

Dynamic Properties of Heat-Treated Butyl Vulcanizates

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INTRODUCTION

It was early recognized that the chain structure of butyl polymers would give rise to a hindered motion that would manifest itself as hysteresis. For instance, Dillon et al.¹ showed that at room temperature butyl rubber was more hysteretic than other materials for both pure gum and compounded stocks. It is also well known that the presence of fillers in an elastomer increases hysteretic properties.²

An important contribution to the literature was made when Gessler³ showed that when butyl was milled with carbon black at high temperatures the contribution of the black to internal friction was much reduced. Working with Ford,⁴ Gessler has shown that this effect could be greatly accelerated by the presence of *p*-dinitrosobenzene during the milling process. Subsequently, other efficient promoters were developed.

The effect of heat treatment in butyl was also discussed by Leeper and his associates.⁵ Buckley⁶ showed that the general durability of butyl tires on severe overload and high-speed wheel tests was greatly improved by the heat treatment, and almost invariably this improvement was accompanied by a major decrease in heat build-up.

Earlier papers by the author⁷ have discussed the structure changes involved in straining, but no study had been made of the effect on these changes of chemically assisted heat treatment. This paper discusses the changes in modulus and hysteresis that occur with straining and with the heat treatment, and investigates these effects in the strain regions which are important in the use of tires and antivibration mountings.

EXPERIMENTAL

The experiments were carried out with the Shawbury dynamic tester, which, together with the type of jig used, has previously been described.⁸ All the dynamic tests were made in shear at the lowest strain obtainable before increasing the strain incrementally to the maximum. This sequence ensured that the rubber had not been overstrained before a particular test, as the dynamic properties of filler-loaded vulcanizates are very sensitive to prior treatment.

The actual measurements made were of the phase angle and of the oscillatory force produced by the sinusoidal deformation. For the very low strains the strain response to a known sinusoidal force was measured. The ratio of stress to strain gave the figure for the modulus, $G^*(\omega) = (G'^2 + G''^2)^{1/2}$, where G' and G'' are the in-phase and out-of-phase components of the components of the complex shear modulus $G^* = G' + iG''$. For convenience, the symbol G will be used.

The compounds used for the investigation were made by adding a high abrasion furnace (HAF) black to a butyl rubber together with the other necessary ingredients, except the sulfur. The masterbatch stock thus made was divided into two parts, the promoting reagent (*N*-methyl-*N*,4-dinitrosoaniline) being added to one which was then heated in a closed mold under pressure for 60 minutes at 120°C., after which it was cooled. Compounding of both parts was then completed by further milling of each with the addition of sulfur, and test pieces 1 in. long and 1/2 in. diameter were molded from each of the two types of compound. These are referred to as "heat-treated" and "normal" in the rest of the text, the presence of the promoter in the heat-treated compound being understood.

RESULTS

Modulus Measurements

Figure 1 shows the shear modulus plotted against the strain amplitude of test for butyl vulcanizates containing up to 23% of HAF black, and Figure 2 continues the plot up to 38.6% by volume.

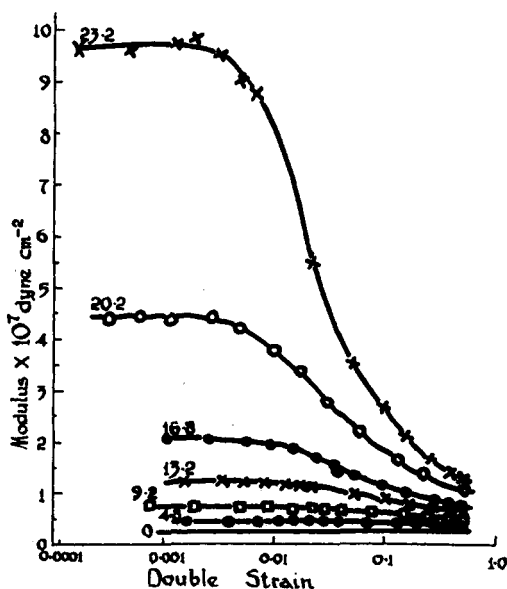


Fig. 1. Variation of shear-modulus G' with strain amplitude (normal compounds).

