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Dynamic Properties of Butyl Containing Attrited Black

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INTRODUCTION

The modification of carbon blacks by severe attrition through ball or two roll (rubber) milling has been described in a series of papers by Gessler.[1–3] It was shown that unexpectedly large increases in the surface area of the black attend this attrition. These increases were attributed partly to the breakage of secondary aggregate structure, and partly due to abrasion and fragmentation occurring at the surfaces of individual particles. The use of attrited blacks leads to butyl vulcanizates with greatly improved properties; tensile strengths, elongation, and elasticity being very significantly increased, while dynamic modulus and heat buildup on flexing are decreased. Abrasion resistance, the collective result of all these effects, is greatly improved. This paper is concerned mainly with examining in greater detail the dynamic properties of butyl rubber containing both normal and attrited blacks, over a wide strain range, and in particular to examine the effect of changes of carbon black structure on these properties.

EXPERIMENTAL

The measurements were carried out on the RAPRA sinusoidal-strain dynamic tester.[4,5] The instrument was used in the following ways: (*a*) a sinusoidal stress was applied to two rubber test pieces in shear (a shear sandwich) and the deformation of the rubber measured (this method was used for the smaller displacements, 0.1–100 μ); (*b*) a sinusoidal strain was applied to the same shear test piece, and the stress measured (this method was used for the larger displacements, 100 μ to 1.25 cm.).

The machine was designed originally for the second method with a displacement maximum of the moving anvils of 1.25 cm. The lower amplitudes were limited by the tolerances in the bearings, etc., but by using a spring between the moving anvil and the rubber test pieces, a large movement of the anvil was reduced to a considerably smaller movement on the rubber. The actual deformation was then dependent on the relative stiffnesses of the spring and the rubber sample. In the first method, the deformation on the rubber was recorded directly by differential displacement pick-up.

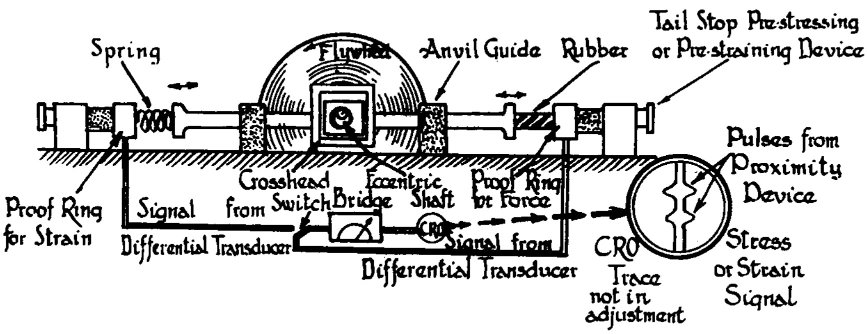

Fig. 1. RAPRA sinusoidal strain machine; forced vibration, non resonant type.

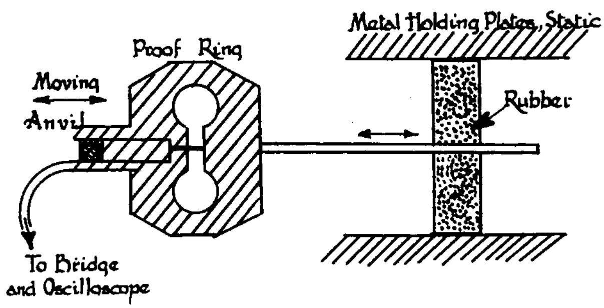

Fig. 2. Schematic drawing of the jig used to cover a wide strain range in shear; method (*a*).

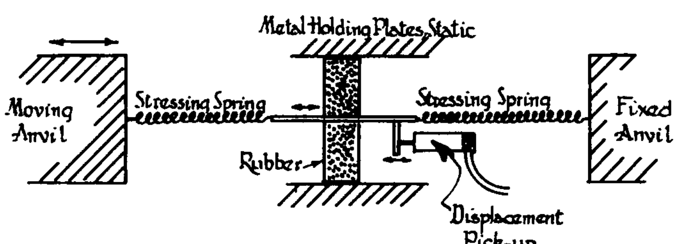

Fig. 3. Schematic drawing of the jig used to cover a wide strain range in shear; method (*b*).

The RAPRA dynamic tester is schematically shown in Figure 1. Figures 2 and 3 show the arrangement used in methods *a* and *b*, respectively. The test pieces were cylinders of rubber 0.8 cm. radius and 2.54 cm. long. The cylinders were securely bonded to the deforming and holding plates. The test frequency was 0.1 cycle/sec. The rubber cylinders were molded in steel molds, lubricated with silicone fluid, so removal from the mold required only very light finger pressure.

All the dynamic tests were made by first oscillating at the lowest stress possible, and then increasing the strain incrementally to the maximum.

This sequence ensured that the rubber was not overstrained before the particular test, the dynamic properties of the filler-loaded vulcanizates being very sensitive to previous treatment. All the tests were carried out at ambient temperature.

The parameters measured were G^*, the complex shear modulus $G^* = (G'^2 + iG''^2)^{1/2}$, where G' is the in-phase component and G'' the out-of-phase component. Also measured was δ, the phase angle between the sinusoidal stress and strain.

