

Creep and Stress Relaxation of Natural Rubber Vulcanizates. Part I. Effect of Crosslink Density on the Rate of Creep in Different Vulcanizing Systems

E. D. FARLIE, *The Natural Rubber Producers' Research Association, Welwyn Garden City, Herts., England*

Synopsis

The physical creep of unfilled natural rubber vulcanizates, prepared with different vulcanizing systems, has been studied. For each of the three vulcanizing systems chosen there is a strong dependence of creep rate on crosslink density, but the rates for accelerated sulfur vulcanizates are two or three times higher than those of peroxide vulcanizates of similar crosslink density. Supplementary experiments, in which the crosslink structure of sulfur vulcanizates is modified either by chemical treatment or by variations in the vulcanizing conditions, show that the nature of the crosslink itself is not a determining factor in the type of vulcanizate. Other features, such as the type and quantity of extranetwork material arising from the vulcanizing process, contribute significantly to the viscoelastic behavior of accelerated sulfur vulcanizates.

INTRODUCTION

The stress developed in a block of vulcanized rubber continuously deformed to a fixed extent relaxes slowly at a rate governed by the nature of the rubber and the experimental conditions. At high temperatures (e.g., $>80^{\circ}\text{C}$) or after long times (e.g., >10 weeks) this effect is mainly the result of thermal or oxidative degradation of the network,¹⁻⁴ but at short times at normal ambient temperatures (e.g., 0° - 30°C) it is attributed to a slow redistribution of stresses on the molecular scale. In unfilled natural rubber vulcanizates at normal temperatures, the rate of stress relaxation has been shown⁵ to be substantially independent of the type and degree of deformation for a given vulcanizate, but it is strongly dependent on the degree of crosslinking of the vulcanizate.^{6,7}

Under constant stress the related phenomenon of creep occurs, when the deformation increases slowly from the value reached immediately after application of the stress. Unlike the rate of stress relaxation, the rate of creep is dependent on the type or degree of deformation^{5,8} as well as on the crosslink density of the vulcanizate.

One result of these phenomena is that it is impossible to obtain equilibrium stress-strain curves on vulcanized rubber,^{9,10} although very low values

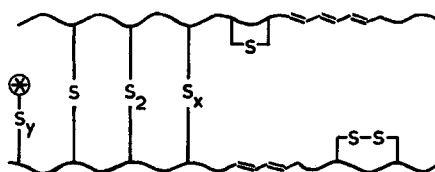


Fig. 1. Structural features of accelerated sulfur vulcanizate network of NR: (⊕) accelerator fragment; $x \geq 3$; $y \geq 1$.

of creep or stress relaxation may be achieved by working with highly swollen vulcanizates.¹¹ In the performance of rubber as a spring material the occurrence of creep is an undesirable feature, particularly in applications such as civil engineering where design lives of 50 years or more are expected. While this has not prevented the extensive use of natural rubber springs in a wide variety of applications, improvement is both possible and desirable.

The most important group of practical vulcanizing systems are those based upon sulfur, whether of the conventional accelerated sulfur types or one of the efficient vulcanization (EV) types.¹² Compared with the simple carbon-carbon crosslink structures of peroxide-cured vulcanizates, sulfur-cured vulcanizates contain various combinations of the structural features shown in Figure 1, in addition to the extranetwork material not found in the peroxide vulcanizate. It is now possible to determine the quantity and quality of the various features in the vulcanizate by the use of chemical probes¹³ and, by comparison with the physical properties of the vulcanizate, to estimate their influence on these properties.

In the present investigation the physical creep behavior of three groups of sulfur-cured vulcanizates of known structure has been examined over a range of crosslink densities and compared with that of a series of peroxide-cured vulcanizates. It is demonstrated that differences of practical significance occur between the different types of vulcanizates, but that these differences are not a function of the crosslink structure itself. Some of the effects observed are shown to accompany the presence of main-chain modification and extranetwork material.

EXPERIMENTAL

Materials

All the vulcanizates were prepared from a blended stock of technically classified RSS1 according to the recipes given in Table I. Peroxide vulcanizates (Ia-Ig) were cured within a few hours of mixing and were pre-moulded for 10 min at 100°C before curing for 60 min at 150°C in a second press. This procedure minimizes the risk of anisotropy in the vulcanizate. In the conventional vulcanizates (IIa-IIf), a constant ratio of sulfur to accelerator was maintained while varying the proportions of these materials in the rubber to obtain different concentrations of crosslinks. The

secondary ingredients (zinc oxide and lauric acid) were held at the same proportion to the rubber throughout the series. A press cure of 35 min at 140°C, which gives the maximum stiffness, was used for all these mixes. In addition, certain of these mixes were cured for 120 min at 140°, giving vulcanizates having different proportions of crosslink types and additional main-chain modifications to those cured for the shorter time. These over-cured vulcanizates are indicated by a prime (e.g., IIb', IIc', etc.). In the