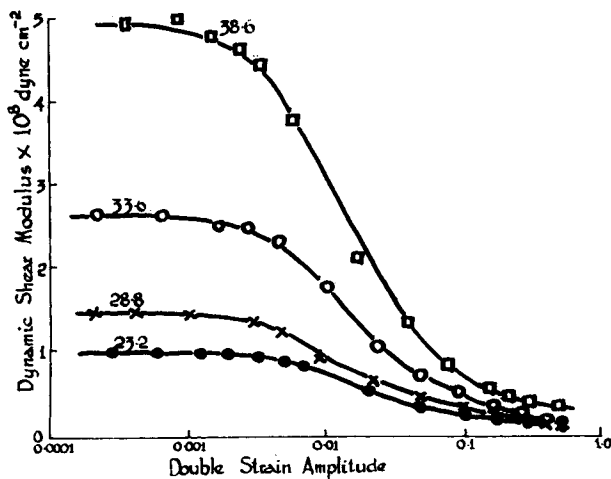


Fig. 2. Variation of shear-modulus G' with strain amplitude (normal compounds).

The strain amplitude given both here and later refers to the total excursion of the deformation and is sometimes known as the double strain. The experimental plots in Figures 1 and 2 show that the curve obtained when the shear modulus is plotted against strain is sigmoidal and at low and high strains appears to approach a constant modulus value. It is also apparent that considerable changes in modulus occur at intermediate strains to which rubber articles are subjected in service. Figure 3 shows some results, corresponding to Figure 1, for heat-treated vulcanizates and a similar shift can be shown for results corresponding to Figure 2. It is quite apparent that there is a drastic change in the properties of the heat-treated vulcanizate as compared with the normal vulcanizate, as is emphasized when the results for one normal and its corresponding heat-treated vulcanizate are plotted together (Fig. 4).

Phase Angle Measurements

Figures 5 and 6 show the phase angle δ plotted against the strain amplitude for the same vulcanizates. It is seen that at low strains the phase angles of all vulcanizates are low and constant and, although there is an increase in phase angle with increasing carbon black content, it is small compared with the changes that occur at higher strains. At higher strains the phase angle increases with increasing strain and passes through a maximum. The greater the concentration of carbon black the greater the phase angle at any given strain.

That there is a close connection between the change in modulus shown in Figures 1 and 2 and the change in phase angle shown in Figures 5 and 6 is obvious, and can be seen clearly in Figure 4, for the reduction in modulus which occurs after heat treatment is accompanied by a reduction of phase angle.

