Since the proof ring and transducer give a linear force-current relationship, the ratio of chart recorder deflection at time t and zero is equal to ratio of stresses (f/f_0).

RESULTS

It is convenient to consider the various vulcanizates separately.

Peroxide Vulcanizates

The peroxide vulcanizates showed typical autocatalytic f/f_0 versus time plots¹⁰ which were somewhat irreproducible. This irreproducibility can be avoided by plotting the rate of degradation $d(f/f_0)/dt$ against extent of degradation $1 - (f/f_0)$ when for a given extension ratio λ straight lines of constant slope k are obtained. This linearity of rate with extent is a feature of autoxidations¹¹ in which similar irreproducibility in f/f_0 versus time plots is often observed. The intercepts of the $d(f/f_0)/dt$ versus $1 - (f/f_0)$ curves which correspond to the initial rates r of degradation, although reasonably constant with rings cut from a single sheet, varied from sheet to sheet. This is believed to be due to variations in the residual hydroperoxide content of the sheets. Tables II and III summarize the stress-relaxation data obtained at 65°C. on peroxide vulcanizates. Figure 1 shows typical rate-extent plots and Figure 2 shows mean f/f_0 versus time plots.

The data for extensions above $\lambda = 3.66$ were very difficult to obtain, owing to the ease with which the samples broke.

TABLE II
Effect of Extension Ratio λ on Slope k of $d(f/f_0)/dt$ vs.
 $1 - (f/f_0)$ for Extracted Peroxide Vulcanizates

λ	$k \times 10^5$, sec. ⁻¹	Standard deviation $\times 10^5$, sec. ⁻¹	No. of results
1.59	5.3	1.1	13
3.66	8.9	2.0	7
4.35	14.0	—	3
5.05	25	—	2

TABLE III
Effect of Elastic Constant C_1 and Extension Ratio on the
Initial Rate r of Degradation of Peroxide Networks

C_1^*	Initial rate $\times 10^6$, sec. ⁻¹		r ($\lambda = 3.66$)
	$\lambda = 1.59$	$\lambda = 3.66$	r ($\lambda = 1.59$)
2.25	1.4	2.8	2.0
1.65	3.3	5.6	1.7
1.52	5.0	7.0	1.4
1.50	1.7	2.8	1.65
1.47	5.6	8.3	1.5
1.35	8.0	16	2.0
1.11	7.5	23.6	3.1

* C_1 is defined in eq. (4).

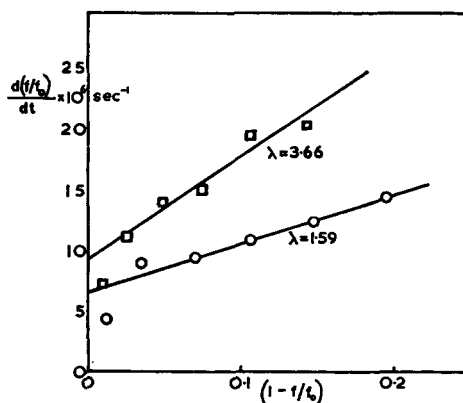


Fig. 1. Typical rate-extent plots for the stress relaxation of peroxide vulcanizate at 65°C. in oxygen at two extension ratios.

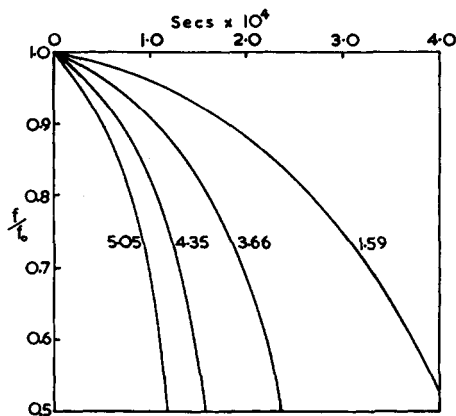


Fig. 2. Mean extent-time plots for the stress relaxation of peroxide vulcanizates at 65°C. in oxygen showing effect of extension ratio.