The rubber used for these experiments was butyl, and the carbon black was a high abrasion furnace black (HAF). Details of the compounding are given in the Appendix. The masterbatch, mixed with 20, 30, 40, 50, and 60 volumes of black, respectively, was split in half. The first half received no further treatment. The second half was hot milled for 10 min. at 300–310°F. Vulcanizing agents were then added to each masterbatch in the conventional manner on a cold mill. Four sets of rubber were therefore prepared and are referred to in this paper as, normal (N), hot milled (H), attrited (A), and attrited and hot milled (A & H).

EXPERIMENTAL RESULTS

G Data

Figure 4*a*–4*e* show the shear modulus plotted against the strain amplitude of test. Each figure contains the results for a single volume of black, and each curve is related to a particular vulcanizate.

Several features of the experimental plots in these figures are cited. (*1*) At any given carbon black concentration, the shear modulus remains essentially unchanged over a range of amplitudes at low strains, as is evident from the flatness in the initial portion of the curves (at extreme left). (*2*) The curves obtained when the shear modulus is plotted against the logarithm of the double strain amplitude are generally sigmoidal, and at high strains converge to approach a constant modulus value. (*3*) It is apparent that the considerable changes in modulus which take place at the intermediate strains are important because they occur in a region of strain to which rubber articles are subjected in service. (*4*) The hot milling treatment of the normal HAF vulcanizate has little effect on the dynamic modulus. Use of the attrited black brings about a considerable reduction in the dynamic modulus at low strains. The combined effect of hot milling and attrition is to decrease substantially the shear modulus at low strains. Indeed, it almost entirely eliminates the structural breakdown effects which are evident on straining.

The effect of differing treatment of the vulcanizate and the concentration of carbon black on the modulus is shown in Figure 5, where the shear modulus at 0.002 and 0.2 double strain amplitude is plotted against the volumes of black per hundred volumes of rubber in the vulcanizate. It is apparent from the curves in Figure 5 that the attrition process has considerably reduced the modulus of the vulcanizate as compared to the normal vulcanizate values. The differences due to the varied treatment of the vulcanizate as shown by these curves becomes smaller as the dynamic amplitude is increased.

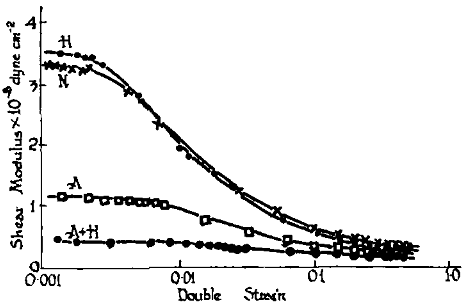

Fig. 4*a*. Shear modulus, G' measurement on butyl vulcanizates containing HAF versus double strain amplitude of testing; (N) normal butyl-HAF vulcanizate; (H) hot-milled normal butyl-HAF vulcanizate; (A) a butyl vulcanizate containing attrited HAF; (A & H) a butyl vulcanizate, containing attrited HAF which has been subjected to a hot milling treatment. 60 volume loading of HAF black.

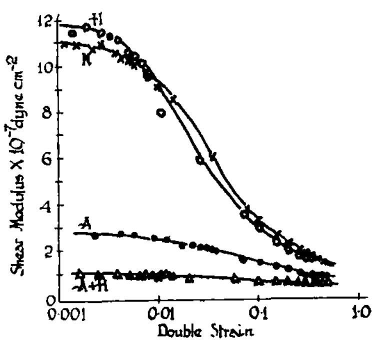

Fig. 4*b*. G' vs. double strain amplitude of testing. 50 volume loading of HAF black.

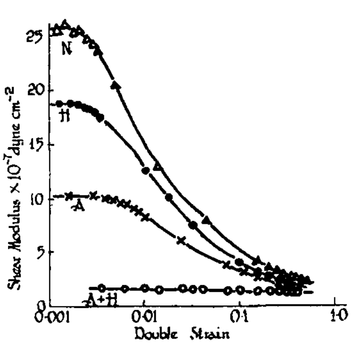

Fig. 4*c*. G' vs. double strain amplitude of testing. 40 volume loading of HAF black.

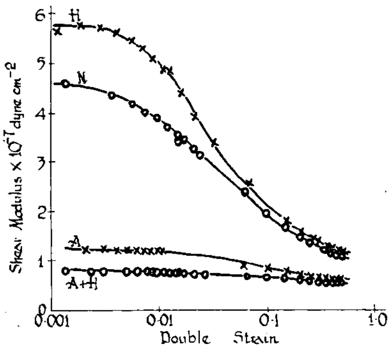

Fig. 4*d*. G' vs. double strain amplitude of testing. 30 volume loading of HAF black.

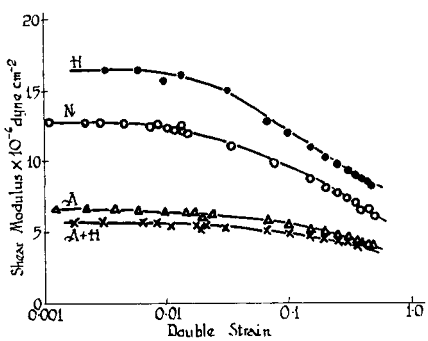

Fig. 4*e*. G' vs. double strain amplitude of testing. 20 volume loading of HAF black.

