Delayed Elasticity of 'Pure-Gum' Rubber Vulcanisates

R. CHASSET and P. THIRION

Institut Français du Caoutchouc, Paris, France

The viscoelastic relaxation in tension of 'pure-gum' vulcanisates based on five types of natural rubber prepared by different methods has been studied. At equal modulus, there is no significant difference in viscoelasticity and, therefore, in dynamic properties at low frequencies. A comparison of the results obtained (a) with different vulcanisation systems and (b) with natural rubber, SBR, and cis-1,4-polybutadiene indicates that the relaxation kinetics of the vulcanisates depend, as equilibrium is approached, on the structure of the macromolecular network rather than on the glass transition temperature of the polymers.

The Plasticity Retention Index (PRI) has been proposed as a criterion of the oxidation resistance of raw natural rubber (BATEMAN AND SEKHAR, 1966; FARLIE AND GREENSMITH, 1966). However, the PRI does not necessarily have any relation to the dynamic properties of the vulcanisates, particularly resilience and heat build-up (RESING, 1967).

In order to appreciate the interest of the PRI to manufacturers, it is necessary to know the physico-chemical factors which could eventually be of importance, in addition to the possible correlations with technological properties. It is this relatively fundamental aspect of the problem which is dealt with in this paper, by analysis of the relaxation in tension of 'pure-gum' vulcanisates used in a general study of the viscoelasticity of elastomers (THIRION AND CHASSET, 1967a and b).

TYPES OF RAW RUBBER EXAMINED AND TEST METHODS

In order to investigate the differences between various types of commercial natural rubbers, an examination was made of the following five types of rubber, which have different impurity contents owing to variations in the degree of washing undergone in the plantation *(Table 1)*.

The rubbers were mixed with 3.5% of

TABLE 1. CHARACTERISTICS OF RAW NATURAL RUBBERS

Type of natural rubber	Nitrogen (%)	Copper (p.p.m.)	Manganese (p.p.m.)	Impurities (% up to sieve 325)	PRI
RSS 1	0.40	2	2	0.015	82
Pale crepe	0.32	2	1.5	0.011	83
Air dried sheet	0.23	1.6	1.3	0.008	75
Tenso-sheet	0.52	3	3	0.017	78
GSK†	–	–	–	0.008	–

†GSK (Guaranteed Super Kleen) rubber is no longer commercially available. It was prepared in Malaya from diluted and filtered latex.

dicumyl peroxide under controlled mastication conditions. This curing agent is rarely used in industry, but, compared with sulphur-accelerator systems*, it has the advantage of producing molecular networks of a simple structure, consisting of carbon–carbon cross-links with no chain modification or risk of reversion.

The weight-average molecular weights were about 600 000 to 800 000 for all the rubbers, as determined by viscometric measurements where degradation of the polymers during mastication was kept to a minimum.

Mastication was prolonged in some cases, however, to reduce the molecular weight to

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*Nevertheless, results relating to a sulphurless GSK natural rubber mix vulcanised by tetramethylthiuram disulphide will be presented later (Mix formulation: see *Table 3*).

about 200 000, so that the effect of this parameter relatively to that of another important variable — degree of cross-linking of the vulcanisates — could be determined. It is a known fact that, other variables being equal, the degree of cross-linking depends very much on the composition of the raw rubber, since the intrinsic cure rate is used as a basis for the classification of the raw rubber. Nevertheless, the authors have tried to cover the widest possible range of moduli, at least in one case, by vulcanising for 20 to 150 minutes at 135°C.

Twenty-eight different natural rubber vulcanisates were obtained in all, as shown in *Table 2*. Samples in the shape of parallelipipeds (70 × 4 × 2 mm) were cut from the sheets,

TABLE 2.   CHARACTERISTICS OF $3\frac{1}{2}$% DICUMYL PEROXIDE NATURAL RUBBER VULCANISATES

Type of rubber	Reference number*	Weight-average molecular weight after vulcanisation $(\overline{M}_w \times 10^{-3})$	Molar cross-link density per cm³ $(\nu \times 10^4)$†	Equilibrium stress at 50% extension F_e (kgf/cm²)
	98 – 20		0.458	1.78
	98 – 30	between 500	0.620	2.36
	98 – 40	and 700	0.805	2.94
	98 – 75		1.205	4.12
	98 – 150		1.700	5.20
	109 A1 20	550	0.470	1.85
	109 A1 40	550	0.752	1.72
GSK	109 A2 40	770	0.810	2.86
	109 A2 75	770	1.280	4.21
	109 A2 150	770	1.860	5.66
	109 B1 20	260	0.289	1.08
	109 B1 40	260	0.585	2.15
	109 B2 40	230	0.583	2.08
	109 B2 75	230	0.890	3.11
	109 B2 150	230	1.525	5.00
ADS	110 A 20	500	0.418	1.60
	110 A 40	500	0.760	2.52
	110 B 20	260	0.290	1.09
	110 B 40	260	0.620	2.20
Pale crepe	111 A 20	500	0.280	1.16
	111 A 40	500	0.600	2.22
	111 B 40	260	0.490	1.84
Tenso-sheet	102 A–30	700	1.170	3.58
	102 B–30	560	1.180	3.61
	102 E–30	330	0.999	2.23
	102 F–30	210	0.610	2.00
RSS 1	113 – 30	between 500	0.655	2.36
	113 – 60	and 700	1.135	3.69

*The second number denotes the vulcanisation time in minutes at 135°C.

