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QUANTITATIVE CHARACTERISATION OF CURE

Part I. **Relationship between "Modulus" and "Strain" in Pure Gum Natural Rubber Vulcanisates**

by
R. F. BLACKWELL

Part II. **Use of Modulus as a Measure of the State of Cure in Pure Gum Natural Rubber Vulcanisates**

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W. P. FLETCHER, GEOFFREY GEE, and S. H. MORRELL

Part III. **Relation between Compound Viscosity and Vulcanisate Stiffness in Pure Gum Natural Rubber Vulcanisates**

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by
GEOFFREY GEE and S. H. MORRELL

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QUANTITATIVE CHARACTERISATION OF CURE

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GENERAL INTRODUCTION

The origin of the work described in this group of four papers was the need for some reliable method of assessing the state of cure of a vulcanisate, and the rate at which this state of cure develops during the course of vulcanisation. The need has been particularly felt in these laboratories during the investigation of possible methods for the technical classification of natural rubber supplies. One important way in which samples of natural rubber differ is in their vulcanisation behaviour.

Every technologist knows roughly what is meant by "well-cured," "under-cured," etc., but there is no generally accepted quantitative sense in which the word "cure" can be used. The purpose of this group of papers is to make some suggestions in this direction, based on modern theoretical studies of rubber elasticity, but keeping to the fore always the desirability of definitions which are simple to apply, and which do not involve difficult or laborious measurements. This last factor is especially important in procedures which might be applied on a very large scale in the technical classification of natural rubber supplies.

This basic purpose has dictated the limitation of the field of experiment to pure gum compounds, and in the main to the one suggested by the Crude Rubber Committee of the American Chemical Society in 1936 and denoted here by ACS1. This has been adopted internationally as the basis of technical classification of rubber supplies.

The first paper of the group is subsidiary to the main theme, preparing the ground for the second paper, in which it is argued that the modulus of a vulcanisate, measured at 100 per cent. elongation, can be used as a quantitative measure of the state of cure. The first paper does, however, have a value of its own in establishing a useful empirical relationship between strain and modulus measurements: this has been found of great practical value in the operation of the scheme of technical classification.

The third paper deals with the effect of the viscosity of the compound on the modulus of the vulcanisate. The practical importance of this matter has now been recognised by the inclusion, in the standard procedure for vulcanisation testing, of a control of compound viscosity.

Finally, the fourth paper sets out a tentative method of evaluating rate of cure from modulus measurements. The theoretical basis is less well established than for our definition of state of cure, and the practical usefulness of this method remains to be assessed in the light of further experience.

I.

Relationship between "Modulus" and "Strain" in Pure Gum Natural Rubber Vulcanisates

BY R. F. BLACKWELL

SUMMARY

The object of this investigation was to determine whether the relationship between strain (elongation) and modulus is sufficiently close for one to be calculated from the other. Stress-strain data have been recorded for loads of 2-10 kg./cm.^{2} for a series of ACS1 and other pure gum compounds. It is shown that the strain at a fixed stress (5 kg./cm.^{2}) is uniquely related to the load required to produce an elongation of 100 per cent. A tentative explanation of this observation is given in terms of the Mooney equation for the stress-strain curve. It is shown that the second constant of this equation does not vary greatly from rubber to rubber.

1. INTRODUCTION

In the past it has been customary to measure the stiffness of a vulcanisate in terms of the load required to produce a fixed elongation—the so-called "modulus." Since the measurement was usually combined with determination of the breaking load it was necessary to choose a high elongation (600 or 700 per cent. for gum stocks) to ensure reasonable precision.

The development of statistical theories of high elasticity has directed attention to the desirability of making modulus measurements at much smaller elongations, of the order of 100 per cent., which can only be done satisfactorily if modulus and tensile determinations are performed separately.

It is, of course, easy to measure the modulus at a low elongation directly, using some form of balance to determine the load; a simple instrument of this type which has been developed and used in these laboratories is described in the following paper. An even simpler procedure, which particularly commends itself when stiffness is used in the routine classification of rubber supplies, involves measurement of the elongation at a fixed load. In these laboratories extensive use has been made of this latter method, the stiffness of a vulcanisate being generally characterised by its "strain," defined as the percentage elongation under a load of 5 kilograms per square centimetre of the unstrained cross-section.[1]

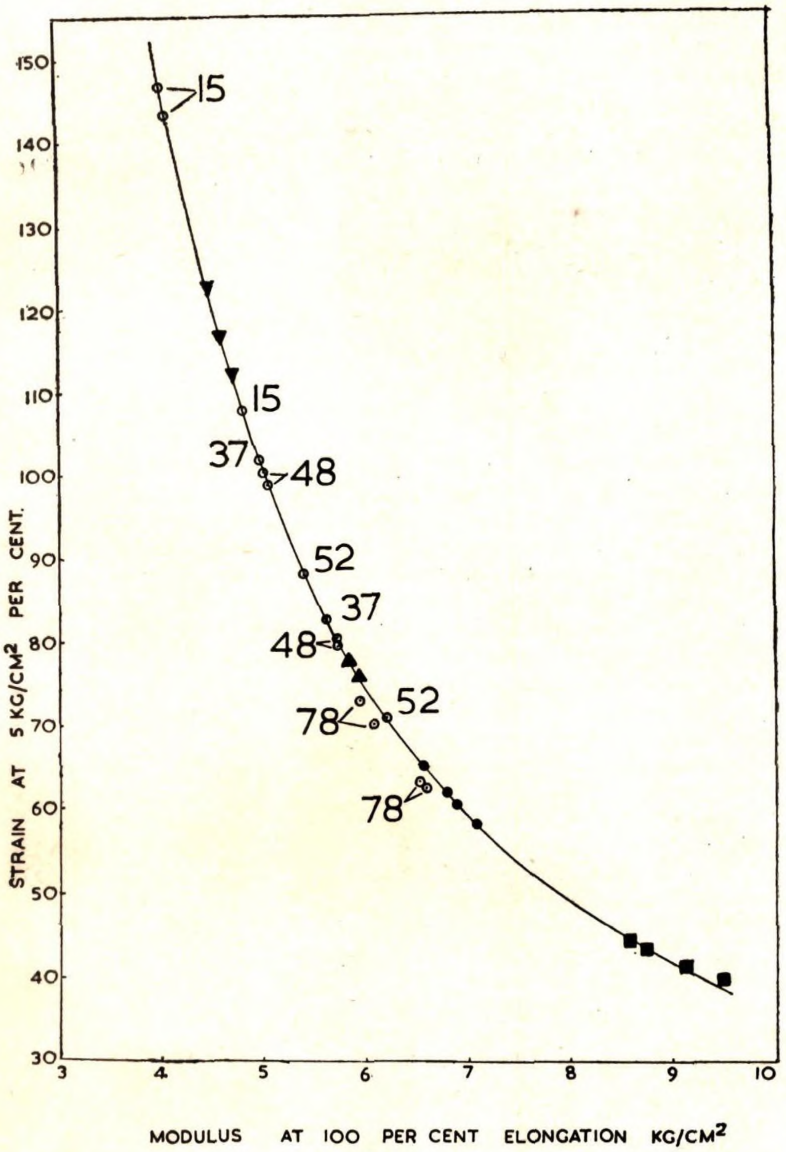

FIG. 1.
The relationship between strain and modulus for ACS1 compounds.

Type of raw rubber	Symbol	Compound Mooney viscosity
High modulus	●	35 ± 2
Low modulus	▲	
Deproteinised	▼	
Skim	■	
Smoked sheet blend . .	⊙	As stated

Curve plotted from equation (3) with $C_2 = 1{\cdot}5$.

While strain is a very simple quantity to measure, it is, of course, an inverse measure of the stiffness, a large figure denoting a soft rubber. This is found in practice to present some slight psychological difficulties, but nevertheless strain measurements are considered to be perfectly satisfactory for most purposes, and in particular there is no reason to criticise their use in the classification of raw rubber supplies. There is little doubt, however, that where any theoretical discussion of the data is intended, it is preferable to have modulus figures.*

Theories of rubber elasticity are not sufficiently developed to predict with any precision the relationship that is to be expected between the three quantities discussed above: modulus at 600 per cent. elongation, modulus at 100 per cent. elongation, and strain; in this paper are recorded the results of an experimental investigation of the relationship between the second and third of these.

2. EXPERIMENTAL

The B.R.P.R.A. Strain Tester[1] was used for the measurements described, being provided with a range of weights giving loads from 2 to 10 kg./cm.^{2} Samples were stretched at the minimum load, allowed to rest 24 hours, then retested at the next higher load, and so on. (As a check, some specimens were further retested at the minimum load, and gave readings not differing by more than one unit from the original value.)

Stress-strain curves from a wide range of available test-pieces were obtained and from each curve readings were taken of the strain at a stress of 5 kg./cm.^{2} and modulus at a strain of 100 per cent.; these pairs of results were plotted and although some scatter was evident, a reasonably smooth curve could be drawn through the points.

A more precise experiment was therefore designed and carried out, using 4 rubbers in 5 different pure-gum compounds. The rubbers were: (*a*) a high modulus smoked sheet blend, (*b*) a low modulus smoked sheet blend, (*c*) a deproteinised crepe, and (*d*) a skim crepe.

The compounds are shown in the Appendix, TC9 not being used for this experiment; in each case they were mixed to a Mooney viscosity of 35 ± 2, and were cured for 30, 40, 50, 60, 80 and 90 minutes at 140° C.

A subsidiary experiment was carried out to determine the effect of mixing the compound to a different viscosity. An ACS1 mix was prepared under nitrogen in an internal mixer, and portions subsequently broken down on the mill so as to give a series of compounds having viscosities ranging from 15 to 78.

3. RESULTS

Figures 1 to 3 record all the data obtained, modulus at 100 per cent. elongation (f_{100}) being plotted against strain at 5 kg/cm.^{2} (S_5). The full curves drawn on the three figures are identical and it is at once apparent that over a wide range of rubbers, mixes and cures, the relationship between f_{100} and S_5 is very good indeed. Detailed examination of the data reveals some systematic departures from the curve; these can conveniently be considered by discussing the three figures in turn.

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*This question is discussed more fully in the following paper.

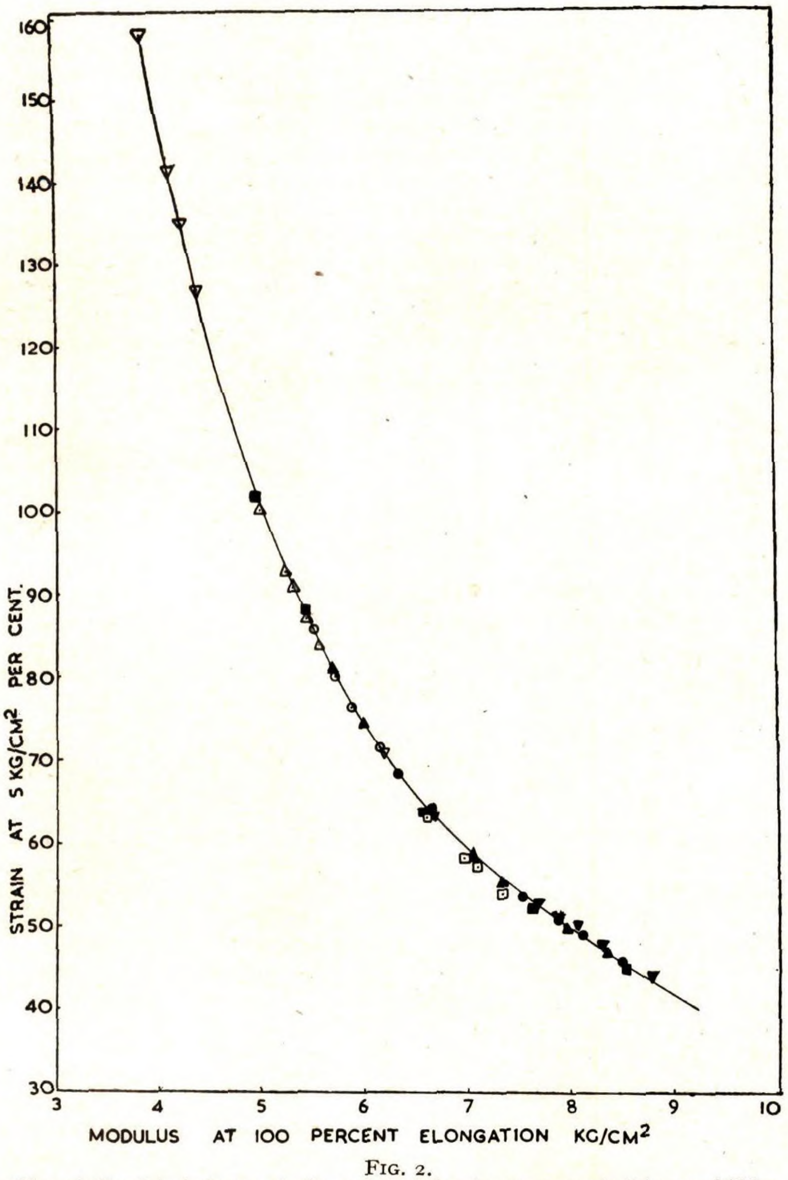

FIG. 2.
The relationship between strain and modulus for compounds TA57 and TC14.

Type of raw rubber	TA57	TC14
High modulus	⊙	●
Low modulus	△	▲
Deproteinised	▽	▼
Skim	⊡	■

All 35 ± 2 Mooney.

Curve plotted from equation (3) with $C_2 = 1\cdot5$.

Fig. 1 (ACS1 compound) shows the curve to represent the relationship extremely well for all the rubbers studied, when the compound viscosity was 35. Using a single sample of smoked sheet, compound viscosity is shown to have no influence so long as it does not exceed about 50° Mooney. Compounds mixed to a higher viscosity appear to deviate slightly, but it is clear that no departure would be expected with any stock mixed in a normal manner.

