Strainwork Dependence of Filler-Loaded Vulcanizates

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Synopsis

The modulus and loss angle of carbon black filler-loaded rubbers varies with the dynamic amplitude of oscillation. The dynamic modulus change with amplitude is of a sigmoid nature. This allows the data to be reduced by a normalization technique. It is the purpose of the paper to show how the normalized data are substantially independent of the carbon black loading and of the polymer type when the normalized modulus is plotted against the energy of deformation (or strainwork).

INTRODUCTION

In previous papers[1-5] the author discussed how the modulus and loss angle of carbon black filler-loaded rubbers vary with the dynamic amplitude of straining. These previous studies were confined to natural and butyl rubbers; this paper extends the dynamic measurements to include a range of these and other polymers. It is known that the dynamic shear modulus decreases with increasing amplitude of straining, and furthermore this modulus change is of a sigmoid nature. These facts allow the data to be reduced by a normalization technique, and it is the purpose of this paper to show how the reduced or normalized data are substantially independent of carbon black loading and of the polymer type.

EXPERIMENTAL

The dynamic measurements were carried out on the RAPRA sinusoidal strain dynamic tester, and previous papers[2,6] have discussed the experimental technique used. All the dynamic tests were made by first oscillating at the lowest strain possible, and then increasing the strain incrementally to the maximum. This sequence ensured that the rubber had not been over-strained before a particular test, as the dynamic properties are very sensitive to previous treatment. All the tests were carried out at ambient temperature. The parameters measured were G^*, the complex shear modulus, where $G^* = (G'^2 + G''^2)^{1/2}$, G' is the in-phase shear modulus and G'' the out-of-phase shear component. Also measured was δ, the phase angle between the sinusoidal stress and strain. The experiments were carried out at 0.1 cps.

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The compounding details of the rubbers used in this investigation are given in the Appendix.

EXPERIMENTAL RESULTS

G' Data

Figure 1 shows the dynamic shear modulus plotted against the strain amplitude of test for four of the rubbers.   Due to the wide range of results, these four rubbers only are presented, but they are typical of the experimental results of all the other rubbers containing carbon black that were used in this investigation.   It is apparent from the shape of the curves in Figure 1 that the shear modulus for a particular vulcanizate is constant over a range of low strains, but the modulus decreases at higher strains and the curve is sigmoidal in shape when plotted against the logarithm of the double strain amplitude.

δ Data

Figure 2 shows typical results for the phase angle *δ* plotted against the strain amplitude of test for four of the rubbers of Series 1.   The particular features of these plots occur at low strains, where the phase angles are low
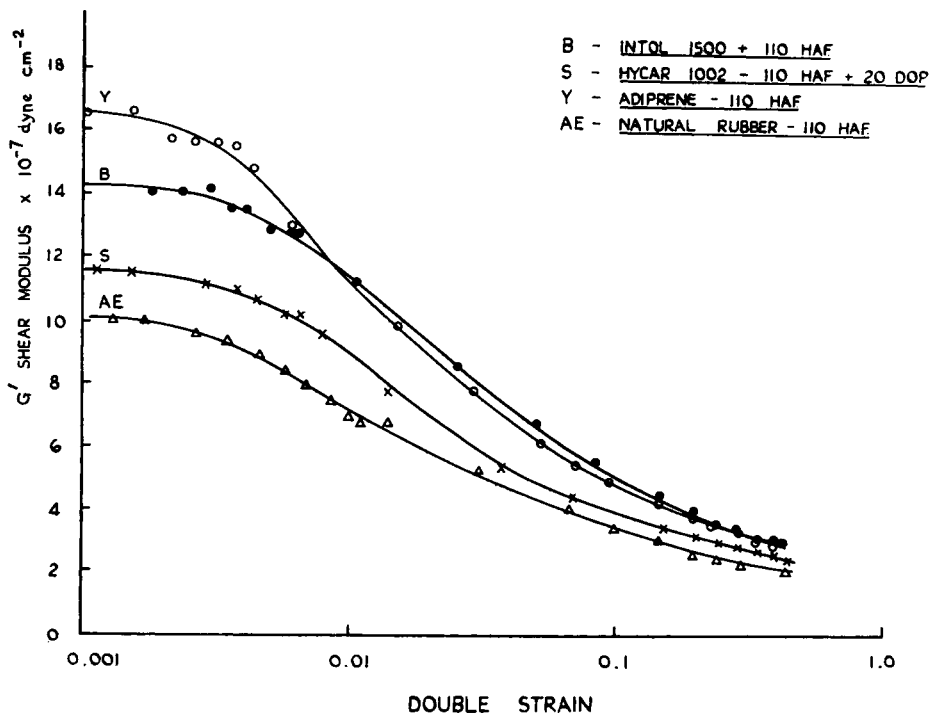

Fig. 1. Shear modulus vs. double strain amplitude of test.   See Table I for identification of curves; Appendix for compounding details.
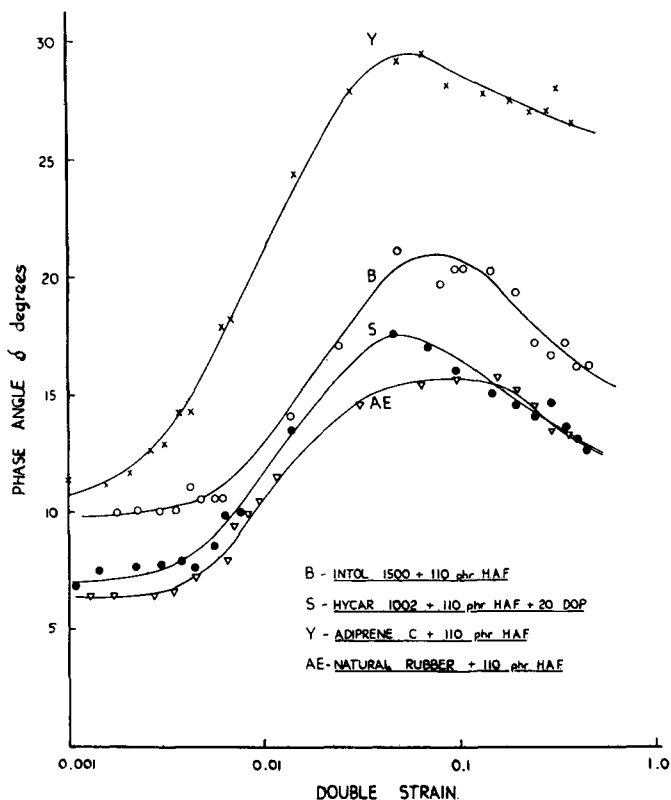
Fig. 2. Phase angle δ vs. double strain amplitude of test.   See Table I for identification of curves.

and constant over a range of low strains.   At high strains the phase angles increase and reach a peak.

G″ Data

Figure 3 shows the corresponding out-of-phase components of the shear modulus plotted against the strain amplitude of test.   As G'' reaches a maximum it is quite apparent that G'' is not a constant, which explains why some workers have noticed a G'' rising with straining, and others a G'' decreasing with strain.   All the curves in Figure 3 reach a peak at very similar amplitudes of straining.