†The molar cross-link density (per cm³) ν is calculated from the maximum swelling in benzene by the Flory-Huggins formula (FLORY, 1950):

$$\nu = \frac{-\log_e \ (1-v_r) - v_r - \mu' v_r^2}{V_o \ (v_r^{\frac{1}{3}} - \frac{1}{2}v_r)}$$

where V_o is the molar volume of benzene, v_r the volume fraction of polymer and μ' the solvent-polymer interaction coefficient. The authors have taken $\mu' = 0.444$ for the natural rubber-benzene system.

TABLE 3.   CHARACTERISTICS OF NATURAL RUBBER/TMTD, SBR/DCP AND
CIS-POLYBUTADIENE/DCP VULCANISATES

Formulation	Reference number*	Weight-average molecular weight after vulcanisation ($\overline{M}_w \times 10^{-3}$)	Molar cross-link density per cm³ ($\nu \times 10^4$)†	Equilibrium stress at 50% extension F_e (kgf/cm²)
Natural rubber	91 – 10	between 500	—	3.22
GSK 100	91 – 15	and 700	—	3.48
Stearic acid 1	91 – 30		—	3.72
Zinc oxide 2	91 – 45		—	3.83
TMTD 3.5	91 – 90		—	3.91
Phenylnaph-thylamine 1				
Vulcanisation temperature 147°C				
SBR (23.5% styrene)	93 – 10	between 300	0.745	2.76
Polysar Krylene 1500 100	93 – 12	and 500	0.940	3.17
	93 – 15		1.320	4.43
Dicumyl peroxide 3	93 – 20		1.765	5.82
	93 – 25		2.030	6.25
Vulcanisation temperature 147°C				
Cis-polybutadiene	116 – 30	460	—	1.15
BR 11 100	116 – 40	460	—	1.65
Dicumyl peroxide 0.4	116 – 75	460	—	3.73
	116 – 150	460	—	5.76
Vulcanisation temperature 135°C				

*The second reference number denotes the vulcanisation time in minutes.

†The molar cross-link density (ν per cm³) was calculated from the maximum swelling in benzene by the Flory-Huggins formula (Flory, 1950):

$$\nu = \frac{-\log_e (1 - v_r) - v_r - \mu' v_r^2}{V_o (v_r^{\frac{1}{3}} - \frac{1}{2} v_r)}$$

where V_o is the molar volume of benzene, v_r the volume fraction of polymer and μ' the solvent-polymer interaction coefficient. We have taken $\mu' = 0.392$ for the SBR-benzene system.

care being taken to avoid any deformation before the tests. The relaxation of dicumyl peroxide cured SBR and cis-1,4-polybutadiene vulcanisates *(Table 3)* was also studied under comparable conditions.

The stress-relaxation of polymers can be measured by various static or dynamic methods. The relaxation test used here involves stretching a test-piece in a dark oven at a constant temperature of $(30 \pm 1)°C$ and maintaining it at constant elongation; a dynamometer records the decrease in tension with time. The precision of the instrument is 0.1 g and is therefore generally better than 0.1% for measurements of the force; elongation was measured using a cathetometer to within 0.1% of the true value, both at the beginning and at the end of the test, no slip in the clamps being detected (Thirion and Chasset, 1967b). The reproducibility of the tests on samples taken from the same sheet is, however, limited by sample variation to about 1 to 2% on average.

DETERMINATION OF PURE VISCOELASTIC RELAXATION REGION

Basic analysis of the stress-relaxation of vulcanisates can only be carried out by regarding it as a physical phenomenon corresponding to a simple reversible rearrangement of the macromolecular network, without appreciable degradation of the structure during the test. At temperatures of the order of 100°C, ageing is the principal cause of rapid relaxation in vulcanisates. This allows the degree of molecular scission under these conditions to be estimated. Although the rate of degradation decreases as the test temperature is lowered, there comes a point when, unlike viscoelastic relaxation, the degradation process, which augments with time, becomes the predominant feature even at ambient temperature (TOBOLSKY, 1960; THIRION AND CHASSET, 1963). A typical illustration of this important point, which has often been neglected in previous studies, will be found in the relaxation curves at 50% extension in *Figure 1*, which plots variations in the stress of a dicumyl peroxide–natural rubber vulcanisate against the logarithm of time, at various test temperatures.

These curves, which at first are always concave towards the abscissa at high temperatures, change shape as the temperature decreases. There is, in fact, a distinct inflection zone at 65°C and, at lower temperatures, the curves become uniformly concave towards the ordinate. The point of inflection is then moved further along the time scale in the periods of time covered, which in this case were limited to about 100 hours.

These radical differences between the relaxation kinetics in different parts of the inflection zone indicate that, except at high temperatures, pure viscoelastic relaxation takes place first. This is characterised by the presence of well-defined elastic moduli and corresponds to states of virtual equilibrium. These states could in theory be reached after very long periods, provided that ageing effects did not interfere and ultimately predominate, so causing the tension to decrease gradually.