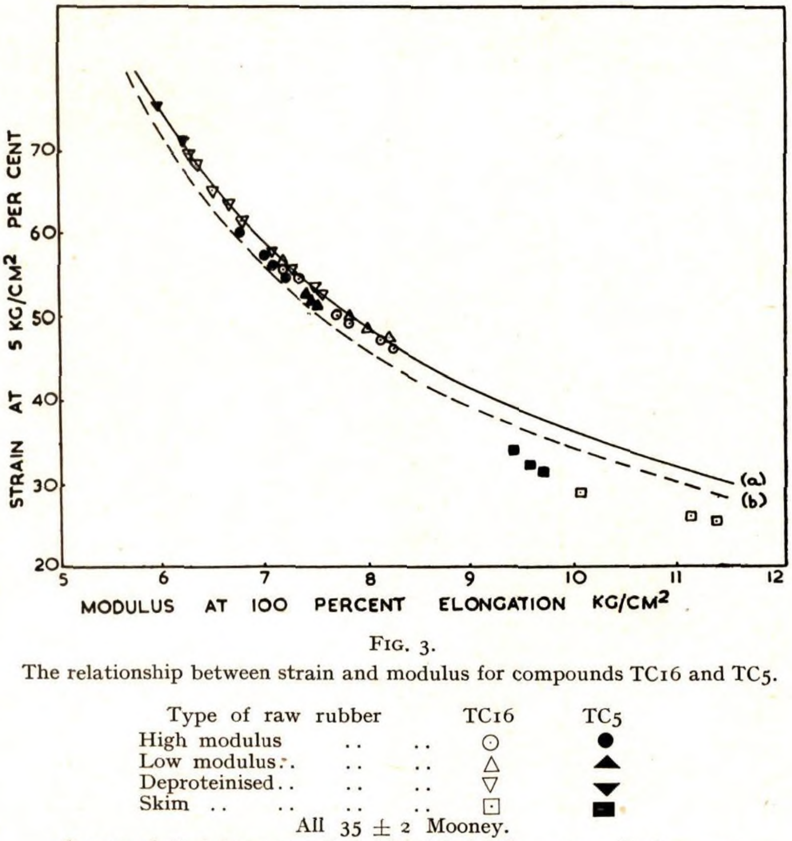

FIG. 3.

The relationship between strain and modulus for compounds TC16 and TC5.

Type of raw rubber	TC16	TC5
High modulus	⊙	●
Low modulus	△	▲
Deproteinised..	▽	▼
Skim	⊡	■

All 35 ± 2 Mooney.

Curves plotted from equation (3) with (*a*) $C_2 = 1\cdot5$; (*b*) $C_2 = 2\cdot5$.

Fig. 2 shows that the behaviour of vulcanisates from two other mixes (TA57 and TC14) is almost equally uniform; results for the skim rubber show a small departure which would be of little importance for most practical purposes.

Fig. 3 (TC16 and TC5) shows a more serious type of deviation; all the results obtained with T.M.T.*–sulphurless compounds appear to fall on a curve different from the normal one, the difference becoming

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*See Appendix for key to abbreviations.

large for the skim rubber. These skim rubbers cured with H.B.S. also resemble the T.M.T. compounds in behaviour.

4. Discussion

The discrepancies which have been noted are of quite secondary importance to the main conclusion that there exists a very nearly unique relationship between strain and modulus for a range of pure gum natural rubber vulcanisates. The existence of this relationship implies that the load-elongation curves of the individual vulcanisates are all of the same general shape; that is to say, if an equation can be found for the load-elongation curve it must contain only one parameter characteristic of the rubber. It is clear that the load-elongation curve deduced from the statistical theory satisfies this condition, for it contains only one parameter:

$$f = C_1 (\alpha - \alpha^{-2}) \qquad \ldots\ldots\ldots\ldots (1)$$

where f is the load at an elongation ratio α given by $S = 100 (\alpha - 1)$. It has, however, been abundantly established[2] that this equation does not describe the form of the curve satisfactorily. Much better agreement with experiment is found with the two-constant equation proposed by Mooney,[3]

$$\begin{aligned} f &= C_1 (\alpha - \alpha^{-2}) + C_2 (1 - \alpha^{-3}) \qquad \ldots\ldots\ldots\ldots (2) \\ &= (C_1 \alpha + C_2)(1 - \alpha^{-3}) \end{aligned}$$

It is readily seen that a series of rubbers whose load-elongation curves are represented by equation (2) will give a unique relationship between f_{100} and S_5 under one of three conditions only: (i) C_1 is independent of the rubber; (ii) C_2 is independent of the rubber; (iii) C_1 and C_2 are related.

These three possibilities have been examined by determining C_1 *and C_2 for the series of vulcanisates employed in the investigation.* It follows from equation (2) that $f/(1 - \alpha^{-3})$ should be a linear function of α with slope C_1 and intercept C_2 at $\alpha = 0$. Figs. 4 and 5 show some typical examples of this plot and Table 1 contains the values of C_1 and C_2 derived from the data. It will be seen that nearly all the values of C_2 lie between 1·5 and 2·0 and that there is no evidence of any systematic relationship between C_1 and C_2. To a first approximation at any rate we may conclude that C_2 is independent of the nature of the vulcanisate *within the range we have examined.* There is some evidence that C_2 increases with compound viscosity when this exceeds 50° Mooney.*

Assuming C_2 to be a constant, it is easy to derive from equation (2) a relationship between $F\ (\equiv f_{100})$ and S_5, in the form

$$F = \frac{875 (S_5 + 100)^2}{(S_5 + 100)^3 - 10^6} + 0{\cdot}875\, C_2 \cdot \frac{S_5 - 100}{S_5 + 100} \qquad \ldots\ldots\ldots\ldots (3)$$

This equation defines a family of curves in which C_2 is a parameter, and all of which pass through the point ($F = 5$, $S_5 = 100$) fanning out on either

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*A more detailed study of the load-elongation curves of a number of rubbers made by Rivlin and Saunders[3c] confirms that C_2 is substantially independent of the rubber, though not quite independent of α.

side. The curves of Figs. 1 to 3 were calculated from equation (3) using a value of $C_2 = 1{\cdot}5$; it should be noted, however, that the curve is not

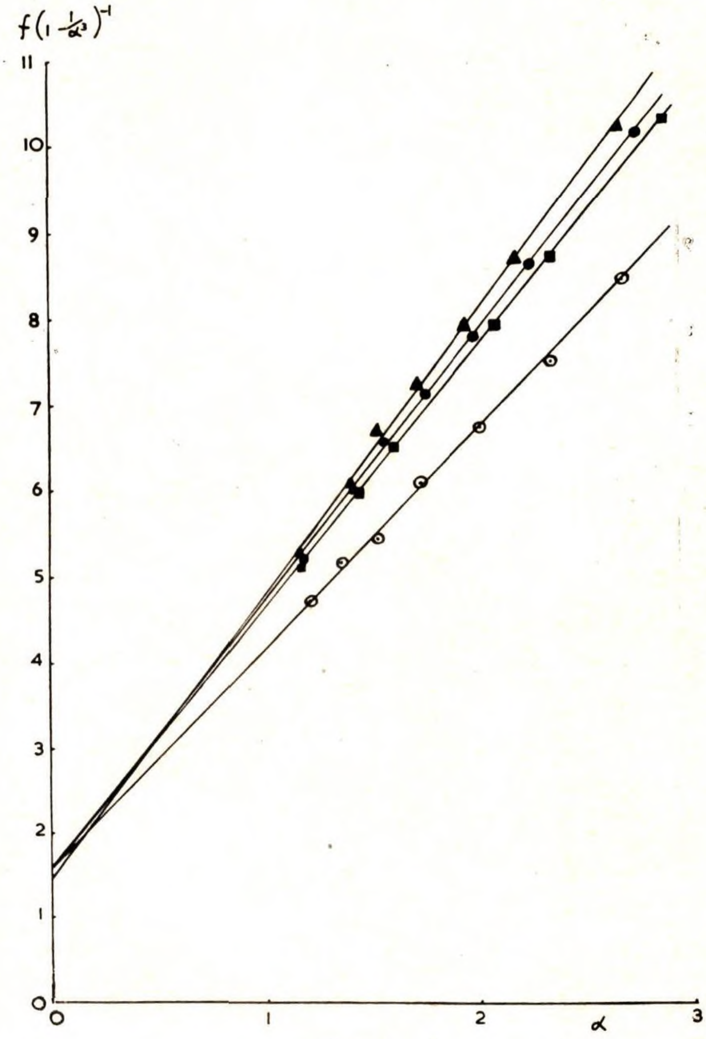

FIG. 4.
Mooney equation for ACS1 compounds.

Cure	Type of raw rubber HM	 LM
30 mins. at 140° C.	▲	
50 mins. at 140° C.	●	⊙
90 mins. at 140° C.	■	

All compounds 35 ± 2 Mooney.

very sensitive to C_2, the broken line in Fig. 3 being calculated with $C_2 = 2{\cdot}5$. The observed departure of the high viscosity compounds in Fig. 1 is doubtless related to their higher C_2 values.

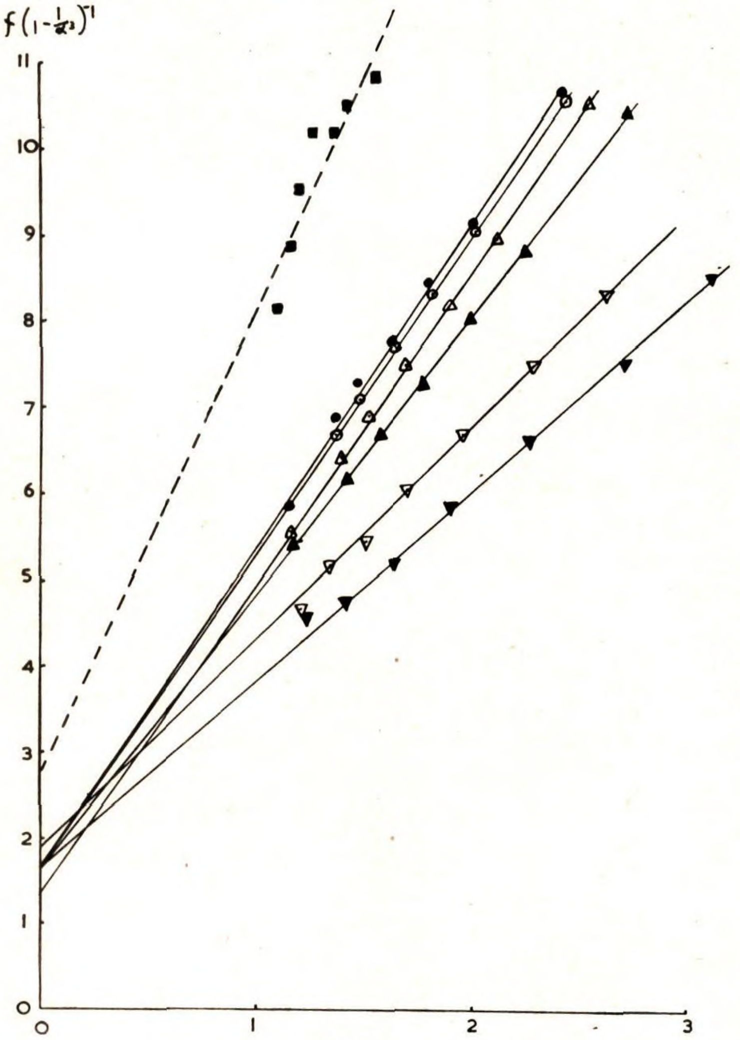

FIG. 5.
Mooney equation for TA57, TC14, TC16.

Compound	Type of raw rubber LM	 HM	 Skim
TC16	●	⊙	■
TC14	▲	△	
TA57	▼	▽	

All compounds 35 ± 2 Mooney.
All cured 50 minutes at 140° C.

TABLE 1

(*a*) VALUES OF C_1 AND C_2 FOR VARIOUS RUBBERS AND COMPOUNDS; VISCOSITY 35 ± 2 MOONEY

		Compound									
		ACS1		TC14		TA57		TC5		TC16	
Rubber	Cure*	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2	C_1	C_2
High-Modulus Smoked Sheet	30	3·2	1·5	2·9	1·5	2·6	1·6	2·9	1·8	3·8	1·7
	40	3·2	1·5	3·0	1·5	2·5	1·6	3·1	1·7	3·8	1·9
	50	3·0	1·6	3·5	1·4	2·3	1·9	3·2	1·8	3·6	1·7
	60	3·0	1·6	3·7	1·4	2·3	1·9	3·2	1·8	3·4	1·8
	80	3·1	1·3	3·8	1·6	2·4	1·8	3·2	1·8	3·2	1·8
	90	3·0	1·6	3·9	1·8	2·2	1·8	3·2	1·8	3·1	1·9
Low-Modulus Smoked Sheet	30	2·5	1·6	2·4	1·7	2·3	1·8	3·1	1·8	3·8	1·7
	40	2·5	1·6	2·6	1·7	2·2	1·8	3·3	1·8	3·7	1·7
	50	2·5	1·6	3·2	1·7	2·2	1·7	3·3	1·8	3·7	1·7
	60	2·5	1·6	3·3	1·7	2·1	1·8	3·3	1·8	3·5	1·7
	80	2·5	1·6	3·7	1·6	2·1	1·8	3·3	1·8	3·3	1·7
	90	2·5	1·6	3·8	1·8	1·9	1·9	3·3	1·8	3·2	1·7
Deproteinised Crepe	30	1·9	1·5	3·2	1·2	1·8	1·4	2·5	1·7	3·3	1·8
	40	1·9	1·5	3·6	1·1	1·6	1·6	2·7	1·7	3·3	1·8
	50	1·9	1·5	4·1	1·1	1·6	1·5	2·7	1·7	3·2	1·8
	60	1·9	1·5	4·4	1·1	1·6	1·6	2·7	1·7	3·2	1·8
	80	1·9	1·5	4·5	1·2	1·5	1·5	2·7	1·7	3·0	1·8
	90	1·9	1·5	4·6	1·3	1·5	1·4	2·9	1·7	2·9	1·7
Skim Crepe	30	3·9	1·9	2·0	1·7	2·8	2·0	4·3	2·3	4·7	2·9
	40	4·2	1·9	2·1	2·0	3·0	2·1	4·4	2·4	5·2	2·8
	50	4·4	1·9	2·7	2·0	2·8	2·0	4·3	2·3	5·2	2·8
	60	4·4	1·9	—	—	3·0	1·9	4·3	2·3	5·0	2·9
	80	4·2	1·9	3·2	2·0	3·2	2·1	4·5	2·4	4·7	3·0
	90	4·4	1·9	3·0	2·4	3·0	2·1	4·3	2·3	4·6	2·8

(*b*) ACS1 compound; viscosity as stated.