Strain and Strainwork Dependence

The various empirical relationships suggested by different authors for the dependence of the dynamic modulus on the strain amplitude have been discussed,[2,3] and it may be noted here, a double logarithmic plot of stress versus strain can also be used.   However, it is proposed here to use a method of presentation which emphasizes the similarity between the modu-
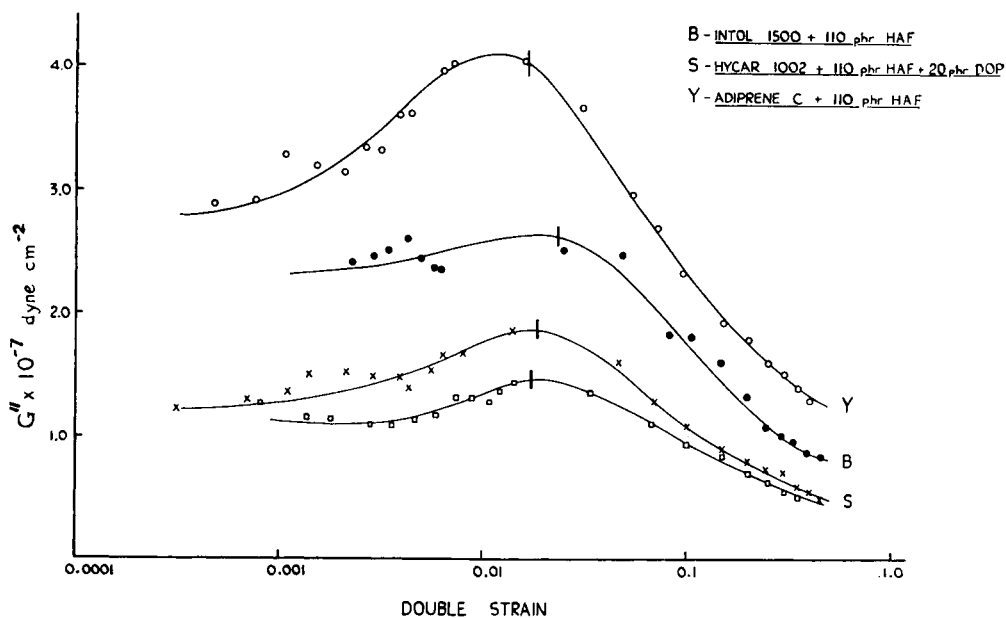
Fig. 3. Out-of-phase shear modulus G'' vs. double strain amplitude of test. See Table I for identification of curves. Bottom curve: AE.

lus breakdown curves for the different polymers containing the same black (HAF). The method proposed here involves "normalizing" the data between the limits at very low and very high strains.

Consider the shear modulus G'. Let G'_0 represent its value at strains approaching zero, G'_∞ its value at very high strains, where there is no
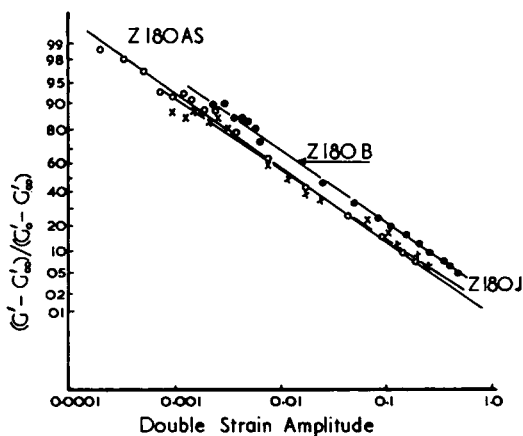

Fig. 4. Normalized dynamic shear modulus Z vs. logarithm of the double strain amplitude for $(Z180AS)$ Hycar + 150 phr HAF; $(Z180J)$ Neoprene + 110 phr HAF; $(Z180B)$ Intol 1500 + 110 phr HAF.
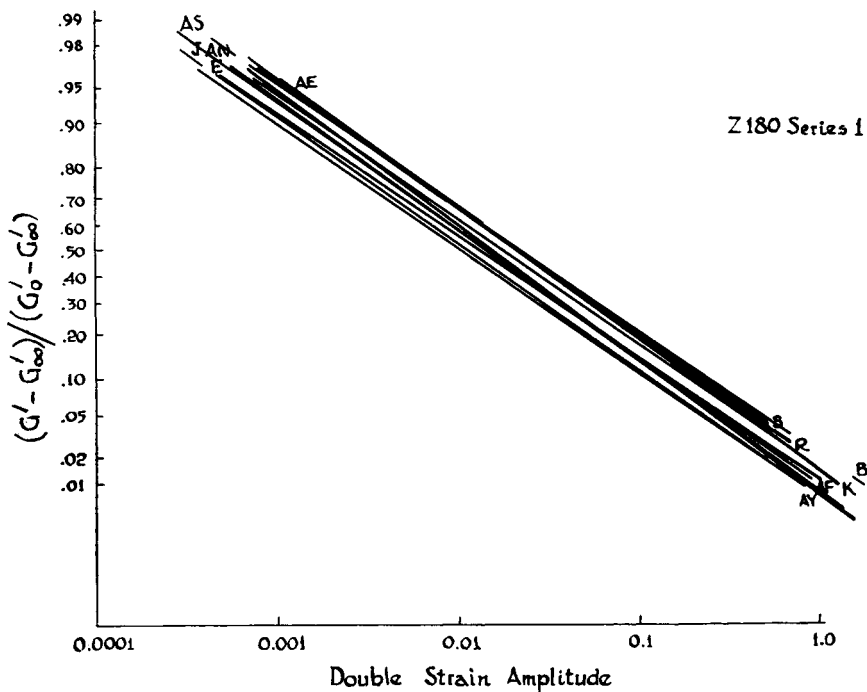
Fig. 5. Normalized dynamic shear modulus Z vs. double strain amplitude for a range of polymers: probability plot. Series 1 rubbers; see Table I for identification.

further change in G' with increase of strain; then the normalized modulus is given by

$$Z = (G' - G'_\infty)/(G'_0 - G'_\infty) \qquad (1)$$

A plot on probability paper against amplitude is shown in Figure 4 for three typical sets of results which refer to the rubbers, Hycar + 150 phr HAF, Neoprene + 110 phr HAF, and Intol 1500 + 100 phr HAF. The G'_0 and G'_∞ values used in the normalization are given in Table I. It will be appreciated that there is some, but very slight latitude in fixing a value for G'_∞, but the variation possible is too small to influence the position of the plot on probability paper. Figure 5 shows the normalized modulus versus double strain amplitude curves for the complete series of different rubbers (Series 1); it can be seen that the resulting plots are all parallel and lie closely together. Table I lists the double strain where $Z = 0.5$, from which it can be seen that they are very similar.

It has been shown in previous papers,[3,5] that neither stress nor strain is the independent parameter which governs the variation of the dynamic modulus with strain, but the product of stress $\times$ strain, which will be referred to as strainwork, will be used in preference. Figure 6 plots on probability paper the normalized modulus for the three rubbers versus strainwork (double stress amplitude $\times$ double strain amplitude), shown in

TABLE I
G'_0, G'_∞, and Stress, Strain, Strength, and Strainwork at $Z = 0.5$ for a Range of Rubber Vulcanizates (Series 1)

Rubber	Designation[a]	Filler (HAF) loading, phr	G'_0, Mdyne cm.$^{-2}$	G'_∞, Mdyne cm.$^{-2}$	Strain-work at $Z = 0.5$ $\times 10^{-4}$, dyne cm.$^{-2}$	Double stress at $Z = 0.5$ Mdyne cm.$^{-2}$	Double Strain at $Z = 0.5$ $\times 10^2$	Double Strength $\times 10$	Spread for 80% change in $G'_0 - G'_\infty$, Log Units	Cole-Cole plots G'_0, Mdyne cm.$^{-2}$	Cole-Cole plots G'_∞, Mdyne cm.$^{-2}$
Intol 1500	A	0	3.2	—							
	B	110	152	22.5	4.1	1.86	2.2	2.1	3.37	163	24
Butyl 301	D	0	2.3								
	E	110	383	10	2.1	1.91	1.1	0.8	2.98	370	17
Neoprene	G	0	12.3	—							
	H	0 + 20[b]	5.0								
	J	110	290	40	2.5	1.79	1.4	1.0	3.61	310	20
	K	110 + 20[b]	220	35	5.0	2.5	2.0	2.0	3.40	240	32
Hycar 1002	N	0	4.9								
	P	0 + 20[b]	2.8								
	R	110	270	45	4.0	2.24	1.8	1.6	3.48	508	30
	S	110 + 20[b]	125	18.5	2.6	1.30	2.0	1.6	3.60	114	15
Adiprene C	X	0	5.7								
	Y	110	173	20	1.8	1.20	1.5	1.0	3.33	203	13