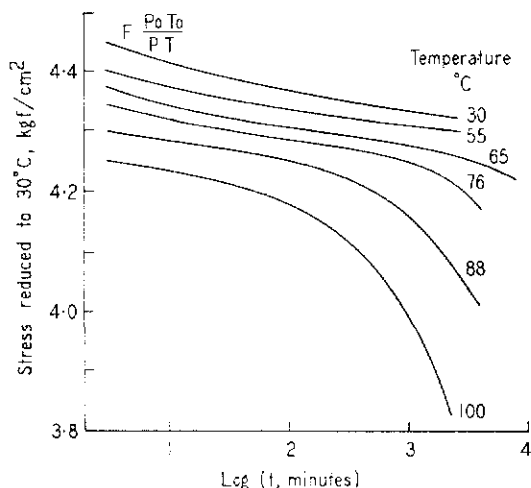Moreover, the portions of the relaxation curves in the neighbourhood of the point of

Figure 1. Relaxation curves showing the respective regions of predominance of viscoelasticity and ageing and their dependence on the temperature of test, for a dicumyl peroxide–natural rubber vulcanisate at 50% extension.

inflection approximate increasingly to a straight line as the precision of the measurements decreases. This has often led to belief in the existence of a linear viscoelastic relaxation law as a function of the logarithm of time (MARTIN *et al.*, 1956; LANDEL AND STEDRY, 1960; GENT, 1962; COTTEN AND BOONSTRA, 1965; ROTH *et al.*, 1965). In reality, this rheological behaviour reveals that viscoelasticity and ageing have an equal effect on relaxation, which is then no longer a reversible phenomenon. For each type of vulcanisate studied, it is therefore necessary to determine, by extrapolation of the high temperature results, the time limit at which the effect of ageing relative to viscoelastic relaxation is no longer negligible. The measurements are no longer of interest in physical stress-relaxation studies beyond this limit, which is generally reached after 15 to 30 hours at 30°C. It is therefore established that, in the useful region of the relaxation curves, the stress of the vulcanisates in all cases decreases less quickly than the logarithm of time, tending towards a non-zero limit.

RHEOLOGICAL ANALYSIS OF RELAXATION CURVES

Separation of Force-Elongation Variables

Since the elasticity of vulcanisates is not linear, the immediate use of classical rheological methods in the analysis of their mechanical properties is not valid, except at small deformations. However, various investigations have shown that tension can be broken down into a two-term product, one term depending solely on deformation and the other on time (Thirion and Chassset, 1967a and b; Landel and Stedry, 1960; Gent, 1962; Mooney *et al.*, 1944; Stern and Tobolsky, 1946). This factorisation principle, which can also be applied to tensile tests at constant rate (Harwood and Schallamach, 1967), enables the tests to be considerably simplified since the above transitory and elastic terms can be analysed independently of each other. Also, data obtained well outside the linear region become strictly equivalent to those obtained from creep tests (Plazek, 1966) or by dynamic tests at periodically varying stresses (Stratton and Ferry, 1964).

There is, however, a limit to the validity of this principle at large elongations, which has been attributed to the onset of crystallisation caused by orientation of the polymer during tensile tests (Harwood and Schallamach, 1967). A detailed examination of the development of these relaxation kinetics as a function of elongation, however, indicates that there is another cause of deviation from the factorisation principle before crystallisation takes place. This is shown, for example, in *Figure 2*, which plots variations in the logarithm of a value proportional to the tension against the logarithm of time. As the origin has arbitrarily been shifted so that the ordinates coincide at 3 minutes, all the relaxation curves in this diagram are superimposed when the factorisation principle is applied, *i. e.*, in the case of the dicumyl peroxide–natural rubber vulcanisate, up to 100% elongation. Above this value the curves separate; until at about 250% elongation, their relative positions indicate that orientation does not modify the nature of the process influencing the stress-relaxation of the vulcanisates, but increases the time constants
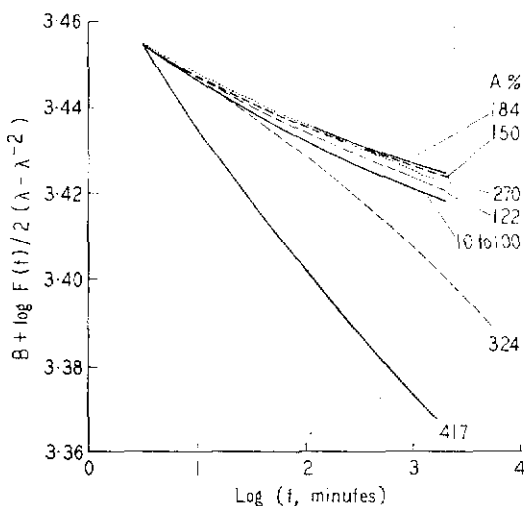

Figure 2. The influence of elongation on the relaxation of a dicumyl peroxide–natural rubber vulcanisate (98–30). Temperature 30°C—F(t) in gf/cm².

which characterise them. Beyond this elongation, at the end of the test, there appears to be an inflection zone; at this point, the change in the curve is accentuated so that the phenomenon is no longer compatible with the existence of a non-zero tension limit, at least in the time range studied. The reason for this is obviously not ageing but crystallisation, which is confirmed, for example, by thermodynamic analysis of the tensile force (Smith *et al.*, 1964) or by X-ray diffraction of the stretched vulcanisates.

Determination of Equilibrium Modulus by Relaxation Curve

Even when the time–elongation variables are separable in the relaxation function, the absolute value of the transitory component of the tensile force can be established only by determining the elastic component, *i.e.*, the limiting value of the stress at equilibrium.