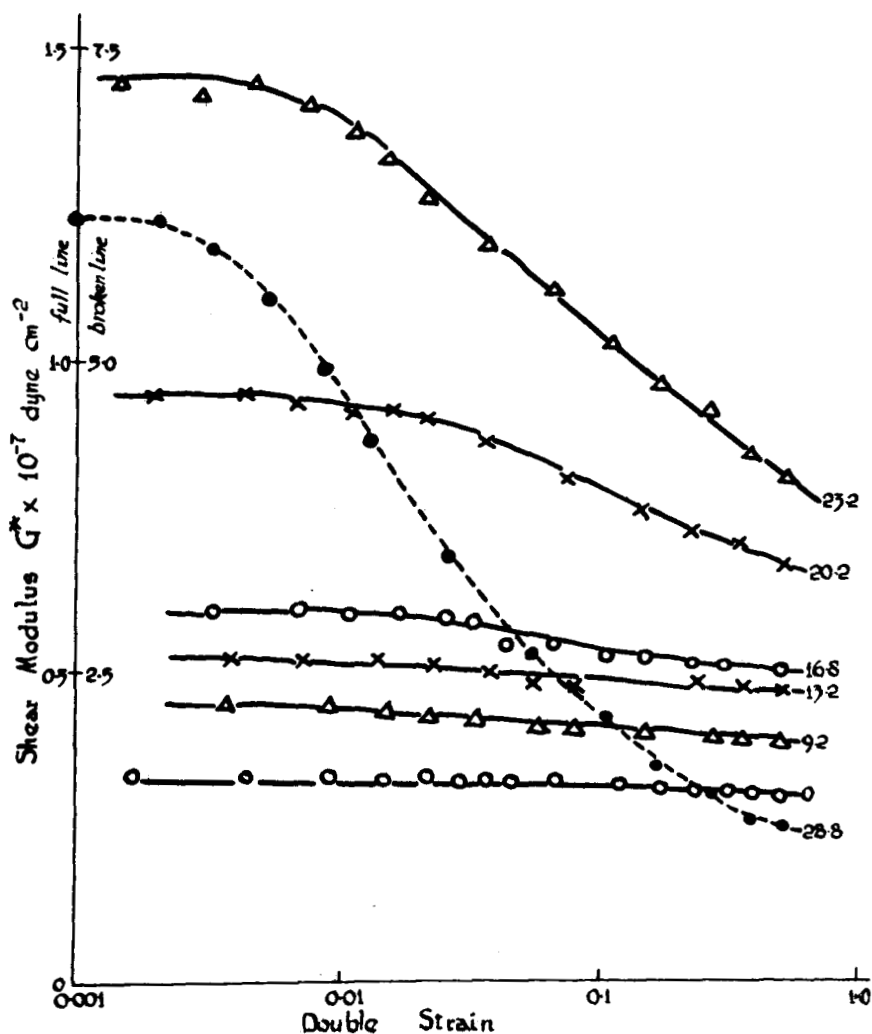


Fig. 3. Variation of shear-modulus G'' with strain amplitude (heat-treated compound).

G'' Measurements

Figures 7 and 8 shows the G'' data for the normal butyl vulcanizates. It is quite apparent that G'' shows a maximum and thus explains why some workers have noticed a G'' rising with straining and others a G'' decreasing with strain.⁸⁻¹¹

Figure 9 shows the G'' results for the heat-treated butyl vulcanizates, and here indeed the differences between the normal and heat-treated rubbers become very apparent, for G'' is approximately constant and very much lower than the G'' of normal vulcanizates.

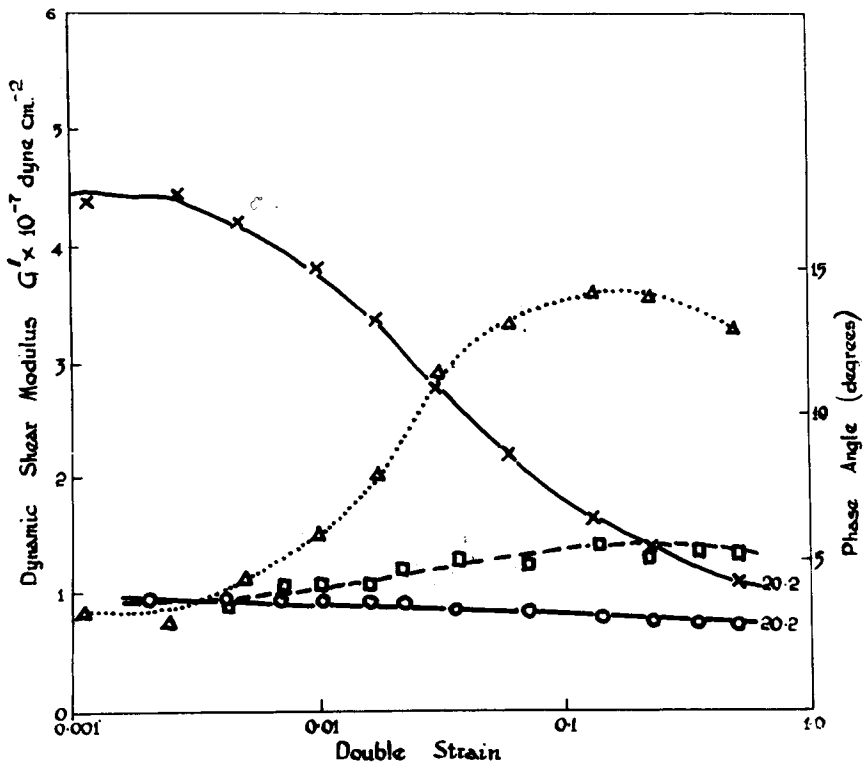


Fig. 4. Comparison of G' and δ for a normal and a heat-treated compound.