Before trying to equate decay in stress with the network damage at various strains, it is necessary to show that the fractional decrease in the stress is constant for a given amount of network damage and is independent of the strain. In order to demonstrate this, a peroxide network was aged to two extents of oxidation and the stress-strain curves of the aged samples compared with that of the unaged samples. It has been demonstrated¹² that during the aging of a peroxide vulcanizate a negligible amount of crosslinking occurs. Therefore the ratio of the stresses of aged and unaged vulcanizates at any strain, derived from these stress-strain curves, is identical with the value of f/f_0 that would be obtained at the same strain. Table IV shows values of f/f_0 at different extension ratios for the two aged vulcanizates. The results indicate that at least up to $\lambda = 4.5$ and 20% degradation, the fractional decrease in stress for a given amount of network breakdown is independent of the strain.

TABLE IV
Effect of Extension Ratio on f/f_0 for Two Aged Peroxide Networks

λ	f/f_0	
	Network I	Network II
1.28	0.900	0.819
1.39	0.898	0.816
1.65	0.896	0.808
2.00	0.887	0.799
2.49	0.885	0.789
2.82	0.885	0.782
3.22	0.878	0.776
3.75	0.902	0.805
4.45	0.899	0.808

Thus, changes in rate of stress decay at any strain truly reflect changes in the rate of network breakdown.

CBS-Accelerated Sulfur Vulcanizates

The stress relaxation behavior of these vulcanizates was more reproducible than that of the peroxide vulcanizates, but showed considerably more vacuum ageing. Plots of $\log(f/f_0)$ versus time were found to be linear over a wide range and although there is no real theoretical reason for this relationship, comparisons of the slopes of these lines offer a convenient means of comparing rates of degradation.

Table V shows the dependence of this slope on λ .

TABLE V
Slope of $\log(f/f_0)$ vs. Time for CBS Vulcanizates at 65°C.

λ	Slope $\times 10^6$, sec. ⁻¹
1.59	3
2.97	3.9
3.66	4.3 ₅
4.35	4.7
5.05	5.8

TMTD and MBT Accelerated Vulcanizates

These may be conveniently discussed together, as the TMTD vulcanizates and the MBT systems gave essentially the same results. At low extensions ($\lambda = 1.59$) the plots of $d(f/f_0)/dt$ versus $1 - (f/f_0)$ were linear, the slopes being as shown in Table VI. However, with these vulcanizates it was impossible to measure the stress relaxation at higher strains, as the rubber broke very shortly after the admission of oxygen, in many cases immediately, and always within 30–40 min. and in all cases before any

TABLE VI

Vulcanizate	$k \times 10^6, \text{sec.}^{-1}$
TMT (2 hr. cure)	10
TMT (7 hr. cure)	28
MBT	2.8

appreciable stress relaxation had occurred. At $\lambda = 1.59$, however, the strips lasted up to 11 hr. and decayed to zero stress without breakage. Furthermore, after breakage the rubber showed no other signs of aging; this is indicative of a rupture process. To try to elucidate this phenomenon the stress relaxometer was modified to enable tensile strength to be measured. For these tests small rings, 1.5 cm. in ID, and 0.1 cm. in width, were used. All measurements were performed at 65°C., the strips being allowed to equilibrate in nitrogen before being stretched. It was found that the stretching motor was too weak to exceed a loading of 121 kg./cm.², and in most cases this was insufficient to break the TMT vulcanizate (7 hr. cure) in vacuum. However in oxygen the strips always broke before this stress was reached. The mean results of a large number of measurements are: tensile strength in vacuum > 121 kg./cm.², tensile strength in oxygen = 104 kg./cm.², both measured at 65°C.

DISCUSSION

Extracted peroxide vulcanizates of purified natural rubber have previously been shown to demonstrate typical olefin autoxidative behavior,¹³ that is¹¹

$$d(\text{O}_2)/dt = k[\text{O}_2] + r_0 \quad (1)$$

where r_0 is the initial rate of oxidation. If it is assumed that the scission efficiency ϵ (number of moles of main chain scissions per molecule oxygen absorbed) remains constant, we have $\epsilon[\text{O}_2] = c$, where c is the number of cuts. This gives