Hycar 1072	AG	0	8.8	—							
	AH	0 + 20[b]	5.1	—							
	AJ	27	26.9	—							
	AK	27 + 20[b]	11.2	—							
	AL	54	56	—							
	AM	54 + 20[b]	19.9	—							
	AN	110	270	30	3.0		1.5	1.4	3.40	—	—
	AP	110 + 20[b]	89	—							
	AS	150	345	55	2.5	1.67	1.5	1.2	3.47	390	26
Hypalon 20	AT	0	5.6	—							
	AW	27	22	—							
	AX	54	37	—							
	AY	110	585	70	3.0	2.73	1.2	0.85	3.47	670	15
Natural rubber	AD	0	3.4	—							
	AE	110	104	19	2.6	1.24	2.1	1.7	3.46	123	10
	AF	150	285	35	3.3	2.06	1.6	1.4	3.30	330	17
				Avg.	Avg. 3.0	Avg.	1.6 Avg.	1.42 Avg.	3.42		

[a] See Appendix.
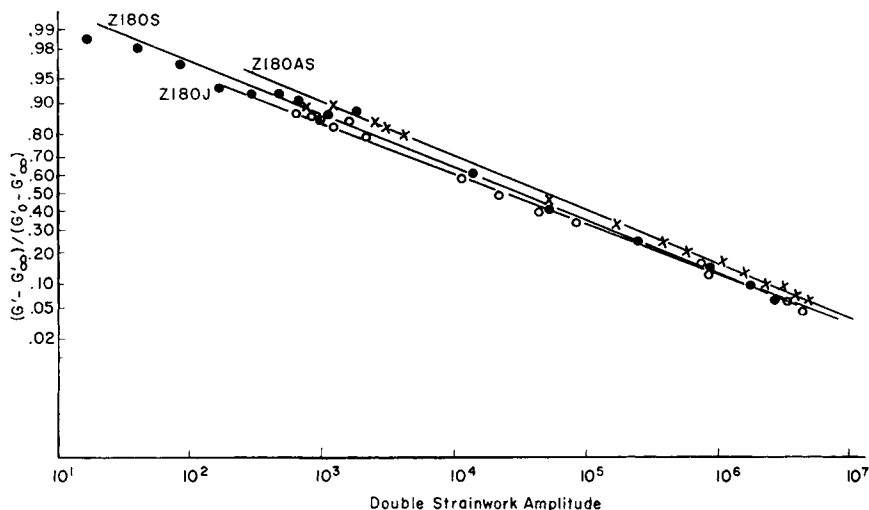[b] Plus 20 phr of DOP (Dioctyl phthalate).

Fig. 6. Normalized dynamic shear modulus Z vs. logarithm of the strainwork (double stress amplitude vs. double strain amplitude) for $(Z180AS)$ Hycar $+$ 150 phr HAF; $(Z180J)$ Neoprene $+$ 110 phr HAF; $(Z180B)$ Intol 1500 $+$ 110 phr HAF. See Table I for identification of curves.
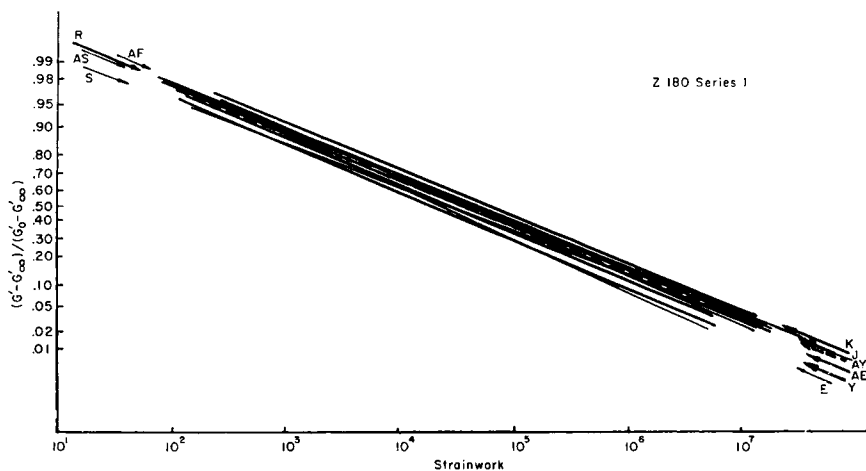

Fig. 7. Normalized dynamic shear modulus Z vs. strainwork for a range of polymers. Series 1 rubbers; see Table I for identification.

Figure 4, and shows that a linear relationship exists between the probit of Z and the strainwork. Figure 7 plots the resulting straight lines for all the vulcanizates of this series which can be analyzed by the normalization procedure.

It is useful to consider the strainwork corresponding to $Z = 0.5$, and Table I lists these values for the different rubbers. It is quite apparent that the strainwork values quoted are very similar irrespective of the type

of rubber. The length of the abscissae for each curve in Figure 7, between $Z = 0.90$ and $Z = 0.10$ is also given in Table I, and this length represents the "spread" of the strainwork for a change of 80% in the modulus G' between G'_0 and G'_∞. An inspection of the values of stress, strainwork and spread at $Z = 0.5$ quoted in Table I shows that these values are very similar for all the different rubbers studied.

The linearity of the plot of the normalized modulus against the logarithm of the strain on the strainwork implies a relationship of the following type:

$$Z = (G' - G'_\infty)/(G'_0 - G'_\infty) \tag{2}$$

$$= (1/\sigma\sqrt{2\pi}) \int_{-\infty}^{x_0} \exp\left\{-(1/2\sigma^2)(x - \mu)^2\right\} dx$$

$$= 1 - P$$

where Z is the normalized modulus, $x = \log X$, where X is the strainwork. The strainwork is the normalizing measure, which has a normally distributed tolerance. μ is the median effective strainwork. As the normalizing transformation is logarithmic, μ is $\log X_{0.50}$, where $X_{0.50}$ is the value of the strainwork at $Z = 0.5$.

It is useful to consider eq. (2) in another form,

$$(G'_0 - G')/(G'_0 - G'_\infty) = (1/\sigma\sqrt{2\pi})$$

$$\int_{-\infty}^{x_0} \exp\left\{-(1/2\sigma^2)(x - \mu)^2\right\} dx = P \tag{3}$$

where $P = 1 - Z$. This equation represents the percentage modulus change that has occurred at a particular strainwork X_0, and the equation represents a type of relationship which has found extensive use in statistics. The use of this type of equation can be considerably simplified by the use of probits, i.e., if

$$dP = (1/\sigma\sqrt{2\pi})\exp\left\{-(1/2\sigma^2)(x - \mu)^2\right\} dx \tag{4}$$

is the distribution of the modulus tolerance over the strainwork ranges studied. This last equation states that a proportion dP of the whole modulus change consists of a fraction whose tolerances lie between x and $x + dx$, where x represents a small interval on the strainwork scale. The equation also states that dP is the length of this interval multiplied by the appropriate value of the distribution function $f(X)$ where

$$f(X) = (1/\sigma\sqrt{2\pi})\exp\left\{-(1/2\sigma^2)(x - \mu)^2\right\} \tag{5}$$

The μ value alone does not fully describe the spread of the modulus changes, which is measured by the variance σ^2. The smaller the value of σ^2, the greater is the effect on modulus of a certain change of strainwork.