TABLE I
Vulcanizate Recipes

I. Peroxide Vulcanizates:							
Base mix: NR, 100; antioxidant, ^a 1.5; dicumyl peroxide (DCP) as below; cured for 60 min at 150°C.							
	Ia	Ib	Ic	Id	Ie	If	Ig
DCP ^b	1.0	1.5	2.0	2.5	3.0	3.5	4.0
II. Conventional Accelerated-Sulfur Vulcanizates:							
Base mix: NR, 100; zinc oxide, 5; lauric acid, 1; antioxidant, ^a 1.5; sulfur and accelerator (CBS) as below; cured for 35 min and 120 min at 140°C; longer cure indicated by prime (e.g., IIb').							
	IIa	IIb	IIc	IIc'	IId	IId'	IIf
Sulfur	1.5	2.0	2.5	2.5	2.7	3.3	4.0
CBS ^c	0.3	0.4	0.5	0.5	0.54	0.67	0.8
III. Efficient Vulcanization Systems:							
Base mix: NR, 100; zinc oxide, 5; lauric acid, 2; antioxidant, ^a 1.5; sulfur and accelerator as below; cured for 50 min at 140°C.							
	IIIa	IIIb	IIIc	IIIc'	IIId	IIId'	IIId''
Sulfur	0.35	0.57	0.8	0.8	1.0	1.0	1.0
TMTD ^d	0.66	1.08	1.51	1.51	1.89	1.89	1.89
MOR ^e	1.40	2.28	3.20	3.20	4.00	4.00	4.00

^a Polymerized trimethyl dihydroquinoline, Flectol H, Monsanto Chem. Co.

^b Recrystallized dicumyl peroxide, Hercules Powder Co.

^c N-Cyclohexylbenzthiazyl sulfenamide, Santocure, Monsanto Chem. Co.

^d Tetramethylthiuram disulfide, Vulcafor TMT, I.C.I. Ltd.

^e 2-(4-Morpholinylmercapto)benzthiazole, Santocure MOR, Monsanto Chem. Co.

third series of vulcanizates (IIIa-IIIId), EV recipes were used, using the same principle of maintaining a constant sulfur-to-accelerator ratio while keeping the zinc oxide and fatty acid level constant. A cure of 60 min at 140°C was given to reach maximum stiffness. Vulcanizates K, L, and M were additional to the main experiment and were also of the EV type.

In some cases replicate mixes were prepared and vulcanized to check the consistency of the data. Where appropriate, results for the individual mixes are given.

Measurement of Creep

The creep of strips 10 cm long by 3 mm wide by 1 mm thick was measured under constant load at a nominal extension of 100% by means of a cathetometer. The strips were enclosed in an air thermostat held at 30°C. Strips were allowed to equilibrate in the thermostat for a minimum of 16 hr before being strained. It has recently been shown¹⁴ that creep rates can be strongly influenced by the ambient humidity. Although the humidity within the cabinet was not controlled, records showed that it varied between fairly narrow limits, and it was estimated that the variation of creep rate from this cause would not exceed 10%.

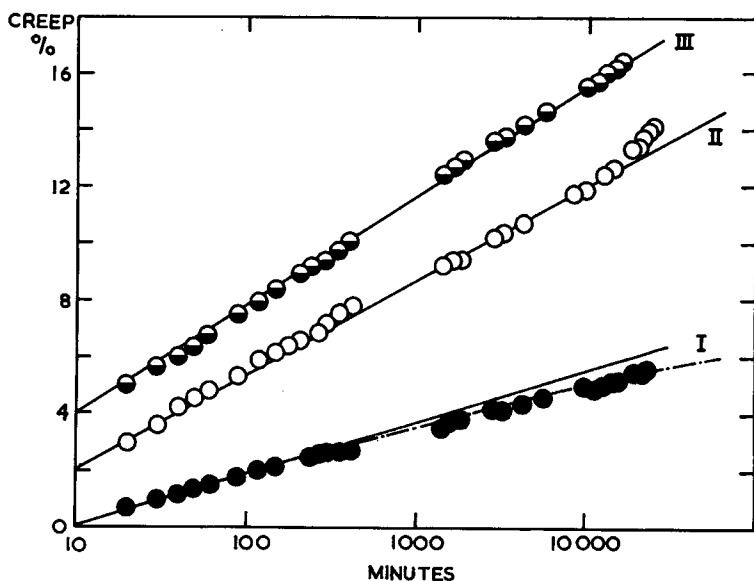


Fig. 2. Typical tensile creep curves from the three types of vulcanizate (see Table I).