Mooney Viscosity	Cure*	C_1	C_2
78	20	2·2	2·4
	20	2·3	2·4
	40	2·6	2·4
	40	2·6	2·4
52	20	2·3	1·8
	40	2·6	1·8
48	20	2·1	1·6
	20	2·1	1·6
48	40	2·4	1·7
	40	2·4	1·7
37	20	2·0	1·6
	40	2·3	1·8
15	20	1·6	1·3
	20	1·6	1·4
	40	2·0	1·4

*Cure — minutes at 140° C.

5. CONCLUSIONS

The main conclusion of this paper is that it is possible to convert train measurements at 5 kg./cm.^{2} (S_5) to modulus at 100 per cent. longation (F) with considerable confidence and precision. Irrespective of the explanation of this fact, it stands as a firmly established experimental observation. For convenience in carrying out this conversion, Table 2 has been calculated from equation (3).

TABLE 2

STRAIN–MODULUS CONVERSION

STRAIN is percentage elongation at 5 kg./cm.^{2}
MODULUS is stress in kg./cm.^{2} to produce 100 per cent. elongation.

STRAIN	0	1	2	3	4	5	6	7	8	9
40	9·27	9·11	8·96	8·80	8·65	8·49	8·36	8·23	8·11	7·98
50	7·85	7·75	7·64	7·54	7·43	7·33	7·24	7·16	7·07	6·99
60	6·90	6·83	6·76	6·68	6·61	6·54	6·48	6·42	6·35	6·29
70	6·23	6·18	6·12	6·07	6·01	5·96	5·91	5·86	5·82	5·77
80	5·72	5·68	5·64	5·59	5·55	5·51	5·47	5·44	5·40	5·37
90	5·33	5·30	5·26	5·23	5·20	5·17	5·13	5·10	5·07	5·03
100	5·00	4·97	4·95	4·92	4·89	4·87	4·84	4·81	4·78	4·76
110	4·73	4·71	4·68	4·66	4·64	4·62	4·59	4·57	4·55	4·52
120	4·50	4·48	4·46	4·44	4·42	4·41	4·39	4·37	4·35	4·33
130	4·31	4·29	4·28	4·26	4·25	4·23	4·21	4·20	4·18	4·17
140	4·15	4·14	4·12	4·11	4·09	4·08	4·06	4·05	4·03	4·02
150	4·00	3·99	3·97	3·96	3·95	3·94	3·92	3·91	3·90	3·88
160	3·87	3·86	3·85	3·83	3·82	3·81	3·80	3·79	3·77	3·76
170	3·75									

The second conclusion is that the constant C_2 of the Mooney load-elongation equation is substantially the same for a range of rubbers and equal to 1·5 kg./cm.^{2} Having regard to the insensitivity to C_2 of the relationship between F and S_5, this second conclusion must be regarded as less certain and the explanation offered for the main conclusion is, therefore, somewhat tentative.

APPENDIX

COMPOUNDING DETAILS

	Compound					
	ACS1	TA57	TC5	TC9	TC14	TC16
Rubber	100	100	100	100	100	100
Sulphur	3·5	2·5	—	1·5	3·5	3
Zinc oxide	6	6	6	6	5	5
Stearic acid..	0·5	0·5	0·5	0·5	—	1
Mercaptobenzthiazole (MBT)	0·5	—	—	—	—	—
Di-benzthiazyl disulphide (MBTS)	—	0·25	—	0·2	—	—
Tetramethylthiuram disulphide (TMT) ..	—	0·04	4	0·1	—	—
Diphenylguanidine (DPG) ..	—	—	—	—	1	—
N-*cyclo*hexyl benzthiazyl sulphenamide (HBS) ..	—	—	—	—	—	0·4

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II.

Use of Modulus as a Measure of the State of Cure in Pure Gum Natural Rubber Vulcanisates

BY W. P. FLETCHER, GEOFFREY GEE AND S. H. MORRELL

SUMMARY

The purpose of this investigation was to develop methods of measuring state of cure which involved only measurements normally available or very readily made. Swelling measurements, although suitable in theory, suffer the practical disadvantage of being time-consuming, but it is shown that they can be replaced very satisfactorily by modulus at 100 *per cent. elongation. This is a good practical measure of state of cure for most purposes, and simple corrections are developed which extend its range of usefulness. An easily constructed machine is described for the accurate measure of modulus at small elongations.*

1. INTRODUCTION

Since vulcanisation consists essentially of the chemical reaction of cross-linking, it seems natural to select as a measure of state of cure some quantity closely related to the extent of cross-linking. It is well-known—and further evidence is described in an accompanying paper (IV)—that the amount of sulphur combined is an unsatisfactory quantity for this purpose, especially when comparisons have to be made between different types of compound. Choice therefore lies between different physical properties of the rubber, or secondary quantities derived from physical measurements.

Statistical theories have related the degree of cross-linking of a vulcanisate with its elastic modulus[1] and with the extent to which it is swollen in a suitable liquid.[2] These theories are based on the assumption that a state of true thermodynamic equilibrium is attained; while this is readily achieved in swelling measurements, it is certainly not reached in a normal modulus determination.*[3] A swelling measurement is, therefore, to be preferred to modulus as a primary measure of cross-linking, i.e. state of cure. We shall, however, show in this paper that over the normal range of cure, modulus at 100 per cent. elongation is a very satisfactory secondary standard, and can, therefore, be used as a highly convenient quantitative measure of state of cure.

* This is easily seen by considering the extreme case of a piece of unvulcanised rubber, whose equilibrium modulus is zero, but for which a finite result would be recorded in any conventional modulus test.

2. "APPARENT" DEGREE OF CROSS-LINKING

Flory[2] has analysed the swelling of an ideal network in terms of the degree of cross-linking of the network and its interaction constant with the swelling agent. In this section we shall treat the vulcanisate as though it were an ideal network and thus arrive at what may be called the "apparent" degree of cross-linking, characterised by the reciprocal of a quantity M_c' which appears in the theory of the ideal network as the molecular weight between junction points of the net.* If Q is the observed equilibrium swelling (c.c. of liquid absorbed per c.c. of rubber) then Flory's theory gives:—

$$\frac{1}{M_c'} = \frac{(1+Q)^{1/3}}{\rho V} \{\ln(1+Q^{-1}) - (1+Q)^{-1} - \mu(1+Q)^{-2}\} \quad \ldots.(1)$$

where ρ is the density of the dry rubber, V the molar volume of the swelling liquid, and μ the interaction constant. μ has to be determined by a supplementary experiment, e.g. a vapour pressure determination on a solution of the unvulcanised rubber in the same liquid, and for natural rubber in benzene has been found[4] to have the value $0{\cdot}39_5$. Once μ is known, the apparent degree of cross-linking can thus be calculated for any vulcanisate by a single measurement of its equilibrium swelling in the appropriate liquid.

The statistical theory of an ideal network[1] leads to a simple expression for the force f needed to elongate a sample in the ratio α:

$$f = \frac{\rho RT}{M_c'}(\alpha - \alpha^{-2}) \quad \ldots\ldots..(2)$$

where ρ is the density of the rubber, R the gas constant, and T the absolute temperature. It is thus reasonable to anticipate a close relationship between modulus at a fixed elongation and M_c', even though the modulus as normally measured cannot be identified with the equilibrium force f calculated in equation (2). Experimentally it is found[5] that, for not too large elongations, the elastic behaviour of a pure gum natural rubber vulcanisate can be represented by the equation

$$f = C_1(\alpha - \alpha^{-2}) + C_2(1 - \alpha^{-3}) \quad \ldots\ldots..(3)$$

The work reported in the preceding paper suggests that C_2 is approximately constant and equal to 1·5 kg./cm.^{2} for a range of rubbers. Inserting this value, and setting $\alpha = 2$, gives for the modulus at 100 per cent. elongation (in kg./cm.^{2})

$$F = 1{\cdot}75\, C_1 + 1{\cdot}31 \quad \ldots\ldots..(4)$$

Comparison of equations (2) and (3) suggests that C_1 is likely to be determined by $1/M_c'$. Experiments to test this view (cf. paragraph 5) were carried out by measuring the modulus and equilibrium swelling in benzene of a series of vulcanisates. In Fig. 1, F is plotted as a function

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*The prime is used to distinguish this quantity from the true molecular weight between junction points in the actual vulcanisate. Cf. paragraph 3.

of $1/M_c'$ (calculated from equation (1)) for one such series; the equation to the full line is:—

$$F = 3{\cdot}6 \times \frac{10^4}{M_c'} + 1{\cdot}31 \qquad \ldots\ldots\ldots(5)$$

It is clear that, except for a grossly undercured compound ($F < 4$ kg./cm.^{2}), equation (5) can be used to evaluate $1/M_c'$. Equation (5) is, of course, essentially empirical, but confidence in its use is increased by noting that the experimental slope ($3{\cdot}6 \times 10^4$ in this example) does not vary widely in the different compounds studied, and is very close to the value ($1{\cdot}75\ \rho\ RT = 4{\cdot}1 \times 10^4$) indicated by the above argument.*

3. "TRUE" DEGREE OF CROSS-LINKING

Although the quantity $1/M_c'$ determines the swelling behaviour of a vulcanisate, it is easily seen that it does not measure directly the number of chemical cross-links present. Before vulcanisation commences, the raw rubber is in the form of a large number of independent molecules, and a network cannot be said to exist at all until sufficient cross-links have been introduced to link together most of these. Flory[6] has pointed out that if we consider a molecule of weight M and the weight between successive junction points is M_c, a fraction $2M_c/M$ will lie outside the network, and will, therefore, not contribute to the elastic properties of the network. Allowing for other types of network defect which may occur in practice, his final result is that, if $1/M_c$ measures the true degree of cross-linking (i.e. M_c = true molecular weight between junction points in the real material), then

$$\frac{1}{M_c'} = g\left\{\frac{1}{M_c} - \frac{2}{M}\right\} \qquad \ldots\ldots\ldots(6)$$

where g is a numerical constant which should be of the order of magnitude 1–10. Flory found that this equation could be applied successfully to a range of butyl rubber vulcanisates, with a value of $g = 3{\cdot}3$.

Combining equations (5) and (6) shows how the modulus depends both on the true degree of cross-linking and on the molecular weight M of the unvulcanised rubber in the mixed compound:

$$F = 1{\cdot}31 + A\left\{\frac{10^5}{M_c} - \frac{2 \times 10^5}{M}\right\} \qquad \ldots\ldots\ldots(7)$$

where A is a new constant.

The molecular weight of the raw rubber in a compound is not of course usually known, but recent investigations in these laboratories

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*The relationship between swelling and modulus has been examined over a wider range by Rivlin and Saunders. Although their conclusions differ somewhat in detail from those presented here, they reinforce the suggestion made here that $1/C_1$ is a reliable measure of $1/M_c'$. It is clear from Rivlin and Saunders' work that if the experimental points plotted in Fig. 1 had been extended to higher values of $10^4/M_c'$, it would have been found that they lay on a curve, concave upwards. Equations (4) and (5) are, therefore, best considered as convenient interpolation formulae covering the range of modulus likely to be encountered in the testing of natural rubber gum compounds.

indicate that it can be calculated with some reliability from the Mooney viscosity of the compound (V_c), using the simple empirical equation*

$$10^{-5}\,M = 0{\cdot}0623\,(V_c + 18{\cdot}7) \qquad \ldots\ldots\ldots(8)$$

By using this result, equation (7) is transformed into

$$F = 1{\cdot}31 + A\left\{\frac{10^5}{M_c} - \frac{32{\cdot}1}{V_c + 18{\cdot}7}\right\} \qquad \ldots\ldots\ldots(9)$$

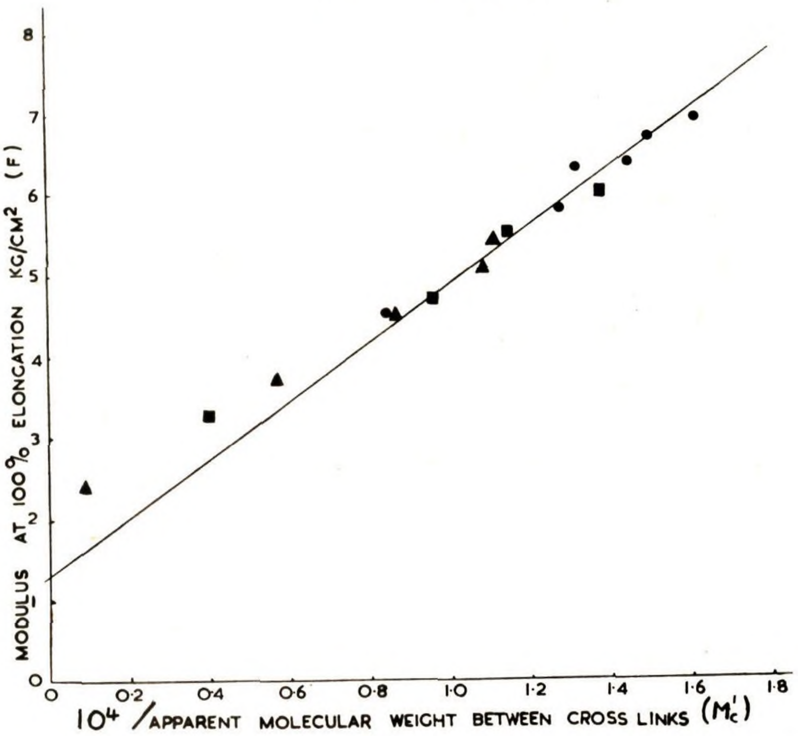

FIG. 1.

Relationship between modulus and "apparent" degree of cross-linking from equilibrium swelling. ACS1 compound. *Line is best fit through* $10^4/M_c' = 0$, $F = 1{\cdot}31$.

Vulcanising temperature

● 140° C. ■ 130° C. ▲ 120° C.