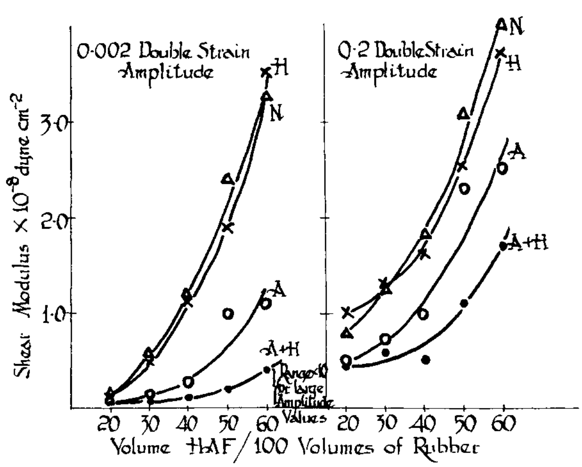

Fig. 5. Shear modulus G' vs. volumes of black per hundred volumes of rubber.

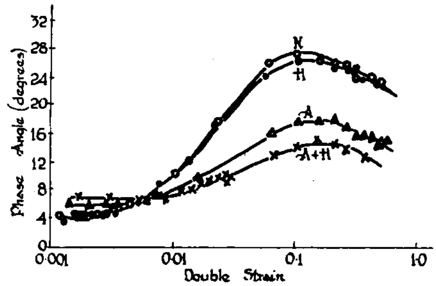

Fig. 6*a*. Phase angle measurements on butyl vulcanizates containing HAF vs. double strain amplitude of testing. 60 volume loading of HAF black.

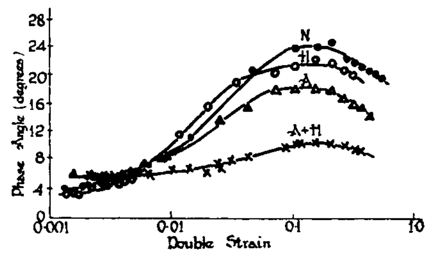

Fig. 6*b*. Phase angle vs. double strain amplitude of testing. 50 volume loading of HAF black.

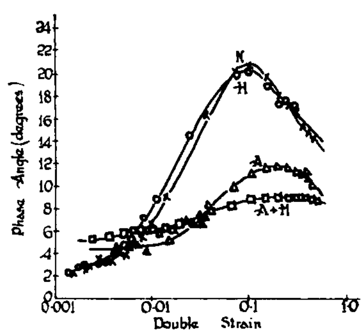

Fig. 6*c*. Phase angle vs. double strain amplitude of testing. 40 volume loading of HAF black.

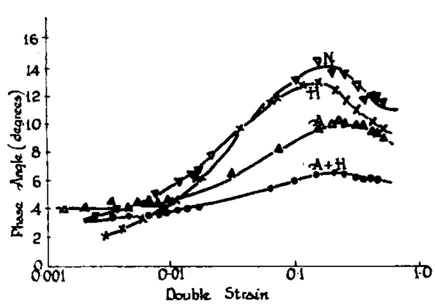

Fig. 6*d*. Phase angle vs. double strain amplitude of testing. 30 volume loading of HAF black.

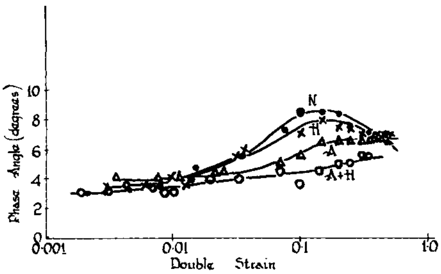

Fig. 6e. Phase angle vs. double strain amplitude of testing. 20 volume loading of HAF black.

δ Data

Figure 6a–6e show the phase angle δ, plotted against the strain amplitude of test. The particular features of these plots are as follows: (1) at low strains, all the phase angles are low and constant over a range of low strains. (2) At higher strains, the phase angles increase and reach a peak. (3) The effect of hot milling treatment of the normal HAF vulcanizate has little effect on the phase angle changes compared to those of the normal vulcanizate. The use of attrited black brings about a considerable reduction in the phase angle at high strains.

The effect of the concentration of carbon black on the phase angle is shown in Figure 7 for systems with differing composition and treatment. In this figure, the phase angle at 0.002 and 0.2 double strain amplitude is plotted against the volumes of black per hundred volumes of rubber in the vulcanizate. It is apparent from the curves (Fig. 7) that the use of attrited black considerably reduces the phase angles at high dynamic strains as compared to the normal vulcanizate values. At low dynamic strains, the use of attrited black increases the phase angles slightly.

G″ Data

Figures 8a–8d show the corresponding out-of-phase component of the shear modulus plotted against the strain amplitude of test. The particular features of these plots are, (1) it is quite apparent that G'' is not a constant as G'' reaches a maximum and then tails off. This fact explains why some workers have noticed G'' rising with increasing strain amplitude and others G'' decreasing with increasing strain amplitude. (2) The hot milling treatment of the normal HAF vulcanizate has little effect on the G''. (3) The use of attrited black brings about a considerable reduction in the G'' peak. (4) The combined effect of hot milling and attrition is to decrease substantially G'', which then shows little change with straining.