The probit of P is Y, where

$$P = (1/\sqrt{2\pi}) \int_{\infty}^{Y-5} \exp\left\{-(1/2)\mu^2\right\} d\mu \tag{6}$$

Comparison of the two formulae for P shows that the probit of the expected proportional change in modulus is related to the strainwork by

$$Y = 5 + (1/\sigma) (x - \mu) \tag{7}$$

By means of the probit transformation, experimental results may be used to give an estimate of this equation, and the parameters of the strainwork distribution may then be estimated. In particular the median effective strainwork is that value of x which gives $Y = 5$. A table giving probits for specified values of P has been prepared by Finney[7] and Fisher and Yates.[8] It is useful to use the values of $P = 0.90$ and $P = 0.10$, i.e.,

$$Y_{0.90} = 5 + (1/\sigma) (x_{0.90} - \mu) \tag{8}$$

and

$$Y_{0.10} = 5 + (1/\sigma) (x_{0.10} - \mu) \tag{9}$$

Thus,

$$Y_{0.90} - Y_{0.10} = 2.56 = (1/\sigma) (x_{0.10} - x_{0.90}) \tag{10}$$

and

$$\sigma = (x_{0.10} - x_{0.90})/2.56 \tag{11}$$

Therefore the difference in logarithmic units between the strainwork at $P = 0.90$ and $P = 0.10$, is directly related to σ and therefore to σ^2. Table I lists the spread of the normalized curves in log units which is then related to σ^2 by eq. (11). The spread appears to be almost independent of polymer type, although butyl does have a slightly smaller spread than the other polymers. The average value of the spread for all the rubbers is 3.42 log units.

The simplest assumption which can be made regarding the modulus changes is that $G'_0 - G'_\infty$ is proportional to the number of weak links that can be broken down on straining, and that there is a normal distribution for the logarithm of the energy of straining of these weak links. The effect on the modulus of various concentrations of black or the different milling procedures during compounding was solely to alter the number but not the distribution of the weak links with respect to the energy of deformation. Another interpretation of the normalized modulus–strainwork plot is that the energy measured relates to the particular energy required to breakdown aggregates of varying dimensions. For instance, a relatively small amount of strainwork would be required to reduce the aggregate size by a factor of 2. More work is then required to reduce each of the residues by another factor of 2, and so on. Hence, so long as there are aggregates one would expect a continuance of the plot of the normalized modulus Z versus strainwork, and one gets a normal "probability" or distribution function.

It is necessary to compare these results with the normalized modulus strainwork curves obtained from other dynamic data previously published. For instance, Figure 8 shows the normalized plots of a natural rubber–HAF
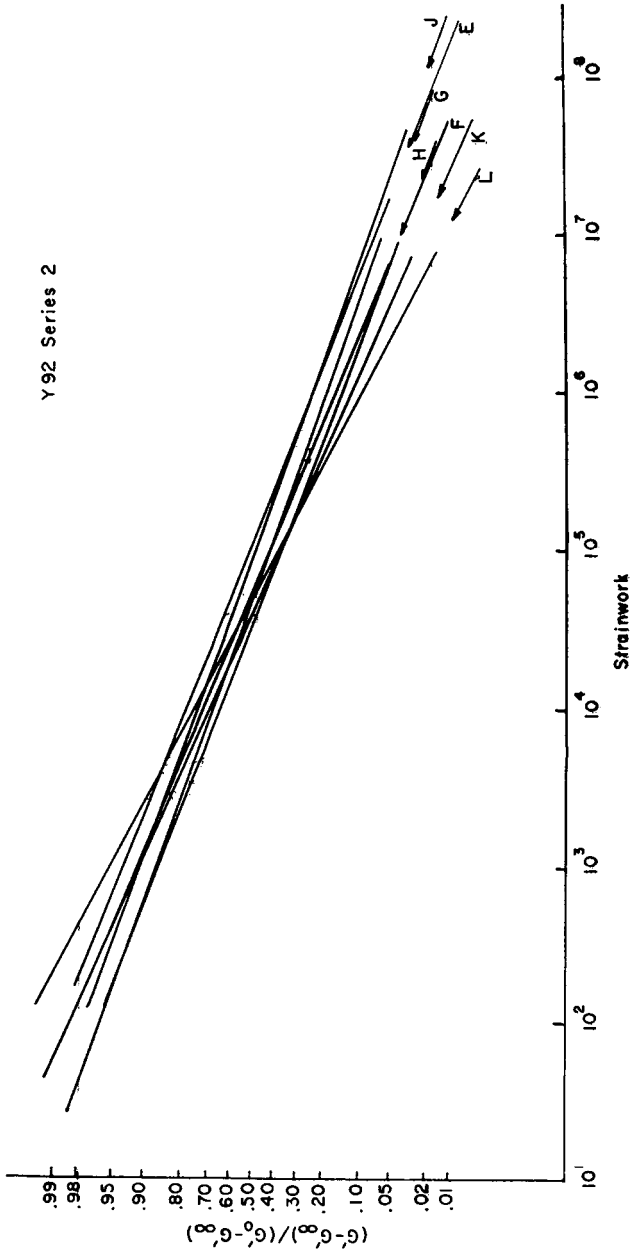
Fig. 8. Normalized dynamic shear modulus Z vs. strainwork for a series of HAF–natural rubber vulcanizates. Series 2 rubbers; see Table II for identification of curves.

TABLE II

G'_0, G'_∞ and Stress, Strain, Strength, and Strainwork at $Z = 0.5$ for Natural Rubber Vulcanizates (Series 2)

Designation	HAF, loading, vol.-%	G'_0, Mdyne cm.$^{-2}$	G'_∞, Mdyne cm.$^{-2}$	Strainwork at $Z = 0.5$ $\times 10^{-4}$, dyne cm.$^{-2}$	Double strain at $Z = 0.5$ $\times 10^2$	Double stress at $Z = 0.5$ Mdyne cm.$^{-2}$	Strength at $Z = 0.5$ $\times 10$	Spread for 80% change in $(G'_0 - G'_\infty)$, log units
A	0	2.5	—					
B	5.6	4.0	—					
C	10.7	5.2	—					
D	15.2	7.7	—					
E	19.3	13.3	6.3	2.8	11.0	0.26	24	3.45
F	23.0	18.1	8.1	4.8	7.0	0.68	11	3.16
G	26.4	39	10.5	2.5	5.0	0.50	5.5	4.00
H	29.5	64	12.0	3.0	3.0	1.00	3.0	3.93
J	32.4	154	14.7	5.5	1.1	5.00	4.5	3.74
K	36.0	295	25.0	3.0	1.5	2.00	1.2	2.98
L	38.4	334	26.0	4.8	1.4	3.43	1.7	2.69
				Avg. 3.77				Avg. 3.43

series of vulcanizates containing different loadings of carbon black[2] (Series 2).   The slopes and the positions of these curves agree with those in Figure 7, the natural rubber–HAF series giving an average value of strainwork of 3.77×10^4 dyne-cm.[2] with a spread of 3.43 log units for the previous series of different rubbers.   Table II lists the normalizing parameters for the natural rubber–HAF vulcanizates.   From the values of the strain at $Z = 0.5$, it should be noted that the strain value decreases with increasing carbon black content, whereas the corresponding stress increases.   It is, however, the product of stress and strain which appears to be independent of filler concentration.

From the normalized curves of butyl vulcanizates containing various amounts of HAF black[4] (Series 3), it can be shown that the plots lie closely
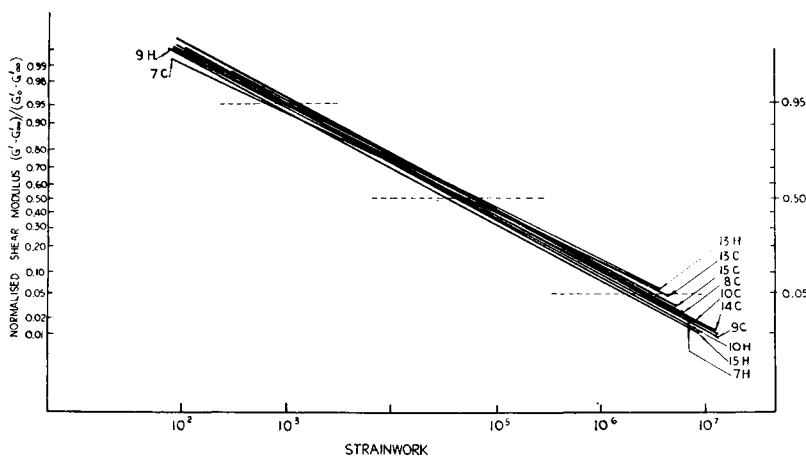

Fig. 9. Nomalized dynamic shear modulus Z vs. strainwork for a series of normal and attrited HAF-in-butyl vulcanizates.   Series 4; See Table IV for identification of the polymers.

together.   Table III lists the normalized parameters for these butyl–HAF vulcanizates from which it is apparent that the average strainwork is 4.16 $\times 10^4$ dyne-cm.[2] with a spread of 2.57 log units.   This shows that the strainwork is similar to the values quoted above for the other rubbers, but the spread is smaller than for the other rubbers.   The difference between the spread between butyl and other rubbers is confirmed by the results obtained from another series of butyl vulcanizates containing varying amounts of normal and attrited HAF blacks[5] (Series 4) (see Fig. 9), and the derived parameters in Table IV.   For this last series, the average strainwork in 4.79 $\times 10^4$ dyne-cm.[2] with a spread of 2.83 log units.   It must be concluded from all these results that the amount of carbon black or the type of rubber has little effect on the strain-work at $Z = 0.5$, and the spread of the modulus changes are not very different.

