

Stress relaxation in carbon-black-filled rubber vulcanizates at moderate strains

C. I. MacKenzie* and J. Scanlan

University of Sheffield, Department of Ceramics, Glasses and Polymers, Northumberland Road, Sheffield S10 2TZ, UK

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Stress-relaxation measurements have been made on rubber vulcanizates containing carbon black. Evidence has been produced for the existence of a distinct relaxation process which occurs within the first 60 s of relaxation at room temperature. This process becomes less important as the strain is increased and disappears when the temperature is increased or the rubber is swollen. It is suggested that this relaxation is the result of breakdown of structure formed from the carbon-black particles.

Keywords Stress relaxation; carbon black; rubber; vulcanizates; low strain

INTRODUCTION

Rubber is an increasingly important engineering material and an improved understanding of its mechanical properties and, particularly, of its viscoelastic behaviour is required. In practice, rubber vulcanizates almost always contain fine-particle fillers of which the carbon blacks are the most important. Such fillers give an increase in the viscoelastic response to deformation and filled vulcanizates show increased creep, stress relaxation and hysteresis.

Stress relaxation in rubber vulcanizates has been widely studied. In early investigations Gent¹ found that for both unfilled (gum) and black-reinforced natural rubber vulcanizates linear plots were obtained of stress against log(time). The slope of such semilogarithmic plots was independent of strain for the unfilled vulcanizates up to levels at which stress-induced crystallization occurs. The slopes of the plots for filled vulcanizates were dependent upon strain and were greater than those from the gum vulcanizates at the same strain. Because of the similar forms found for the plots for filled and unfilled vulcanizates, Gent proposed a similarity in viscoelastic mechanism for both types of vulcanizate.

In later investigations Cotten and Boonstra² and Voet, Sircar and Cook³ preferred fully logarithmic plots of log(stress) against log(time). Again linearity was found, implying a power-law relationship

$$\sigma(t) = at^{-n} \quad (1)$$

between stress and time. In practice it is not possible to distinguish between the semilogarithmic and fully logarithmic plots unless the fractional decrease in stress is large (see below). These workers found a variation in slope with strain for both filled and unfilled vulcanizates when rubbers other than natural were investigated.

Bartenev and his coworkers⁴⁻⁶ investigated relaxation

in filled and unfilled SBR vulcanizates and attempted to calculate approximate relaxation spectra. They concluded that the same processes with relaxation times $< 10^4$ s occurred in both filled and unfilled vulcanizates and could be attributed to movements of segments of the polymer chain. In the filled vulcanizate there was in addition a process with a relaxation time between 10^5 and 10^6 s which could be attributed to breakdown of rubber-filler bonds. This latter process was found to be strain dependent whereas the earlier processes were not.

A study of the effect of strain on stress relaxation in black-filled vulcanizates was initiated. Early experiments showed up strain dependence at short times rather than at the longer times suggested by Bartenev *et al.* and subsequent work was concentrated on this part of the timescale.

EXPERIMENTAL

Materials

All rubber formulations were mixed and provided by the Rubber and Plastics Research Association. The recipes are given in Table 1. Similar gum (unfilled) and black-loaded vulcanizates were prepared so that the effect of the carbon-black filler could be observed. The recipes were simple ones with usually just the rubber, vulcanizing ingredients and filler as required although sometimes an antioxidant, Flectol H, was also added.

The vulcanizates were in the form of sheets about 2 mm thick from which the test pieces were cut. Two types of test pieces were used (Figure 1) but type 1 was used solely with vulcanizate NRI in the first series of tests performed. Type II with its long gauge length and square shoulders was more suitable for stress-relaxation measurements.

Apparatus

An Instron 1026 Table Model Tester was used for all the stress-relaxation measurements. The load time data

* Present address: I.C.I. Ltd, Petrochemicals and Plastics Division, Bessemer Road, Welwyn Garden City, Hertfordshire, AL7 1HD, UK

Table 1 Vulcanization recipes

	NR I	NR II	NR III	BR	SBR
Natural rubber – RSS1	100		100		
Natural rubber – SMR5		100			
Butadiene rubber – Cariflex BR1220				100	
SBR – Intol 1509					100
Zinc oxide	5	5	5	3	5
Stearic acid	2	2	2	1.5	1.5
Octamine	1		1		
MBT	0.75		0.75		
Santocure MOR		0.75		1	1
TMTD					0.25
Flectol H		1		1	1
Sulphur	2.5	2.5	2.5	2	2
HAF black	0, 60	0, 60	0, 40, 60, 80	0, 60	0, 60

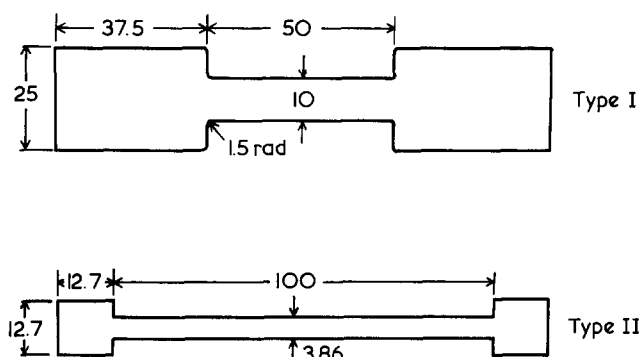


Figure 1 Test pieces. Dimensions given in mm

were traced out by the pen recorder of this machine which has a maximum response time of 0.5 s full scale. A Claude-Lyons Automatic Voltage Stabilizer type BTR-2 was used to regulate the input voltage to the tester as it was found that the recorder could be disturbed by mains voltage surges caused by switch operation on nearby apparatus. Even so calibration of the load cell and recorder was not reliable for longer than 6 h so that no measurements were made over a longer period.

Experimental techniques

Nominal stress values were used throughout this investigation. The dimensions of the test piece were measured with a standard micrometer and it is estimated that the maximum error in the cross-sectional area was about 6%. Errors in the load were considerably less, readings being made to better than 0.1% full scale, and errors in the stress would be similar to those in area. Strain in the test piece was calculated from straining time, estimated from the load-time chart, and crosshead speed. Accurate strain estimation requires fast chart speed but considerations of chart usage generally dictate a slow speed during stress-relaxation measurements. The accuracy in the strain is therefore limited. At the slowest chart speed elongation of a few millimetres could have been in error by as much as 50% but for higher strains errors would usually be less than 10%.

In order to conserve chart paper after an initial period a rotary switch was brought into operation and the chart then moved for a few seconds every 10 min. At the slowest chart speed short times were measurable to within 0.3 s and errors except at the shortest times were small.

Some measurements were made on swollen NR III

vulcanizates, both gum and filled, the swelling liquid being a light machine oil (Coopers WA/23). In order to obtain differently swollen samples strips of the vulcanizates were immersed in the oil for different lengths of time. After removal from the oil strips were surface dried and placed in individual stoppered tubes. They remained in these tubes for seven days in order for the swelling to become uniform within each strip. Stress-relaxation measurements were made at approximately 10% strain.