All tests were carried out on freshly cut testpieces, care being taken to avoid prior deformation of the rubber, which has been shown^{9,15} to affect the subsequent creep behavior. Plots of the percentage increase in elongation against the logarithm of the time after loading were substantially linear up to 10^4 min in most cases. Typical plots for three vulcanizates are shown in Figure 2. The slope of such plots gives the creep rate C , where $C = (1/e) \{ \partial e / [\partial (\log t)] \}$ and e is the elongation after 1 minute. In some cases the elongation after 10 min was used to calculate C , but no difference was found between values calculated from either origin. The rate is expressed throughout in per cent per decade in time, and the values quoted were normally the mean of measurements on two or more replicate test pieces.

Crosslink Density Measurements

Estimates of the crosslink density of vulcanizates were made from stress-strain measurements using the Mooney-Rivlin equation^{16,17}

$$\delta = 2(C_1 + \lambda^{-1}C_2)(\lambda - \lambda^{-2})$$

where λ is the ratio of the strained to the unstrained length ($\lambda = 1 + e$) at stress δ calculated on the unstrained cross section and C_1 and C_2 are constants. The measurements were made on a specially designed machine on which the strips are extended by predetermined increments of extension arranged to give a uniform progression in the values of λ^{-1} . The sample is held for a constant time at each extension, the force being measured at the end of each time period. Values of C_1 and C_2 were obtained graphically from plots of $\delta/[2(\lambda - \lambda^{-2})]$ versus λ^{-1} .

The average molecular weight between physically effective crosslinks has been calculated from the relation

$$C_1 = \frac{1}{2}\rho RT M_c^{-1}(\text{phys}).$$

In addition, estimates of the average molecular weight between chemical crosslinks were made using the following equation¹⁷:

$$C_1 = [\frac{1}{2}\rho RT M_c^{-1}(\text{chem}) + 0.78 \times 10^6][1 - 2.3 M_c(\text{chem}) \cdot M_n^{-1}] \text{dynes cm}^{-2}.$$

TABLE II
Vulcanizate Physical Properties^a

Vulcanizate no.	C_1 , (dynes/cm ²) $\times 10^{-6}$	C_2 , (dynes/cm ²) $\times 10^{-6}$	$M_c(\text{phys})$ $\times 10^{-4}$
Ia	0.69	0.66	1.65
Ib	1.11	0.77	1.08
Ic	1.29	0.77	0.87
Id	1.66	0.84	0.68
Ie	2.04/2.22	0.81/0.79	0.55/0.56
If	2.32/2.40	0.90/0.79	0.49/0.47
Ig	2.67/2.78	0.84/0.77	0.42/0.41
IIa	0.99	1.07	1.19
IIb	1.29/1.34	1.35/1.38	0.92/0.88
IIc	1.62	1.45	0.74
IId	1.77/1.86	1.31/1.32	0.67/0.64
IIe	2.14/2.03	1.26/1.39	0.55/0.59
IIf	2.40/2.35	1.45/1.41	0.50/0.51
IIb'	1.23	1.24	0.97
IId'	1.45	1.24	0.82
IIe'	1.61	1.23	0.73
IIf'	1.70	1.20	0.71
IIIa	1.17/1.17	1.31/1.49	1.01/1.01
IIIb	1.83/1.82	1.45/1.70	0.65/0.65
IIIc	2.41/2.44	1.69/1.87	0.49/0.49
IIId	2.75/2.87	1.84/1.96	0.43/0.42

^a Where more than one result is given, the figures refer to vulcanizates prepared from replicate mixes.

Values of the initial molecular weight prior to vulcanization were derived from solution viscosity measurements in toluene¹⁸ where

$$[\eta] = 9.00 \times 10^{-6} \bar{M}_n^{1.026}.$$

The values of $M_c(\text{chem})$ were used in the calculations on structural analysis; values of C_1 , C_2 , and $M_c(\text{phys})$ are given in Table II.

Vulcanizate Structural Analysis

The estimation of the relative proportion of mono-, di-, and polysulfide crosslinks in the sulfur vulcanizates followed the procedure described by Watson and Saville¹³ except that the more recently developed hexane thiol

TABLE III
Sulfur Vulcanizate Characterization

Vulcanizate no.	$M_c(\text{chem})$ $\times 10^{-4}$	Crosslink distribution			
		%S _x	%S ₂	%S ₁	SMI ^a
IIb	1.49	70	30	—	2.86
IIc	0.94	75	25	—	1.86
IId	0.73	73	27	—	1.92
IIe	0.63	73	27	—	1.90
IIb'	1.71	46	20	34	5.25
IIc'	1.24	44	19	37	5.08
IId'	1.05	44	18	38	4.70
IId'	0.98	49	16	35	4.37
IIIa	1.65	—	—	100	1.29
IIIb	0.84	—	15	85	1.04
IIIc	0.60	—	6	94	1.15
IIId	0.52	—	11	89	1.22

^a Sulfur Modification Index: number of sulfur atoms combined in an average network chain at points other than at the crosslinks.

treatment²⁰ was used instead of the sodium dibutyl phosphite probe. Details of the other treatments are given elsewhere.^{13,21,22} The results are given in Table III.