TABLE III

G'_0, G'_∞, and the Stress, Strain, Strainwork, and Stength Values at $Z = 0.5$ of Butyl–HAF Vulcanizates (Series 3)

Designation	HAF loading, vol.-%	Condition of vulcanizate[a]	G'_0, Mdynes cm.$^{-2}$	G'_∞, Mdynes cm.$^{-2}$	Strainwork at $Z = 0.5$ $\times 10^{-4}$, dynes cm.$^{-2}$	Stress at $Z = 0.5$ Mdynes cm.$^{-2}$	Strain at $Z = 0.5$ $\times 10^2$	Strength at $Z = 0.5$ $\times 10$	Spread for 80% change in $(G'_0 - G'_\infty)$, log units
A	0	H	3.3	3.0	b				
B		N	4.2	3.5	b				
C	9.2	H	4.6	3.9	b				
D		N	6.9	4.7	b				
E	13.2	H	5.3	4.7	b				
F		N	12.1	5.5	5.5	0.69	8.0	11.5	3.01
G	16.8	H	6.1	5.0	b	—		—	—
H		N	20	7.0	5.7	0.95	6.0	7.2	2.52
J	20.2	H	9.5	6.8	b	—		—	—
K		N	44.4	9.0	4.0	1.14	3.5	4.0	3.02
L	23.2	H	14.4	8.1	b	—		—	—
M		N	98	10	4.8	1.55	3.1	3.5	2.32
N	28.8	H	62	11.5	2.3	0.89	2.6	1.5	2.56
P		N	144	12.5	4.2	2.47	1.7	3.5	2.44
S	33.6	N	260	15	4.0	2.35	1.7	0.95	2.30
W	38.8	N	500	30	4.0	3.08	1.3	0.95	2.18
					Avg. 4.16				2.57
									Avg.

[a] N = normally compounded vulcanizate; H = heat-treated vulcanizate.

[b] Too small a change in modulus for G_∞ and strainwork to be derived.

Strength Dependence

According to Blanchard and Parkinson,[9-12] the modulus of filler-loaded vulcanizates can be resolved into the one component $G_r F(S)$, which is a function of the prestress and is due mainly to the filler, and a further component G^* surviving high prestresses attributed to strong (primary) linkages formed by sulfur and by carbon blacks. This quantitative description of softening is expressed by eq. (12)

$$G = G^* + G_r F(S) \tag{12}$$

and

$$F(S) = K^3/4 \int_x^\infty S^{1/2} \exp\left\{-(KS^{1/2})\right\} dS$$

where K is a constant, and theoretically for low prestresses $F(S)$ approaches unity 1 and after high prestresses $F(S)$ approaches zero. These equations were found by a theoretical treatment, which attributes the softening with prestressing fundamentally to a breakage of rubber–filler attachments. Thus the quantity S, when these secondary bonds are broken, is a measure of their strength (linkage strength factor). It is a function of the prestress σ, extension ratio α, and the residual modulus G after prestressing, and is defined by:

$$S = \alpha\sigma/G^{1/2} \tag{13}$$

Figure 10 shows the normalized modulus plotted against the strength factor S' for the three rubbers Neoprene, Hycar, and Intor 1500, S' being defined as:
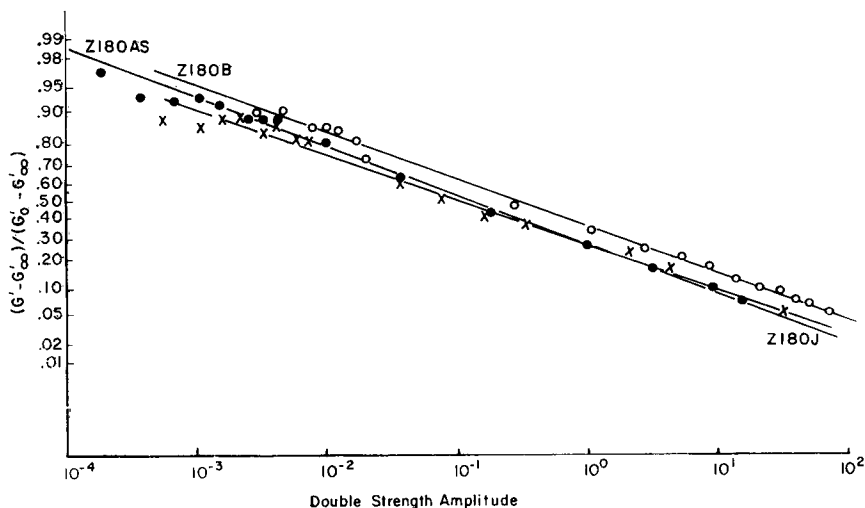
$$S' = \beta\sigma'/G^{2/3} \tag{14}$$

Fig. 10. Normalized dynamic shear modulus Z vs. strength for ($Z180AS$) Hycar + 150 phr HAF; ($Z180J$) Neoprene + 110 phr HAF; ($Z180B$) Intol 1500 + 110 phr.

TABLE IV

G'_0, G'_∞ and the Stress, Strain, Strainwork, and Strength Values at $Z = 0.5$ of Butyl–HAF Vulcanizates (Series 4)

Designation	Condition of vulcanizate[a]	Loading HAF vol.-%	G'_0, Mdynes cm.$^{-2}$	G'_∞, Mdynes cm.$^{-2}$	Strainwork at $Z = 0.5$ × 10^{-4} dynes cm.$^{-2}$	Double strain at $Z = 0.5$ × 10^2	Double stress at $Z = 0.5$, Mdynes cm.$^{-2}$	Strength at $Z = 0.5$ × 10	Spread for 80% change in $(G'_0 - G'_\infty)$ log units
6C	N	20	16.6	8.6	b		—		
6H	H		17.8	6.3	b		—		
11C	A		5.8	3.9	b		—		
11H	A + H		5.5	4.5	b		—		
7C	N	30	45.6	7.5	4.7	4.25	1.13	5.8	2.98
7H	H		58.5	8.0	5.1	4.24	1.20	6.0	2.64
12C	A		13.0	4.5	5.5	7.92	0.69	17.0	2.95
12H	A + H		8.0	5.0	b	—	—	—	—
8C	N	40	112.5	10	5.0	2.85	1.74	3.7	2.79
8H	H		120	10	4.0	2.48	1.61	2.5	2.69
13C	A		28	7.5	6.0	5.8	1.03	8.5	2.91
13H	A + H		20	5.5	b	—	—	—	—
9C	N	50	260	15	4.3	1.77	2.43	1.0	2.94
9H	H		195	10	4.0	1.98	2.03	1.8	2.71
14C	A		105	10	6.1	3.41	1.78	4.6	2.72
14H	A + H		16	10	b	—	—	—	—
10C	M	60	337	22.5	4.3	1.55	2.79	0.4	2.79
10H	H		335	15.0	4.0	1.53	2.60	1.3	2.94
15C	A		100	10	5.4	2.93	1.85	2.4	2.85
15H	A + H		12.5	12.5	4.0	3.89	1.02	3.6	2.77
					Avg. 4.79				Avg. 2.83

[a] N = normally compounded vulcanizates; H = normally compounded by a hot milling technique; A = vulcanizates containing attrited black (HAF); A + H = vulcanizate containing attrited black (HAF) compounded by a hot milling process.