The following paper is concerned with the practical use of this equatio in studying the dependence of modulus on compound viscosity. Antici pating its conclusions, we may note that the equation is found valuable

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*This equation is based on simultaneous measurements of the osmotic molecula weight and Mooney viscosity of a series of milled rubbers.[10] The Mooney viscosit of a compound and the molecular weight of the raw rubber extracted therefrom hav also been shown to be in agreement with this equation.

and that while experimental estimates of A vary rather widely, a mean value of 3·27 kg./cm.^{2} (equivalent to a value of $g = 7$ in equation (6)) is finally adopted. Using this value, it is now possible to calculate the *true* degree of cross-linking from the modulus and the compound viscosity:

$$\frac{10^5}{M_c} = \frac{1}{3{\cdot}27}\left(F - 1{\cdot}31 + \frac{105}{V_c + 18{\cdot}7}\right) \qquad \ldots\ldots\ldots(10)$$

4. The Definition of "State of Cure"

In the preceding sections F has been shown to be a linear function of two different quantities $1/M_c'$ and $1/M_c$ which measure respectively what we have termed the "apparent" and "true" degrees of cross-linking. We have now to discuss which of these three related quantities can best be regarded as a measure of the state of cure of a vulcanisate. Arguments can be advanced in favour of any one of them, but from a practical point of view there are obvious advantages in selecting modulus, in that it is the only one of the three possibilities which we measure directly. For most purposes, modulus at 100 per cent. elongation is an eminently satisfactory measure of state of cure, but we shall see in the two following papers that it requires modification when we wish to discuss (*a*) the dependence of modulus on compound viscosity and (*b*) the rate of development of modulus during vulcanisation. To meet these difficulties while still preserving the practical advantages of a scheme based on modulus measurements, we therefore make the following proposals:—

(i) Modulus at 100 per cent. elongation is regarded as the normal measure of state of cure.

(ii) If we are interested in relating mechanical properties with swelling behaviour it is necessary to deduct from the modulus that part of it, estimated as 1·31 kg./cm.^{2}, which is independent of the rubber. Under such circumstances we therefore measure state of cure by $(F - 1{\cdot}31)$, which is seen from equation (5) to be proportional to $1/M_c'$.

(iii) According to either of these estimates, state of cure is dependent on the viscosity of the raw compound as well as on vulcanisation. If we wish to have a quantity which is a function only of the raw rubber and vulcanisation, we must add a further term to correct for the effect of the finite molecular weight of the rubber in the compound. We then arrive at the quantity $\left(F - 1{\cdot}31 + \frac{105}{V_c + 18{\cdot}7}\right)$ which, according to equation (10), is proportional to $1/M_c$. It will be noted that this correction is opposite in sign to the first one, and usually somewhat larger, so that the net correction to F is additive. This is the quantity which we use in the two succeeding papers.

One other concept which may be mentioned is that of "percentage cure." If F is the chosen measure of state of cure, we may speak of a "full cure" as the maximum modulus attainable with a given compound at a specified temperature. Percentage cure is then 100 times the ratio of any other modulus to the maximum.

The most serious exception to these conclusions arises in the behaviour of grossly undercured rubbers. For such materials, determination of modulus becomes very unsatisfactory, the value recorded being extremely dependent on the time of measurement. Fig. 1 shows a typical example of the departure of modulus measurements from values calculated from equation (5). At very low states of cure swelling measurements give a more reliable estimate of $1/M_c'$, though even these become uncertain when an appreciable fraction of the rubber is soluble. Normally, we are

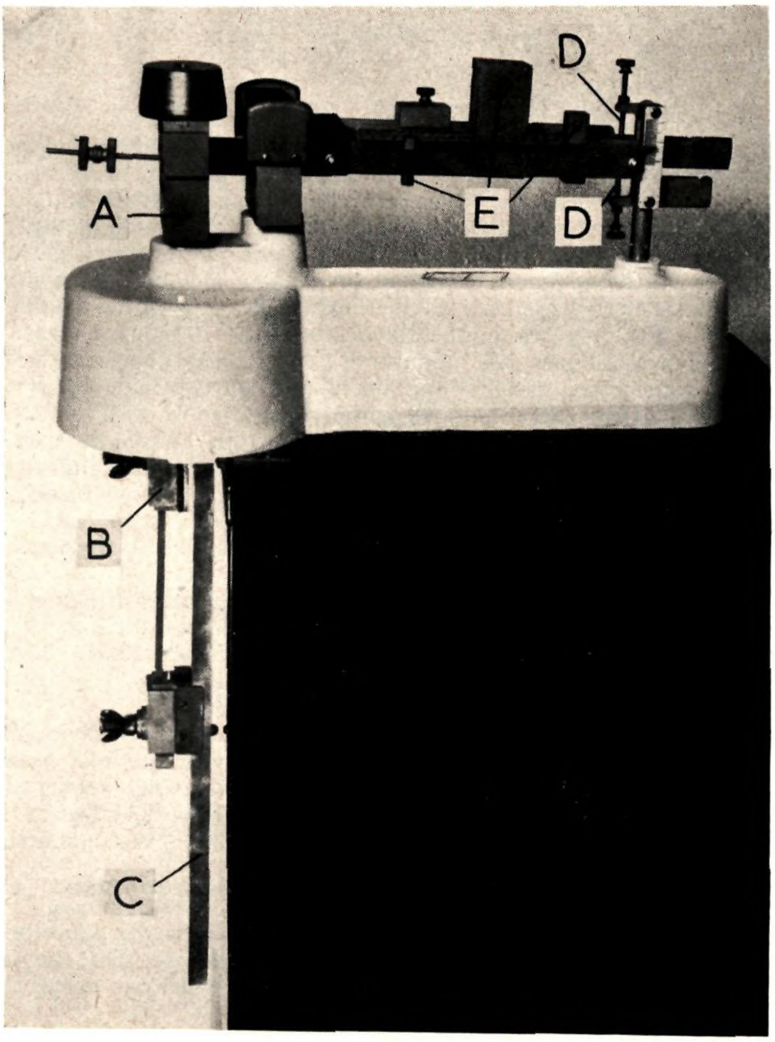

FIG. 2.
Modulus testing machine.

not concerned with this region of cure, but the analysis presented above can be formally extended back even to the start of vulcanisation by replacing F by an "equilibrium" modulus F*, so defined that the above equations always hold. These ideas find application in the study of "rate of cure" presented in part IV of this series.

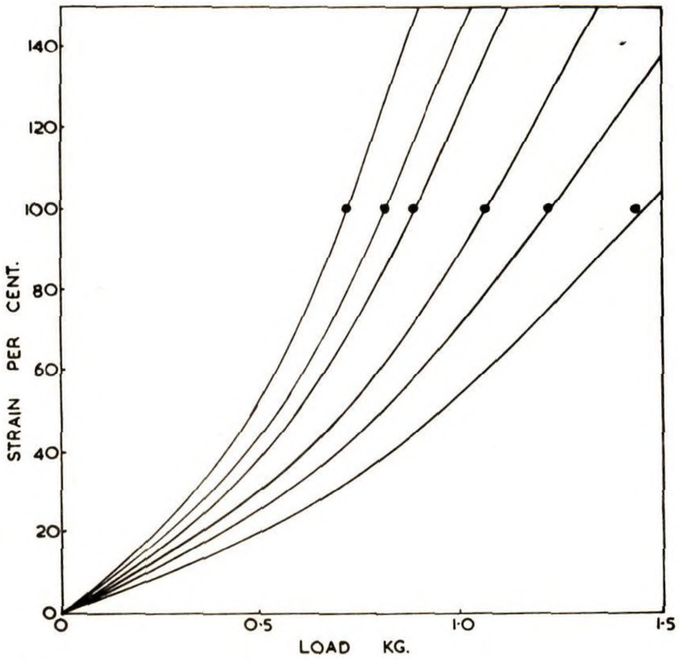

FIG. 3.

Load extension curves from strain test results.

— Strain tester
● Modulus tester

5. EXPERIMENTAL COMPARISON OF SWELLING AND MODULUS

Portions of a single blend of No. 1 RSS were compounded according to the ACS1 recipe (see Appendix to Paper I) and cured for a range of times and temperatures in the form of test pieces as used in the B.R.P.R.A. strain test.[7] Measurements of modulus at 100 per cent. elongation were made on a simple machine developed in these laboratories and described in paragraph 6.

The equilibrium swelling in benzene was determined by Garvey's method.[8] The ends of the same test pieces were removed and the central strips (10 cm. long) swollen in benzene for several days at 20° C. until the length was constant. The volume swelling $\underset{\sim}{Q}$ was calculated from the measured increase in length, and the apparent degree of cross-linking from equation (1).

The results of a typical experiment are recorded in Fig. 1, the compound being mixed to a Mooney viscosity of $V_c = 50$. A second series, in which the compound viscosity was 35 ± 2, gave very similar results, except that the departure of F from the linear relationship was somewhat smaller.

6. A Simple Machine for the Measurement of Modulus

The machine is of the same general type as described by Flory[9] and is shown in the photograph, Fig. 2. It consists of an "ETA" triple beam laboratory balance modified in the following manner. The moulded plastic pan which normally carries the article to be weighed is removed and its support A, which passes through a clearance gap into the interior of the hollow base casting, is fitted with an extension rod. In the balance as supplied the lower part of the support is used in conjunction with a small pivoted lever to allow only vertical movement of the pan assembly, and this mechanism is retained intact. The extension rod carries a grip B of the type used in the B.R.P.R.A. strain tester.[7] Extending downwards and rigidly fixed to the base casting is a rod C. A second grip fitted with a cylindrical stud may be "plugged" into any of six holes drilled in the vertical rod. When the device is in its balancing position the distance between the two grips is such that the extension of the test piece held therein is 0, 25, 50, 100, 150 or 200 per cent., depending upon which hole is occupied by the plug.

In use, a standard strain test-piece is fixed into the upper and lower grips, and the lower grip is plugged in at the position giving say 100 per cent. extension. The tension force of the rubber unbalances the machine, but the beam-stops D prevent more than a fractional movement of the beam and upper grip. Balance is restored by the sliding weights E and from the graduated beam the load can be read. With gum rubbers, the device is sensitive to a change of 1 gm. in the load, the range being 0 to 2,000 gm. An average reading for well cured compounds is in the region of 1,000 gm. The balance is usually adjusted over a period of 1 minute in conformity with the stress relaxation, the modulus being recorded after that period under strain.

As a check on the performance of the modulus tester, measurements of modulus at 100 per cent. elongation were made on a series of test-pieces, stress/strain curves for which had previously been obtained using the B.R.P.R.A. strain tester. Fig. 3 shows the closeness of fit of the modulus points on these curves.

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III.

Relation between Compound Viscosity and Vulcanisate Stiffness in Pure Gum Natural Rubber Vulcanisates*

BY R. F. BLACKWELL, W. P. FLETCHER AND GEOFFREY GEE

SUMMARY

The aim of this investigation was to study the dependence of vulcanisate stiffness upon the compound Mooney viscosity, and if possible to derive a method by which account could be taken of variations in viscosity in order to reduce the so-called mixing error in batches of test compound. Investigations covering a range of compounds, raw rubbers and curing times, gave results which for the practical range indicated a relation between modulus at 100 per cent. elongation and Mooney viscosity. Using the relationship thus established, a method of adjusting modulus results to correspond to a standard Mooney viscosity was derived. Application of the scheme to batches of ACS1 compound mixed from parts of the same lot of homogeneous raw rubber led to a considerable reduction in the range of modulus values.

1. INTRODUCTION

Experienced rubber compounders are well aware that the viscosity or plasticity of an unvulcanised compounded rubber has an effect on the modulus of the vulcanisate. It is a common experience, for instance, to find that the higher plasticity (softer) laboratory-mixed batch has a lower modulus when vulcanised than a corresponding factory-mixed batch. As long ago as 1925 a committee of the American Chemical Society in a report gave figures showing how the Williams plasticity and modulus were related; no application of this observation seems to have been made, although attention was recently redirected to its importance.[1] In another investigation in these laboratories, it was found that pure-gum compounds mixed in nitrogen so as to avoid breakdown, generally gave vulcanisates of much higher modulus than those obtained from conventionally mixed compounds.

These observations suggest strongly that the considerable "mixing" error observed both within and between laboratories in the evaluation of the vulcanising characteristics of rubber would be substantially

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*The data discussed in this paper formed the substance of that read by C. M. Blow before the Division of Rubber Chemistry of the American Chemical Society at its meeting in Cleveland in October, 1950. Subsequent work led to a re-examination of the results and it appeared that considerable simplification would be possible if the data were considered in terms of modulus rather than strain values.

reduced if compounds were always mixed to the same viscosity. As this would obviously be troublesome to achieve in practice, we have examined the alternative possibility of "adjusting" the results of vulcanisation tests for variations in compound viscosity. It will be shown below that this is indeed possible. The adjustment is only approximate, but does in practice result in a significant reduction of mixing error.

We therefore recommend that in all vulcanisation testing which aims at precision the compound viscosity should be measured, and an adjustment made to convert the results to a standard viscosity.

2. Experimental

A study was made of the effect of compound viscosity on vulcanisate modulus, in which the aim was to cover the widest possible range of modulus and viscosity. A number of types of rubber were used, including skim sheet and skim crepe. Three different mixes (ACS1, TA57 and TC9) were employed; details of these are given in the appendix to paper I.

To produce a range of stocks differing only in viscosity, the general method was to mix a large batch of compound, keeping breakdown to a minimum, and then to divide the mixed batch into smaller lots for further breakdown. Each lot was used to mould test pieces on which either the strain at 5 kg./cm.^{2} or the modulus at 100 per cent. elongation was measured by methods described in the second paper of this series and elsewhere[1]. Where the primary measurement was in the form of strain, it was converted to modulus using the relationship established in the first paper of this series. All data are recorded and discussed in the form of modulus.