$$dc/dt = kc + \epsilon r_0 \quad (2)$$

A number of workers have developed theoretical treatments relating network structure with elastic properties.¹⁴⁻¹⁸ These theories all attempt to relate the number of elastically effective chains N with the initial number N_0 and the number of cuts made. In applying these results to stress relaxation behavior, it is assumed that

$$f/f_0 = N/N_0 \quad (3)$$

Direct experimental verification of these theories has not yet been possible since, during stress relaxation, accurate assessment of actual numbers of cuts has not been possible. However, Mullins¹⁹ has derived an empirical relationship between the chemically determined values of crosslink density,

main chain molecular weight, and the elastic constant C_1 determined from stress-strain behavior²⁰ and given by

$$F = 2A_0[\lambda - (1/\lambda^2)][C_1 + (C_2/\lambda)] \quad (4)$$

where A_0 is cross-sectional area, C_1 and C_2 are constants, and F is force at extension λ and in which according to Mullins

$$C_1 = (1/2\rho RT/M_c + 0.78 \times 10^6) (1 - 2.3 M_c/M) \quad (5)$$

where ρ is density, R is the gas constant, M_c is molecular weight between crosslinks and M is molecular weight of main chains.

From eq. (4), we have

$$F/F_0 = [C_1 + (C_2/\lambda)]/[C_{10} + (C_{20}/\lambda)] = f/f_0 \quad (6)$$

where the subscript zero refers to the initial values. It has been shown that for small extents of degradation C_2 is proportional to C_1 , and thus we have:

$$f/f_0 = C_1/C_{10} \quad (7)$$

which, when substituted in eq. (5) gives

$$f/f_0 = (1 - 2.3 M_c/M)/(1 - 2.3 M_c/M_0) \quad (8)$$

since only M is affected in the ageing of a peroxide vulcanizate, M_c remaining constant.

Since the number of cuts is $c = (1/M) - (1/M_0)$,

$$f/f_0 = 1 - [2.3 M_c/(1 - 2.3 M_c/M_0)]c \quad (9)$$

This expression for f/f_0 gives an initial rate of degradation more than twice as great as that predicted by all of the theoretical treatments mentioned above apart from that due to Flory which is only some 15% slower. The reason for this discrepancy is not entirely obvious, and in view of the uncertainties involved, the author considers that the use of the semi-empirical expression (9) is preferable.

Combining eq. (9) with eq. (2) readily gives

$$\frac{d}{dt} (1 - f/f_0) = k(1 - f/f_0) + \frac{2.3\epsilon r_0 k M_c}{1 - 2.3 M_c/M_0} \quad (10)$$

i.e., the rate of degradation is proportional to the extent. Comparing eq. (10) with eq. (1) we see that not only is the slope of the rate-extent plot for change in f/f_0 independent of the scission efficiency ϵ , but it is identical with the slope of the rate-extent plot for oxidation. Furthermore, in view of the variability of the initial rate of oxidation r_0 , the agreement between the ratios of r (in Table III) and the ratios of k at $\lambda = 3.66$ and 1.59 (in Table II), is quite good. This implies that ϵ is independent of strain and that the increase of k with strain reflects the effect of strain on the kinetics of the oxidation process.

The mean strain energy per isoprene unit for typical gum vulcanizate is about 5×10^{-18} ergs; this corresponds to about 5×10^4 ergs/g., which is insufficient to cause a detectable change in reactivity. However, owing to the random distribution of chain lengths, some bonds will be very highly strained, and it is plausible that these will as a result show a higher chemical reactivity.

Interpretation of the stress relaxation of CBS networks is complicated by the lack of detailed knowledge of the kinetics of their oxidation. The increase in rate of degradation with increasing strain is less for this vulcanizate than it is for a peroxide vulcanizate; this could well be due to the slipping of the polysulfide crosslinks preventing very high strains being reached in the short or unfavorably placed chains, an explanation which has been put forward to account for the high tensile strength of this type of vulcanizate.²¹

The very rapid failure of the TMT and MBT strips due to rupture was unexpected but is consistent with the effect of strain on the rate of oxidation and hence on the rate of stress relaxation. The stretched sample is liable to have small flaws in which there will be large stress concentrations. In the presence of oxygen, rapid degradation will occur at these sites and ultimately lead to failure. Thus the tensile strength in oxygen will be less than in its absence.