RESULTS AND DISCUSSION

The Dependence of Creep Rate on Crosslink Density

The measured creep rate C for each of the vulcanizates of the three principle series is given in Table IV, including the results for replicate mixes. Also given is the stress relaxation rate S , calculated from the expression⁵

$$C = S(\delta/e)(\partial e/\partial \delta)_t$$

where δ is the stress and e the elongation and $(\partial e/\partial \delta)$ is the slope of the strain-stress curve at e . Measured stress relaxation rates on selected vulcanizates showed good agreement with calculated values.

The reproducibility of creep results from replicate mixes is good and confirms that the differences between types of vulcanizates are significantly greater than the variability within the types. The marked dependence of creep rate on crosslink density, as represented by the value of C_1 is illustrated in Figure 3. The form of dependence is similar for the three groups of vulcanizates, but over most of the range of crosslink density examined the sulfur vulcanizates as a whole show rates 2-3 times higher than the corresponding peroxide vulcanizates. Below C_1 values of 1×10^6 dynes cm^2 , the characteristics appear to converge for all three types, but at the higher end of the range there is a clear difference between the conventional and EV

TABLE IV
Rates of Creep (C) and Stress Relaxation (S)

Vulcanizate no.	C , %/dec	S , ^a %/dec
Ia	4.8	2.7
Ib	2.2	1.3
Ic	1.5	0.90
Id	1.0	0.61
Ie	0.75/0.80	0.47/0.51
If	0.65/0.70	0.41/0.45
Ig	0.62/0.70	0.40/0.46
IIa	4.5	2.4
IIb	3.3/2.9	1.8/1.6
IIc	2.5	
IId	2.6/2.3	1.5/1.3
IIe	2.2/2.2	1.3/1.3
IIf	2.1/2.0	1.3/1.2
IIb'	3.3	1.8
IId'	2.6	1.5
IIe'	2.4	1.4
IIf'	2.2	1.3
IIIa	3.9/4.2	2.1/2.2
IIIb	3.2/2.9	1.8/1.6
IIIc	2.6/2.5	1.5/1.4
IIId	2.6/2.3	1.5/1.4

^a Calculated from creep rate.

sulfur vulcanizates. Overcuring of the conventional vulcanizates does not alter the creep behavior except insofar as the level of crosslinking is reduced.

The observed differences between sulfur and peroxide vulcanizates are apparently in conflict with the data of Gent.³ The solid line in Figure 4 is reproduced from Bateman, chap. 8,⁶ the plotted points being some of the values of stress relaxation rate calculated from the present results. Most of the present peroxide vulcanizates lie well below the line, while the results for sulfur vulcanizates are in good agreement at values of C_1 about 1.5 dynes/ cm^2 and much higher at high values of C_1 . The present data also appear to give lower rates of stress relaxation than reported by Chasset and Thirion⁷ for peroxide vulcanizates of similar crosslink densities. Reasons

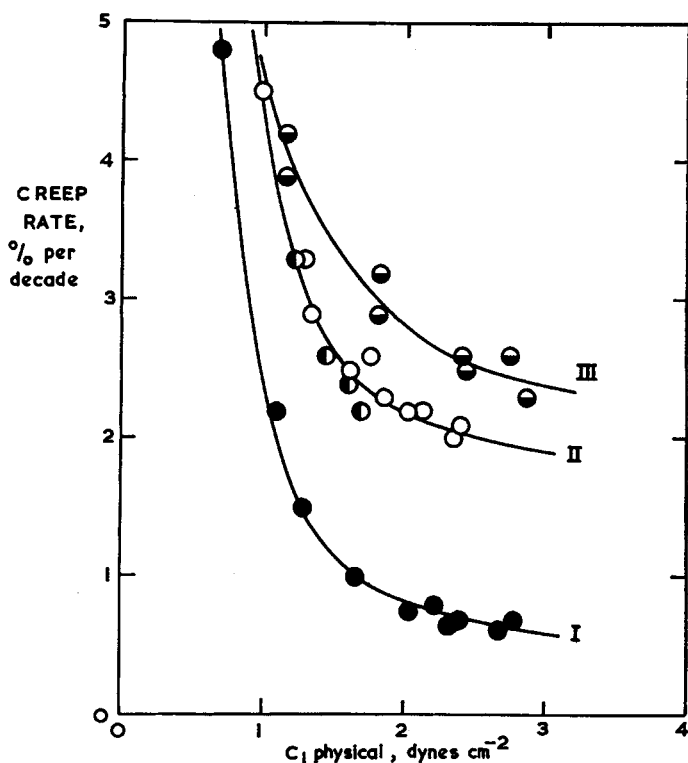


Fig. 3. Dependence of creep rate on physical estimate of crosslink density.

for the apparent discrepancy between these and previously reported results have not been established.