3. Analysis of the Data

Although the aim of this paper is essentially practical, there are obvious advantages in considering what dependence of modulus on viscosity is to be expected on theoretical grounds. This problem is discussed in the preceding paper, where it is shown that the modulus at 100 per cent. elongation (F) should be a function of two quantities, (i) the number of chemical cross-links introduced during vulcanisation (measured by $10^5/M_c$) and (ii) the Mooney viscosity V_c of the uncured compound. An equation was derived which contained only one adjustable constant A, the value of which was expected to be close to 1 kg./cm.^{2}:—

$$F = 1{\cdot}31 + A\left(\frac{10^5}{M_c} - \frac{32{\cdot}1}{V_c + 18{\cdot}7}\right) \qquad \ldots\ldots\ldots(1)$$

It is convenient to write this in a new form by making the substitutions

$$B = 32{\cdot}1\,A$$
$$\epsilon = (V_c + 18{\cdot}7)^{-1}$$

Then
$$F = 1{\cdot}31 + \frac{B}{32{\cdot}1} \times \frac{10^5}{M_c} - B\epsilon \qquad \ldots\ldots\ldots(2)$$

ϵ is now our new measure of compound viscosity and is chosen because theory predicts that F should decrease linearly with increase of ϵ, if

M_c is kept constant. Now M_c is a measure of the number of chemical cross-links in the vulcanisate, and should, therefore, depend only on the time of cure and not on V_e. For the purpose of this investigation we may, therefore, simplify the equation still further to the form:

$$F = C - B\epsilon \qquad \ldots\ldots\ldots(3)$$

This equation implies that if we take a series of similar compounds mixed from the same rubber but to different viscosities and give them the same cure, their moduli will vary linearly with ϵ. Moreover, if we repeat the experiment using a different mix, there is no reason to expect a different dependence of F on ϵ. We should indeed anticipate a family of parallel plots of F against ϵ, the absolute values of F and C differing widely, but with the slope B substantially constant. This then is the starting point of the analysis of the data, and in the following paragraphs we use the data obtained in this investigation to examine in turn a number of questions:—

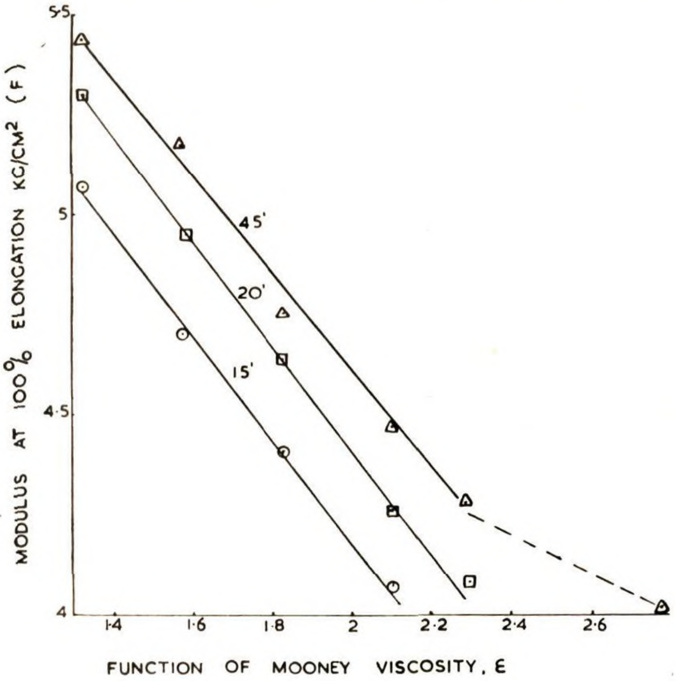

FIG. 1.

Relationship between modulus and function ϵ of Mooney viscosity, TA57 compound 3 times of cure at 140° C.

(i) Is F found in practice to be a linear function of ϵ ?

(ii) If so, does the slope B depend systematically and significantly on any identifiable experimental factor, including (*a*) the absolute value of F at fixed ϵ, (*b*) the time of cure, (*c*) the mix, or (*d*) the particular sample of rubber ?

(i) Figs. 1 and 2 are typical of the many plots which have been made of F against ϵ. The scatter of the points as shown here is typical, and it is difficult to be certain of the precise form of the relation between these quantities. Over the range of $\epsilon = 1{\cdot}35$ to $2{\cdot}30$ (Mooney viscosity 55–25) the plot is in general reasonably linear, but there are systematic departures outside this range: the dependence of F on V_c is greater at high V_c and less at low V_c than indicated by the linear F versus ϵ plot. Over this central range there is, however, no systematic evidence of general curvature, and no empirical equation has been found which, when tested on the whole body of data, is more successful in covering a wide range of ϵ.

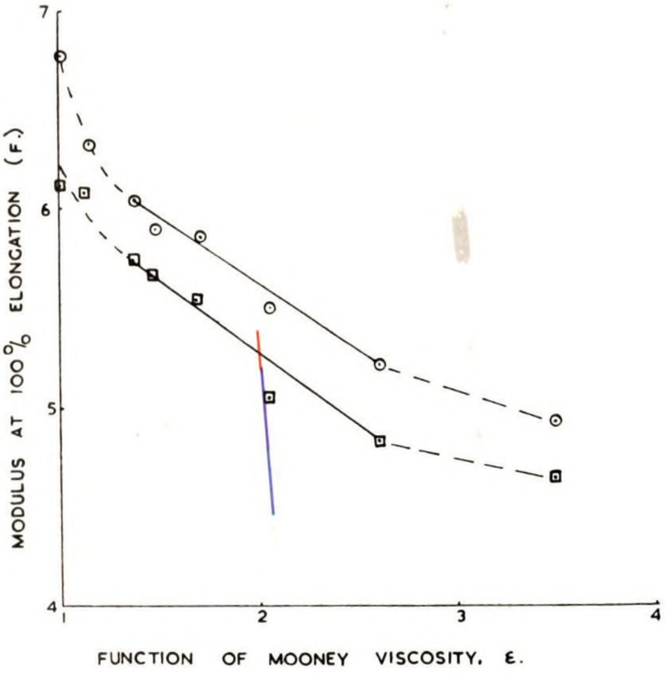

FIG. 2.

Typical relationships between modulus and function ϵ of Mooney viscosity.

(ii) Tables 1, 2 and 3 record values of the slope of F versus ϵ plots for a large number of vulcanisates in three different mixes, the recipes for which are given in the appendix to part I. All these slopes refer to the linear part of the plot, covering the Mooney ranges indicated in the tables, and were in most cases estimated by regression analysis. In considering the rather wide scatter of the values it is of importance to note the substantial discrepancies between replicates (cf. e.g. triplicate observations on rubbers 7 and 8 in Table 1). This is not surprising, having regard to the fact that the total effect of compound viscosity is not very large, but it does of course limit the precision with which the effects of the different experimental factors can be isolated.

TABLE 1

SLOPES OF F VERSUS ϵ LINES FOR TA57 COMPOUNDS MIXED FROM VARIOUS RUBBERS

Rubber	Mooney range	Modulus at optimum cure and $V_c = 40$	Cure range	Slope at each cure in range				
1	38·5–51·5	5·6	A	159	126	141		
2	35–51·5	5·6	,,	119	100	123		
3	38–52	5·65	,,	172	169	167		
4	36–52	5·8	,,	91	125	105		
5	35–49	5·9	,,	90	73	92		
6	34–54	6·0	,,	91	86	106		
7	30–57	5·9	,,	101	119	107		
7	28·5–54·5	5·9	,,	93	102	82		
7	30–54	5·8	,,	87	102	92		
8	31–55	5·6	,,	129	137	146		
8	29–52	5·8	,,	90	128	125		
8	29·5–55	5·8	,,	111	117	115		
9	37–55	5·2	B	130	133	133	136	
10	25–59	7·9	C	162	173	162	174	196
11	25–57	5·0	D	128	129	109	112	124
12	26–60	5·3	C	133	148	124	130	138
13	31–46	6·3	E	136	135	126	120	111
13	33–51	6·2	,,	151	99	85	116	100
14	26–43	5·1	,,	69	82	91	79	70

Mean value 119.

Cure ranges: A 30, 40, 50 mins. at 140° C.
B 25, 35, 50, 65 ,, ,, ,,
C 15, 20, 35, 60, 100 ,, ,, ,,
D 15, 20, 45, 60, 100 ,, ,, ,,
E 15, 25, 35, 45, 55 ,, ,, ,,

TABLE 2

SLOPE OF LINEAR PART OF F VERSUS ϵ LINES FOR TC9 COMPOUND WITH TWO RUBBERS

Rubber	Mooney range	Cure temp.°C.	Modulus at optimum cure and $V_c = 40$	Slope for stated times of cure at 140° C.								
				20	**30**	**35**	**40**	**50**	**60**	**65**	**80**	**100** MINS.
15	20–49·5	120° C.	8·8	53	—	—	71	—	76	—	90	78
15	,,	130	8·8	79	—	81	—	84	—	88	95	—
15	,,	140	7·8	90	87	—	86	95	100	—	—	—
16	20–48	120	6·2	—	—	—	83	—	89	—	86	85
16	,,	130	6·2	93	—	101	—	100	—	102	91	—
16	,,	140	5·4	80	83	—	101	100	113	—	—	—

Mean value 88.

Table 3

Slope of F versus ϵ Lines for ACS1 Compound with Various Rubbers

Rubber	Mooney range	Modulus at optimum cure and $V_c = 40$	Slope for stated times of cure at 140° C., minutes		
			20	**40**	**80**
W1	28–48	7·0	99	112	123
,,	28–48·5	6·8	86	70	93
W2	25–42	6·1	93	78	76
,,	25·5–43·5	6·3	106	81	90
W3	25·5–43	5·8	104	87	115
,,	25·5–40·5	5·7	84	71	105
W4	27–41	6·2	125	89	115
,,	28·5–40	6·5	140	111	123
W5	24–39·5	5·8	80	72	85
,,	27–38·5	5·8	90	74	97
W6	24–38	6·4	77	91	101
,,	22·5–35	6·4	90	69	93
W7	25·5–44	5·9	116	85	94
,,	25–45	5·9	126	81	70
W8	23·5–38	6·1	120	98	110
,,	24·5–39	6·1	140	112	116
W9	23·5–38	6·1	110	84	115
,,	24·5–40	6·1	132	107	98
W11	25–37	6·2	127	107	119
,,	24–38	6·2	84	84	83
Mean value for each cure:			106	89	101
Grand mean				98	

(*a*) The effect of modulus level is always confounded with one of the other variables, but the data in Table 2 show some small systematic effect of modulus level which is more clearly brought out by a plot of slope against modulus level. Tables 1 and 3 show no similar trend and it is clear that if present the effect is masked by other variations.

(*b*) In the ACS1 mix (Table 3) the slope shows an apparent minimum at the intermediate time of cure—which corresponds roughly to the time to maximum modulus. No such effect is shown by either of the dual-accelerated mixes (Tables 1 and 2).

(*c*) Taking grand means of the results in the three separate tables shows an effect of mix, but it is small compared with the overall spread of the results.

(*d*) Considering any one mix, the largest source of variation appears to be in the rubber. Evidence is lacking as to whether a rubber which gives a high slope in one mix will also give a high slope in other mixes.

4. Adjustment of Modulus Data for Compound Viscosity Variation

If we average the slope B over all the rubbers and mixes studied, a value of 105 is obtained. This then is the value to use if a single adjustment scheme is to be applied to all rubbers and all mixes. We write for the modulus F measured at any arbitrary value of ϵ:

$$F = C - 105\epsilon$$

The value F_s calculated for the standard value of $\epsilon = \epsilon_s$ is

$$F_s = C - 105\ \epsilon_s$$

whence $$F_s - F = 105\ (\epsilon - \epsilon_s)$$

The values of this function for $\epsilon_s = 0{\cdot}0170$ ($V_c = 40$) are given in Table 4 for a range of V_c from 25 to 55; the figures give the amount to be added

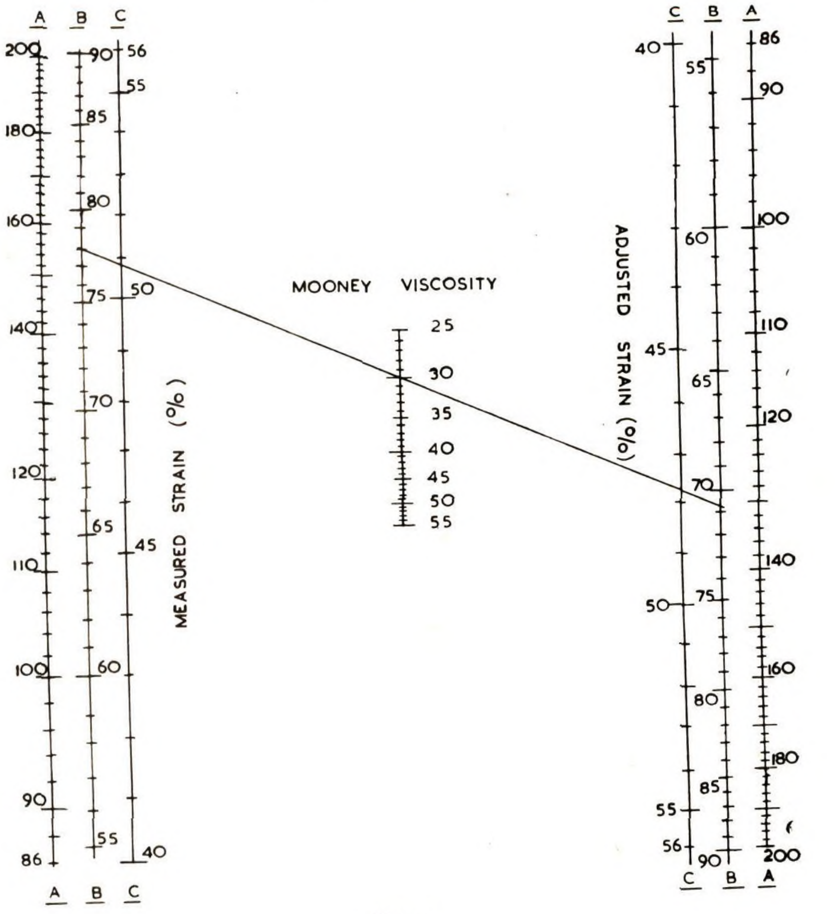

FIG. 3.

Nomogram for adjusting strain values to a Mooney compound viscosity of 40.

Example: A compound mixed to 30 Mooney gives a strain of 78 per cent. The nomogram shows the adjusted value to be about 70·8 per cent.

to the measured modulus in order to calculate the modulus to be expected if the compound had been mixed to viscosity 40.*

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*This value is the average attained in routine mixing of pure gum compounds for the purpose of the technical classification of natural rubber.

Two further questions have now to be examined: (i) In view of the large scatter of B values recorded in paragraph 3, can we be sure that a single adjustment scheme will always *reduce* the mixing error ? (ii) Would it be possible to devise more accurate adjustments applicable only to more limited conditions, e.g. to one mix only, and possibly to a single time of cure ?

TABLE 4

ADJUSTMENT OF 100 PER CENT. MODULUS VALUES TO MOONEY COMPOUND VISCOSITY OF 40

This table gives adjustments to be added to 100 per cent. modulus values for Mooney viscosity (V_c) between 25 and 55. Values may be linearly interpolated.