Systematic study of various elastomers shows that progressive cross-linking leads to considerable reduction in the amount of relaxation observed in a given time, as can be seen in *Figure 3* for a natural rubber–dicumyl peroxide mix. Strictly, except in the case of the most
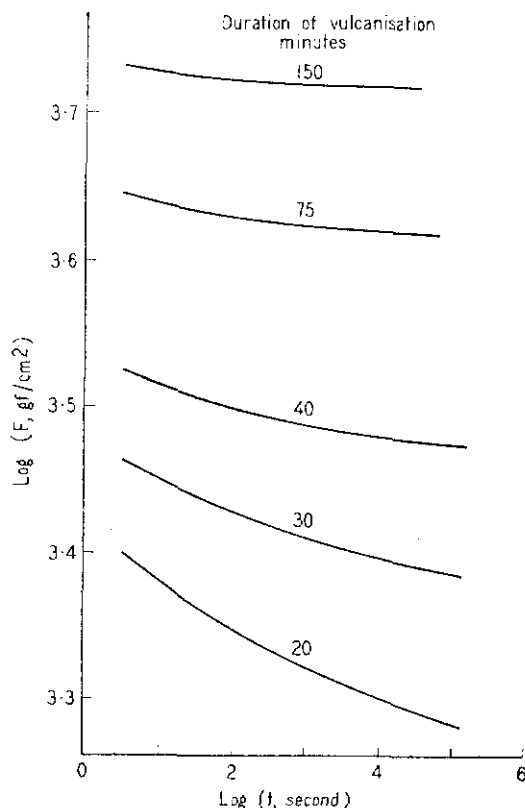
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Figure 3. The influence of vulcanisation time on the relaxation of a dicumyl peroxide–GSK vulcanisate (Series 98). Temperature 30°C. Extension 50%.

highly cross-linked vulcanisate, the equilibrium stress cannot obviously be deduced from experimental data on the vulcanisate considered, unless using extrapolation procedures, and an arbitrary method has been used previously for want of a better one (THIRION AND CHASSET, 1967a and b; TOBOLSKY AND SPERLING, 1968).

However, as already established by PLAZEK (1966) for the retardation spectrum in creep, the terminal region of the relaxation spectrum does not depend on the degree of cross-linking, at least for a given polymer and curing system. For example, the various isothermal relaxation curves $\log f$ ($\log t$) obtained from ten GSK natural rubber vulcanisates coincide to within 1/5000 with a single master

curve, when they are suitably shifted relative to each of the co-ordinate axes *(Figure 4)*. In other words, as long as the glass transition zone is avoided, the degree of cross-linking can be considered as a reduced variable affecting the viscoelasticity of the vulcanisates in the same way as temperature or degree of swelling in solvent (FERRY, 1961).

Yet the very concept of degree of cross-linking raises a delicate problem, if one is trying to define it by molecular quantity, such as the number of network chains per unit volume v calculated either from the modulus or from maximum solvent swelling (FLORY, 1950; MULLINS, 1956). There is in fact a serious ambiguity regarding its significance, since, at least in its classical form, the statistical theory of elasticity does not quantitatively take into account experimental stress–strain relationships (RIVLIN AND SAUNDERS, 1951; KRIGBAUM AND ROE, 1965; THIRION AND CHASSET, 1967c; VAN DER HOFF AND BUCKLER, 1967). As this cross-link density is widely used, we have amplified it by using a more direct macroscopic test: the equilibrium stress F_e corresponding to a uniform elongation of 50%.

Let us therefore consider an arbitrary reference curve corresponding to the lowest degree of cross-linking v_0 for the series of
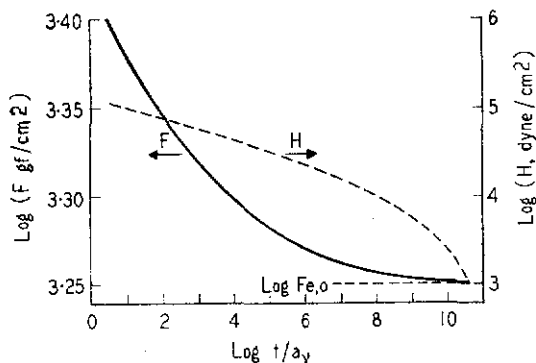

Figure 4. Relaxation (F) master curve (at 50% extension) and function of relaxation time distribution (H) obtained from 10 dicumyl peroxide–natural rubber vulcanisates (Series 98 and 109A). Reference vulcanisate 98–30. Temperature 30°C.
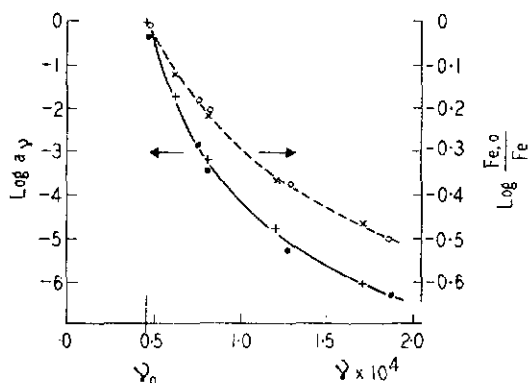
Figure 5. The shift factors log av and log $F_e,o/F_e$ relative to the time and stress axes as a function of the cross-link density ν. Dicumyl peroxide–natural rubber vulcanisates—series 98 ($+$, $\times$), series 109A ($\bullet$, $\bigcirc$). Temperature 30° C. Reference vulcanisate 98–30.