RESULTS

Measurements at different strain

Linear plots were found for σ/σ_0 against $\log_{10} t$ and for $\log_{10} \sigma$ against $\log_{10} t$ at all strain levels for gum vulcanizates. (The time at which the maximum load was recorded by the tensile tester was taken as the time zero and the maximum load value was used to calculate the reference stress σ_0 .) The semilogarithmic plots for the NRI gum vulcanizate are shown in Figure 2. There appears to be a slight initial curvature in the results at the highest strain, possibly because of the long straining time; otherwise the lines are straight over the whole experimental timescale.

The results for all the gum vulcanizates are summarized in Table 2 which gives for each strain level used the slope of the semilogarithmic plot of σ/σ_0 against $\log t$. The slopes vary little with strain for the natural rubber vulcanizates, NRI and NR II, but for the butadiene rubber and SBR there is some decrease in slope with increase in strain, with the slope levelling off at high strain. Similar results have been reported by Voet, Sircar and Cook³.

Results for the black-loaded NRI vulcanizates are shown as a similar semilogarithmic plot in Figure 3. The experimental points now appear to lie upon two straight lines rather than one, the first line of greater slope applying for times less than about 1 min and the second for greater times. It can also be seen that increase in the strain reduces the initial slope but has little or no effect upon the latter slope. Plotting these results as a fully logarithmic graph gives similarly a graph consisting of two straight lines with the greater slope appearing at short times.

The experimental results for a given vulcanizate at a given strain can be summarized by four values, the slopes of the two straight lines and their intercepts upon the σ/σ_0 or $\log \sigma$ axis at $\log t = 0$ (i.e. at $t = 1$ s). These quantities from the semilogarithmic plots for the filled vulcanizates tested are given in Table 3. In all cases the results are

similar to those for natural rubber vulcanizate NRI. Although the later slope is more dependent upon strain for rubbers other than natural, the dependence on strain of the early slope is always greater. A measure of the relative importance of the early process is given by dividing the difference of the intercepts by the intercept of the early line. This fraction in percentage form is also given in the Table. The declining importance of the short-time relaxation process is evident from the decrease in this measure as strain increases (see also Figure 6).

The difference in slope between the early and later lines and the difference in the intercepts are not independent. Figure 4 shows a plot of intercept difference against slope difference in stress relaxation at 20°C of vulcanizates containing 60 phr HAF black. All points lie close to a

single line through the origin regardless of the type of rubber or the strain. The same interrelation is apparent in the approximate constancy of the time at which the two straight lines of the semilogarithmic plot intercept. This time represents a change-over time at which a mechanism operating at short time becomes exhausted.

Black concentration

Natural rubber vulcanizates NRIII contained different black loadings, 40, 60 and 80 parts per hundred rubber. Results obtained from each of these vulcanizates at approximately 10% strain are shown in Figure 5. The modulus of the vulcanizate increases markedly with black concentration and so also do the peak stress and the stress at 1 s. Otherwise the effect of black concentration is limited.

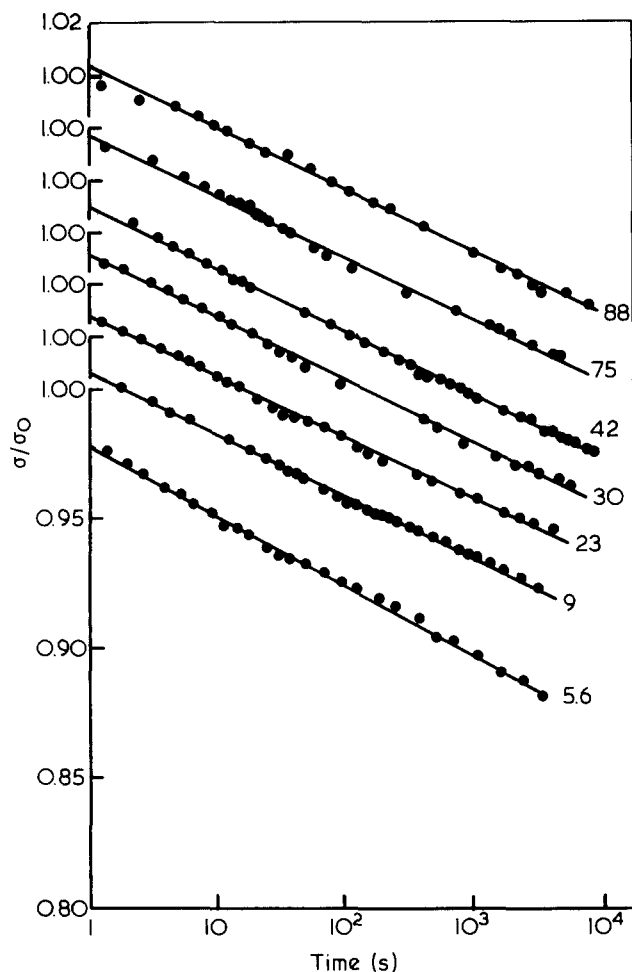


Figure 2 Relaxation results for NRI gum vulcanizate. Successive graphs are displaced upwards by 0.02 for clarity. Figures against lines give elongation

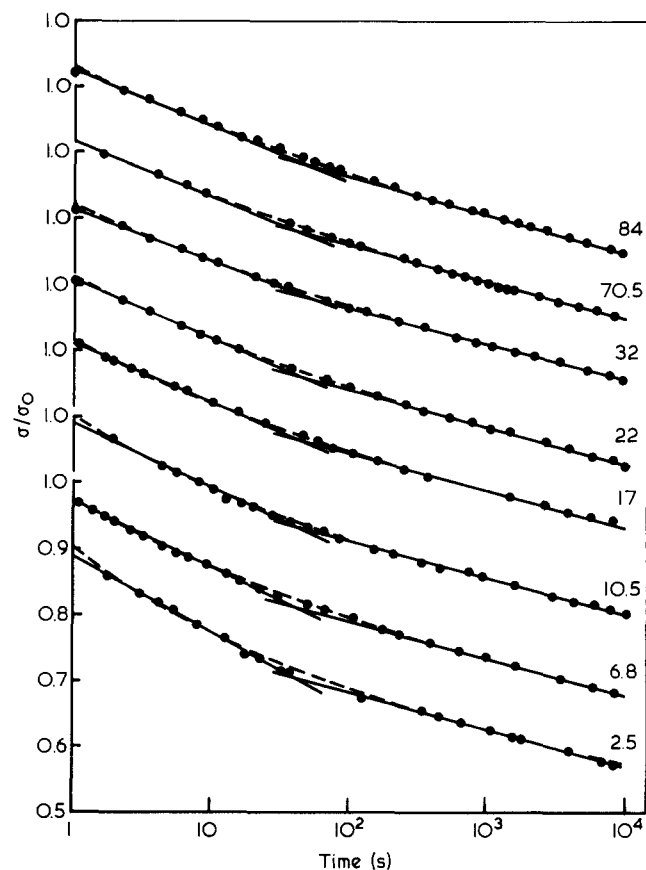


Figure 3 Relaxation results for black-filled NRI vulcanizate. Full lines fitted to experimental points for times < 20 s and times > 100 s; dashed curves calculated from fitted double power law. Successive graphs are displaced upward by 0.1 for clarity. Figures against curves give elongations