V_c	0	1	2	3	4	5	6	7	8	9
20						+0·61	+0·56	+0·51	+0·46	+0·41
30	+0·37	+0·33	+0·29	+0·25	+0·21	+0·17	+0·13	+0·09	+0·06	+0·03
40	0	−0·03	−0·06	−0·09	−0·11	−0·14	−0·17	−0·19	−0·22	−0·24
50	−0·26	−0·28	−0·30	−0·32	−0·35	−0·37				

TABLE 5

ADJUSTMENT TO MOONEY VISCOSITY 40 OF 100 PER CENT. MODULUS VALUES GIVEN BY 26 BATCHES OF ACS1 COMPOUND

	Measured value modulus at 100 per cent. elongation kg./cm.^{2}	Adjustment from Table 4 kg./cm.^{2}		Adjusted value modulus at 100 per cent. elongation kg./cm.^{2}
	6·29	−·38		5·91
	5·72	−·16		5·56
	5·72	·13		5·85
	5·68	·10		5·78
	5·47	·06		5·53
	6·01	−·24		5·77
	6·07	−·28		5·79
	5·91	−·24		5·67
	5·86	·21		6·07
	5·55	·28		5·83
	5·64	·06		5·70
	5·44	·33		5·77
	5·20	·33		5·53
	6·01	−·21		5·80
	5·68	−·14		5·54
	5·68	−·11		5·57
	5·59	−·08		5·51
	5·68	−·11		5·57
	5·68	·03		5·71
	5·86	−·02		5·84
	6·01	−·08		5·93
	5·86	−·05		5·81
	6·07	−·11		5·96
	6·07	−·02		6·05
	5·72	−·11		5·61
	5·82	−·08		5·74
Range	1·09		Range	0·56

The answer to the first of these questions seems to be fairly certainly in the affirmative. In no single case of the many recorded in Tables 1 to 3 is the measured slope more than twice or less than half the average. Allowing for the large experimental error, it appears safe to conclude that the true spread is not so large that adjustment could ever be positively harmful. In the vast majority of cases a substantial diminution of the effect of compound viscosity is to be anticipated, with a consequent reduction in the mixing error. An indication of the order of improvement found in practice is presented in Table 5, which records the observed and adjusted modulus given by 26 batches of ACS1 compound, all mixed from a single lot of raw rubber: the range is seen to be approximately halved by the adjustment.

As regards the second question, it is true that a smaller spread of slopes is found if instead of considering Tables 1 to 3 as a whole we restrict attention to one time of cure and one mix. Having regard to the conclusion that the main source of variation arises from the rubber samples, it is doubtful whether any advantage which resulted from such a treatment would be sufficient to outweigh the disadvantages of having to use a number of different systems of adjustment.

5. Routine Use of the Adjustment

Where measurements are made of modulus the adjustment is made simply by addition or subtraction of the amount corresponding to the compound viscosity indicated in Table 4. For measurements of strain at 5 kg./cm.^{2} the adjustment varies with the level of strain, and may then be made with reference to the nomogram, Fig. 3. Thus in the example shown, the compound was mixed to $V_c = 30$ and gave a vulcanisate having $S_5 = 78$; the adjusted figure at $V_c = 40$ is seen to be $S_5 = 70{\cdot}8$.

Reference

1. Fletcher, W. P., *Rubber Chem. and Technol.*, 1950, **23**, 107.

IV.

Definition and Measurement of "Rate of Cure" for Pure Gum Natural Rubber Compounds[*]

By GEOFFREY GEE and S. H. MORRELL

SUMMARY

The purpose of this paper is to develop a simple practical method of assessing rate of cure, based on sound theoretical principles, and using only measurements which are normally available or easily made. Mathematical and experimental studies of modulus-time curves are presented, and it is shown that several types of gum compound give curves of a simple mathematical form, equivalent to that of a first order chemical reaction. It is concluded that in such cases "rate of cure" can be defined and measured by the value of a first-order velocity constant, having dimensions time^{-1}*, the reciprocal of which determines the vulcanisation period needed to produce a given percentage cure. Application to a substantial number of rubbers has shown that the method is capable of yielding reproducible results for the rate of cure of a single compound, and of distinguishing with high significance between different compounds. A connection is predicted between rate of cure, as thus measured, and scorch; preliminary data are consistent with expectation.*

INTRODUCTION

Despite the widespread use of the terms "fast-curing" and "slow-curing," it is safe to assert that there is no generally accepted definition which would attach a quantitative significance to "rate of cure." The purpose of this paper is to put forward some suggestions as to the lines along which this problem can be approached, and to present some relevant experimental results recently obtained in these laboratories. The relation of this method to another recently proposed is discussed in the appendix.

It is shown in part II of this series (referred to below as II) that the state of cure of a vulcanisate is very satisfactorily determined by the modulus at 100 per cent. elongation (F), corrected if necessary to remove contributions which do not change during vulcanisation. It is with the corrected modulus that we are concerned in this paper, since our aim is to discuss methods of determining the rate at which the cross-linked

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[*] Parts of this Paper were presented before the Rubber Division of the American Chemical Society at Cleveland in October, 1950.

structure is built up during vulcanisation. Our measure of state of cure in this paper will therefore be:—

$$X \equiv F - 1{\cdot}31 + \frac{105}{V_c + 18{\cdot}7} \qquad \ldots\ldots\ldots(1)$$

where V_c is the Mooney viscosity of the compound.

THE UNCURED COMPOUND

Since X measures the number of chemical cross-links it must be zero at zero time, and equation (1) then gives a calculated value for the modulus F_o of the uncured compound.

$$F_o = 1{\cdot}31 - \frac{105}{V_c + 18{\cdot}7} \qquad \ldots\ldots\ldots(2)$$

In general, this quantity will be negative (unless $V_c > 61$) and it is clear that it does not correspond with anything physically measurable. We have here indeed an extreme case of the difficulty discussed in (II), where it was pointed out that at very low cures the modulus fails to measure the degree of cross-linking. Equation (1) should therefore be written in terms of the "equilibrium" modulus F^* where this differs from F, and in particular, for the uncured compound, (2) should be replaced by

$$F_o{}^* = 1{\cdot}31 - \frac{105}{V_c + 18{\cdot}7} \qquad \ldots\ldots\ldots(3)$$

Although $F_o{}^*$ is unobservable, it is nevertheless a quantity of considerable importance, as it gives a measure of the state of the unvulcanised rubber. Moreover, in any attempt to represent the time dependence of F, it fixes the initial point through which the curve should pass at zero time.

RATE OF CURE

Our definition of rate of cure should describe some quantitative measure of the way in which F (strictly, X) increases with time. The alternatives would seem to be (*a*) the absolute rate of increase of F with t, i.e. $\frac{dF}{dt}$, measured e.g. in kg./cm.$^{-2}$ min.$^{-1}$; and (*b*) a velocity constant (if one can be found) which defines the shape and slope of the modulus-time curve. The latter alternative is much the more attractive since $\frac{dF}{dt}$ is difficult to measure and varies rapidly during the course of vulcanisation. On the other hand, there is no *a priori* reason to expect the time-dependence of F to follow any simple kinetic law: vulcanisation is not a simple chemical process and our knowledge of its detailed course is still scanty. In what follows, therefore, the immediate objective is only to find convenient ways of defining and measuring a velocity constant which can be used to characterise the time-dependence of modulus. The interpretation of such a constant in terms of chemical reactions lies outside the scope of this paper.

NON-REVERTING COMPOUNDS

In the absence of reversion, F^* increases with time from the initial value F_0^* calculated from equation (3) to an observable limit F_∞ at long times of cure. Following the argument set out above, we have to find an empirical kinetic equation for X. The simplest type of equation, which we shall see later is in fact very satisfactory, represents the increase in X as kinetically of the first order, i.e.

$$X = X_\infty (1 - e^{-kt}) \qquad \ldots\ldots\ldots(4)$$

Thus a vulcanisation rate constant k, having dimensions time^{-1}, can be unambiguously defined and can very reasonably be termed the "rate of cure" of the compound. The modulus F, at time t, is given by

$$F = F_\infty - (F_\infty - F_0)\, e^{-kt} \qquad \ldots\ldots\ldots(5)$$

or, taking logs,

$$kt = \ln (F_\infty - F_0) - \ln (F_\infty - F) \qquad \ldots\ldots\ldots(5')$$

The two parameters in this equation are F_∞ and k. The former is determinable experimentally by carrying out a long-time cure; k can then be calculated from a second modulus measurement, preferably chosen so that $F \simeq 0{\cdot}8\, F_\infty$. In principle it is unnecessary to carry out the long-time cure needed to measure F_∞ since any two modulus measurements can clearly be used to obtain k and F_∞. A convenient method is to make two measurements F_1 and F_2 at times τ and 2τ, whence

$$F_\infty = F_0 + \frac{(F_1 - F_0)^2}{2F_1 - F_2 - F_0} \qquad \ldots\ldots\ldots(6)$$

$$k = \frac{1}{\tau} \ln \left\{ \frac{F_\infty - F_0}{F_\infty - F_1} \right\} \qquad \ldots\ldots\ldots(7)$$

(F_0 being given by equation (3)).

REVERTING COMPOUNDS

It is well known that the modulus of many compounds passes through a maximum as the time of cure is progressively increased. This implies either that some at least of the cross-links are unstable, or that vulcanisation is accompanied by a reaction in which molecular chains are broken; this latter process would reduce the modulus in the same way as would loss of cross-links. In order to describe the complete vulcanisation curve it is necessary to introduce at least one further parameter to define the breakdown or reversion process. If, as the data in paragraph 8 suggest, reversion is never complete, still a fourth parameter becomes necessary to describe the modulus at infinite time.

We are not concerned in this paper with a detailed study of reversion, but it is necessary to discuss how the occurrence of reversion affects the problem of estimating the rate of cure. The first point to be noted is that the reaction responsible for reversion presumably starts right from the beginning of vulcanisation, so that the modulus only measures the net effect of cross-linking *minus* reversion. Two methods of analysis are therefore possible:

(*a*) Ignore the fall of modulus at long times of cure, take the maximum modulus as a measure of F_∞ and characterise the rising modulus as in paragraph 4.

(*b*) Attempt to separate the effects of cross-linking and reversion by a more detailed analysis of the whole curve. In this case F_∞ must be understood to mean the maximum modulus which would have been attained had reversion been absent. It thus becomes an unobservable quantity and all we can say in general is that it must be somewhat larger than the observed maximum modulus F_m.

Although we have not made much progress in applying the second method of analysis to actual data, it is perhaps of interest to illustrate the kind of behaviour predicted by a very simple theoretical treatment. We assume that all the cross-links are unstable, and that they break down unimolecularly, with a rate constant λ times that of the cross-linking process. (Rate constant for reversion $k_r = \lambda k$.) It is then easily shown that equation (4) must be replaced by:

$$X = \frac{X_\infty}{1 - \lambda}\left(e^{-\lambda kt} - e^{-kt}\right) \qquad \ldots\ldots\ldots(8)$$

The maximum modulus F_m and the time t_m to attain it are given by

$$\frac{X_m}{X_\infty} = \frac{F_m - F_0}{F_\infty - F_0} = \lambda^{\frac{\lambda}{1-\lambda}} \qquad \ldots\ldots\ldots(9)$$

$$t_m = \frac{1}{k(1 - \lambda)} \ln\left(\frac{1}{\lambda}\right) \qquad \ldots\ldots\ldots(10)$$

These equations can be used to examine the validity of (i) the approximation (*a*) above and (ii) the widely accepted method of regarding t_m as an inverse measure of rate of cure. Table 1 records values of X_m/X_∞ and of kt_m calculated from equations (9) and (10), while Fig. 1 gives plots of equation (8) for $\lambda = 0$, 0·01 and 0·05; with $k = 0{\cdot}10$ min.$^{-1}$, $X_\infty = 10$ in each case.

TABLE 1

λ	X_m/X_∞	kt_m
0	1·000	∞
0·002	0·989	6·22
0·005	0·974	5·33
0·01	0·955	4·65
0·02	0·923	3·99
0·05	0·854	3·16
0·1	0·774	2·56

The controlling effect of λ (the ratio between velocity constants for reversion and cross-linking) is clearly brought out, and two conclusions may be drawn: (*a*) If reversion is small (e.g. $\lambda = 0{\cdot}02$) a good estimate of k will result from a study of the rising modulus curve, neglecting reversion. (*b*) The time to optimum cure gives a rough relative measure of $1/k$ so long as λ is not too small (e.g. in the region of $\lambda = \cdot 02$, t_m is some five times as sensitive to k as it is to λ). This method can, of course, never be precise, as is indeed obvious from the fact that the very *existence* of a maximum in the modulus curve depends on the occurrence of reversion. It is clear that if the method is to be used a fairly "peaky" mix should if possible be chosen.

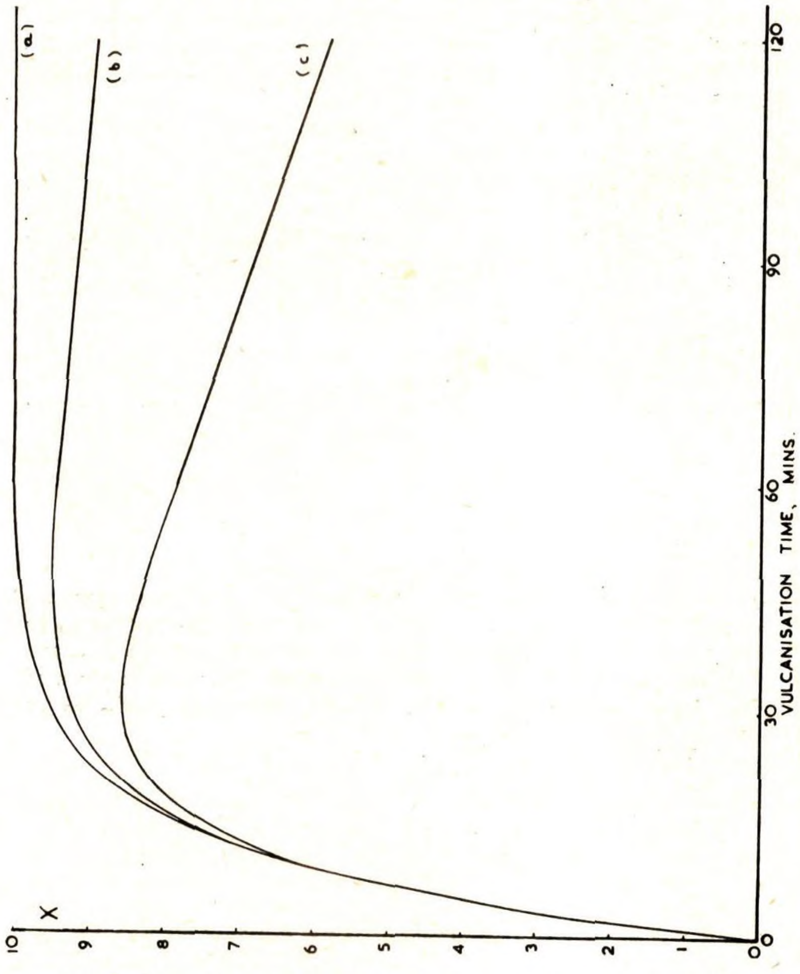

FIG. 1.