The effect of differing treatment of the vulcanizate and the concentration of carbon black on the G'', is shown in Figure 9, where the G'' at 0.002 and 0.2 double strain amplitude is plotted against the volumes of black per hundred volumes of rubber in the vulcanizate. It is apparent from the

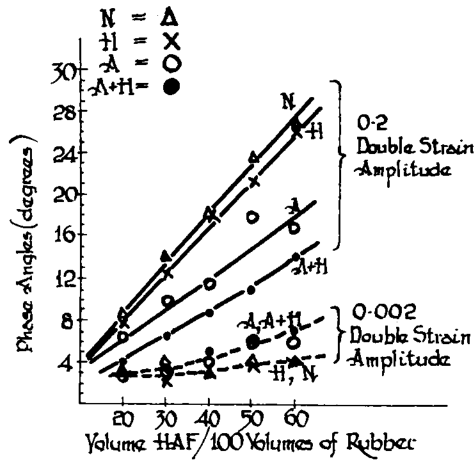

Fig. 7. Phase angle vs. volumes of black per hundred volumes of rubber (—) results at 0.002 double dynamic strain amplitude; (–) results at 0.2 double dynamic strain amplitude. The symbols are the same as in Fig. 4*a*.

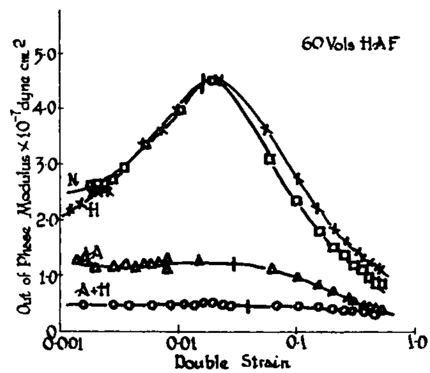

Fig. 8*a*. Out-of-phase modulus G'' vs. double strain amplitude of testing. 60 volume, loading of HAF black.

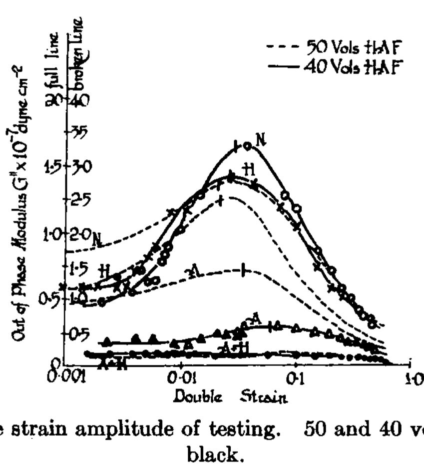

Fig. 8*b*. G'' vs. double strain amplitude of testing. 50 and 40 volume loading of HAF black.

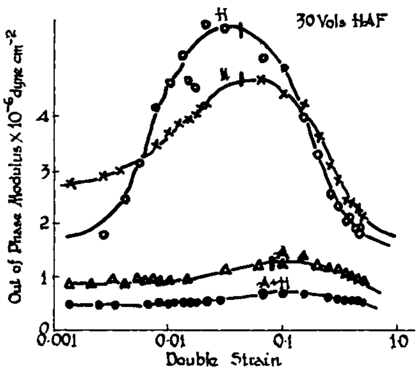

Fig. 8c. G'' vs. double strain amplitude of testing. 30 volume loading of HAF black.

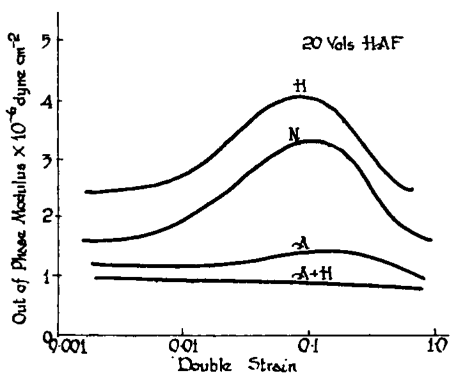

Fig. 8d. G vs. double strain amplitude of testing. 20 volume loading of HAF black.

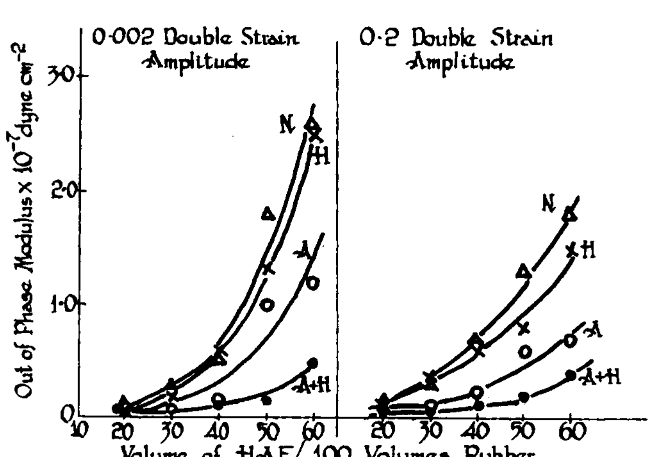

Fig. 9. Out-of-phase modulus G'' vs. volumes of black per hundred volumes of rubber.

curves in Figure 9 that the attrition process has considerably reduced the G'' over the whole strain range as compared to the G'' values of the normal vulcanizate. Also it is clear that considerable changes have been brought about in the dynamic properties of the butyl vulcanizate by the attrition of the carbon black.