Table 2 Slopes of semilogarithmic plots of σ/σ_0 against $\log_{10} t$ for gum vulcanizates

Natural rubber I		Butadiene rubber		SBR		Natural rubber II	
Strain (%)	Slope	Strain (%)	Slope	Strain (%)	Slope	Strain (%)	Slope
5.6	0.0122	5.6	0.0175	4.8	0.0175	8.0	0.0078
9.0	0.0114	13.2	0.0150	8.8	0.0157	30	0.0074
22.8	0.0110	27.6	0.0125	35	0.0150	52.5	0.0066
30	0.0116	54	0.0117	66	0.0111	76	0.0067
42	0.0113	80	0.0095	100	0.0116	105	0.0067
75	0.0110	99.5	0.0085				
88	0.0114						

Table 3 Results of stress-relaxation measurements on filled vulcanizates

Strain (%)	Semilogarithmic plot								
	Early slope	Later slope	Intercepts at 1 s		Contribution early process (%)	a_1 (N m ⁻²) x 10 ⁻⁶	a_2 (N m ⁻²) x 10 ⁻⁶	n_1	n_2
			Early line	Later line					
Natural rubber I									
2.5	0.117	0.059	0.89	0.80	9.6	0.027	0.18	0.4	0.035
6.8	0.101	0.058	0.87	0.81	7.1	0.042	0.54	0.4	0.037
10.5	0.0995	0.054	0.89	0.82	8.5	0.070	0.65	0.4	0.034
17	0.0895	0.0545	0.91	0.85	6.4	0.063	1.01	0.4	0.034
22	0.088	0.0565	0.91	0.85	6.0	0.052	1.08	0.4	0.036
32	0.078	0.052	0.915	0.87	5.2	0.061	1.28	0.4	0.032
70.5	0.079	0.0565	0.92	0.88	4.3	0.076	2.34	0.4	0.034
84	0.0755	0.061	0.92	0.89	3.4	0.076	2.43	0.4	0.036
Natural rubber II									
3.2	0.079	0.055	0.89	0.86	3.8	0.012	0.31	0.4	0.033
7.2	0.069	0.051	0.92	0.89	3.3	0.022	0.77	0.4	0.029
20	0.062	0.046	0.93	0.90	2.9	0.040	1.52	0.4	0.025
29	0.055	0.044	0.95	0.93	1.7	0.040	1.68	0.4	0.023
52.5	0.073	0.053	0.92	0.89	3.7	0.061	3.02	0.4	0.032
80	0.069	0.055	0.93	0.91	2.8	0.060	3.36	0.4	0.032
SBR									
2.5	0.112	0.065	0.84	0.77	8.4	0.018	0.26	0.4	0.047
12.5	0.089	0.051	0.88	0.87	6.6	0.088	0.89	0.4	0.028
27	0.068	0.044	0.93	0.89	4.6	0.103	1.98	0.4	0.024
46.5	0.076	0.048	0.92	0.88	4.8	0.164	2.83	0.4	0.026
61	0.074	0.049	0.92	0.88	4.8	0.172	3.46	0.4	0.028
83	0.078	0.050	0.92	0.88	4.4	0.244	4.73	0.4	0.028
Butadiene rubber									
5.2	0.062	0.041	0.93	0.90	3.7	0.015	0.43	0.4	0.023
10.5	0.059	0.042	0.95	0.92	2.8	0.020	0.62	0.4	0.022
17	0.059	0.044	0.95	0.93	2.5	0.027	0.78	0.4	0.021
27	0.051	0.038	0.97	0.94	2.7	0.023	1.37	0.4	0.021
48	0.048	0.040	0.96	0.95	1.9	0.036	1.78	0.4	0.020
83	0.053	0.043	0.96	0.94	1.8	0.044	2.96	0.4	0.023

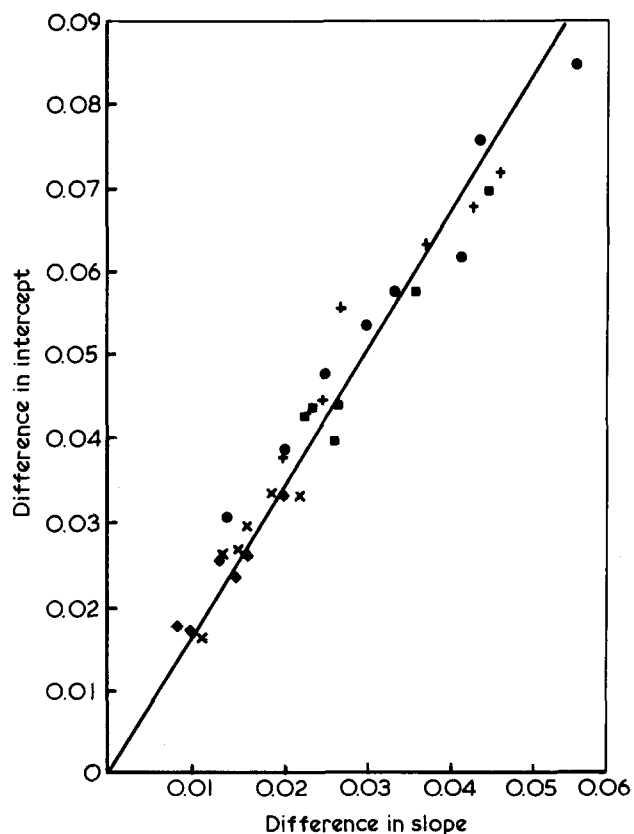


Figure 4 Relation between intercept differences and slope differences in graphs for relaxations at 20°C in all vulcanizates containing 60 phr HAF black: ●, NRI; ×, NRII; +, NRIII; ◆, BR; ■, SBR

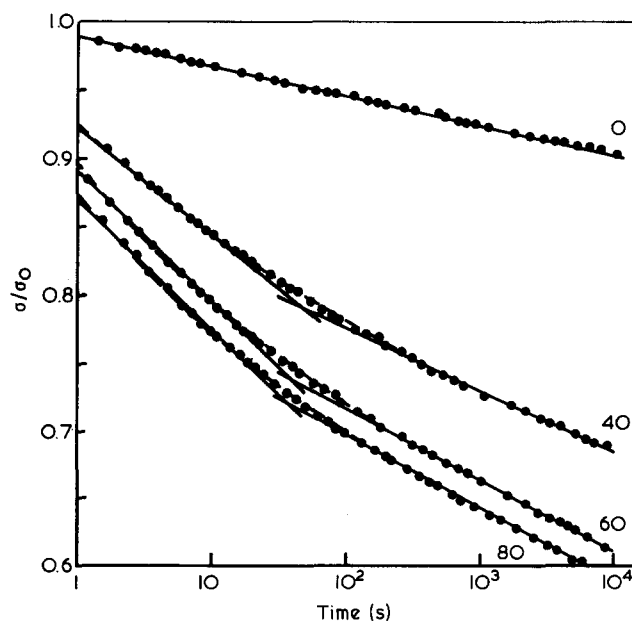


Figure 5 Relaxation results for NRIII vulcanizates containing varying black concentrations. Figures against curves give black loadings in parts per hundred rubber

Figure 6 summarizes the experimental results at different black concentrations. The later slope and the ratio of the intercept difference to the intercept of the early line used above as a measure of the importance of the short-time process are both plotted against strain for each of the black concentrations. The decrease in importance of the short-time process as strain increases, previously noted, is again obvious but effects of the variation in black concentration are minor, increasing black concentration increasing the later slope a little but changing the relative contribution of the early process by only a very small amount.