The observed differences between the peroxide and sulfur vulcanizates are in broad agreement with other aspects of viscoelastic behavior: thus, peroxide vulcanizates show lower hysteresis than sulfur vulcanizates as indicated by rebound resilience tests. Working with small samples in shear, Ferry et al.²³ observed differences in $\tan \delta$ between peroxide-cured and sulfur-cured vulcanizates over a range of crosslink densities, with a tendency for the results to converge at low levels of crosslinking. The logarithmic plot of S versus M_c (phys) in Figure 5 from the data on Table IV is exactly analogous to Ferry's plot of $\tan \delta$ versus M_c (cf. Fig. 6 in Ferry²³). The considerable differences in experimental conditions make quantitative comparisons hazardous but the linearity of the plots over a range of M_c values, and the differences in slope for the two types of vulcanizate, are alike in both sets of results.

The Effect of Sulfur Crosslink Length and Creep Rate

Polysulfide crosslinks are believed to rupture and reform under certain conditions.²⁴ If this process occurs in a deformed vulcanizate, creep or

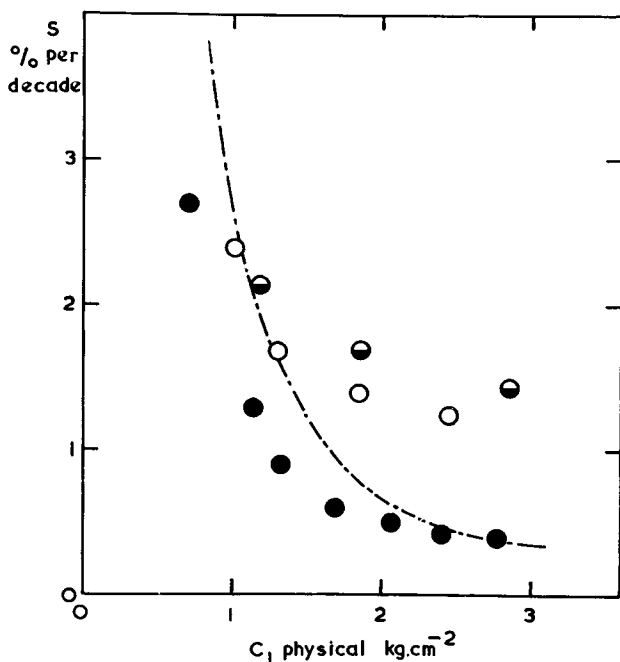


Fig. 4. Dependence of stress relaxation rate (calculated) on physical estimate of crosslink density. Curve reproduced from Bateman.⁶

stress relaxation will be enhanced and part of the deformation will be irrecoverable.²⁵ At ordinary ambient temperatures deformation of conventional accelerated-sulfur vulcanizates is almost completely recovered after compression for 10^5 min^{5,26} and crosslink rearrangement is thus believed to be insignificant under these conditions.

The following experiment provides additional confirmation that the primary creep rate at 30°C of the sulfur-CBS vulcanizate is not affected by the presence of polysulfide crosslinks. By treatment of a conventional vulcanizate containing mainly polysulfide crosslinks with triphenyl phosphine,²¹ a vulcanizate is produced having the same crosslink density (as indicated by the value of C_1 before and after treatment) and substantially the same main chain modifications but which now contains only monosulfide crosslinks. Removal of some soluble extranetwork material will however occur during the treatment, which includes solvent extraction of the test piece.

In Figure 6, creep curves are shown for treated and untreated test pieces from vulcanizate IIc, together with a "control" test piece subject to the same preliminary extraction and swelling procedures but without addition of triphenyl phosphine. In this case the value of C_1 is found to increase by about 10%. While the creep plots of the treated materials show earlier departures from linearity, probably because antioxidant removal during extraction advances the time at which a significant contribution occurs

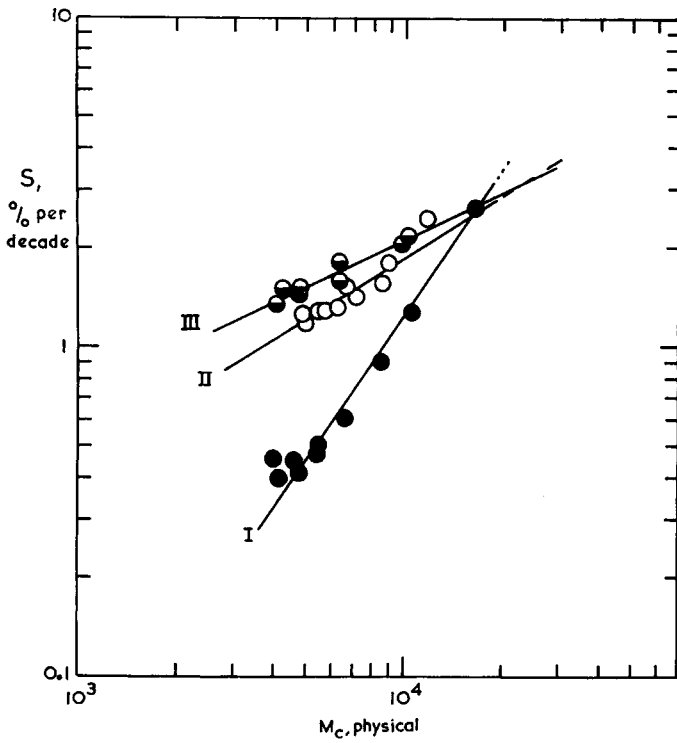


Fig. 5. Logarithmic plot of stress relaxation rate against physical estimate of chain length between crosslinks.