STRAINWORK DEPENDENCE

The various empirical relationships suggested by different authors for the dependence of the dynamic modulus on strain amplitude have been discussed,[5] and it may be noted here, a double logarithmic plot of stress versus strain can also be used. However, it is proposed to develop a method of presentation which emphasizes the similarities between the curves derived for the different treatment and for the various loadings of black. The method involves "normalizing" the data between the limits at a very low and very high strain. Consider the shear modulus G';

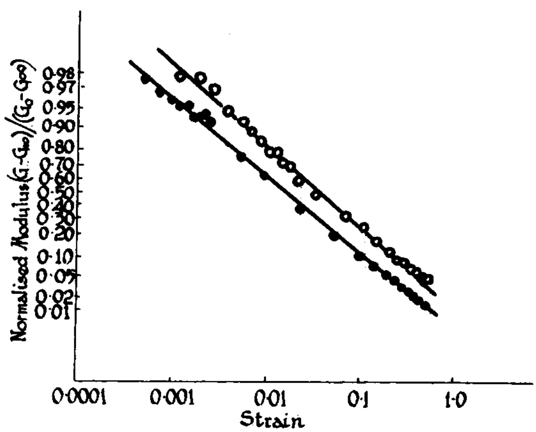

Fig. 10. Normalized modulus $(G' - G_\infty)/(G_0 - G_\infty)$ vs. double strain amplitude of test.

let G_0 represent its value at strains approaching zero; G_∞ its value at the high strains, where there is no further change in G' with increase of strain. Then the normalized modulus, Z, is given by $(G' - G_\infty)/(G_0 - G_\infty)$, and is shown in Figure 10 plotted* against the log of the double strain amplitude for two typical sets of results. The latter refers to butyl heat treated with 30 volumes of normal HAF black (compound 7H) and to butyl mixed but not heat treated, with 60 volumes of the same black (compound 10 c). The G_0 and G_∞ values used in the normalization are given in Table I. It will be appreciated that there is some, but not very much, latitude in fixing a value for G_∞, but the variation possible is too small to influence the position of the plot.* Linear plots are also obtained

* Original plotted on probability paper.

TABLE I. G_0, G_∞, and the Stress, Strain, and Strainwork Values at $Z = 0.5$ of Butyl–HAF Vulcanizates

Volume loading of black	Condition 1[a]	Condition 2[b]	G_0, $\times 10^{-7}$ dyne cm.$^{-2}$	G_∞, $\times 10^{-7}$ dyne cm.$^{-2}$	Value at $Z = 0.5$: Double stress $\times 10^{-6}$ dyne cm.$^{-2}$	Value at $Z = 0.5$: Double strain, dimensionless	Value at $Z = 0.5$: Strainwork, $\times 10^{-4}$ dyne cm.$^{-2}$	Value at $Z = 0.5$: Width for 90% change in $G_0 - G_\infty$, logarithms
20	6C	N	1.66	0.86[c]	—	—	—	—
	6H	H	1.78	0.63[c]	—	—	—	—
	11C	A	0.58	0.39[c]	—	—	—	—
	11H	A & H	0.55	0.45[c]	—	—	—	—
30	7C	N	4.56	0.75	1.125	0.0425	4.7	3.79
	7H	H	5.85	0.80	1.196	0.0424	5.1	3.36
	12C	A	1.30	0.45	0.692	0.0792	5.5	3.75
	12H	A & H	0.80	0.50[c]	—	—	—	—
40	8C	N	11.25	1.0	1.74	0.0285	5.0	3.55
	8H	H	12.0	1.0	1.61	0.0248	4.0	3.42
	13C	A	2.8	0.75	1.03	0.0582	6.0	3.71
	13H	A & H	2.0	0.55[c]	—	—	—	—
50	9C	N	26.0	1.5	2.43	0.0177	4.3	3.74
	9H	H	19.5	1.0	2.03	0.0198	4.0	3.44
	14C	A	10.5	1.0	1.78	0.0341	6.1	3.46
	14H	A & H	1.6	1.0[c]	—	—	—	—
60	10C	N	33.7	2.25	2.79	0.0155	4.3	3.55
	10H	H	33.5	1.50	2.60	0.0153	4.0	3.74
	15C	A	11.6	1.0	1.85	0.0293	5.4	3.62
	15H	A & H	4.0	1.25	1.02	0.0389	4.0	3.52
						Average	4.8	

[a] Identification in Figures 10, 11, and 12.
[b] Identification in other figures.
[c] Too small a change between G_0 and G_∞ to allow normalization of the data.