vulcanisates mentioned above. The vertical shifts log $F_e,o/F_e$ necessary to superimpose each of the curves relating to the other vulcanisates on the reference curve reveal the variations of the elastic components, and the horizontal shifts, log av, indicate the variations in position of the transitory function along the time scale *(Figure 5)*. It then appears that the total molecular processes delaying the establishment of equilibrium of the vulcanisate are multiplied uniformly by these last coefficients, which depend principally on the cross-linking index. Although the theoretical meaning of this result is still not clear, it is nevertheless of great importance in the analysis of the viscoelastic behaviour of the vulcanisates. Extrapolation using the master curve of each relaxation curve allows the corresponding elastic stress, as well as the transitory component at a given moment, to be determined as precisely as in the case of the most highly cross-linked rubber, *i.e.*, to better than 1/1000. From this point of view, the improvement is of the order of 10 to 100 fold, according to the degree of cross-linking, in comparison with thermo-mechanical conditioning procedures.

Moreover, the relaxation spectrum can be determined directly by this method over a range

of about ten decades without varying the temperature or the test method *(Figure 4)*.

Calculation of Dynamic Properties from Relaxation Results

It has been established (Thirion and Chasset, 1967a and b) that, in the time range actually covered for each vulcanisate, the relaxation kinetics deviate little from a power law with respect to time of the form:

$$F(t) = F_1 [1 + C t^{-m}] \qquad \ldots(1)$$

where F_1 represents a limiting stress value for a given elongation, C is a coefficient expressing the amount of relaxation, and m is a constant which generally varies from about 0.10 to 0.25 in value.

In theory, this elucidation of the kinetics allows the dynamic properties at any given frequency to be deduced by Carson-Laplace transformation. In reality, this calculation is only valid where the response times considered in each case are sufficiently close. The error with respect to the true kinetics, particularly when disregarding the glass transition, does not then falsify the results obtained when integrating between zero and infinite time.

If G_e refers to the equilibrium shear modulus at small deformations, $G'(\omega)$ the storage modulus and $G''(\omega)$ the loss modulus for frequency ω, Γ the gamma function, transformation of Equation (1) gives:

$$G' = G_e [1 + C\omega^m \Gamma(1 - m) \cos m\pi/2] \ \ldots(2)$$

$$G'' = G_e C\omega^m \Gamma(1 - m) \sin m\pi/2 \quad \ldots(3)$$

The values of G', G'' and $\tan \delta = G''/G'$, calculated by this method have been compared with those obtained for the same samples, in the laboratory of Professor Ferry, by measuring their dynamic properties over wide temperature and frequency ranges. As is seen in *Figures 6* and 7, which refer to a natural rubber vulcanisate of average degree of cross-linking, the two methods are quantitatively in agreement where the frequency does not exceed 100 Hertz. The increasing deviations at higher frequencies reflect the existence of rapid relaxation processes differing from those which affect the terminal zone of the spectrum of the vulcani-
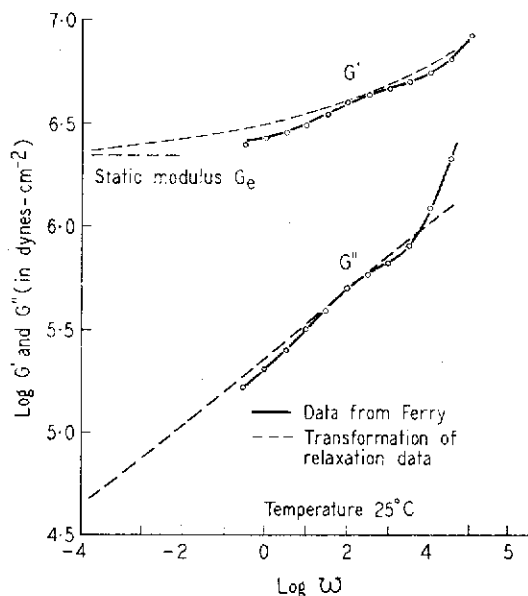
*Figure 6. Variation of the storage modulus G'
and loss modulus G" as a function of frequency
ω. Dicumyl peroxide–natural rubber vulcanisate
(102 F 30).*

sates. In fact, the first are much more closely
related to the flexibility of the molecular chains
of the polymers than to the degree of cross-
linking of the vulcanisates, although the reverse
is true for the second.

COMPARISON OF DIFFERENT TYPES OF NR AND SBR CROSS-LINKED WITH DICUMYL PEROXIDE

It has been established that each of the relaxa-
tion curves characterising the different natura
rubber–dicumyl peroxide vulcanisates can coin-
cide, whatever type of rubber is considered,
with part of the master curve obtained for
GSK. Therefore, the most rational way of
comparing the viscoelastic properties of these
rubbers is to look for existing correlations
between the relative position log a_v on the
time scale of the relaxation curves and the
cross-link index v and F_e. *Figure 8* shows
that there is no significant difference under
similar mastication conditions, with the excep-
tion perhaps of Tenso-sheet rubber, which

seems rather less elastic than the other types at
equal modulus.