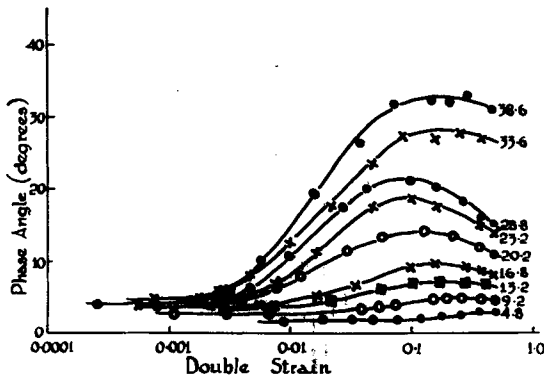


Fig. 5. Variation of phase angle with strain amplitude (normal compound).

Swelling and Tensile Measurements

It has been thought that the heat treatment process tends to form more carbon-polymer linkages.³ However, swelling measurements show little or no difference between normal and heat-treated rubbers. Indeed, the

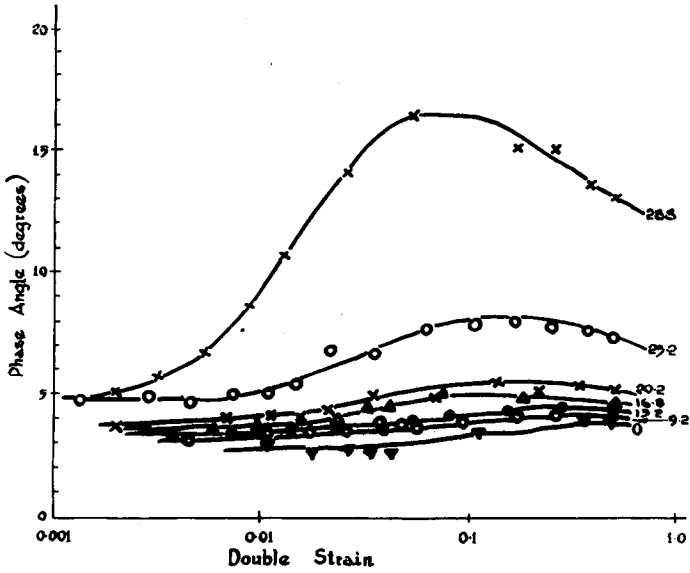


Fig. 6. Variation of phase angle with strain amplitude (heat-treated compound).