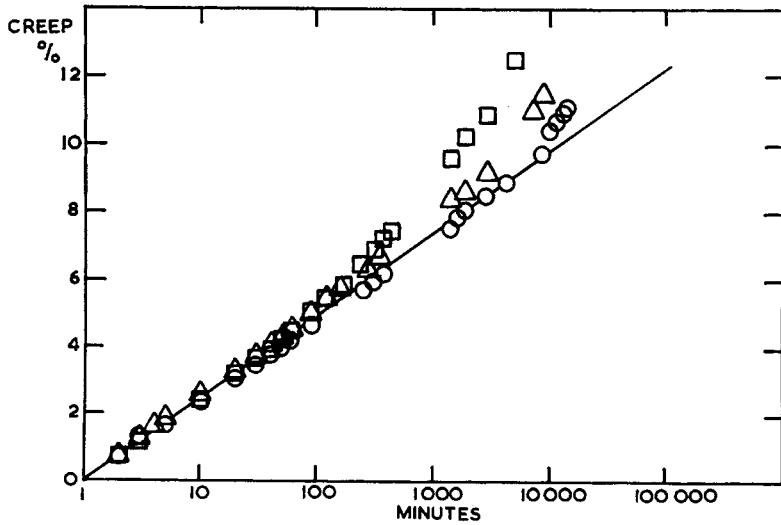


Fig. 6. Creep plots for vulcanizate IIc, with and without treatment to remove polysulfide crosslinks: (O) untreated; (□) treated; (Δ) blank treatment.

from oxidation, creep results over the first two decades are almost identical. Thus, polysulfidic crosslinks do not, under these experimental conditions, contribute to the physical creep of conventional sulfur-cured vulcanizates.

The Effect of Main Chain Modifications on Creep

During the vulcanization of natural rubber with sulfur systems, modifications to the polymer chains may take place other than at crosslink sites, examples being the formation of conjugated triene groups and *cis-trans* isomerization of isoprene units.¹³

Other modifications involving combination of sulfur include the formation of cyclic sulfide groups and the attachment of pendent groups derived from the vulcanization accelerator. Both kinds of modification will to some extent locally modify the chain flexibility.

In particular, both cyclic sulfides and pendent accelerator units offer possibilities for polar interaction either directly between groups on adjacent chains or through intermediates among the extranetwork materials. The strength of such interactions might vary from that of a weak entanglement to that of an ionic bond. Such effects might well show a dependence on humidity.

An indication of the concentration of such groupings in the vulcanizate can be deduced from the network characterization procedure.¹³ From these data the average number of sulfur atoms combined in each network chain other than in the crosslinks is found. This number, called the sulfur modification index (SMI), does not indicate the particular form of the modifications and this must be adduced from other evidence. Values of SMI for the sulfur vulcanizates are given in Table III. In vulcanizates I Ib–I If there are about two atoms of sulfur combined in each network chain. Recent work²⁷ has shown that the molar proportion of pendent groups in this type of vulcanizate does not exceed about 5% of the crosslinks, so that most of this sulfur is probably combined as cyclic sulfide groups. In vulcanizates I Ib', I Id', I Ie', and I If', vulcanized for a longer time, the value of the SMI has risen to about 5 per network chain, again mostly in the form of cyclic groupings. Since the creep rates of vulcanizates cured for the longer times were equal to those of comparable crosslink density cured for the shorter times, the creep of conventional vulcanizates appears to be independent of the concentration of cyclic sulfide groups in the network.

In the EV mixes the value of the SMI is much lower and mainly represents sulfur combined in pendent groups. Work both on vulcanizates prepared from tetramethyl thiuram disulfide/zinc oxide EV recipes²⁸ and on EV vulcanizates in which a high ratio of accelerator to sulfur was used²⁹ has shown that at full cure about one pendent group is combined for every two crosslinks. Other EV recipes would be expected to show the same result, the nature of the attachments depending on the accelerator(s) employed.