As a whole, these results indicate that the
proportion of non-rubber materials influences
the viscoelasticity of the vulcanisates only by
way of the cross-link density, which is itself
connected with the reactivity of each type of
rubber under the vulcanisation conditions
defined. As the cure rate can easily be varied by
the manufacturer by adapting the mix formula-
tion, it is believed there is little chance of
finding significant correlation between the dyna-
mic properties of industrial vulcanisates and the
non-rubber content or the PRI of the rubbers
(RESING, 1967). Moreover, the influence of the
degree of mastication on the rubbers tends to
reduce still further the effect of plantation
preparation conditions on the dynamic proper-
ties. As is shown in *Figure 9*, reduction of the
initial molecular weight from 600 000 to 200 000
by prolonged mastication leads to a significant
acceleration of the viscoelastic processes, for
a given modulus, and the representative points
deviate from the relationship found for the
above masticating conditions.

On the other hand, the correlation found
with the SBR–dicumyl peroxide vulcanisates
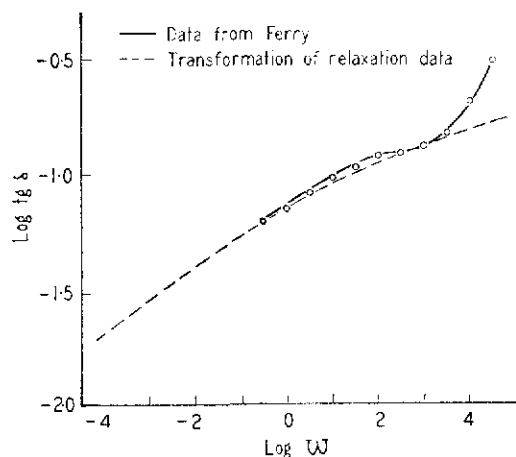reveals slower viscoelastic behaviour than for

*Figure 7. Variation of mechanical loss as a
function of frequency ω. Dicumyl peroxide–
natural rubber vulcanisate (102 F 30). Tempera-
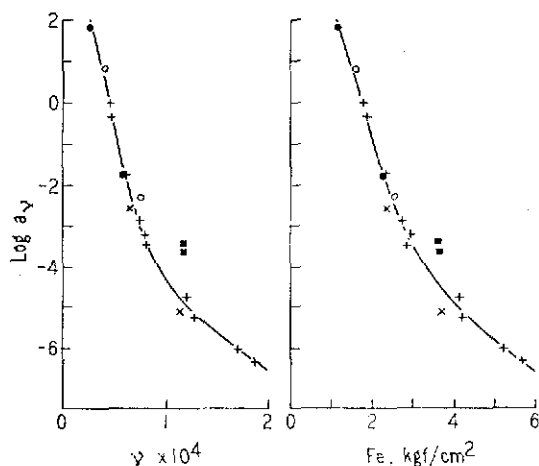ture 25°C.*

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Figure 8. Comparison of the viscoelastic properties of five types of lightly masticated natural rubber. The correlation is shown between the shift factor log a_v and the cross-link densities v and F_e for dicumyl peroxide. Reference vulcanisate 98–30. Temperature 30°C. GSK(+), ADS (○), crepe (●), RSS1 (×), Tenso-sheet (■).

natural rubber *(Figure 9)*. Despite the structural differences between these polymers, direct comparison using a_v is possible since the master relaxation curves are identical for dicumyl peroxide vulcanisates.

In a general way, for both natural rubber and SBR, the log a_v — F_e correlations found emphasise the very marked influence of the cross-link density on the viscoelastic response time of the vulcanisates, since this is reduced by a factor of 10^7 when the modulus varies in a ratio of 1 to 4 only.

NATURAL RUBBER–TETRAMETHYL THIURAM DISULPHIDE (TMTD) AND CIS-1,4-POLYBUTADIENE–DICUMYL PEROXIDE VULCANISATES

The only mix similar to industrial formulations which has been examined at present is a pure gum natural rubber–TMTD mix. This has excellent ageing resistance, so good in fact that pure viscoelastic relaxation can be conveniently followed. However, we have not been able to determine the number of network chains v by

maximum swelling, as can be done for peroxide vulcanisates, since the polymer-solvent interaction coefficient can never be determined with sufficient precision for sulphur vulcanisates (Saville and Watson, 1967). The only indication of cross-link density is then the equilibrium stress F_e determined directly from the relaxation curves.

Again, these are reduced to a single master curve represented in *Figure 10*. The time interval covered, about six decades, is, however, smaller than for the dicumyl peroxide vulcanisates, as such high moduli cannot be obtained with TMTD, since prolonged vulcanisation leads to reversion However, the master curve obtained has not the same shape as that for
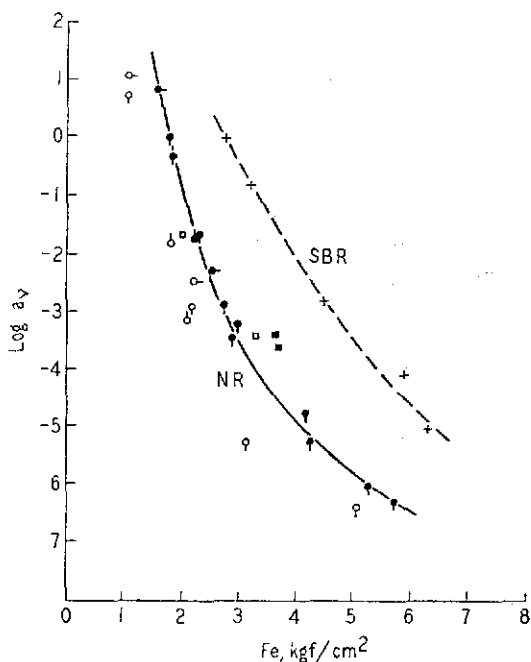