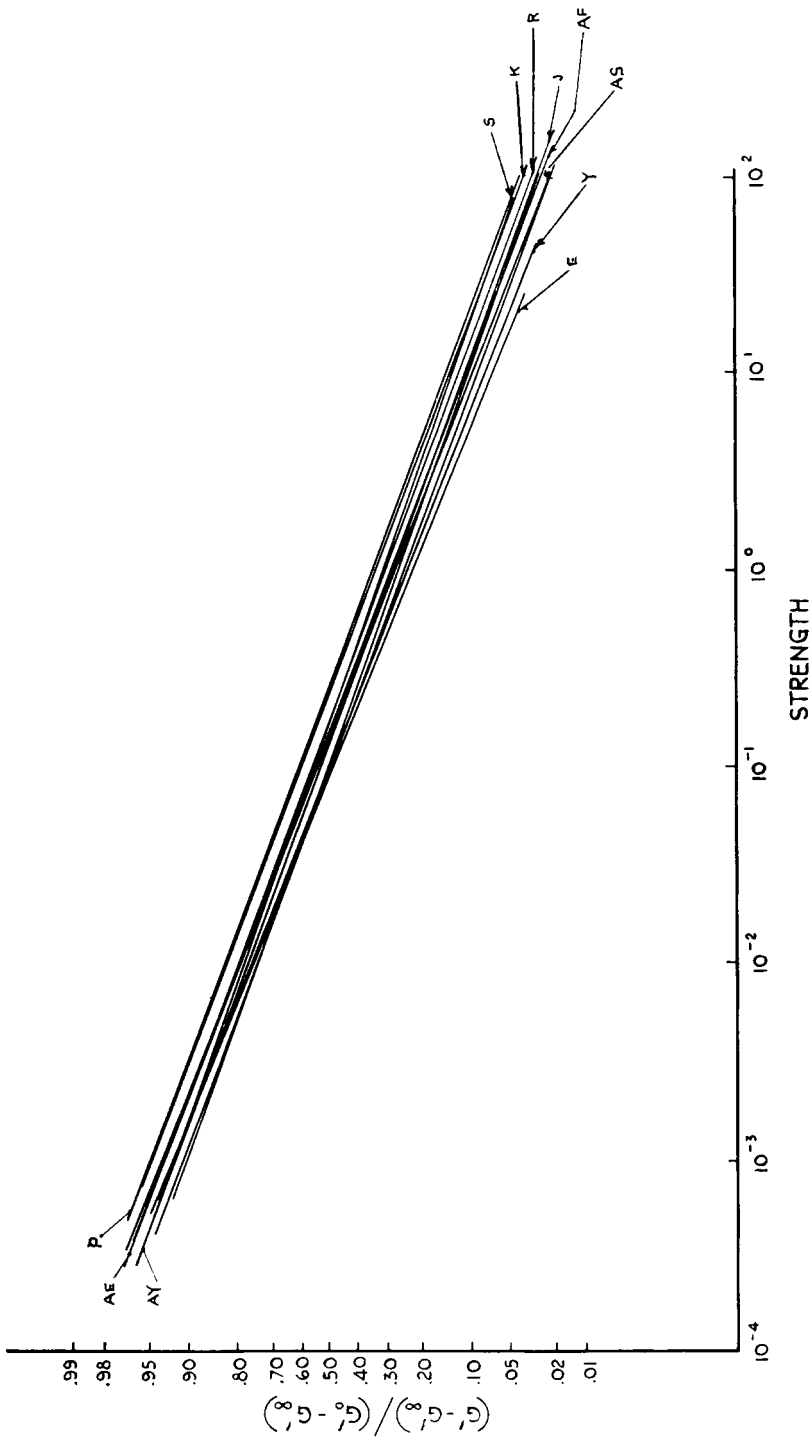[b] Too small a change in modulus for G'_∞ and strainwork to be determined.

Fig. 11. Normalized dynamic shear modulus vs. strength for a range of polymers; probability plot. Series 1.
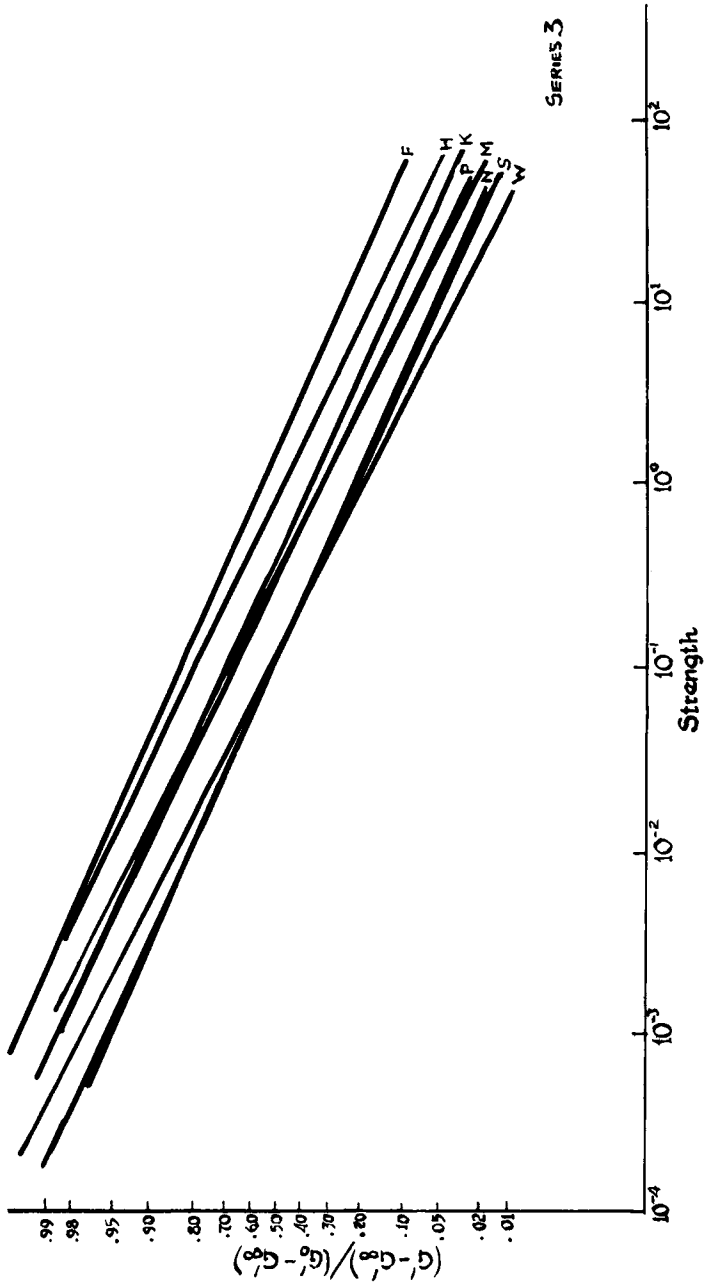
Fig. 12. Normalized dynamic shear modulus vs. strength for a range of HAF–butyl vulcanizates; probability plot. Series 3; See Table III for identification of curves.

where β is the dynamic double strain amplitude, σ' is the dynamic double stress amplitude, and G is the corresponding dynamic shear modulus. This equation is analogous to the Blanchard and Parkinson equation, eq. (13). The plots in Figure 10 are linear and are given in this paper as typical plots of the normalized modulus against strength. Figure 11 plots the results for the first series of different rubbers, from which it can be seen that the plots for the different rubbers lie closely together and have approximately the same slopes. This infers that the normalized modulus–strength curves for different polymers containing the same amount of black must be very similar. However, it must not be concluded that there is a strength distribution, similar for all concentrations of filler, even though the distribution may be similar for the same amount of black in a wide range of polymers. For instance, Figure 12 plots the normalized modulus versus strength for a range of concentrations of HAF in butyl (Series 3) and the strainwork position of the curve decreases with increasing carbon black content. Similar results were obtained for the natural rubber–HAF series (Series 2). Strength as a criterion of structure is therefore not independent of the concentration as was the strainwork criterion. Tables I–IV list the strength values, S', at $Z = 0.5$, and an inspection of these values for series 2, 3, and 4 confirms that strength is dependent on the concentration of the black.