Fitting the experimental data

The results for the black-filled vulcanizates indicate the existence of two distinct relaxation processes. For the second, longer-time, process the data are well represented by a power law in the time. However, the data for the short-time process, obtained by subtracting extrapolated long-time measurements from the observed values, are much less precise and it is not possible to be so definite about a suitable empirical form. Nevertheless an attempt has been made to fit the experimental data over the whole experimental time by a double power law

$$\sigma(t) = a_1 t^{-n_1} + a_2 t^{-n_2} \quad (2)$$

Attempts to fix the four parameters, a_1 , a_2 , n_1 and n_2 by least-squares fits using computer optimization were not successful as the program frequently failed probably because of very shallow minima. However, the linearity of the plot of intercept differences against slope differences (Figure 4) suggests a similar dependence upon time for the short-time process in all cases. If it is assumed that the initial straight lines approximate the tangents at $\log t = 0.5$ then equation (A.18) (see Appendix) indicates

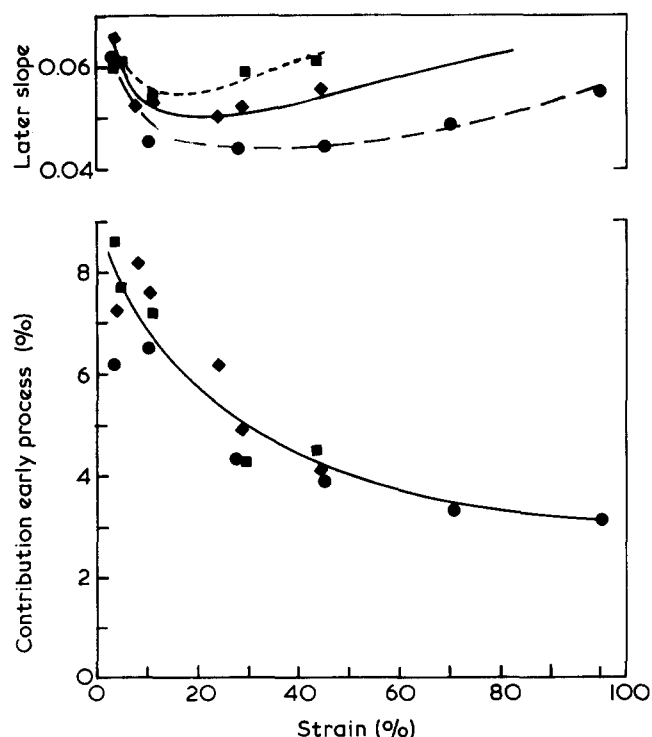


Figure 6 Effects of strain and black concentration on relaxation in NR III vulcanizates; ●, 40 phr; ◆, 60 phr; ■, 80 phr

that in all cases $n_1 \approx 0.4$. If this value of n_1 is taken, least-squares fits to the experimental data give the parameter values given in Table 3 and the dashed curves of Figures 3 and 5 were calculated from equation (2) using parameter values obtained in this way. The results of the curve fitting for NR II shown in Figure 9 are typical. The exponent n_2 apparently varies somewhat with strain in line with the similar variation in final slope. The plots of a_1 and a_2 against strain are equivalent to isochronous (at 1 s) stress-strain curves for the two relaxation processes; the dependence of a_2 upon strain is similar to that of stress in a rubbery material but a_1 exhibits a yield-like behaviour.

Strain rate

In an ideal stress-relaxation measurement the initial straining of the sample would be carried out infinitely rapidly. In practice, of course, only a finite strain rate can be used and, moreover, in the measurements reported here the same strain rate (0.0667 s^{-1}) was usually used so that straining time varied with the strain. The effects of strain rate upon the subsequent relaxation of vulcanizate NRI were therefore investigated. As far as possible a constant strain was used, but limits to the reproducibility of operation of the limit switches on the tensile tester meant that there was some change in strain with change in strain rate.

The results are shown in Figure 7a. In the tests made with a very slow strain rate (long straining time) the plots of stress against $\log(\text{time})$ showed a marked initial curvature but the usual two straight line form was eventually established. The slopes of the two straight lines are little if at all affected by straining time but even when no initial curvature can be seen the intercepts on the axis at $\log t = 0$ do vary with straining time.

Effect of prestrain

Stress-relaxation measurements were made upon samples which had previously been stretched to 100% elongation, released and then allowed to recover for varying time periods. The results are summarized in Table 4 which gives some parameters derived from fully

Table 4 Effect of prestrain on the stress relaxation of filled vulcanizates

Recovery time (min)	Strain (%)	Fully logarithmic plot		
		Early slope	Later slope	Intercept difference
NR II vulcanizate				
No prestrain	9.5	0.031	0.027	0.0049
2	8.0	0.0335	0.028	0.0071
5	7.3	0.034	0.028	0.0067
10	6.6	0.034	0.029	0.0064
40	7.3	0.034	0.030	0.0061
180	7.4	0.032	0.027	0.0061
1260	7.9	0.031	0.027	0.0066
SBR vulcanizate				
No prestrain	8.8	0.045	0.034	0.0154
1	11.0	0.042	0.028	0.0176
2	10.6	0.043	0.029	0.0180
5	11.2	0.042	0.028	0.0187
10	10.4	0.043	0.030	0.0172
60	12.4	0.041	0.030	0.0146
1225	10.0	0.042	0.031	0.0165