A high rate of stress relaxation has been previously reported⁶ for a tetramethyl thiuram disulfide (TMTD) vulcanizate. Three mixes based upon

TABLE V
Additional EV Vulcanizate Recipes

	Vulcanizate		
	K	L	M
NR	100	100	100
Zinc oxide	5	5	5
Lauric acid	—	1.0	—
Stearic acid	0.5	—	1.0
TMTD	3	3	3
Antioxidant	1 ^a	1.5 ^a	1 ^b
Cured at 140°C for	45 min	45 min	20 min

^a Flectol H.

^b Phenyl- β -naphthylamine.

this system were prepared (K, L, and M, Table V) having minor variations in ingredients. The results (Table VI) failed to confirm a higher creep rate for this material than for a comparable conventional sulfur vulcanizate. It follows that at this level of crosslinking the presence of pendent groups in

TABLE VI
Creep of TMTD Vulcanizates

Vul- canizate	C_1 , (dynes/cm ² $\times 10^{-6}$)	C_2 , (dynes/cm ² $\times 10^{-6}$)	C , %/dec
K	1.23	1.19	3.1
L	1.10	1.39	2.9
M	1.07	1.30	2.9

EV vulcanizates cannot be the primary cause of difference between the creep rates of the two types of sulfur vulcanizate. Thus, at conventional levels of crosslink density ($C_1 = 1.0 - 1.5$ dynes/cm²), main-chain modifications alone may not be an important factor in determining physical creep rates of gum vulcanizates. The role of pendent groups at the higher crosslink densities in EV vulcanizates cannot be determined from the present data.

The Contribution of Extranetwork Material to Creep Behavior

The extranetwork materials in a vulcanizate arise either from nonrubber present in the raw material or from unreacted materials and reaction by-products from the vulcanizing process. Some of the material present may be rubber soluble, while others will be insoluble and act as filler particles. The amount of solvent-extractable material present depends on the type of vulcanizate (Table VII).

Solvent extraction has previously been shown to improve the creep behavior of one type of EV vulcanizate⁶ and results are given in Table VIII of creep measurements on several extracted vulcanizates, including two (K and

TABLE VII
Typical Amounts of Solvent-Extractable Material in Vulcanizates

Vulcanizate	% Extract ^a	Contents of extract
Raw	2.2	nonrubber constituents (nrc's)
If	4.9	nrc's + DCP residues + antioxidant
IIb	3.5	nrc's + fatty acid + acc. residues + antioxidant
IIe	3.5	nrc's + fatty acid + acc. residues + antioxidant
IIIa	5.2	nrc's + fatty acid + acc. residues + antioxidant
IIIc	6.8	nrc's + fatty acid + acc. residues + antioxidant
IIId	7.3	nrc's + fatty acid + acc. residues + antioxidant
K	4.4	nrc's + fatty acid + acc. residues + antioxidant

^a Extraction for 48 hr with chloroform-acetone-methanol azeotrope in water-jacketed Soxhlet apparatus.

TABLE VIII
Creep of Extracted Vulcanizates

Vulcanizate	Treatment ^a	C_1 , (dynes/cm ² $\times 10^{-6}$)	C_2 , (dynes/cm ² , $\times 10^{-6}$)	C , % dec
IIb	none	1.29	1.35	3.3
	A	1.45	1.32	3.4
IIIa	none	1.17	1.31	3.9
	A	1.36	1.32	3.5
IIIb	none	1.83	1.45	3.2
	A	2.10	1.45	2.8
IIIc	none	2.41	1.69	2.6
	A	2.76	1.52	2.7
IIId	none	2.75	1.84	2.6
	A	3.38	1.29	2.4
K	none	1.23	1.19	3.1
	A	1.35	1.17	2.7
	B	1.33	1.10	2.4
L	none	1.10	1.39	3.5
	A	1.31	1.29	2.9

^a A: 48 hr extraction with azeotrope of chloroform, methanol, and acetone in water-jacketed Soxhlet apparatus; B: 24 hr extraction with hot acetone in Soxhlet apparatus.

L) vulcanized with TMTD. Values of the elastic constant C_1 after extraction are included; it was invariably found that this value was higher than that obtained on the original material, while the value of C_2 was for the most part unaffected. In no case was the treatment expected to affect the number of chemical crosslinks present, nor is it obvious how the number of

permanent entanglements could be altered. This was confirmed by comparison of swelling measurements in *n*-decane before and after extraction. Thus the permanent network should be unchanged by the treatment and this assumption is made in comparing the creep rates before and after treatment.

The results confirm the reported improvement in creep rate of TMTD vulcanizates on extraction, but of the other EV vulcanizates, only IIIa and IIIb show significant improvement on extraction. The conventional sulfur vulcanizate shows no decrease in creep rate after extraction. The role of the extractable extranetwork material in the creep process is thus apparently different for different vulcanizing systems and may vary within one system at different concentrations of crosslinks and main-chain modifications.