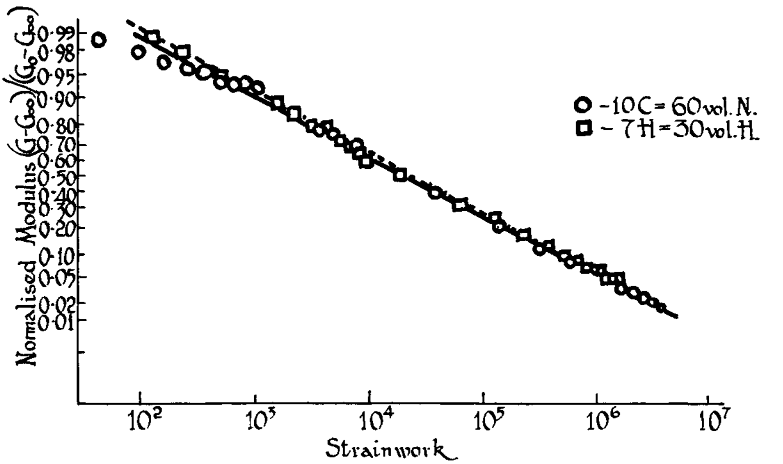

Fig. 11. Normalized modulus $(G' - G_\infty)/(G_0 - G_\infty)$ vs. logarithm of the strainwork for the same two vulcanizates as in Fig. 10.

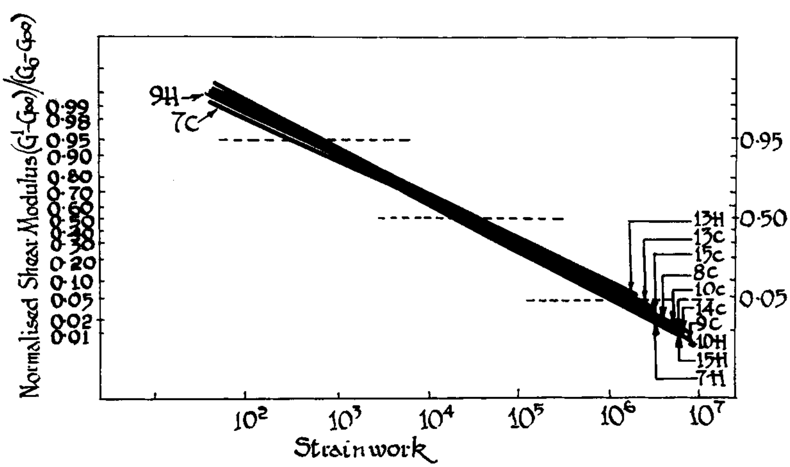

Fig. 12. Normalized modulus $(G' - G_\infty)/(G_0 - G_\infty)$ vs. logarithm of the strainwork for a number of butyl–HAF vulcanizates. The number on the appropriate curve refers to the volume loading of HAF and the letter to the condition of the vulcanizate. See Table I for identification.

when the normalized modulus Z is plotted against the log of the double stress amplitude.

It has been shown in previous papers,[5–7] that neither stress nor strain are the independent parameters which govern the variation of modulus with strain, but the product of stress × strain, which will be referred to as strainwork, will be used in preference. Figure 11 indicates the normalized modulus Z versus strainwork (maximum stress × maximum strain) for the same two vulcanizates as given in Figure 10. It is seen that a linear

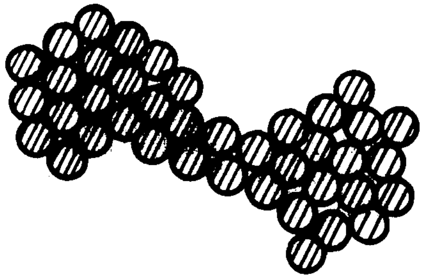

Fig. 13. Carbon black aggregates.

relationship exists between Z and strainwork. Figure 12 is the plot of the resulting straight lines for all the vulcanizates which could be so analyzed. (See footnote to Table I.)

It is convenient to consider the strainwork corresponding to $Z = 0.5$, and this is used in Table I. It is quite apparent that this strainwork is very similar irrespective of the treatment of the black. The slopes of the plot are quite close, and no consistent variation could be detected. The length of the abscissae between $Z = 0.95$ and $Z = 0.05$ is also given in Table I; the value represents the width of the change in the strainwork for 90% change in G' between G_0 and G_∞. An inspection of the values of stress, strain, and strainwork at $Z = 0.5$ (Table I) shows that, in general, as the strain values decrease, the stress values increase, whereas the strainwork remains approximately constant. These conclusions are similar to those derived in earlier papers on other polymer–black systems.[5,7]

The linearity of the plot of the data implies a relationship of the following type:

$$Z = (G' - G_\infty)/(G_0 - G_\infty) = 1 - (2/\sqrt{\pi}) \int_0^u e^{(-u^2/2)}\, du$$

where u is a linear function of strainwork.

The simplest assumption that 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 on straining, and that there is a normal distribution for the logarithm of the energy of straining of those weak links. The effect of the various treatments of the vulcanizate is solely to alter the number, but not the distribution of the weak links with respect to the energy of deformation.

