

## Crosslink Formation during Aging of Natural Rubber Vulcanizates

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Combination of continuous and intermittent stress relaxation measurements in the manner of Andrews et al.<sup>1</sup> has amply demonstrated that degradation of rubber vulcanizates during aging is frequently accompanied by a network-building reaction which is always assumed to be crosslinking. The occurrence of such a crosslinking reaction in a sulfur vulcanizate of natural rubber has more recently been confirmed by observation<sup>2</sup> of the stress-strain properties during aging. Sulfurless natural rubber vulcanizates show much smaller amounts of crosslinking and the crosslinking observed has been considered a continued vulcanization, although it has already been shown<sup>3</sup> that the reaction occurs during the aging of vulcanizates that have been extracted for the removal of residual vulcanizing agents.

Measurements have now been made of extent of crosslinking reaction in a number of accelerated sulfur vulcanizates of natural rubber under conditions that would reduce or prevent oxidative reactions, i.e., in the presence of antioxidant or *in vacuo*. In the case of reactions in air, the extent of crosslinking was estimated in the usual way, by comparison of intermittent and continuous stress relaxation. For reaction in a vacuum, however, the continuous relaxation was compared with the change in elastic modulus determined from equilibrium swelling in *n*-decane.

### EXPERIMENTAL

#### Preparation of Samples

Sheets of vulcanizates 0.02 cm. thick were prepared in a suitable press and mold from the following recipes.

DPG is diphenylguanidine, MBT is mercaptobenzothiazole, ZDC is zinc diethyldithiocarbamate.

After cure the sheets were extracted with hot acetone under nitrogen in a Soxhlet extractor for 24 hrs., dried under vacuum, and stored in vacuum.

	A	B	C
Pale crepe	100	100	100
Zinc oxide	5	5	5
Stearic acid	1.5	1.5	1.5
Sulfur	3	2.5	2.5
MBT	1.0	—	—
DPG	—	1.5	—
ZDC	—	—	0.375
Cure	40 min. at 141°C.	80 min. at 141°C.	90 min. at 100°C.

### Incorporation of Antioxidants

When necessary, antioxidants 2,2'-methylene-bis(4-methyl-6-*tert*-butyl-phenol)(Antioxidant 2246 of American Cyanamid Company) and phenyl- $\beta$ -naphthylamine were introduced by swelling strips of the vulcanizates in 1% ethyl acetate solutions of the antioxidant overnight and removing the solvent under vacuum.

Since the strips took up approximately their own volume of solution the final concentration of antioxidant in the strip could be expected to be approximately the same as that in the swelling solution. Accurate estimates are not required for the present purposes.

### Stress Relaxation Measurements

Continuous relaxation measurements were made in a manually operated relaxometer essentially similar to that described by Berry.<sup>4</sup> The design of this instrument enables measurements to be made either in air or in vacuum ( $10^{-4}$  mm.).

Intermittent relaxation measurements were made on an automatic instrument previously described.<sup>5</sup>

### Determination of Equilibrium Swelling

Equilibrium swellings in *n*-decane were measured for samples of each of the vulcanizates, both before and after heating in vacuum, by a procedure similar to that of Moore and Watson.<sup>6</sup> Weighed samples were placed in tubes containing *n*-decane in a thermostat at 25°C. and after 2 days, allowed for attainment of equilibrium, were removed, quickly surface-dried with filter paper, placed in a stoppered weighing bottle, and weighed again. The samples were then dried under vacuum to constant weight.

Use is made of the calibration established by Mullins<sup>7,8</sup> to relate these swelling measurements to the elastic constant  $C_1$  for the vulcanizates.