There is an important point to be noted when comparing the dynamic results with those obtained by Blanchard and Parkinson, viz., that modulus changes occur at much lower values of S' than do those (S) in a tensile test. This, however, may be due to an artifact in the methods of being able to obtain a modulus value from a tensile stress–strain curve.

The results of Blanchard and Parkinson show clearly that there is an anomalous softening by low prestresses between 15 and 30 kg./cm.^{2}, i.e., $F(S) > 0.9$, of which their analysis in terms of eqs. (12) and (13) does not take account and which has been neglected as a secondary effect although this effect is obvious in many published results.

Analysis of G'' Data

It is clear that G'' is not a constant, and in fact G'' reaches a definite peak value. It is interesting to note that the maximum of the G''–strain amplitude coincides approximately with the strain corresponding to the modulus value at $Z = 0.5$, i.e., the strain corresponding to the modulus value halfway between G'_0 and G'_∞. The double strain at which $Z = 0.5$ has been noted as a vertical line on the appropriate curves in Figure 3, for example in order to stress this coincidence of G'' on the breakdown of the shear modulus with the amplitude of straining.

Figure 13 is a plot of G' against G'' for four of the series 1 measurements on different polymers. In all cases the results can be made to fit on to the arc of a circle in a manner reminiscent of the Cole-Cole[13-15] plots for electrical permittivity and mechanical compliances. The values of G'_0 and G'_∞
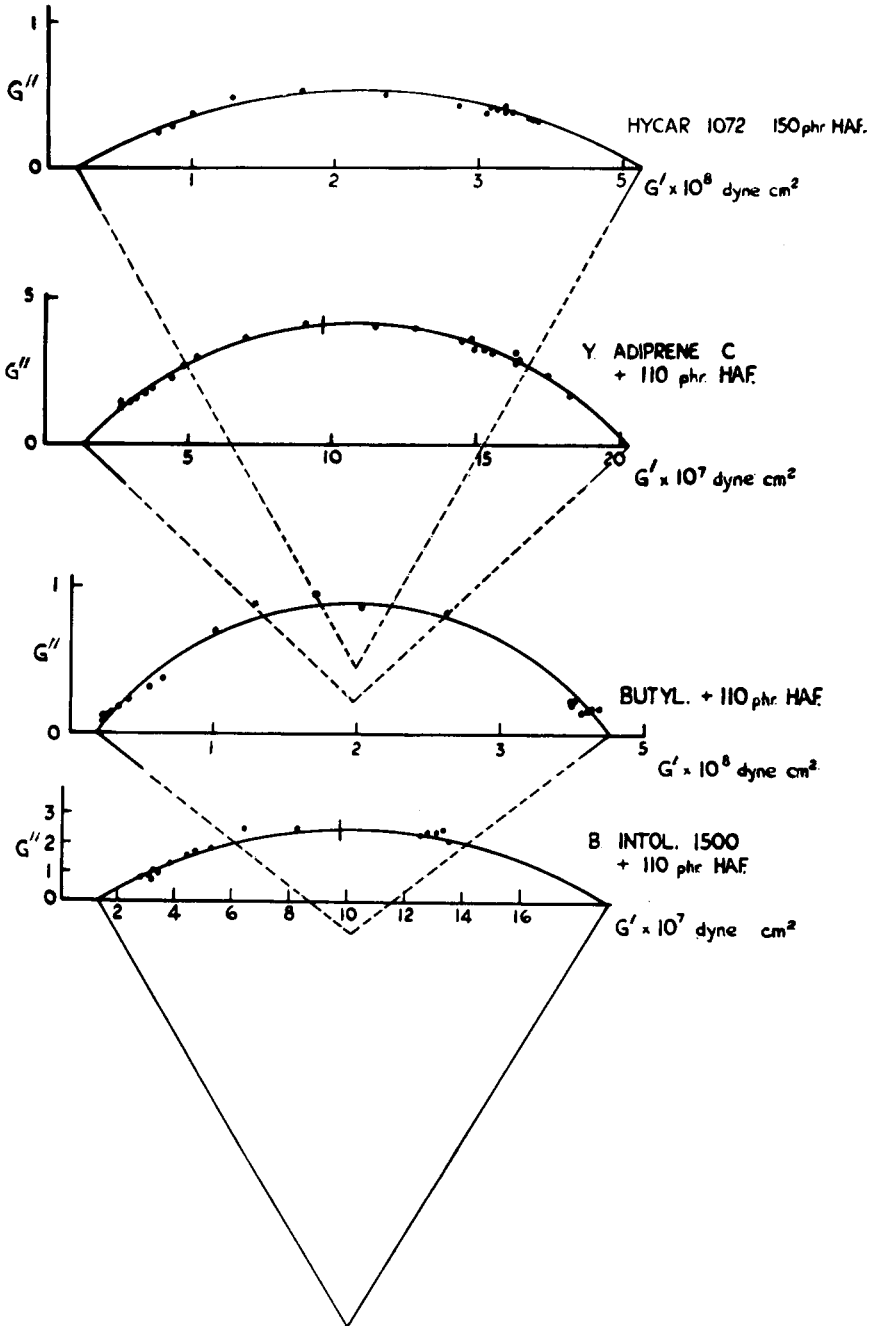
Fig. 13. G'' vs. G' plots for a series of HAF–polymer vulcanizates.   (Four of the series 1 rubbers.)
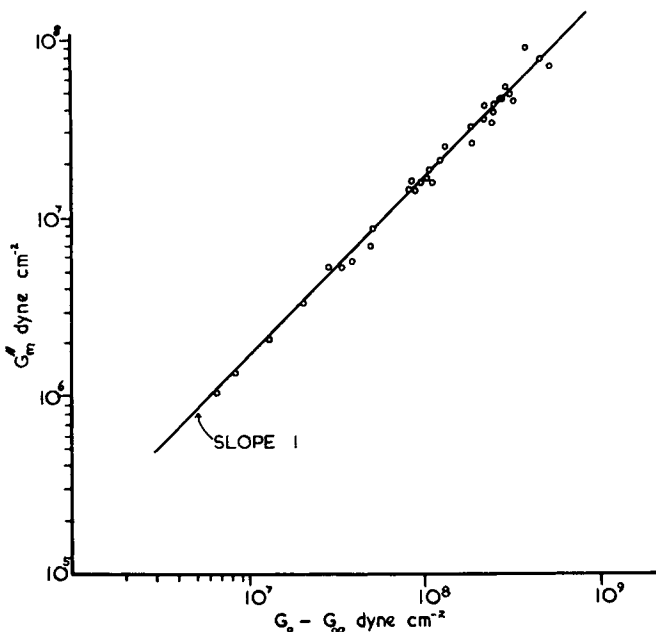
Fig. 14. G''_m vs. $G_0 - G_\infty$ for 32 rubber–black vulcanizates.

obtained from these plots are similar to those derived from the normalization procedure, although G'_0 is usually higher and G'_∞ is lower than the normalized values.   Table I lists the G'_0 and G'_∞ values from the Cole–Cole plot for comparison with those obtained from the normalization procedure. The mean value position of $G'_0 - G'_\infty$ from the normalization procedure has been indicated by a vertical line on the arc of the circle to stress the fact that G'' reaches a maximum approximately at $(G'_0 - G'_\infty)/2$.   The use of the Cole–Cole plot technique is, nevertheless, limited because the G'' strain curve is not symmetrical; G'' does not approach zero at very low strains because of the finite viscosity inherent in the rubber itself and the probably large contribution to the viscosity due to hydrodynamic effects of the agglomerates (whose effect diminishes considerably on straining). The effect of this "background" G'' is, therefore, not known, so it is not possible to separate it out from the change in G'' due solely to structural changes.   The approximate dependence of G'' with G' is, however, quite apparent, and certainly associates a large fraction of the hysteresis properties of a carbon black-loaded vulcanizate with the modulus breakdown phenomena.