One interpretation of the normalized modulus–strainwork plot is that the energy measured is that energy required to break down aggregates of varying dimensions. For example, if we had an aggregate like that shown in Figure 13, a relatively small amount of strainwork would be required to reduce it by a factor of two. More work would then be required to reduce each of the residues by another factor of two and so on. Hence, as long as there are aggregates one would expect a continuation in the plot of normalized modulus Z versus strainwork and one obtains a normal "probability" or distribution function. As the original extent of aggregation is reduced, a lower initial G_0 and a lower $G - G_\infty$ results, eventually culminating in attrited black heat-cycled stock, where G_0 tends to G_∞, and it is presumed that few aggregates exist which are capable of being broken down by deformation.

It is of further interest to note that the maxima of the G''-strain amplitude curves in Figure 8 coincide 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 $Z = 0.5$ has been noted as a vertical line on the appropriate curves in Figure 8 in order to stress this coincidence which indicates the dependence of G'' on the breakdown of the shear modulus with the amplitude of straining.

TENSILE TESTS

The various treatments of the HAF–butyl vulcanizates produce a shift in the stress–strain curve. Figure 14 shows a typical series of curves for the 40 volume loading of HAF. The effect of hot milling with normal HAF black is to reduce the tensile modulus slightly, but with very little alteration in tensile strength and ultimate elongation. The attrition process brings about substantial changes for there is a lowering of the tensile modulus below 350% elongation, but a substantial increase in the ultimate tensile strength and elongation. The effect of attrition and hot milling is to further reduce the modulus at low strains, but to increase the modulus at high strains. This will cause a crossover of the stress–strain curves of the attrited, and the attrited and hot milled stocks at just over 100%

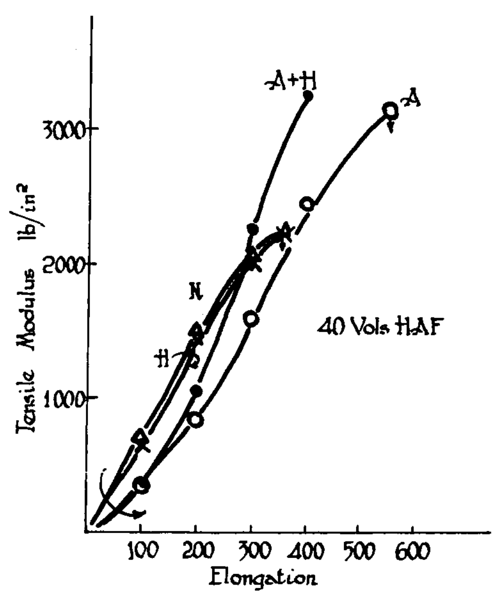

Fig. 14. Typical tensile stress–elongation curves for a 40 volume loading of HAF in a butyl vulcanizate.

TABLE II
Tensile Modulus, Elongation at Break, and Tensile Product of Butyl–HAF Vulcanizates

Volume black	Condition	Hardness (Shore)	Tensile modulus, lb. in.^{2}				Tensile strength, lb. in.^{2}	Elongation at break, %	Tensile product. lb. in.^{2} $\times 10^{-4}$
			100%	200%	300%	400%			
20	N	56	270	625	1075	1725	2230	480	107
	H	55	300	675	1175	1825	2450	500	122
	A	50	200	425	825	1415	2750	580	159
	A & H	50	220	500	970	1750	2600	540	141
30	N	66	425	980	1640	2170	2270	410	93
	H	64	480	990	1675	2250	2325	420	98
	A	55	265	600	1185	1980	2700	550	149
	A & H	51	280	735	1620	2720	3200	470	150
40	N	73	700	1500	2075	—	2225	360	80
	H	73	660	1460	2050	—	2225	360	80
	A	62	350	840	1600	2480	3110	530	165
	A & H	58	350	1070	2275	3260	3460	440	153
50	N	83	950	1715	—	—	2050	290	59
	H	82	875	1670	—	—	1825	270	49
	A	70	415	1125	2050	2700	2900	470	136
	A & H	65	450	1460	2720	—	3200	370	118
60	N	86	1100	1420	—	—	1430	200	29
	H	86	950	—	—	—	1275	180	23
	A	76	550	1450	2430	—	2875	400	115
	A & H	—	630	1740	2875	—	3025	330	100

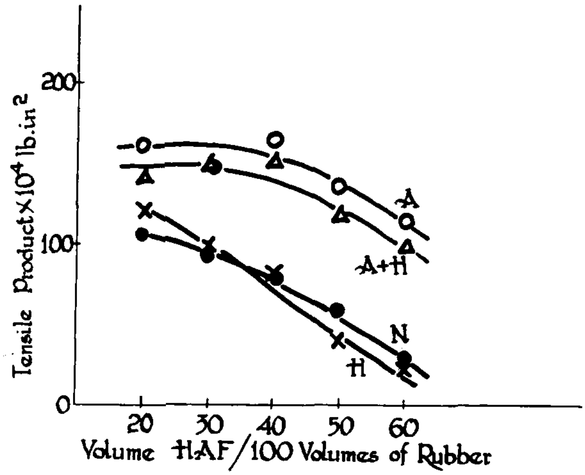

Fig. 15. Tensile product vs. volume loading of HAF in butyl.

elongation. The tensile modulus and elongation at break for the various butyl HAF vulcanizates are given in Table II.