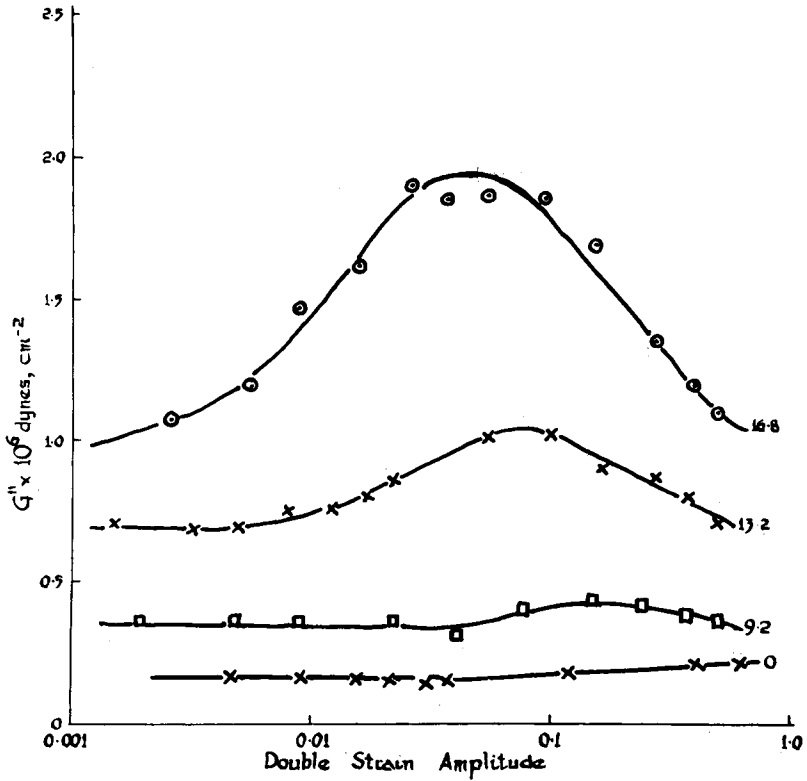


Fig. 7. Variation of G'' , out-of-phase modulus, with strain amplitude (normal compound).

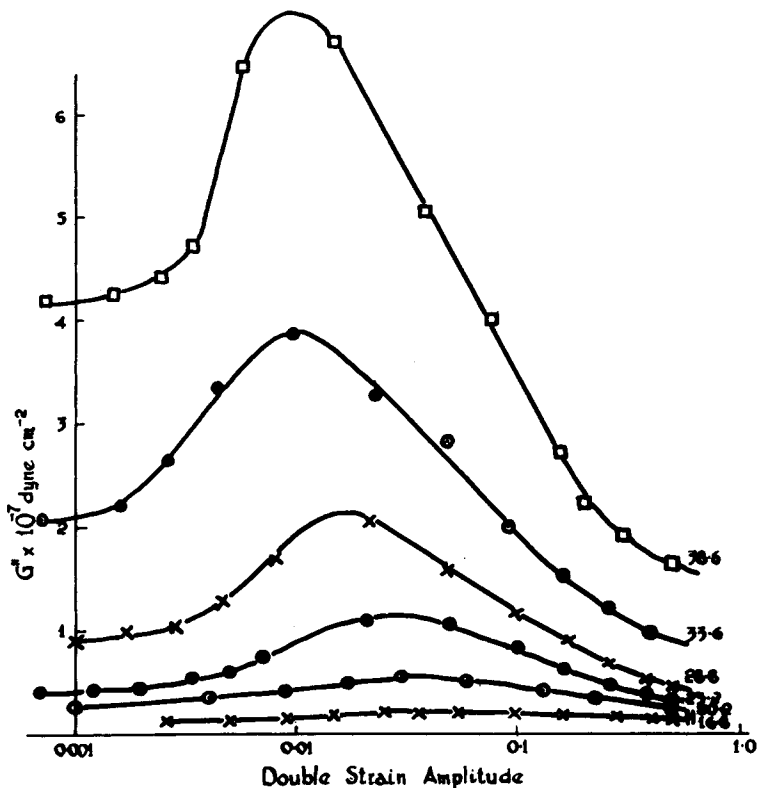


Fig. 8. Variation of G'' , out-of-phase modulus, with strain amplitude (normal compound).

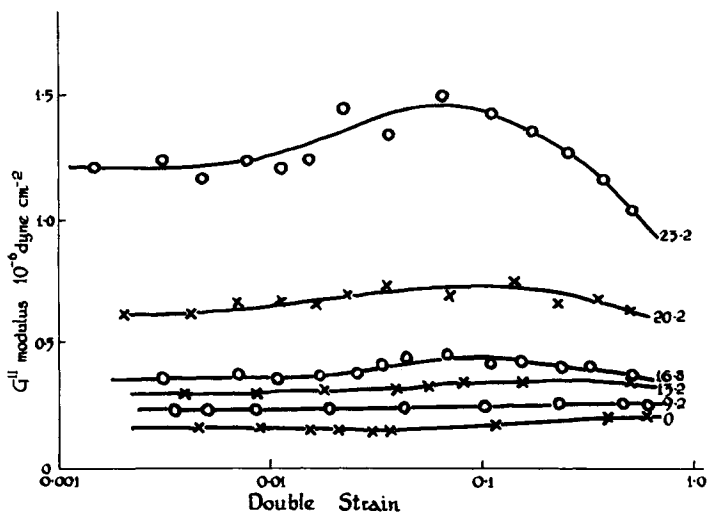


Fig. 9a. Variation of G'' , out-of-phase modulus, with strain amplitude (heat-treated compound).

pure gum heat-treated vulcanizate actually shows a slightly lower effective crosslinking than the normal vulcanizate. The percentage volume increases on swelling are given in Table I.