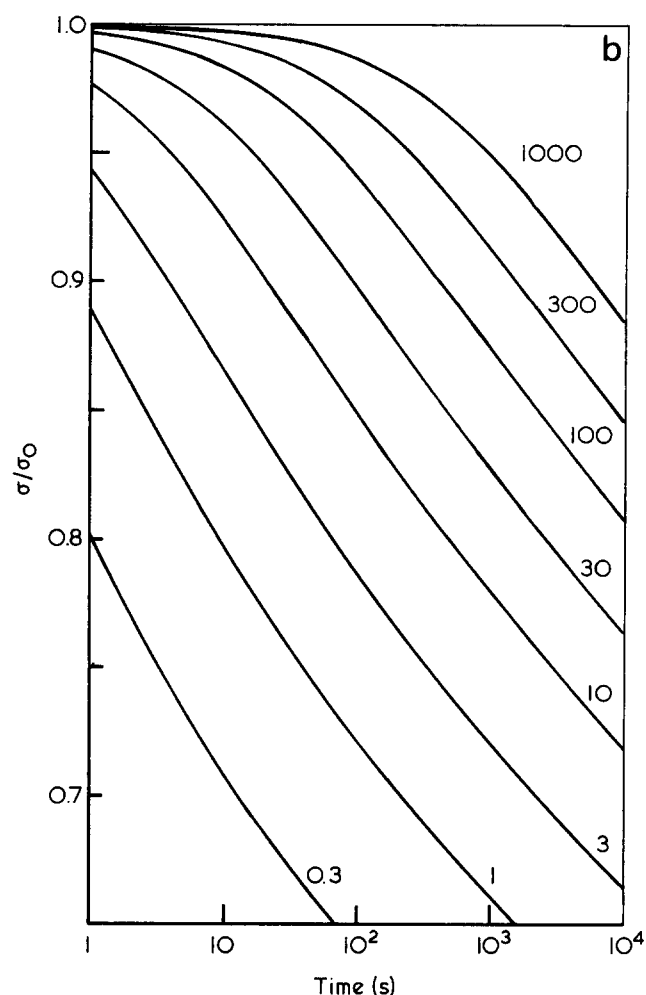
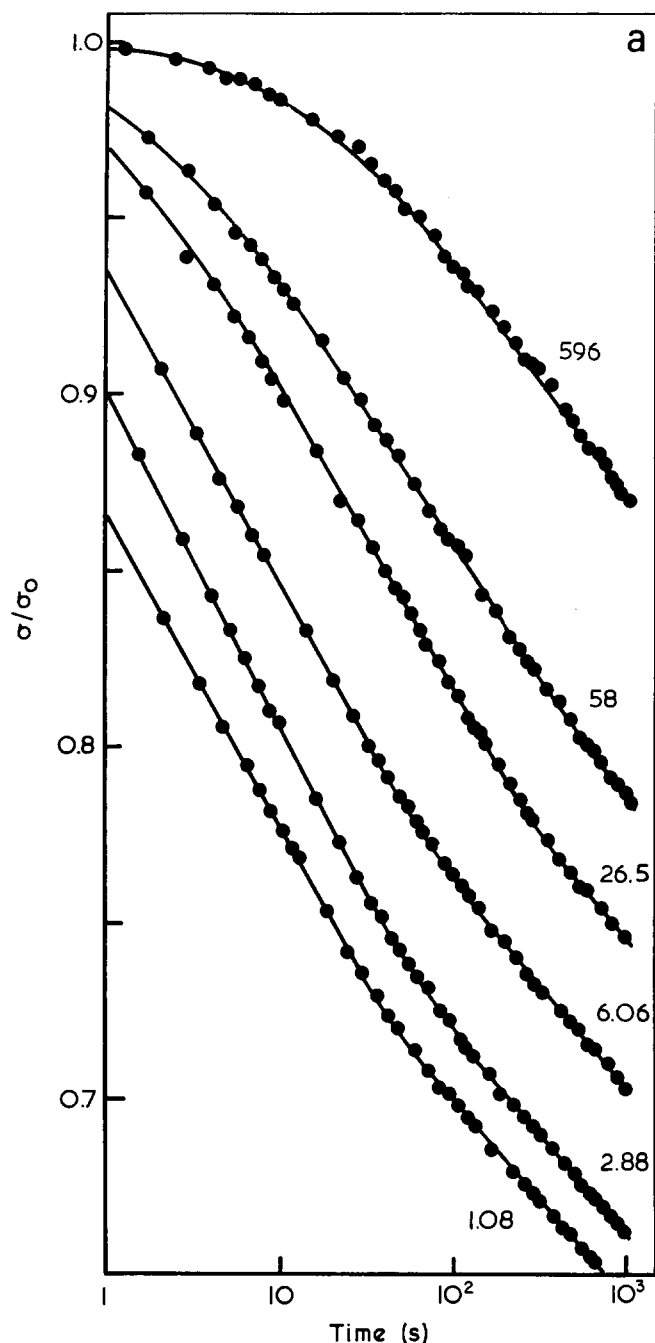


Figure 7 Effect of straining time on relaxation of filled vulcanizate. Figures give straining times in seconds. (a) experimental results for NRI filled vulcanizate. (b) Theoretical curves

logarithmic plots. Prestrain does not appear to produce any marked effect. However, the shortest recovery period which was experimentally attainable was 1 min and it may be that the vulcanizate was able to recover from the prestrain within this period.

Effect of temperature

Stress-relaxation measurements have been made at various temperatures. The range of temperatures which can be covered is, however, limited. Above about 60°C the rubber vulcanizates become susceptible to atmospheric oxidation and stress relaxation of chemical origin is added to that arising from viscoelastic processes. On the other hand, the glass transition is approached when the temperature is lowered so that additional relaxation processes become important; the relaxation plots for the gum vulcanizates then become curved. No measurements were made at temperatures above 60°C for any rubber, below -10°C for natural rubber or polybutadiene or

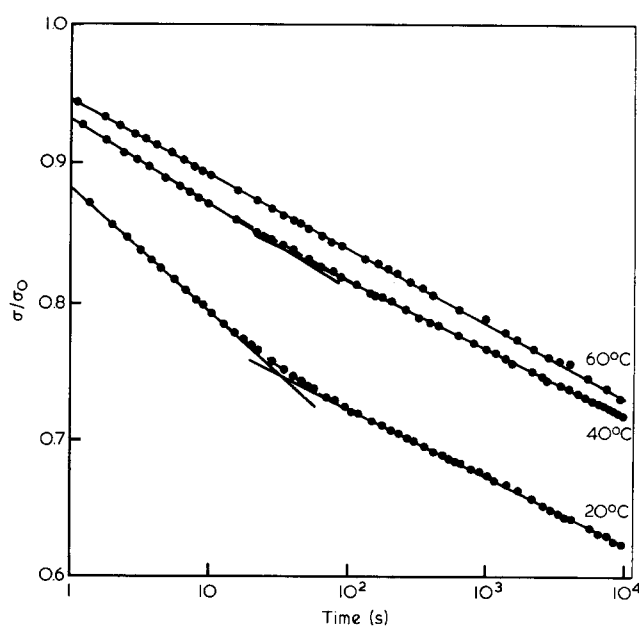


Figure 8 Effect of temperature on relaxation in filled SBR vulcanizate.

below 20°C for SBR. Figure 8 shows relaxation curves obtained at various temperatures for SBR at strains near 12.5%. Results for all vulcanizates are summarized in Table 5 and those for NRII are illustrated in Figure 9.

Increase in temperature reduces the relative importance of the short-time relaxation process as is shown by the reduction in a_1 and neither for NRII nor for SBR was it possible to distinguish an initially greater slope at 60°C, and at 40°C such a greater slope could be found only at low strains for SBR and not at all for NRII. The limited results obtained for butadiene rubber were however anomalous and did not show the decrease in a_1 with increase in temperature. The effect of change of temperature upon longer-time relaxation was remarkably small.

Stress relaxation in swollen vulcanizates

The results of stress-relaxation measurements on a NRIII gum vulcanizate containing variable amounts of

an oil diluent but all at approximately the same strain are shown in Figure 10. The results for a similar series of measurements on the corresponding black-filled vulcanizate are shown in Figure 11.