From the Cole–Cole plots the top of the arc of the circle was obtained. Figure 14 plots G''_m, the maximum value against $G'_0 - G'_\infty$.   The $G'_0 - G'_\infty$ values were those obtained by the normalization procedure.   As the results covered a wide range of both G''_m and $G'_0 - G'_\infty$, the data have been plotted on logarithmic paper.   It is clear that nearly all the results fall close

to the line which has a slope of unity. The mean overall value of $G''_m/(G'_0 - G'_\infty)$ for the 32 rubber vulcanizates was 0.17, and therefore

$$G''_m = 0.17(G'_0 - G'_\infty) \tag{15}$$

One can infer from this simple relationship that the viscous contribution to the complex modulus (beyond that of the polymer itself) is mainly due to the amount of "structure" which can be broken down on oscillation, that is on the value $(G'_0 - G'_\infty)$.

DISCUSSION

Mullins[16-18] originally proposed a dual mechanism of softening by bond rupture with the emphasis on the breakage of carbon–carbon chains. Blanchard and Parkinson,[9,12] in later papers, have contested Mullins' interpretation of softening, which is based on chainlike groupings of filler particles (chain structure). They attribute the softening almost entirely to breakage of attachments between carbon particles and rubber. Following the arguments of Ladd and Wiegand[19] that characteristic black chain structures survive milling into rubber, Blanchard and Parkinson concluded that such structures are not broken by prestretching the vulcanized stock. A distinction was made between characteristic structure and the temporary structure formed by contacts between fortuitously adjacent particles. These latter contacts can be broken by stretching and remade by heating in accordance with electrical evidence that conducting paths can thus be broken and reformed. Later Blanchard[10-12] arrives at the conclusion that contact forces between particles are weak but contribute to the modulus at very low stresses, and that disruption of contacts by prestresses between 15 and 40 kg./cm.² is mainly responsible for the departure from their law of softening when $F(S) > 0.9$. It is also to be noted that the stress at $Z = 0.5$ for the highest loading of fillers approach 1–5 kg./cm.⁻² (see Tables I–IV). The stress ranges thus quoted by Blanchard as causing anomalous behavior are not greatly different from the stresses required to cause the maximum rate of breakdown of dynamic modulus with stressing.

Bueche[20] has analyzed the stress–strain curves in tension on the assumption that a polymer chain can bridge two particles of black. The segment of the rubber chain between the particles becomes extended on stretching the rubber and must ultimately break or part from the surface. This analysis was carried out for high strains only, and he derived parameters which are orders different from those required to account for the dynamic modulus changes at the lower strains.

Recent experiments in our laboratories[21] have shown that a three-dimensional structure possessing a high modulus can be obtained from relatively low quantities of reinforcing fillers in paraffin, thus proving the possibility of a large elastic contribution due to the black alone to the modulus of carbon black filler-loaded rubber.

The dynamic results show that the black–black structure is almost completely eliminated at dynamic strains of less than 1, whereas Bueche[20] has shown that the Mullins effect still persists at high elongations. This could be accounted for by a dual mechanism the black–black structure being responsible for the modulus and hysteretic performance of carbon black stocks at low strains, and the rubberlike entropic nature of a polymer chain bridging two particles of black mechanism, which becomes apparent only at high strains. The Bueche mechanism then might be responsible for the properties at high strains, but would have no or very little effect at low strains. Unfortunately some of the experiments at high strains in tension have not taken into account the fact that even if all the structure has been broken down at strains less than 1, the hysteresis, as shown up by the large phase angle values, is then very large, and differences in successive stress–strain loops may be solely due to the very large hysteresis. Further work is obviously needed to clarify these discrepancies in observations.

APPENDIX

Compounding details and designations of the rubbers used are given in Tables A-I–A-IX.

TABLE A-I

	A	B
Intol 1500	100	100
Philblack O	—	110
Dutrex R	5	5
ZnO	5	5
Stearic acid	1	1
CBS	0.8	0.8
DPG	0.6	0.6
Sulfur	1.75	1.75

Cure 40 min. at 141°C.

TABLE A-II

	D	E
Polysar Butyl 301	100	100
Philblack O	—	110
Zinc oxide	5	5
Stearic acid	1	1
ZDC	2	2
WRT	1	1
Sulfur	2	2

Cure 20 min. at 153°C.

TABLE A-III

	G	H	J	K
Neoprene WRT	100	100	100	100
Philblack O			110	110
Zinc oxide	5	5	5	5
L.C. MgO	4	4	4	4
DOP	—	20	—	20
Stearic acid	1	1	1	1
Robac 22	0.35	0.35	0.35	0.35

Cure 40 min. at 141°C.

TABLE A-IV

	N	P	R	S
Hycar 1002	100	100	100	100
Philblack O	—	—	110	110
DOP	—	20	—	20
Zinc oxide	5	5	5	5
Distec 108	1.5	1.5	1.5	1.5
MBTS	1.5	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5	1.5

Cure 35 min. at 153°C.

TABLE A-V

	X	Y
Adiprene C	100	100
Philblack O	—	110
Dicumyl peroxide	1.1	1.1

Cure 60 min. at 153°C.

TABLE A-VI

	AM	AN	AP	AS
Hycar 1072	100	100	100	100
Philblack O	54	110	110	150
Zinc oxide	5	5	5	5
Distec A108	1	1	1	1
DOP	20	—	20	20
TMT	3.5	3.5	3.5	3.5

Cure 35 min. at 155°C.

TABLE A-VII

	AT	AW	AX	AY
Hypalon 20	200	200	200	200
Slaybile resin	10	10	10	10
Litharge	40	40	40	40
MBTS	1	1	1	1
Thiuram P25	1.5	1.5	1.5	1.5
Philblack O	54	108	220	

Cure 40 min. at 153°C.

TABLE A-VIII

	AD	AE	AF
Smoked sheets (natural rubber)	100	100	100
Philblack O	—	110	150
Stearic acid	2.5	2.5	2.5
Zinc oxide	5	5	5
CBS	0.5	0.5	0.5
Sulfur	2.5	2.5	2.5

Cure 30 min. at 141°C.

TABLE A-IX

	AG	AH	AJ	AK	AL
Hycar 1072	100	100	100	100	100
Philblack O	—	—	27	27	54
Zinc oxide	5	5	5	5	5
Distec A108	1	1	1	1	1
DOP	—	20	—	20	—
TMT	3.5	3.5	3.5	3.5	3.5

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A. R. PAYNE

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Résumé

Le module et l'angle de perte des caoutchoucs chargés de noir de carbone varient avec l'amplitude dynamique de l'oscillation. La variation dynamique du module avec l'amplitude est de nature sigmoïde. Ceci permet de réduire les résultats par une technique de normalisation, et le but de cet article est de montrer comment le résultat normalisé est essentiellement indépendant de la charge en noir de carbone et du type de polymère quand le module normalisé est porté en fonction de l'énergie de déformation (ou travail d'élongation).

Zusammenfassung

Modul und Verlustwinkel von mit Russ gefülltem Kautschuk hängt von der dynamischen Amplitude der Schwingung ab. Die Abhängigkeit des dynamischen Moduls von der Schwingung ab. Die Abhängigkeit des dynamischen Moduls von der Amplitude hat sigmoiden Charakter. Dies gestattet, die Ergebnisse durch ein Normalisierungsverfahren zu reduzieren; es ist Aufgabe dieser Arbeit zu zeigen, dass die normalisierten Ergebnisse im wesentlichen von der Russfüllung und vom Polymertyp unabhängig sind, wenn man den normalisierten Modul gegen die Deformationsenergie (oder Verformungsarbeit)aufträgt.