Theoretical vulcanisation curves, showing effect of reversion. Calculated from equation (8) with $\lambda = 0$ (curve a), 0·01 (b), 0·05 (c).

Attempts to fit equation (8) or similar equations to our data reveal the difficulties inherent in the use of multi-parameter equations. Unless data are available over an exceedingly wide time range, the constants deduced are very sensitive to experimental uncertainties, and are therefore of limited significance. If, for example, we measure X at $t = 20$, 40 and 80, we can easily fit the data to equation (8) and so calculate λ, k and X_∞. Generally, however, a very small change in one of the X values would lead to substantial changes in the constants. It is easy to see how this can arise, since the effect of increasing λ is to a considerable extent offset by an appropriate increase of X_∞. The actual rate of reversion in a typical practical mix is therefore difficult to assess, but the analyses we have made suggest that in the ACS1 mix, reversion is of the order of 100 times slower than vulcanisation.

The whole problem of reversion requires further investigation. Meantime we conclude that rate of cure even of a reverting compound is best measured on the rising modulus curve, neglecting reversion. We do not recommend the use of time to maximum modulus, except as a very rough indication of rate of cure.

SCORCH TIMES

The rubber in the uncured compound is in the form of individual molecules; scorch (incipient vulcanisation) occurs when sufficient cross-links have been introduced to bind most of these into a network. At this point the rubber just ceases to be soluble in benzene and it follows directly from the argument of II that the onset of scorch can be defined by $\frac{1}{M_c'} = 0$ or $F^* = 1{\cdot}31$. If then we can find some method of measuring t_s, the time to scorch, it is possible to use this, with a knowledge of F_∞, to calculate k. If we put $F = 1{\cdot}31$ and $t = t_s$ in equation (5), we find, on rearrangement,

$$kt_s = \ln\left\{1 + \frac{105}{(V_c + 18{\cdot}7)(F_\infty - 1{\cdot}31)}\right\} \qquad \ldots\ldots\ldots(11)$$

This equation is not very sensitive to F_∞ and it would be sufficient to take for F_∞ the measured modulus from a good technical cure. The real difficulty lies in measuring the scorch time, and it is doubtful whether present methods of doing so are sufficiently good to make the quantitative use of equation (11) practicable; this matter is further discussed in paragraph 9. It may be noted that the well-known factory method of reducing scorching by increased mastication finds a rational explanation in equation (11); decreasing V_c will clearly increase t_s if k remains constant.

SULPHUR COMBINATION AND CROSS-LINKING

Although this paper is not concerned with the chemistry of vulcanisation it is pertinent to point out that cross-linking does not in general go hand-in-hand with sulphur combination. Experimental evidence presented in the next section shows that even when both processes can be described by first order constants, the two constants may differ widely. It must, therefore, be re-emphasised that the velocity constants discussed in this paper are only intended to describe the observed cross-linking and do not necessarily bear any simple relation to the underlying chemical reactions.

AN EXPERIMENTAL STUDY OF RATE OF CURE

In order to try out the methods of measuring rate of cure outlined above, a number of vulcanisation curves have been followed in some and X_∞. Generally, however, a very small change in one of the X values would lead to substantial changes in the constants. It is easy to see how this can arise, since the effect of increasing λ is to a considerable extent offset by an appropriate increase of X_∞. The actual rate of reversion in a typical practical mix is therefore difficult to assess, but the analyses we have made suggest that in the ACS1 mix, reversion is of the order of 100 times slower than vulcanisation.

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AN EXPERIMENTAL STUDY OF RATE OF CURE

In order to try out the methods of measuring rate of cure outlined above, a number of vulcanisation curves have been followed in some detail. Rubber from a single bale of No. 1 R.S.S. was blended on the mill to provide a uniform material which was used throughout the investigation. Test pieces of the type used for the B.R.P.R.A. strain test were moulded, and modulus measurements made after 1 minute loaidng at 20° C. on the machine described in II. In many cases the

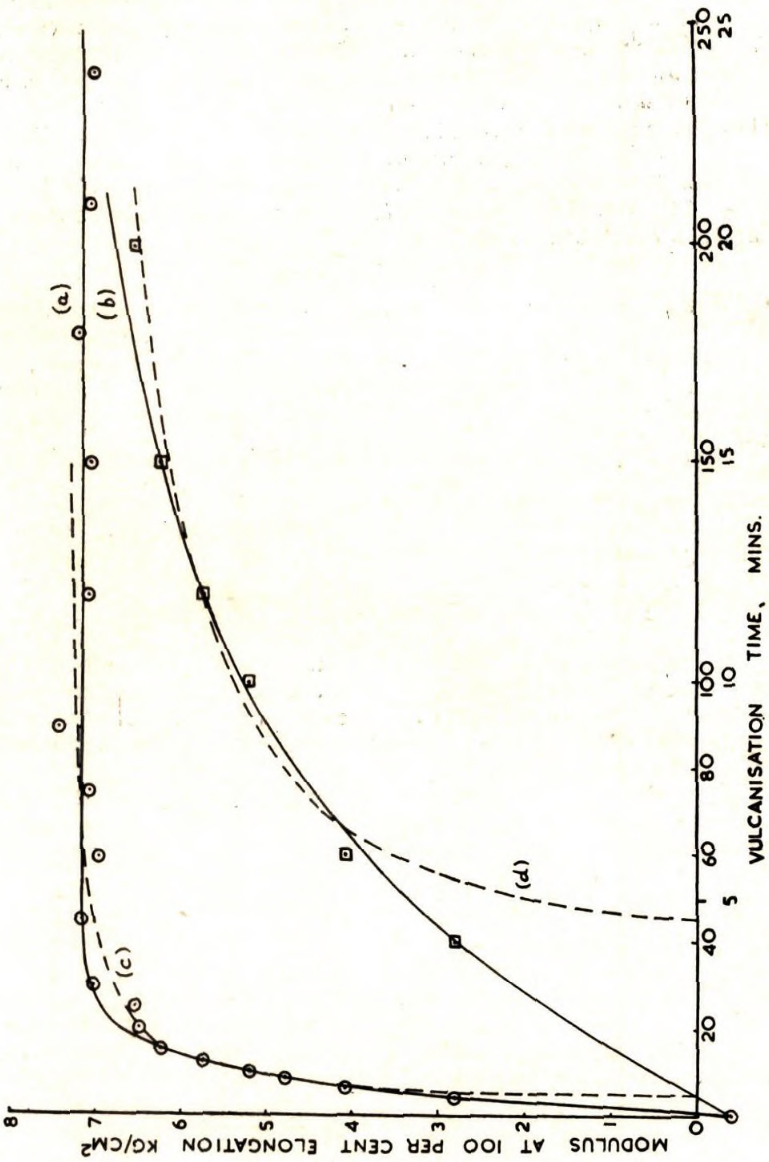

FIG. 2.

Vulcanisation of TC5 compound at 140° C. Curves (b) and (d) are on time scale ÷ 10. Broken curves (c) and (d) calculated from strain hyperbola (paragraph 13).

equilibrium swelling in benzene was also recorded, so that when the rubber was grossly undercured it was possible to compute and use the

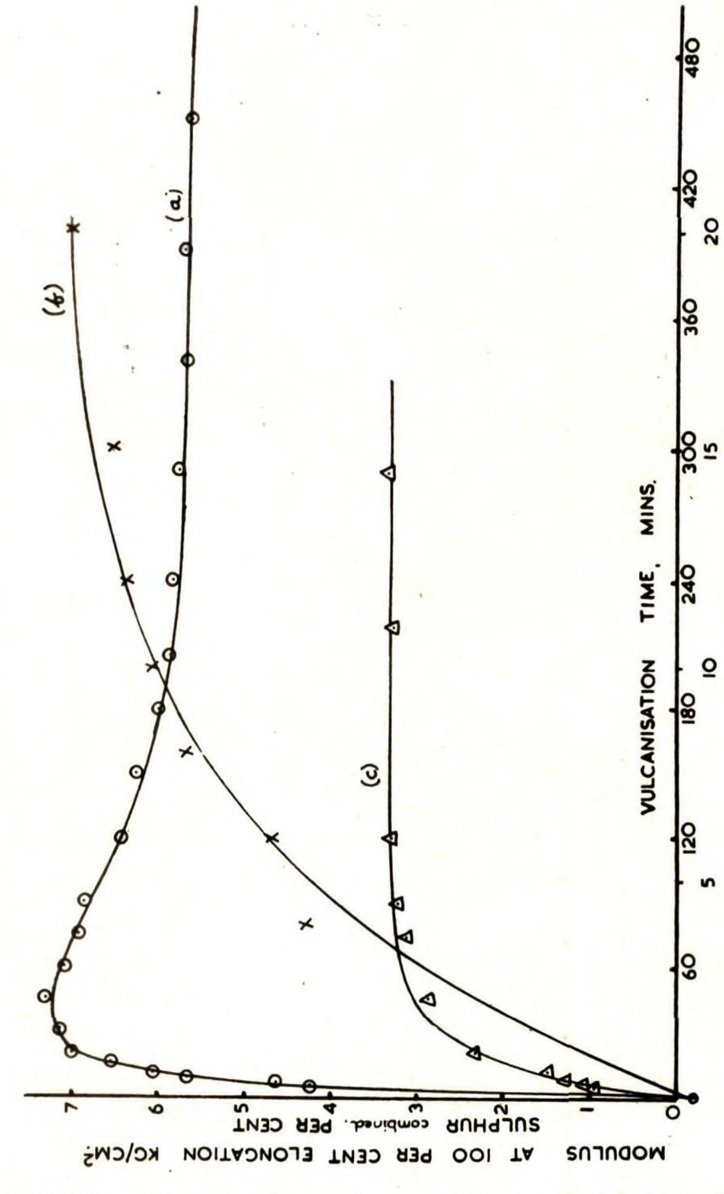

Fig. 3.
Vulcanisation of ACS1 compound at 140° C. Curves (a), (b) modulus (b on lower-time scale); (c) combined sulphur.

equilibrium modulus F* in place of the measured value. In general it was found that these two quantities only differed significantly when F was less than 4 kg./cm.^{2}. Where F* has been used in the data discussed below, a note is added to this effect. In some cases combined sulphur was also determined; this was done by a combustion method, using acetone-extracted samples. The figures recorded, therefore, include sulphur in the form of zinc sulphide, in addition to sulphur combined with rubber.

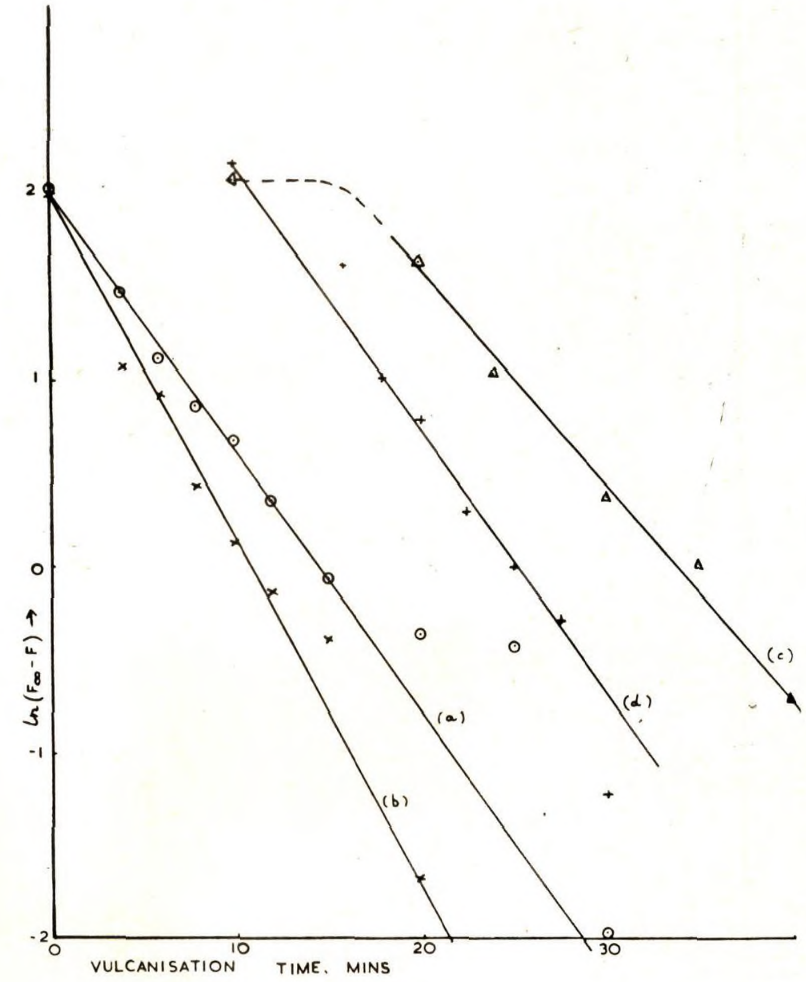

FIG. 4.

Estimation of rates of cure from equation 5′. Time scale displaced 10 min. for curves (c) at 120° C. and (d) at 140° C.

Vulcanisations were followed for a number of different compounds; typical results are shown in Figs. 2 to 4 and discussed below:

(*a*) A non-reverting mix (TC5, see Appendix to paper I) was cured at 140° C.; modulus data are plotted in Fig. 2, curve (*b*) showing the early stages of the reaction on an extended time scale. Combined sulphur was measured at 9 times of cure, ranging from 4 min. to 450 min.: all the values lay between 0·48 and 0·58. The value of F_0^*, calculated from $V_c = 43$, was $-$ 0·39. Since the mix does not revert appreciably we read off from curve (*a*) $F_\infty = 7{\cdot}20$. We can, therefore, evaluate k by using equation 5′, plotting ln $(F_\infty - F)$ against t, as shown in Fig. 4, curve (*a*). Data for the first 15 minutes give a very satisfactory linear plot and the value of k calculated from the slope is 0·138 min.$^{-1}$. The line in Fig. 2 (*b*) is, therefore, calculated from the equation

$$F = 7{\cdot}20 - 7{\cdot}59\, e^{-0{\cdot}138t}$$

(*b*) The ACS1 compound is well known to show a certain measure of reversion; some data recorded for this mix at 140° C. are plotted in Fig. 3. The value of F_0^*, calculated from $V_c = 51$, was $-$ 0·20; F_∞ is not directly observable, but it must be equal to or greater than the maximum modulus F_m, which is read from curve (*a*) as 7·20. An alternative method of estimating F_∞ is by applying equation (6) to suitable pairs of modulus determinations; values obtained in this way are very close to 7·20 and this value can accordingly be adopted with some confidence. The velocity constant k can, therefore, be estimated as before from a plot of ln $(7{\cdot}20 - F)$ against t (Fig. 4, curve (*b*)). A satisfactory straight line gives $k = 0{\cdot}182$ min.$^{-1}$, whence the curve of Fig. 3 (*b*) is calculated from $F = 7{\cdot}20 - 7{\cdot}40\, e^{-0{\cdot}182t}$. Sulphur combination was also measured in this series; Fig. 3 (*c*) shows that the data are consistent with the equation

$$\text{Combined sulphur} = 3{\cdot}30\,(1 - e^{-0{\cdot}056t})$$

Although this is similar in form to the initial part of the modulus curve, the velocity constant is smaller by a factor of 3.