## RESULTS AND DISCUSSION

The results of the stress relaxation measurements for the three vulcanizates are given in Figures 1*a*, 1*b*, and 1*c*. The results of the swelling

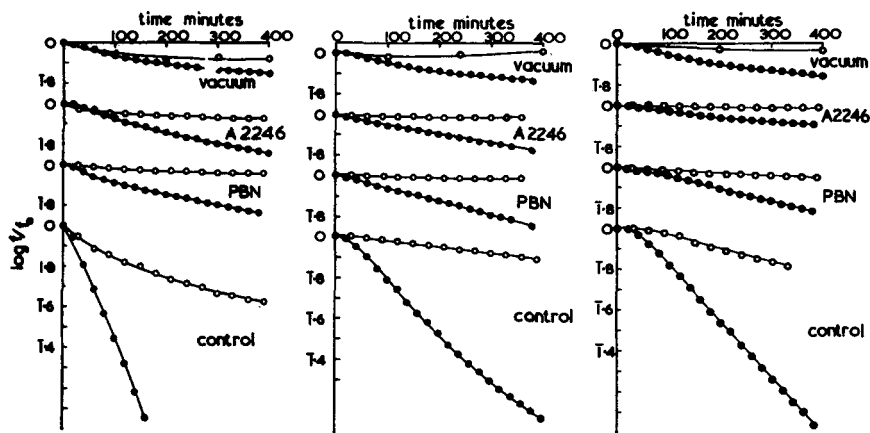


Fig. 1. Results of stress relaxation measurements: (a) MBT vulcanizate; (b) DPG vulcanizate; (c) ZDC vulcanizate.

measurements made before and after heating in vacuum are given in Table I and are also included in the figures,  $\log (C_1/C_{1,0})$  being plotted instead of  $\log (f/f_0)$ . In theory, the relative change in the elastic constant  $C_1$  derived from equilibrium swelling should be equivalent to the relative change in tension in intermittent relaxation. It has previously been shown<sup>9</sup> that, in

TABLE I  
Results of Swelling Measurements on Vulcanizates during Heating *in vacuo*

Heating time, min.	Vol. fract. rubber in swollen vulcanizate	$C_1$ dynes, $\text{cm.}^2 \times 10^{-6}$	$C_1/C_{1,0}$
Vulcanizate A			
0	0.285	1.54	1
103	0.272	1.37	0.89
200	0.263	1.26	0.82
301	0.267	1.31	0.85
393	0.265	1.29	0.84
Vulcanizate B			
0	0.307	1.84	1
100	0.303	1.78	0.97
240	0.306	1.81	0.98
400	0.313	1.93	1.05
Vulcanizate C			
0	0.336	2.31	1
200	0.329	2.17	0.94
400	0.325	2.13	0.92

spite of deficiencies in the theory, there is satisfactory agreement during aging of vulcanizates between the two types of measurement.

In Figures 2a, 2b, and 2c are plotted  $[(f/f_0)_{\text{int}} - (f/f_0)_{\text{cont}}]$  or  $[(C_1/C_{1,0}) - (f/f_0)_{\text{cont}}]$  against time for the three vulcanizates. These quantities give