TABLE I
Volume Swelling Ratios, Per Cent

Volume of HAF, %	Values quoted after 14 days' swelling (equilibrium values), %	
	Normal	Heat-treated
0	188	192
9.2	178	184
13.2	163	166
16.8	150	152
20.2	139	141
23.2	129	131
28.8	121	120
33.6	112	113
38.8	108	108

Following the line of thought advanced in earlier papers,⁷ these similarities would imply that the curves of modulus against strain should approach each other at high strain if strong linkages alone survive straining. This appears to be a possibility, from the nature of the curves shown in Figure 4. It has been argued that the weak forces holding particles of the filler together in cohesive pigment structures are replaced by strong forces that link the polymer and the black much more permanently in the resulting

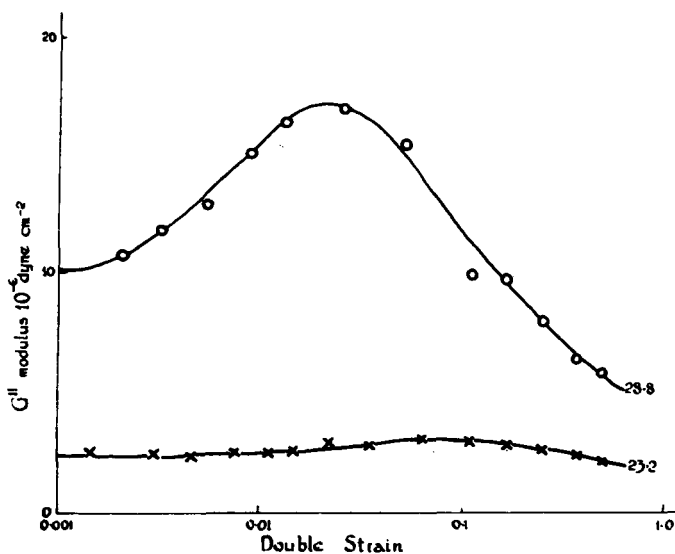


Fig. 9b. Variation of G'' , out-of-phase modulus, with strain amplitude (heat-treated compound).

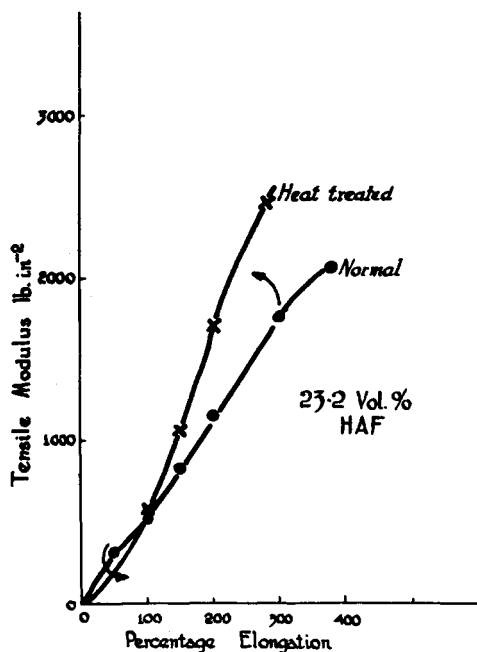


Fig. 10. Comparison of the tensile curves of a normal and a heat-treated compound.