It is clear that butyl vulcanizates with attrited black are characterized by increased tensile strength and extensibility, and this confirms earlier work by one of the present authors.[2,3] As with the dynamic results, the tensile properties show that the attrited black compounds respond much more sharply to heat treatment than those containing normal HAF.

It is also interesting to note the changes in the tensile product with the various treatments. For example, Figure 15, which plots the tensile product, shows a clear difference between the normal and attrited black stocks. Again, the effect of hot milling the attrited black stock is to slightly reduce the tensile product. Work at the Esso Laboratories[2] has shown a good correlation between tensile product and Lambourn abrasion resistance, therefore, the marked improvement in the tensile product on attrition is of interest. Gessler[2] has previously proved that the abrasion losses in butyl are reduced 25–50% by the substitution of attrited for standard blacks.

The hardness results given in Table II parallel the tensile modulus values at low elongations, and indicate the effect of a lowering of the hardness of the vulcanizate by attrition and by attrition and hot milling.

CONCLUSIONS

Drastic changes were noticed in the dynamic behavior of butyl containing attrited black as compared to the normal vulcanizate. These changes were apparent in all the properties measured, both dynamic and tensile. When the dynamic modulus changes (i.e., between G_0 and G_∞) were normalized and plotted against strainwork, the experimental data, irrespective of the concentration of the black or condition of the vulcanizate, were found to lie close together. Although the various treatments of the blacks or the vulcanizates altered the number of linkages that could be broken down by stressing, the distribution of these linkages with respect to the logarithm of the strainwork was unaltered. The strain at the maximum value of G'' coincided approximately with the strain at the modulus equal to $(G_0 - G_\infty)/2$ therefore indicating a direct dependence of G'' on the rate of change of G' with the amplitude of straining.

The specific action of oxygen on the carbon surface was reported in the literature.[8,9] It was pointed out that nonoxyblacks (the furnace and thermal blacks) did not respond directly to heat treatment or hot milling, selected chemical agents being required to promote the interaction. The attrition of carbon black, since it yields oxyblacks from nonoxy blacks, produces pigments which respond directly and readily to heat treatment. This is again apparent from the marked effect hot milling has on the dynamic properties of the attrited black vulcanizate as compared to the effect of heat treatment on the normal HAF compound.

Appendix

The compounds used are given in Table III:

TABLE III

Compound number		Volume of black
Standard black HAF	Attrited black HAF	
6C, 6H	11C, 11H	20
7C, 7H	12C, 12H	30
8C, 8H	13C, 13H	40
9C, 9H	14C, 14H	50
10C, 10H	15C, 15H	60

The letters C and H in each of these series are used to refer to compounds in which the masterbatch was conventionally used and heat treated (hot milled), respectively. These butyl–HAF compounds were compounded conventionally and cured for 45 minutes at 307°F. The formulation is given in Table IV.

TABLE IV
Compound Formulation

Masterbatch	
Enjay Butyl 217	100
Black	as indicated
Stearic acid	1.0
Curing Agents	
Zinc oxide	5.0
Sulfur	2.0
Tetramethylthiuram disulfide[a]	1.0
2,2′-Benzothiazyl disulfide[b]	1.0

[a] Tuads.
[b] Altax.

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Synopsis

The dynamic modulus and loss angle of butyl vulcanizates containing both normal and attrited carbon black (HAF) have been studied over a wide strain amplitude range. Large changes are observed in the modulus with the attrition of the black. Hot milling treatment accentuates these changes. The decrease of modulus with the logarithm of the strainwork is shown to be sigmoidal in form. When the modulus is normalized between, G_0, the shear modulus at very low strains and, G_∞, the shear modulus at high strains, the resulting plots with respect to strainwork are independent of the concentration of the black and the condition of the vulcanizate.

Résumé

On a étudié dans un large domaine de tension le module dynamique et l'angle de perte de vulcanisats butyliques contenant du charbon de bois (HAF) normal et pulvérisé. Le module varie fortement avec le degré de pulvérisation du charbon de bois. Un broyage à chaud accentue ces variations. La diminution du module en fonction du logarithme du travail de tension présente une allure sigmoïde. Lorsqu'on normalise le module entre G_0, c'est à dire le module de cisaillement pour de très faibles tensions et G_∞, c'est à dire le module à de très fortes tensions, les courbes en fonction du travail de tension qui en résultent sont indépendantes de la concentration en charbon de bois et des conditions de vulcanisation.

Zusammenfassung

Der dynamische Modul und der Verlustwinkel von Butylvulkanisaten mit normalem und abgeriebenem Russ (HAF) wurden in einem weiten Bereich der Verformungsamplitude untersucht. Mit der Zerreibung des Russes traten grosse Moduländerungen auf. Heissmahlung verstärkt diese Änderungen. Die Abnahme des Moduls mit dem Logarithmus der Verformungsarbeit hat *s*-Kurvengestalt. Bei Normierung des Moduls zwischen G_0, dem Schubmodul bei sehr kleiner Verformung, und G_∞, dem Schubmodul bei hoher Verformung ergeben sich Diagramme, in denen die Verformungsarbeit unabhängig von der Russkonzentration und der Vulkanisationsbedingung ist.

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