Figure 9. Correlation between shift factor log a_v and cross-link density F_e for dicumyl peroxide showing the difference between SBR (+) and natural rubber subjected to either a small or large amount of mastication before vulcanisation. Reference vulcanisate 98–30. Temperature 30°C. Molecular weights before vulcanisation: 5 to 7 × 10^5 (●, ■), 2 × 10^5 (○, □).
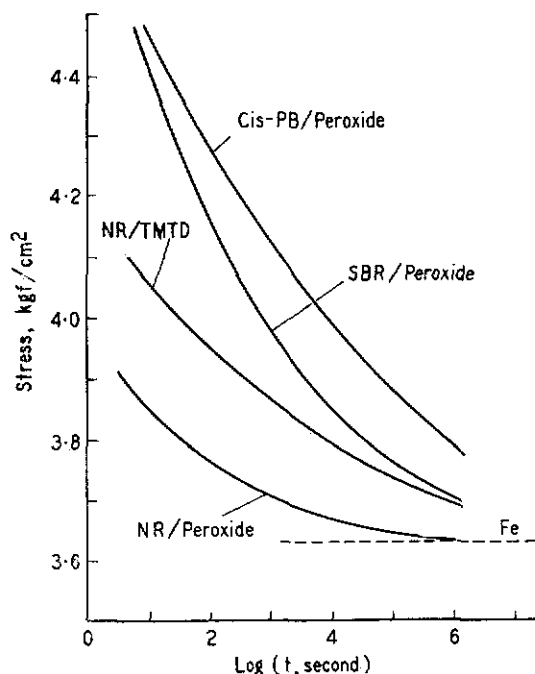
Figure 10. Comparison at equal modulus of the relaxation curves of peroxide or TMTD vulcanised natural rubber with those of dicumyl peroxide vulcanised cis-PB and SBR. Extension 50%. Temperature 30°C.

peroxide-vulcanised SBR and natural rubber. This difference cannot be attributed solely to the different vulcanisation system since the master curve of a *cis*-1,4-polybutadiene vulcanised with dicumyl peroxide is not obtained by horizontal shifting of the curve for the peroxide-vulcanised SBR and natural rubber *(Figure 10)*.

From the viewpoint of practical value, the fact that the master curves may intersect proves that the classification of different polymers by the viscoelastic properties of their vulcanisates depends essentially, in certain cases, on the time or frequency range considered, and not only on the two classical criteria: glass transition temperature and resilience. For example, under usual service conditions, which correspond more closely to the terminal zone of the relaxation time spectrum, peroxide-vulcanised pure gum *cis*-polybutadiene is slightly less

elastic at equal modulus than natural rubber vulcanisates *(Figure 10)*. The current opinion that polybutadiene is always superior in this respect should therefore be reconsidered.

CONCLUSIONS

In measurements where comparison is made at equal degrees of cross-linking or equal moduli, under similar mastication conditions, no significant difference is detected between the viscoelastic properties of dicumyl peroxide–pure gum vulcanisates prepared from various types of raw natural rubber. Also, the Plasticity Retention Index (PRI) of the raw rubbers can only be correlated with the dynamic properties of the vulcanisates by the use of a single variable, cross-link density, which depends directly on the specific reactivity of the rubbers to vulcanisation agents.

These factors are at least as important to the viscoelastic properties as the type of polymer so that for example, in the present case, natural rubber was found to be more elastic than *cis*-1,4-polybutadiene, in spite of its higher glass transition temperature.

REFERENCES

BATEMAN, L. AND SEKHAR, B.C. (1966) Significance of PRI in raw and vulcanised natural rubber. *J. Rubb. Res. Inst. Malaya*, **19(3)**, 133.

COTTEN, G.R. AND BOONSTRA, B.B. (1965) Stress relaxation in rubbers containing reinforced fillers. *J. appl. Polym Sci.*, **9(10)**, 3395.

FARLIE, E.D. AND GREENSMITH, H.W. (1966) The processing and vulcanized properties of commercial grades of natural rubber. Part III. Accuracy and reproductibility of the plasticity retention test for characterising oxidation resistance of raw natural rubber. *Trans. Instn Rubb. Ind.*, **42(5)**, 227.

FERRY, J.D. (1961) *Viscoelastic Properties of Polymers.* New York: John Wiley and Sons, Inc.

FLORY, P.J. (1950) Statistical mechanics of swelling of network structures. *J. Chem Phys.*, **18(1)**, 108.

Gent, A.N. (1962) Relaxation processes in vulcanized rubber. I. Relation among stress relaxation, creep recovery and hysteresis. *J. appl. Polym. Sci.*, **6(22)**, 433.

Harwood, J.A.C. and Schallamach, A. (1967) Dynamic behaviour of natural rubber during large extensions. *J. appl. Polym. Sci.*, **11(10)**, 1835.

Krigbaum, W.R. and Roe, Ryong-Joon (1965) Survey of the theory of rubberlike elasticity. *Rubb. Chem. Technol.*, **38(5)**, 1039.

Landel, R.L. and Stedry, P.J. (1960) Stress as a reduced variable: stress relaxation of SBR rubber at large strains. *J. appl. Phys.*, **31**, 1885.