The stress-log(time) curves for the swollen gum vulcanizates are initially linear with slopes which vary little with diluent concentration. There is an upward curvature at longer times and it was thought that this must have been due to a small loss of swelling liquid during the test. However, weighing the test pieces before and after the relaxation measurements failed to demonstrate any such loss; the loss required to account for the observed curvature can be estimated from equation (A.14) (see above) and although small should have been observable. No explanation can be offered for the curvature at this time and therefore further discussion will be limited to the linear parts of the relaxation curves.

The relaxation curves for the black-filled vulcanizate show the usual two straight line form at low

Table 5 Results of stress-relaxation measurements on filled vulcanizates at various temperatures

Temp. (°C)	Strain (%)	Fully logarithmic plot							
		Early slope	Later slope	Intercept at 1 s		a_1 (N m ⁻²) x 10 ⁻⁶	a_2 (N m ⁻²) x 10 ⁻⁶	n_1	n_2
				Early line	Later line				
Natural rubber II/HAF black									
-10	3.8	0.048	0.040	5.664	5.653	0.018	0.44	0.4	0.039
	16.8	0.042	0.029	6.198	6.178	0.105	1.48	0.4	0.027
	42	0.042	0.032	6.446	6.431	0.143	2.66	0.4	0.031
20	3.2	0.041	0.034	5.502	5.492	0.012	0.31	0.4	0.033
	7.2	0.034	0.029	5.897	5.888	0.022	0.77	0.4	0.029
	20	0.030	0.025	6.193	6.184	0.040	1.52	0.4	0.025
	29	0.027	0.023	6.235	6.228	0.040	1.68	0.4	0.023
	52.5	0.035	0.032	6.479	6.472	0.061	3.02	0.4	0.032
	80	0.035	0.032	6.533	6.527	0.060	3.36	0.4	0.032
40	2.4	—	0.039	—	5.517	—	0.33	—	0.039
	26	—	0.026	—	6.196	—	1.57	—	0.026
60	12	—	0.026	—	5.940	—	0.87	—	0.026
	31	—	0.026	—	6.216	—	1.64	—	0.026
SBR/HAF black									
20	2.5	0.060	0.048	5.437	5.415	0.018	0.26	0.4	0.047
	12.5	0.047	0.030	5.989	5.962	0.088	0.89	0.4	0.028
	27	0.034	0.025	6.316	6.300	0.103	1.98	0.4	0.024
	46.5	0.038	0.028	6.474	6.457	0.164	2.83	0.4	0.026
	61	0.037	0.029	6.558	6.543	0.172	3.46	0.4	0.028
	83	0.039	0.030	6.696	6.683	0.244	4.73	0.4	0.028
40	4.0	0.043	0.037	5.548	5.536	0.013	0.34	0.4	0.037
	12.4	0.029	0.027	5.988	5.983	0.014	0.96	0.4	0.027
	32	—	0.027	—	6.298	—	1.99	—	0.027
60	2.5	—	0.045	—	5.411	—	0.26	—	0.045
	13.2	—	0.027	—	5.943	—	0.88	—	0.027
	34	—	0.025	—	6.309	—	2.04	—	0.025
Butadiene rubber/HAF black									
-10	2.5	0.048	0.029	5.454	5.428	0.027	0.26	0.4	0.026
	15.2	0.033	0.024	5.921	5.905	0.041	0.80	0.4	0.023
	59	0.029	0.025	6.350	6.343	0.051	2.19	0.4	0.024
20	5.2	0.030	0.024	5.648	5.638	0.015	0.43	0.4	0.023
	10.5	0.028	0.023	5.807	5.798	0.020	0.62	0.4	0.022
	17	0.029	0.022	5.905	5.895	0.027	0.78	0.4	0.021
	27	0.024	0.021	6.144	6.139	0.023	1.37	0.4	0.021
	48	0.023	0.020	6.258	6.251	0.036	1.78	0.4	0.020
	83	0.025	0.023	6.476	6.471	0.044	2.96	0.4	0.023
60	6.4	0.024	0.018	5.616	5.601	0.016	0.40	0.4	0.018
	16	0.024	0.016	5.948	5.932	0.041	0.85	0.4	0.016
	30.5	0.023	0.015	6.158	6.140	0.071	1.38	0.4	0.015

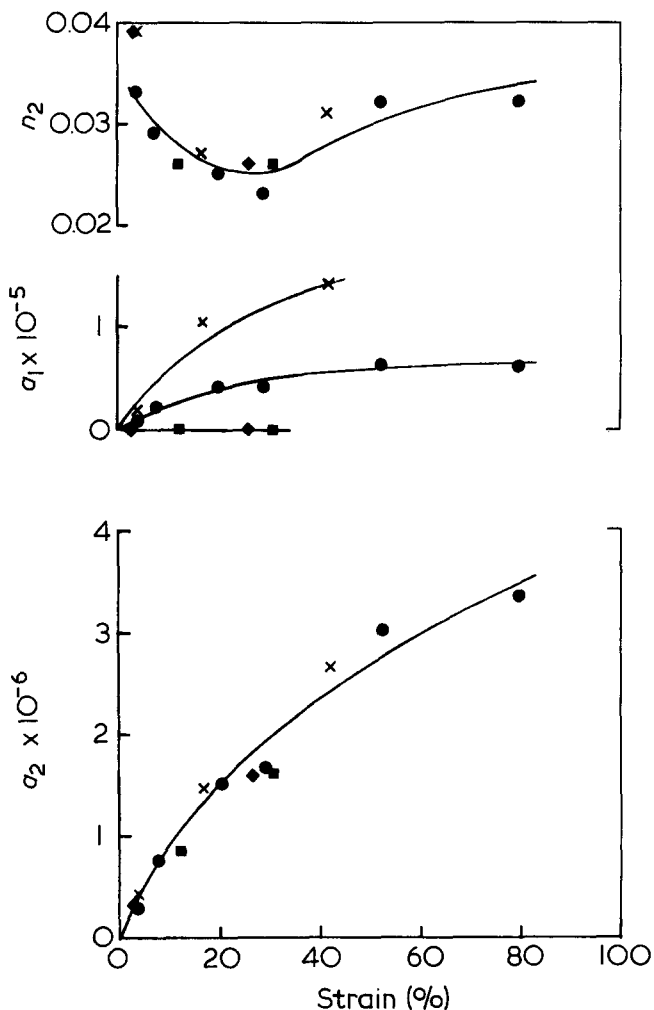


Figure 9 Double power-law parameters for NR/II filled vulcanizate at various temperatures: x, -10°C; ●, 20°C; ◆, 40°C; ■, 60°C

concentrations of the oil diluent (with, again, a small upward curvature at long times for the swollen samples). The steeper initial slope disappears, however, at higher degrees of swelling ($\geq 17.7\%$) and there is then only one linear region.