This work forms part of a program of research conducted by the Natural Rubber Producers' Research Association.

References

1. Lake, G., and P. B. Lindley, *J. Appl. Polymer Sci.*, **9**, 1233 (1965).
2. Tobolsky, A. V., I. B. Prettyman, and J. H. Dillon, *J. Appl. Phys.*, **15**, 380 (1944).
3. Berry, J. P., *J. Polymer Sci.*, **21**, 505 (1956).
4. Scanlan, J., and W. F. Watson, *Trans. Faraday Soc.*, **54**, 740 (1958).
5. Dunn, J. R., J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.*, **54**, 730 (1958).
6. Maisey, L. J., and J. Scanlan, *J. Appl. Polymer Sci.*, **5**, 518 (1961).
7. Neumann, P. D., and J. C. Griess, *Corrosion*, **19**, 345 (1963).
8. Braden, M., and A. N. Gent, *J. Appl. Polymer Sci.*, **3**, 90 (1960).
9. Watson, W. F., *Trans. Inst. Rubber Ind.*, **34**, 237 (1958).
10. Dunn, J. R., J. Scanlan, and W. F. Watson, *Trans. Faraday Soc.*, **55**, 667 (1959).
11. Bateman, L., *Quart. Rev.*, **8**, 147 (1954).
12. Dunn, J. R., and J. Scanlan, *Trans. Faraday Soc.*, **57**, 160 (1961).
13. Colclough, T., private communication.
14. Flory, P. J., *Chem. Revs.*, **35**, 51 (1944).
15. Tobolsky, A. V., D. J. Metz, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **72**, 1946 (1950).
16. Berry, J. P., and W. F. Watson, *J. Polymer Sci.*, **18**, 201 (1955).
17. Scanlan, J., *J. Polymer Sci.*, **43**, 501 (1960).
18. Yu, H., *J. Polymer Sci.*, **B2**, 631 (1964).
19. Mullins, L., *J. Polymer Sci.*, **19**, 225 (1956).
20. Gumbrell, S. M., L. Mullins, and R. S. Rivlin, *Trans. Faraday Soc.*, **49**, 1495 (1953).
21. Bateman, L., Ed., *The Chemistry and Physics of Rubber-like Substances*, MacLaren, London, 1963.

Résumé

On a étudié l'influence d'une forte tension sur la force de relaxation oxydante de plusieurs caoutchoucs naturels vulcanisés. Dans le cas de vulcanisats accélérés au moyen de peroxyde et de CBS, la vitesse de relaxation de la tension augmente avec l'augmentation de la tension et cette augmentation semble être due à une augmentation de vitesse d'oxydation du réseau. Les vulcanisats de TMTD et de MBT montrent un défaut prématuré et important sous de fortes tensions, et on n'a pas pu effectuer de mesure de la force de relaxation oxydante. On a trouvé que la force d'élongation du vulcanisat TMTD était au moins de 20% plus élevée sous vide qu'en présence d'oxygène; ceci est dû, semble-t-il à une dégradation oxydante induite sous tension à l'extrémité d'un défaut de surface dans le caoutchouc.

Zusammenfassung

Der Einfluss hoher Verformung auf die oxydative Spannungsrelaxation einiger Naturkautschukvulkanisate wurde untersucht. Im Falle von Peroxyd- und CBS-beschleunigten Vulkanisaten nahm die Geschwindigkeit der Spannungsrelaxation mit steigender Verformung zu; diese Zunahme scheint durch eine Zunahme der Oxydationsgeschwindigkeit des Netzwerks bedingt zu sein. TMTD- und MBT-Vulkanisate zeigten ein ausgeprägtes vorzeitiges Versagen bei hoher Verformung, und es konnten daher keine Messungen der oxydativen Spannungsrelaxation ausgeführt werden. Die Zugfestigkeit eines TMTD-Vulkanisats war im Vakuum um mindestens 20% höher als in Sauerstoff, was, wie angenommen wird, auf einen spannungsinduzierten Abbau an der Spitze von Oberflächenrissen des Kautschuks zurückzuführen ist.

Received April 26, 1965