CONCLUSIONS

It has been shown that distinct differences in creep behavior exist between different types of natural rubber vulcanizates, confirming the results reported by Ferry et al.²³ In vulcanizates containing sulfur crosslinks, the number of sulfur atoms in the crosslink does not affect the rate of creep and it is probable that the presence of sulfur crosslinks does not itself account for the higher creep rate of sulfur-cured vulcanizates relative to peroxide-cured vulcanizates of the same stiffness. These remarks relate only to the *primary* creep of the vulcanizates; under conditions where *secondary* (chemical) creep occurs, it is known³ that vulcanizates containing mainly polysulfidic crosslinks show very different behavior from those containing mainly monosulfidic crosslinks.

The results have not provided a complete understanding of the effects of either the main-chain modifications or the extranetwork materials on the creep of vulcanizates. Variations in the concentration of cyclic sulfide groups seem to have no significant effect on the creep rate, but the contribution of the pendent groups present in EV vulcanizates remains conjectural. It is possible that polar interaction occurs between groups attached to the chain, either directly or through intermediates among the extranetwork material. Removal of some of this extranetwork material by solvent extraction in some cases reduces the creep rate, but in others there is no effect. In any case, appreciable amounts of insoluble zinc compounds remain in the rubber after extraction and this may be an important factor. The possibility of polar interactions is consistent with the observed effect of humidity on creep rates.¹⁴

It has been clearly demonstrated that factors other than the crosslink density and crosslink type can contribute significantly to the viscoelastic behavior of vulcanizates.

Many thanks are due to G. Skellern and B. Abbott for experimental assistance both on creep measurements and vulcanizate characterization. The work forms part of the program of research of the Natural Rubber Producers' Research Association.

References

1. A. V. Tobolsky, J. B. Prettymann, and J. H. Dillon, *J. Appl. Phys.*, **15**, 380 (1943).
2. L. Bateman, Ed., *The Chemistry and Physics of Rubberlike Substances*, Maclaren, London, 1963, Chap. 18.
3. A. N. Gent, *J. Appl. Polym. Sci.*, **6**, 442 (1962).
4. P. Thirion and R. Chasset, Proc. 4th Rubb. Tech. Conf., Inst. Rubb. Ind., London, 1963, p. 338.
5. A. N. Gent, *J. Appl. Polym. Sci.*, **6**, 433 (1962).
6. L. Bateman, Ed., *The Chemistry and Physics of Rubberlike Substances*, Chap. 8, p. 219.
7. R. Chasset and P. Thirion, Proc. Internat. Conf. Physics of Noncrystalline Solids, Delft, 1964, p. 345.
8. D. H. Cooper, *Ind. Eng. Chem.*, **43**, 365 (1951).
9. G. M. Martin, F. L. Roth, and R. D. Stiehler, *Trans. Inst. Rubb. Ind.*, **32**, 189 (1956).
10. A. Ciferri and P. J. Flory, *J. Appl. Phys.*, **30**, 1498 (1959).
11. G. Gee, *Trans. Faraday Soc.*, **42**, 585 (1946).
12. T. D. Skinner and A. A. Watson, *Rubber Age*, **99**, (11) 76 (1967).
13. B. Saville and A. A. Watson, *Rubb. Chem. Tech.*, **40**, 100 (1967).
14. C. J. Derham, G. J. Lake, and A. G. Thomas, *J. Rubb. Res. Int. Malaya*, **22**(2), 191 (1969).
15. C. J. Derham and A. G. Thomas, *Nature*, **218**, 81 (1968).
16. M. Mooney, *J. Appl. Phys.*, **11**, 582 (1940).
17. R. S. Rivlin and D. W. Saunders, *Phil. Trans. Roy. Soc. A*, **243**, 251 (1951).
18. L. Mullins, *J. Appl. Polym. Sci.*, **2**, 1 (1959).
19. G. M. Bristow, *J. Polym. Sci. A-1*, **1**, 2261 (1963).
20. D. S. Campbell and B. Saville, Proc. Rubb. Tech. Conf. IRI, London, 1968, p. 1.
21. C. G. Moore and B. R. Trego, *J. Appl. Polym. Sci.*, **5**, 299 (1961).
22. B. R. Trego, Ph.D. Thesis, University of London, 1965.
23. J. D. Ferry, R. G. Mancke, E. Maekawa, Y. Oyanagi, and R. A. Dickie, *J. Phys. Chem.*, **68**, 3414 (1964).
24. B. A. Dogadkin and Z. M. Tarasova, *Rubb. Chem. Tech.*, **27**, 883 (1954).
25. R. D. Andrews, A. V. Tobolsky, and E. E. Hanson, *J. Appl. Phys.*, **17**, 352 (1946).
26. E. D. Farlie, unpublished results.
27. D. S. Campbell, *J. Appl. Polym. Sci.*, in press.
28. C. G. Moore and A. A. Watson, *J. Appl. Polym. Sci.*, **8**, 581 (1964).
29. D. S. Campbell, *J. Appl. Polym. Sci.*, in press.

Received September 22, 1969

Revised October 3, 1969