DISCUSSION

Logarithmic and semilogarithmic plots of stress-relaxation data

Two types of plot have been used in investigations of stress relaxation in rubber vulcanizates. Gent¹ and Derham and Thomas⁷ used a semi-logarithmic plot of $\sigma(t)/\sigma(1)$ against $\log_e t$ ($\sigma(1)$ is the stress after a standard time—usually 1 s). Voet *et al.*³ and Cotten and Boonstra² preferred a plot of $\log \sigma$ against $\log t$; a linear plot here implies a power-law relationship, $\sigma = at^{-n}$, between stress and time. Both types of graph have been claimed to be linear. Since the slope of a semilogarithmic plot is $\sigma(1)^{-1} d\sigma/d \log t$ and that of a fully logarithmic plot is $\sigma(t)^{-1} d\sigma/d \log t$, linearity in both plots implies that $\sigma(t)$ remains always approximately equal to $\sigma(1)$. That is, no distinction can be made between the two types of plot so long as the extent of relaxation remains small. Trial plots show that if a linear semilogarithmic plot is assumed, the deviation from linearity of a fully

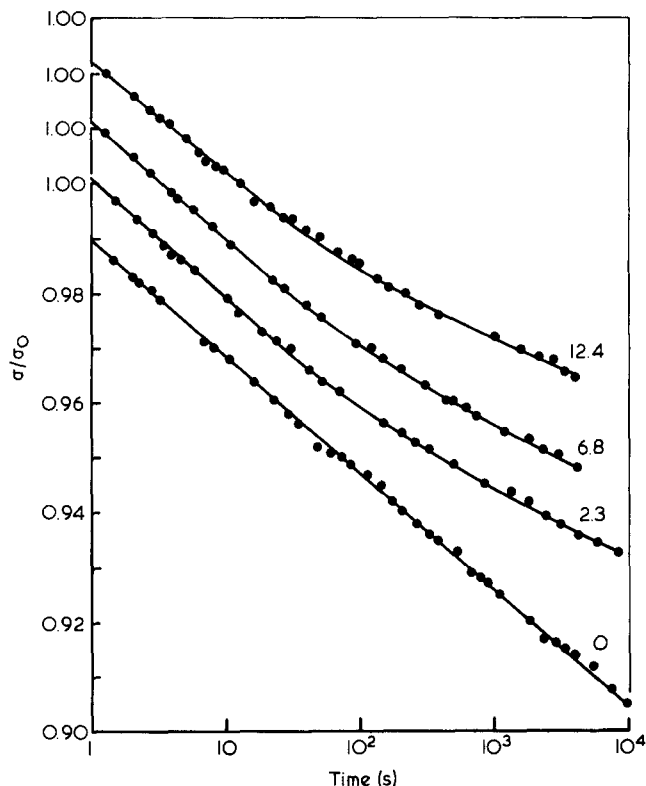


Figure 10 Effect of swelling by solvent on stress relaxation in NR/II gum vulcanizate. Figures against curves give oil concentrations in wt%. Successive curves are displaced upward by 0.01 for clarity

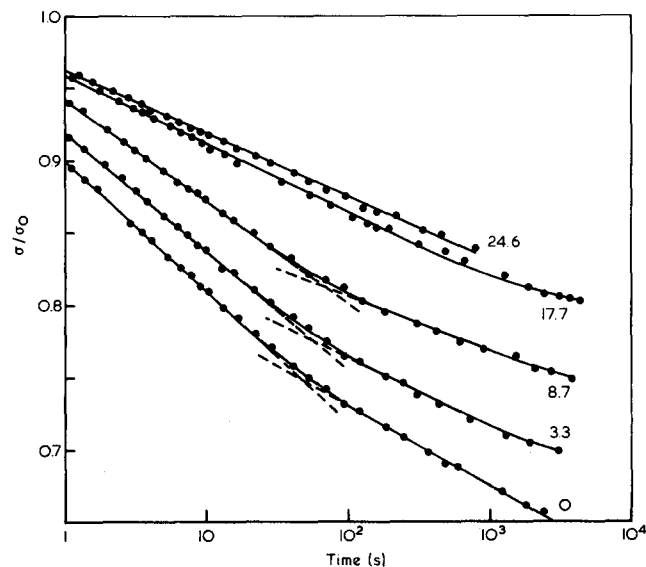


Figure 11 Effect of swelling by solvent on stress relaxation in NR/II vulcanizate containing 60 phr HAF black. Figures against curves give oil concentrations in wt%

logarithmic plot is not perceptible while $\sigma(t)/\sigma(1) > 0.75$ and conversely that assumption of a linear fully logarithmic plot leads to an apparently linear semilogarithmic plot under the same condition.

In this investigation both types of plot have been used as seemed most convenient and, as stated above, both gave graphs which were either linear or consisted of two linear portions. However only the fully logarithmic plot suggests a simple relationship, the power law, which is

readily extended to include two distinct relaxation processes. This extended form including two power-law terms has been used as equations (2) and (A.1) both to fit the data empirically and as a base for theoretical calculations.

Effect of changes in straining time on relaxation in black-filled rubbers

The experimental stress-relaxation curves for the black-filled NRI vulcanizate shown in *Figure 7a* may be compared with the theoretical curves of *Figure 7b* obtained by use of Boltzmann superposition (see Appendix). The values of the parameters used in the construction of the theoretical curves were those given in *Table 3* for the same NRI vulcanizate at the similar strain of 10.5%, the ratio A/B of equations (A.2) to (A.9) being assumed equal to a_1/a_2 .

The calculated and experimental curves show striking qualitative similarities. For short straining times, curves of both sets consist principally of two linear sections joined by a short curved portion. As straining time is increased, an initial curvature develops in the plots and the change-over from one linear portion to the other is delayed to later times although there is little change in slope of either straight line.

The application of Boltzmann superposition is strictly justified if the viscoelastic processes involved are linear in their behaviour. In this application both processes are non-linear, especially the earlier. It is not surprising, therefore, that the theory and experiment should not agree at all well quantitatively.

That non-linearity is a major cause of the imperfect agreement is supported by the observation that improved agreement is obtained if the straining times are divided by factors of 3 to 6. Some such effect is to be expected as relaxation will only occur during extension for the later part of the straining time when strain and stress are already high.

Another possible cause of disagreement between theory and experiment cannot be excluded: the existence of additional relaxation mechanisms active in the period of a few seconds before observations can be made.

CONCLUSIONS

The results obtained in the experiment described in this paper support the existence of a relaxation process in rubber vulcanizates containing HAF carbon black which occurs at relatively short times and is more important at small elongations and which is different from the relaxation processes observed in gum vulcanizates and in black-filled vulcanizates at higher elongations and longer times.

Evidence for the existence of the separate short-time relaxation process is provided by:

(i) the existence of two linear sections in the plots of stress against time in either fully logarithmic or semilogarithmic form;

(ii) the effect of variation of strain rate during the extension is qualitatively very similar to that predicted by a simplified linear theory which allows for two concurrent relaxation processes; and

(iii) the reduction in importance or complete disappearance of the initial steeper line from the stress-time plots when

- (a) the elongation is increased,
- (b) the temperature is raised, and
- (c) the rubber is swollen.

The nature of the relaxation process involved in the short-time process must remain to some extent a matter for speculation. However, the fact that the observed relationship between intercept difference and slope difference (*Figure 4*) does not depend upon the nature of the rubber suggests that the process involves the black only.