Martin, G.M., Roth, F.L. and Stiehler, R.D. (1956) Behaviour of 'pure gum' rubber vulcanisates in tension. *Trans. Instn Rubb. Ind.*, **32(6)**, 189.

Mooney, M., Wolstenholme, W.E. and Villars, D.S. (1944) Drift and relaxation of rubber. *J. appl. Phys.*, **15**, 324.

Mullins, L. (1956) Determination of degree of crosslinking in natural rubber vulcanizates Part I. *J. Polym. Sci.*, **19(92)**, 225.

Mullins, L. (1959) Determination of degree of crosslinking in natural rubber vulcanizates Part III. *J. appl. Polym. Sci.*, **2(4)**, 1.

Plazek, D.J. (1966) Effect of crosslink density on the creep behaviour of natural rubber vulcanizates. *J. Polym. Sci. Part A-2*, **4(5)**, 745.

Resing, W.L. (1967) Factors affecting the PRI of natural rubber and relations between the PRI and some properties of vulcanizates. *Revue gén. Caoutch. Plastq.*, **44(7-8)**, 899.

Rivlin, R.S. and Saunders, D.W. (1951) Large elastic deformations of isotropic materials, VII Experiments on the deformation of rubber. *Phil. Trans.*, **A 243**, 251.

Roth, F.L., Bullman, G.W. and Wood L.A. (1965) Compliance-time-temperature relationships from indentation measurements on a pure-gum rubber vulcanizate. *J. Res. natn. Bur. Stand.*, **69A(4)**, 347.

Saville, B. and Watson, A.A. (1967) Structural characterization of sulfur-vulcanized rubber networks. *Rubb. Chem. Technol.*, **40**, 100.

Smith, Jr, K.J., Greene, A. and Ciferri, A. (1964) Crystallisation under stress and non-gaussian behaviour of macromolecular networks. *Kolloidzeitschrift Z., Polym.*, **194(1)**, 49.

Stern, M.D. and Tobolsky, A.V. (1946) Stress-time-temperature relations in polysulfide rubbers. *J. Chem. Phys.*, **14**, 93.

Stratton, A. and Ferry, J.D (1964) Dynamic viscoelastic properties of natural rubber vulcanized by different agents. *Revue gén. Caoutch. Plastq.*, **41(4)**, 635.

Thirion, P. and Chasset, R. (1963) Relative contributions of viscoelasticity and ageing to the relaxation of rubber vulcanisates. *Proc. 4th. Rubb. Technol. Conf. London, 1962*, 338.

Thirion, P. and Chasset, R. (1967a) Viscoelastic relaxation of rubber vulcanizates between the glass transition and equilibrium. *Revue gén. Caoutch. Plastq.*, **44(9)**, 1041.

Thirion, P. and Chasset, R. (1967b) Viscoelastic relaxation of vulcanizates in extension. *Chim. Ind. Génie chim.*, **97(5)**, 617.

Thirion, P. and Chasset, R. (1967c) Linear empirical relation between the unfolding of macromolecular network chains and macroscopic deformations. *C.r. Acad. Sci. Paris Ser.C.*, **264(11)**, 958.

Tobolsky, A.V. (1960) *Properties and Structure of Polymers*, 105. New York: John Wiley and Sons, Inc.

Tobolsky, A.V. and Sperling, L.H. (1968) Volume dependence of the equation of state for rubber elasticity: Poly(dimethyl siloxane) *J. phys. Chem.* **72(1)**, 345.

van der Hoff, B M.E. and Buckler, E.J. (1967) Transient changes in topology and energy on extension of polybutadiene networks. *J. makromolek. Sci. (Chem.)*, **A4**, 747.

DISCUSSION

Chairman: Dr. H. W. Greensmith

Mr. A.G. Thomas commented that the linearity between stress–relaxation and logarithm of time for accelerated sulphur vulcanisates was observed at 40 and 50°C as well as at 20°C. It was therefore unlikely to be due to a fortuitous balance between physical and chemical effects, because their respective temperature coefficients would be very different. Dr. Thirion replied that deviations from the linear relationship between stress–relaxation and log time could only be detected by very precise measurements of the stress (0.1%). Radical differences were found between the viscoelastic relaxation of compounds cured with TMTD and with dicumyl peroxide.

Dr. S. Banerjee asked how the greater elasticity of natural rubber compared with *cis*-polybutadiene was explained. Dr. Thirion replied that co-operative work with Prof. J.D. Ferry indicated quite different viscoelastic mechanisms in the rubbery and glass transition states, so that the micro-structure of the molecular chains should have no effect. However, it was by no means certain that network topology and chain entanglements were not involved.

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Dr. L. Bateman remarked that although PRI (Plasticity Retention Index) was discussed in the opening and concluding paragraphs, the paper reported no experimental investigations on, or directly relevant to, PRI. Inferences concerning PRI should not be quoted out of context or without qualification. Neither PRI nor any other property was claimed to be a single unique indicator of rubber quality. When rubbers of the wide range obtained in ordinary factory operations (instead of the narrow range tested in the experiments reported) were subjected to standard processing, differences were found in the Mooney viscosity of the compounds which affected the physical properties of the derived vulcanisates; these could be corrected by appropriate adjustments in cure and processing on the basis of PRI determinations. The paper elegantly quantified the relationship between network structure and elastic behaviour showing the importance of vulcanising characteristics, but this did not deny the significance of the polymer component as indicated by PRI.