TABLE II
Tensile Properties of Normal and Heat-Treated Vulcanizates

Volume HAF, % ^a	Tensile modulus, lb.-in. ⁻² , at % elong.					Tensile strength, lb.-in. ⁻²	Elong. at break, %
	50	100	150	200	300		
0 H	60	120	210	310	510	970	400
N	70	100	160	240	450	1000	430
9.2 H	80	160	280	450	1060	1690	400
N	80	130	210	310	650	1670	500
13.2 H	100	180	370	700	1580	2280	400
N	110	210	310	490	850	2280	550
16.8 H	140	290	630	1110	2070	2690	370
N	170	280	460	640	1450	2210	470
20.2 H	180	410	830	1390	1730	2640	350
N	200	370	590	920	1500	1950	400
23.2 H	230	590	1050	1710		2460	280
N	300	520	830	1150	1770	2040	380
28.8 H	370	880	1470	1910		2090	240
N	390	800	1270	1610	1920	2050	350
33.6 H	590	1050	1280			1320	160
N	630	1100	1310	1570		1550	200
38.8 H	710	800				800	100
N	830	990				1090	120

^a H, heat-treated vulcanizate; N, normal vulcanizate.

network. The swelling measurements and the asymptotic approach of the normal and heat-treated curves in Figure 4 suggest that the weak linkages are removed by heat treatment, but there remains the *same number of* strong linkages in both cases, giving a modulus figure referred to as G_{∞} in the earlier papers.

The heat treatment of butyl produces a shift in the tensile stress-strain curve. Figure 10 shows, for instance, the typical properties of normal and heat-treated butyl vulcanizates. At the higher strains, the heat-treated butyl has a higher stress than the normal.

Table II gives the tensile modulus values for the normal and heat-treated vulcanizates. From this it can be seen that at low strains the heat-treated rubber is softer than the normal, but is harder at the higher strains. There is a fractional improvement in the tensile strength of the material with heat treatment for the lower concentrations of filler.

ELECTRON MICROSCOPE EVIDENCE

Figures 11 and 12 are photomicrographs of a carbon black-loaded butyl vulcanizate (16.8 vol.-% HAF), Figure 11 is the normal and Figure 12 the heat treated. The photographs are replicas of torn surfaces taken by a technique similar to that used by Andrews and Walsh¹² and are magnified 10,000 times.

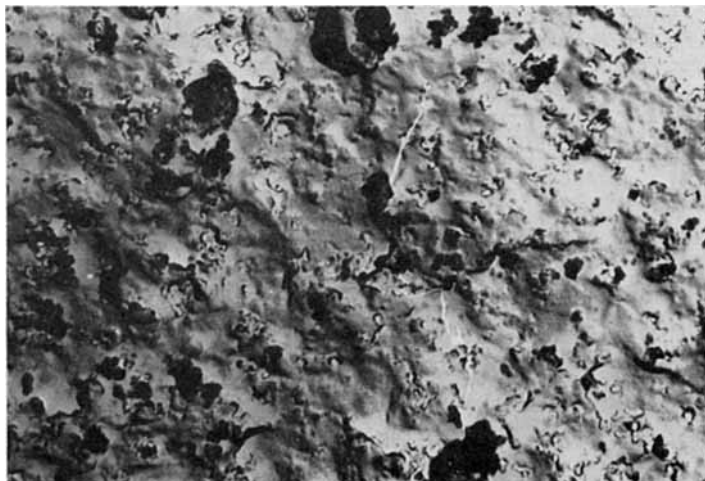


Fig. 11. Electron microscope photograph for the 16.8% volume HAF (normal compound).

In each case a piece of rubber was torn steadily by hand, and the torn piece used to form a heavy first-stage gelatin replica. This replica was stripped from the rubber, and the replica surface was then coated with a thin layer of evaporated carbon which was then metal-shadowed obliquely

with a gold-palladium alloy. The gelatin was then removed by trypsin in the final stage.

Particles of carbon black appear in the image of such a replica in three different ways. Some are extracted by the gelatin from the rubber surface, then remain embedded in the final replica but do not give metal shadows because they are embedded in the reverse side from that shadowed. Particles that were retained in one or other of the torn rubber surfaces, and were not removed by the gelatin, appear as shadowed bumps and hollows in the final replica.