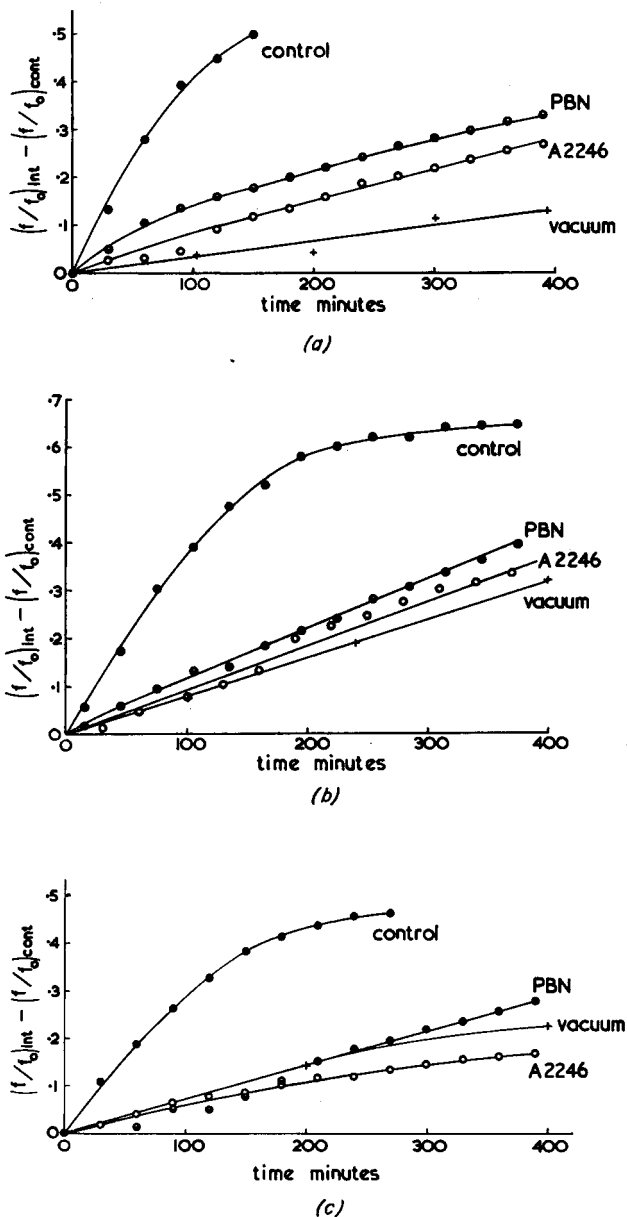


Fig. 2. Crosslinking during aging and heating *in vacuo*: (a) MBT vulcanizate; (b) DPG vulcanizate; (c) ZDC vulcanizate.

measures of the number of crosslinks formed during the heating in air or in vacuum. It will be seen that, although neither the breakdown reaction nor the crosslink formation is completely halted by addition of antioxidant or removal of oxygen, both are very markedly reduced under either condition.

It must be concluded, then, that the crosslink formation, observed in air in the absence of antioxidant, must, like the degradation, be either an oxidative reaction or part of a reaction sequence started by an oxidation.

The continuous relaxation under vacuum was appreciable with these vulcanizates and the antioxidants also reduced the relaxation to a similar rate. In the presence of antioxidants the intermittent tension after a small initial fall became almost constant and, although the measurements are less accurate, the equilibrium swelling appears to behave similarly with heating in vacuum. Whatever the nature of the oxidative degradation reaction observed by continuous relaxation in air, the only plausible explanation for the continuous relaxation in vacuum appears to be a rearrangement of some labile crosslinks, and such a rearrangement must also account for at least a major part of the continuous relaxation in the presence of antioxidant observed in these experiments.

### References

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### Synopsis

The effect of antioxidant on the crosslinking reaction occurring during the oxidation of sulphur vulcanizates of natural rubber was investigated by using both continuous and intermittent stress relaxation measurements. Similarly, by means of continuous stress relaxation and equilibrium swelling measurements the crosslinking reaction in vacuum was followed. The presence of antioxidant or removal of air reduced considerably both continuous and intermittent relaxation and also the difference between them, which measures the crosslinking. The crosslink formation must therefore form part of the sequence of oxidative reactions.

### Résumé

L'effet d'un antioxydant sur la réaction de pontage se produisant durant l'oxydation du caoutchouc naturel vulcanisé au soufre a été étudié à l'aide de mesures continues et intermittentes de relaxation de tension. De façon semblable, à l'aide de mesures continues de tension de relaxation et de gonflement à l'équilibre, la réaction de pontage sous vide a pu être suivie. La présence d'antioxydant ou l'absence d'air diminue fortement à la fois la relaxation continue et intermittente et aussi la différence entre celles qui mesurent le pontage. Ainsi la formation du pontage doit faire partie de la série des réactions d'oxydation.

### Zusammenfassung

Der Einfluss von Antioxydantien auf die bei der Oxydation von Naturkautschuk-Schwefelvulkanisaten auftretende Vernetzungsreaktion wurde anhand kontinuierlicher und intermittierender Spannungsrelaxationsmessungen untersucht. In ähnlicher Weise wurde die Vernetzungsreaktion im Vakuum durch kontinuierliche Spannungsrelaxations- und Quellungs-gleichgewichtsmessungen verfolgt. Die Gegenwart von Antioxydantien oder der Luftausschluss setzte sowohl die kontinuierliche als auch die intermittierende Relaxation beträchtlich herab; auch der Unterschied zwischen beiden, ein Mass für die Vernetzung, wurde reduziert. Die Bildung von Vernetzungen muss daher ein Teil der Folge der oxydativen Reaktionen sein.

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