Payne⁸⁻¹⁰ has observed in dynamic mechanical measurements on black-filled rubbers that at high black loadings and at low strain amplitudes the magnitude of the dynamic modulus is very strongly dependent upon strain amplitude. He attributed this dependence to the existence within the black-filled vulcanizate of a structure which is progressively destroyed as the stress increases. Payne appears to assume that the breakdown of the structure occurs instantaneously when stress is increased and from his failure to observe any dependence of dynamic modulus upon frequency (over quite a narrow frequency range) concluded that the re-formation of the structure was also very rapid. The magnitudes of the modulus changes observed in these present experiments are small compared with those found by Payne and it is suggested that the initially increased rate of relaxation can be attributed to the final stages of the breakdown of the structure involving the carbon black.

The reduced importance of the short-time relaxation process as strain increases is clearly consistent with its attribution to breakdown of black structure similar to that postulated by Payne. So also is the disappearance of the early relaxation process when the rubber is swollen in solvent to quite a modest extent for Voet *et al.*³ have shown that swelling a black-filled vulcanizate markedly reduced the magnitude of the low-strain dynamic modulus and consequently also the strain sensitivity similarly to reduction in black concentration. The effect of temperature can be attributed to breakdown of the structure by thermal as well as mechanical energy, and is again similar to the effect on dynamic modulus. Payne's conclusion that the structure is rapidly re-formed after breakdown is reinforced by the failure in this investigation to observe any effect of prestrain on the early process.

Payne concluded tentatively that the labile structure involved carbon black alone with direct involvement of the rubber since similar effects could be observed in paraffin oil containing black and suggested that the structure was held together by van der Waals forces only. Our observation that the form of the initial relaxation-time plot did not depend upon the nature of the rubber would support this conclusion.

APPENDIX

Effect of initial rate of strain — theory

If it is assumed that stress relaxation is the result of two linear power-law processes acting in parallel, the relaxation function may be written

$$E(t) = At^{-n_1} + Bt^{-n_2} \quad (\text{A.1})$$

and Boltzmann superposition may be used to calculate the effect of variations in straining time.

The Boltzmann superposition principle states that for any strain history in the stress, $\sigma(t)$, at time t is given by

$$\sigma(t) = \int_{-\infty}^t E(t-\tau) \frac{de(\tau)}{d\tau} d\tau \quad (\text{A.2})$$

is $e(t)$ is the strain at time t . Assuming that the strain is given by

$$e(t) = \begin{cases} 0 & t < -T \\ \frac{e_0}{T}(t+T) & -T \leq t < 0 \\ e_0 & 0 \leq t \end{cases} \quad (\text{A.3})$$

so that e increases linearly during a time interval T to the strain e_0 at which the relaxation occurs, then

$$\sigma(t) = \frac{e_0}{T} \int_{-T}^0 E(t-\tau) d\tau \quad 0 \leq t \quad (\text{A.4})$$

Thus

$$\sigma(t) = \frac{Ae_0}{(1-n_1)T^{n_1}} \left(\frac{t}{T}\right)^{1-n_1} \left[\left(1 + \frac{T}{t}\right)^{1-n_1} - 1 \right] + \frac{Be_0}{(1-n_2)T^{n_2}} \left(\frac{t}{T}\right)^{1-n_2} \left[\left(1 + \frac{T}{t}\right)^{1-n_2} - 1 \right] \quad (\text{A.5})$$

or

$$\frac{\sigma(t)}{\sigma(0)} = \frac{\alpha}{\alpha+\beta} \left(\frac{t}{T}\right)^{1-n_1} \left[\left(1 + \frac{T}{t}\right)^{1-n_1} - 1 \right] + \frac{\beta}{\alpha+\beta} \left(\frac{t}{T}\right)^{1-n_2} \left[\left(1 + \frac{T}{t}\right)^{1-n_2} - 1 \right] \quad (\text{A.6})$$

where

$$\alpha = \frac{A/B}{(1-n_1)T^{n_1}} \quad \beta = \frac{1}{(1-n_2)T^{n_2}} \quad (\text{A.7})$$

For $T \ll t$, (A.6) reduces correctly to

$$\sigma(t) = Ae_0 t^{-n_1} + Be_0 t^{-n_2} = e_0 E(t) \quad (\text{A.8})$$

for when $T/t \ll 1$

$$\frac{1}{T^n} \left(\frac{t}{T}\right)^{1-n} \left[\left(1 + \frac{T}{t}\right)^{1-n} - 1 \right] \simeq \frac{1}{T^n} \left(\frac{t}{T}\right)^{1-n} \left[1 + (1-n)\frac{T}{t} - 1 \right] = (1-n)t^{-n}$$

Loss of solvent from a strained swollen test piece

The loss of solvent from a strained swollen rubber strip results in a decrease in the volume V and hence to a decrease in the unstrained length l_0 . If the strained length l is held constant, as in a stress-relaxation measurement, the tensile strain e increases and so does the retractive force.

From the kinetic theory it may be deduced that the tensile stress in a strained swollen rubber strip is given by

$$p = Cv_2^{-1/3}(\lambda - 1/\lambda^2) \quad (\text{A.9})$$

where p is the tensile stress per unit unstrained, unswollen, cross-sectional area, $\lambda = 1 + e = l/l_0$ is the extension ratio

and v_2 , is the volume fraction of dry rubber in the swollen vulcanizate, $= V_r/V$ if V_r is the volume of dry rubber in the sample. For small strains ($e \ll 1$)

$$p = \frac{3C}{V_r^{1/3}} V^{1/2} e \quad (\text{A.10})$$

since

$$\frac{de}{dV} = \frac{d}{dV} \left(\frac{l}{l_0} - 1 \right) = -\frac{l}{l_0^2} \frac{dl_0}{dV} = -\frac{l_0}{l_0^2 3V} = -\frac{(1+e)}{3V} \quad (\text{A.11})$$

$$\frac{dp}{dV} = -\frac{3C}{V_r^{1/3}} \frac{1}{3V^{2/3}} = -\frac{p}{3eV} \quad (\text{A.12})$$

Thus for loss of a small volume, $-\Delta V$, of solvent from the swollen strip there is an increase Δf in the tension f given by

$$\frac{\Delta f}{f} = \frac{\Delta V}{3eV} \quad (\text{A.13})$$

The effect increases therefore as the strain decreases.

Intercepts in semilogarithmic plots for the power-law function

If

$$\sigma = at^{-n} \quad (\text{A.14})$$

then

$$\frac{d\sigma}{dt} = -nat^{-n-1}$$

$$\frac{d\sigma}{d \log t} = t \frac{d\sigma}{dt} = -nat^{-n} = -n\sigma \quad (\text{A.15})$$

The tangent at $t = t_1$ to the semilogarithmic plot σ vs. $\log t$ is

$$\sigma = \sigma(t_1) [1 - n \log(t/t_1)] \quad (\text{A.16})$$

The intercepts on the σ and $\log t$ axes are

$$\sigma(t_1)(1 + n \log t_1) \quad \text{and} \quad \log t_1 + 1/n \quad (\text{A.17})$$

The ratio of intercept on σ axis to slope is then

$$(1 + n \log t_1)/n \quad (\text{A.18})$$

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