An approximate idea of the temperature coefficients of the two velocity constants can be obtained by comparing the above figures with some obtained for similar mixes cured at 120° C. or 105° C. Measurements were made only at short times of cure (up to 25 min. at 120° C., 50 min. at 105° C.) and it was necessary to use F^* in place of F for the shortest times. As the highest modulus reached was 5·40, F_∞ could not be estimated accurately by extrapolation, and was, therefore, taken from the 140° data. The velocity constants obtained were: rate of cure 0·062 min.$^{-1}$ at 120° C., 0·024$_4$ at 105° C.; sulphur combination at 0·0168 min.$^{-1}$ at 120° C. The calculated energies of activation, which can only be considered very approximate, are 18 and 20 kcal. respectively.

(*c*) A less complete study was made of two other mixes which show reversion (TA57 vulcanised at 120° C. and TC16 at 140° C.; see Appendix to paper I). Vulcanisation was carried beyond the maximum and the highest modulus observed taken as F_∞. Plots of ln $(F_0 - F)$ against t are included in Fig. 4 (curves c and d respectively). While the latter gives a satisfactory straight line, the behaviour of the former is quite different: there is strong indication of a marked delay before vulcanisation commences appreciably, and the rate of cure can no longer be represented (*a*) A non-reverting mix (TC5, see Appendix to paper I) was cured at 140° C.; modulus data are plotted in Fig. 2, curve (*b*) showing the early stages of the reaction on an extended time scale. Combined sulphur was measured at 9 times of cure, ranging from 4 min. to 450 min.: all the values lay between 0·48 and 0·58. The value of F_0^*, calculated from $V_c = 43$, was $-$ 0·39. Since the mix does not revert appreciably we read off from curve (*a*) $F_\infty = 7{\cdot}20$. We can, therefore, evaluate k by using equation 5′, plotting ln (F_∞ $-$ F) against t, as shown in Fig. 4, curve (*a*). Data for the first 15 minutes give a very satisfactory linear plot and the value of k calculated from the slope is 0·138 min.$^{-1}$. The line in Fig. 2 (*b*) is, therefore, calculated from the equation

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Table 2 summarises the constants obtained for the three mixes to which this method has been found to apply.

TABLE 2

				Estimated Rates of Cure		
Compound	F_0*	F_∞	Vulcanisation Temp. °C.	k min.$^{-1}$	t_m min.	kt_m
ACS1	0·20	7·20	140	0·182	40	7·3
	0·22	(7·18)	120	0·062	Not measured.	
	0·31	(7·09)	105	$0{\cdot}024_4$	,,	
TC5	0·39	7·20	140	0·138	No reversion.	
TC16	0·34	8·25	140	0·140	40	5·6

The sixth column records t_m, the time to reach maximum modulus estimated by eye from plots of F versus t. It will be observed that for the ACS1 and TC16 compounds, the product kt_m is of the order derived in Table 1; TC5 does not revert sufficiently for t_m to have much significance.

This analysis shows that the rate of increase of modulus in several types of compound can be very satisfactorily described by a first order equation defining a velocity constant which forms a suitable measure of rate of cure. That the method is not universally applicable is clearly shown by its failure with TA57, and it should, therefore, not be used with a new type of compound until a complete vulcanisation curve has been examined in some detail.

ESTIMATION OF SCORCH TIMES

It was argued, in paragraph 6, that the scorch time must be intimately related to rate of cure. In attempting to verify this conclusion we have made some measurements of scorch time, using a Mooney viscometer. It was found possible to identify a reasonably well-defined time at which the viscosity suddenly began to rise, and we have tentatively used this figure. We do not, however, consider this method of estimating scorch very suitable for the present purpose. A thermocouple inserted into the rubber shows that the temperature of the centre of the mass does not reach the viscometer temperature quickly enough for short scorch-times to be of much significance: even after 5 minutes, temperature differences between centre and outside of 2 to 7 degrees were recorded. Alternative methods of estimating scorch-times are, therefore, under investigation; meantime it is of interest to note the results of some preliminary measurements on an ACS1 compound under different conditions.

Scorch-times were determined in the Mooney viscometer for a series of ACS1 compounds, covering a wide range of initial viscosities, and three different temperatures. In Table 3 the results are compared with scorch-times calculated from equation (11). In making the calculations,

X_∞ was assumed to be 7·40 in all cases, F_0^* calculated from V_c and F_∞ obtained from $X_\infty + F_0^*$; values of the rate of cure k were taken from Table 2.

TABLE 3

Scorch-times for ACS1 compound

Temp. (° C.)	k (min.$^{-1}$)	V_c	Scorch-time (min.) calc.	Scorch-time (min.) obs.
140	0·182	51	1·3	$2\frac{1}{4}$
120	0·062	80	2·7	$4\frac{1}{4}$
		50	3·7	$5\frac{1}{2}$
		43	4·1	5
		31	5·0	$5\frac{1}{2}$
		21	6·0	$5\frac{1}{4}$
105	$0{\cdot}024_4$	46	10·3	14
		32	13·5	15
		15	22·5	22

The agreement between calculation and observation is good enough to establish the general dependence of scorch-time on rate of cure. On the other hand, much better experimental data would be needed to test equation (11) properly, or to permit the accurate estimation of rate of cure from a measured scorch-time.

PRACTICAL APPLICATIONS

The experimental work reported in paragraph 8 shows that it is legitimate to characterise the rate of cure of a compound by means of a first-order velocity constant. One of the practical applications envisaged for this method is in the characterisation of raw rubber supplies. If the mix and the vulcanisation temperature are fixed, the rates of cure of a series of rubbers constitute a criterion by which the variability of the rubbers can be assessed.

To apply the method it is necessary to know three quantities:

(i) The viscosity V_c of the mixed compound, from which F_0 can be obtained. This is given by equation (2) and for convenience is tabulated in Table 4. The final value of k is not very sensitive to F_0 and no serious error would result if, in the absence of any figure for V_c, any reasonable value for V_c were assumed.

(ii) The modulus at full cure F_∞. If data are available for several times of cure this is best taken equal to the maximum modulus. Failing this, it is permissible to take for F_∞ the value of a single modulus determined on a well-cured sample. For the ACS1 mix, suitable times of cure for most rubbers would be 40 min. at 140° C. or 80 min. at 134·5° C. For an unusually slow curing rubber this F_∞ value may be somewhat low, which would result in k being overestimated. A second approximation is then readily obtained by applying equation 5 (with the approximate k) to calculate F_∞ and thence a better value for k; this refinement should seldom be needed in practice.

(iii) The modulus F on an undercured sample. Ideally this should be ca. 0·8 F_∞, but in practice it is sufficient to fix a single time of cure.

Our experience with the ACS1 mix suggests that this should be about 10 min. at 141° C. or 20 min. at 134·5° C.

TABLE 4

Calculation of F_0 from V_c.

V_c	0	1	2	3	4	5	6	7	8	9
20	−1·40	−1·33	−1·27	−1·21	−1·13	−1·09	−1·03	−0·99	−0·94	−0·89
30	− ·84	− ·80	− ·76	− ·72	− ·68	− ·64	− ·61	− ·57	− ·54	− ·51
40	− ·48	− ·45	− ·42	− ·39	− ·36	− ·34	− ·31	− ·29	− ·26	− ·24
50	− ·22	− ·20	− ·17	− ·15	− ·13	− ·11	− ·09	− ·08	− ·06	− ·04
60	− ·02	·00	+ ·01	+ ·03	+ ·04	+ ·06	+ ·07	+ 0·8	+ ·10	+ ·11

We have examined in this way two sets of suitable vulcanisation data available in our laboratory records. The first set concerns 29 ACS1 mixings carried out at intervals over a period of several months employing a single blend of No. 1 R.S.S. The second set involves duplicate ACS1 mixes on each of 35 samples of natural rubber supplied to us at one time by a remilling company. These samples comprised 10 sheets of 1 R.S.S., 2 of 2 R.S.S., 8 of 3 R.S.S., 2 of 4 R.S.S., 8 of 5 R.S.S. and 5 of low grade crepes.

The 99 mixes in the two sets were all cured at 134·5° C. for times of 20, 30, 40, 60 and 80 minutes; V_c was measured for each mix. The 20 minute modulus was taken as F, and F_∞ estimated from the optimum cure; this value did not usually differ seriously from the 80 minute modulus. k was then calculated from equation 5′.

The mean rate of cure of the set of 29 replicates was 0·062 min.$^{-1}$, the extreme values being 0·056 and 0·071 and the standard deviation 0·004. Analysis of the set of 35 different rubbers disclosed a range of 0·058 to 0·118 min.$^{-1}$, the 1 R.S.S. results lying between 0·070 and 0·113. The standard deviation between duplicate mixes was 0·007, somewhat larger than that found for the first set. We can say, therefore, that if single determinations of rate of cure in the ACS1 mix at 134·5° C. on each of two rubbers differ by more than 0·020 min.$^{-1}$ there is a 95 per cent. probability that the rubbers do genuinely differ in rate of cure. If duplicates are performed on each rubber, a difference between means of 0·015 is significant at this level. Judged by this criterion, these results show a highly significant variation in rate of cure among the 10 samples of 1 R.S.S. and a still more significant variation over the whole group of rubbers.

Another interesting point may be noted in connection with these results. It seems highly probable that the variability found between rubbers derives mainly from the presence of variable quantities of non-rubber materials which boost the M.B.T. acceleration. Now it is well known that addition of e.g. D.P.G. to an M.B.T.-accelerated mix increases the modulus of the resulting vulcanisate and also makes the mix more scorchy. We might, therefore, expect to find some degree of correlation between rate of cure (k) and full cure ($X_\infty = F_\infty - F_0$). Analysis of the results as a whole reveals a general positive correlation of this type.

The other practical application of k which may be mentioned is in determining the time required to produce a given degree of cure. It is generally desirable in production to avoid over-cure; it may for some applications be desirable to cure to less than the maximum modulus. If C is the percentage of the full cure to be developed, i.e. $C/100 = (F - F_0)/(F_\infty - F_0)$, then the required time of cure t_c is

$$t_c = \frac{1}{k} \ln\left(\frac{100}{100 - C}\right) \qquad \ldots\ldots\ldots(12)$$

Equation (12) gives a clear picture of the significance of k: 80 per cent. of the full cure requires $t = 1{\cdot}61/k$; 90 per cent., $2{\cdot}30/k$; 95 per cent., $3{\cdot}00/k$. Moreover, comparison of the k values with times t_m to maximum modulus for a range of rubbers in the ACS1 mix showed that kt_m was approximately constant, with an average value of 6·4. It is clear, therefore, that $1/k$ is a valuable measure of the vulcanisation time required to give the maximum modulus, or any specified degree of undercure.

Further experience will be needed to establish the value of this method of assessing rate of cure: the authors will be glad to hear from any other workers who may apply it to their own data or problems.

APPENDIX

Comparison with the Strain Hyperbola.

It is interesting to compare the method of determining rate of cure developed in this paper with that put forward by Roth and Stiehler[1] and recently elaborated by Schade.[2] This method is entirely empirical, being based on the observation that the strain-time curve can be represented as a rectangular hyperbola. If S is the strain at time t and S_∞ its value at infinite time, then

$$(S - S_\infty)(t - t_0) = 1/C \qquad \ldots\ldots\ldots(13)$$

where t_0 and C are constants. In the recommended application of this method S_∞ is not determined directly, but the equation is fitted to three experimental points on the S—t curve. Our limited experience with this equation suggests that it suffers from the same defect as our own equation (8): there are too many parameters for any of them to be precisely determined. Schade's[2] recent paper implies the same difficulty, in that he reports wide variability of the constants found for rubbers which are technologically very similar.

In Fig. 2 the broken curves (*c*) and (*d*) are calculated from equation (13), with $S_\infty = 54{\cdot}5$, $t_0 = 4{\cdot}5$ min., $1/C = 186$, strain values being converted to modulus by the relationship established in paper I of this series. The difference between these curves and our own is insignificant over the major portion of the vulcanisation period, but they differ completely at short times of cure. It is clear that the constant t_0 has no more experimental significance than our own F_0. On the other hand, whereas F_0 is a well defined theoretical quantity, calculable and highly significant, t_0 has no theoretical basis whatsoever. A positive value of t_0 implies a definite time-lag before vulcanisation starts; the results presented in this paper show that, while a time-lag may occur with certain accelerators, it is not a general feature of vulcanisation and is certainly negligible for the T.M.T. mix whose vulcanisation curve is shown in Fig. 2, fitted to a hyperbola for which $t_0 = 4{\cdot}5$ minutes.

The basis of Schade's suggestion that rubbers are equally cured when they have similar values of dS/dt or d^2S/dt^2 is also empirical. These quantities depend partly on the constant C, and partly on the amount by which the strain exceeds its asymptotic value:—

$$-\frac{dS}{dt} = C\,(S-S_\infty)^2; \frac{d^2S}{dt^2} = 2C^2\,(S - S_\infty)^3$$

It follows that equality in respect to one or other of these quantities does not necessarily imply that rubbers are cured to the same strain or to the same percentage of the attainable cure.

In considering how to define cure and rate of cure we have therefore rejected the methods based on the strain hyperbola as unsatisfactory and have sought to develop methods which have a sound theoretical basis, yet are simple to apply in practice.

REFERENCES

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2. Schade, J. W., *ibid.*, 1950, **123**, 311.

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