Fig. 12. Electron microscope photograph for the 16.8% volume HAF (heat-treated compound).

The photomicrographs of the normal and heat-treated rubbers then differ in two ways. One difference is immediately obvious: more particles are extracted from the normal rubber by the gelatin than from the heat treated. The other difference is that among all the particles, extracted or not, there is more aggregation in the normal than in the heat-treated vulcanizate.

It is interesting to note also that both the rubbers gave very high dispersions according to the Dunlop technique.¹³ The optical dispersion did, however, show more large agglomerates for the heat-treated than for the normal vulcanizate. The agglomerates in the heat-treated vulcanizate had a brown tinge which indicated that the agglomerate was not that of dry black, but was a rubber-black complex. It is probable, then, that the tear surface used for the electron microscope photographs were obtained by a tear which avoided these regions of high black density. The two conclusions from optical and electron microscopy are therefore apparently contradictory, unless one concludes that "structure" effects disappear when some of the black is concentrated in regions of high density in a wet rubber-carbon black complex and that the rest of the black, in the regions of low black density, are effectively microdispersed.

CONCLUSIONS

Heat treatment, when it is adequately performed, can reduce and, in some cases, almost entirely eliminate "structure" effects in carbon black-loaded vulcanizates, although swelling measurements indicate that G_{∞} is unaltered.

The additional hysteresis, beyond that expected from hydrodynamic and steric effects, of a well-dispersed black is entirely connected with the breakdown of structure. This conclusion is of practical importance as it shows that, in order to lower the damping and heat build-up tendencies of carbon black-loaded stocks, it is necessary to eliminate "structure." This elimination is adequately carried out with moderate loadings of HAF in butyl rubber by heat-treating the stock with *N*-methyl-*N*,4-dinitrosoaniline. The effect of lowered structure appears in the conventional tensile test used in rubber technology as a lowering of the modulus at low strains but a raising of the modulus at high strains with heat treatment.

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Synopsis

Heat treatment of butyl rubber containing carbon black can considerably reduce "structure effects" in the dynamic properties of the vulcanizate, although swelling measurements indicate that G_{∞} the shear modulus at very high amplitudes is unaltered. This paper compares the G' , G'' and phase angle δ changes that occur with the amplitude of oscillation for both a normal butyl rubber containing HAF black and a vulcanizate of the same composition but which has been subjected to an additional heat-treatment process with *N*-methyl-*N*,4-dinitrosoaniline.

Résumé

Le traitement à chaud du caoutchouc butylique contenant du noir de carbone, peut suivant les propriétés dynamiques du vulcanisat, réduire considérablement les effets de

structure, bien que des mesures de gonflement indiquent que G_{∞} , le module de cisaillement à haute amplitude, est altéré. Ce travail comprend G' et G'' et les changements de l'angle de phase δ qui se produisent avec l'amplitude de l'oscillation, pour deux caoutchoucs butyliques normaux: ceux-ci contenant du noir HAF et un vulcanisat de la même composition mais qui a été soumis dans un processus à chaud par traitement additionnel à la *N*-méthyl-*N*-4-dinitrosoaniline.

Zusammenfassung

Hitzebehandlung von Butylkautschuk mit einem Gehalt an Russ kann die "Struktureinflüsse" bei den dynamischen Eigenschaften des Vulkanisats beträchtlich herabsetzen, obgleich Quellungsmessungen erkennen lassen, dass G_{∞} , der Schubmodul bei sehr hohen Amplituden, unverändert bleibt. In der vorliegenden Mitteilung werden Änderungen von G' und G'' und solche des Phasenwinkels δ verglichen, die mit der Schwingungsamplitude sowohl bei einem normalen, mit HAF-Russ gefüllten Butylkautschuk als auch bei einem Vulkanisat der gleichen Zusammensetzung auftreten, das aber einer zusätzlichen Hitzebehandlung bei Gegenwart von *N*-Methyl-*N*-4-dinitrosoanilin unterworfen worden war.

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