Effect of Dispersion on the Dynamic Properties of Filler-Loaded Rubbers

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Synopsis

A study has been made of the effect of increased time of mixing carbon black in rubber on the dynamic properties of the carbon black–rubber vulcanizates.   Increased time of mixing reduces the dynamic modulus and dynamic viscosity as well as the phase angle at moderate amplitudes of oscillation.   The changes in dynamic properties with mixing time are shown to be associated with the dispersion of the carbon black.

Introduction

Recent studies of the dynamic properties of filler-loaded rubbers have emphasized the relationship between a three-dimensional carbon black network and the dynamic modulus and viscosity changes with the amplitude of oscillation, therefore it is to be expected that dynamic measurements should sensitively reflect the degree of dispersion of the carbon black fillers.   This paper attempts to ascertain how the degree of dispersion does effect the dynamic properties.

It has been generally recognized that to achieve a high degree of reinforcement, adequate dispersion is necessary;   it is therefore rather surprising to note that there have been few published studies in which the rubber properties were actually studied systematically as a function of the degree of dispersion.   However, a recent paper by Boonstra and Medalia[1] discusses the results of a systematic study of how the degree of the dispersion as measured by microscopic observation and counting methods correlates with mechanical behavior.   It is the intention of this paper to study and extend a particular aspect of this work, that pertaining to dynamic properties, a stage further.

In order to keep the study in line with the work of Boonstra and Medalia, similar mixing formulations were used;   therefore the results presented in this paper should be considered in conjunction with those on other properties presented by the above authors.

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Compounding Procedures

Dannenberg[2] showed that an extremely short mixing time suffices for the development of reasonably good mechanical properties; thus with HAF black in natural rubber, 1.1 min. at 77 rpm in a laboratory model (Model B) Banbury gave properties indicative of a good dispersion, while with HAF or EPC black in cold SBR 1.25 min. was sufficient. Boonstra and Medalia[1] carried out a similar study with ISAF black (Vulcan 6) in SBR-1712. An "upside-down" mix was used, i.e., the black and all the powdered ingredients were placed in the Banbury and the SBR was added on top. The ram was lowered and the batch was run for the necessary time, then dumped and sheeted out by three passes on the mill without banding. The Banbury starting temperature and speed were 120°F. and 77 rpm, respectively. The compounds were cured without remill. An exactly similar procedure was adopted for the single-stage mixing discussed in this paper.

The designations given to the compounds are shown in Table I.

TABLE I

Mix designation	Time of mixing, min.
A	1.5
B	2.0
C	2.5
D	3.0
E	4.0
F	8.0
G	16.0
H	Two-stage mix

TABLE II
Two-Stage Mixing Formulation with All Black Added in First Stage

	Parts
Stage I[a]	
SBR-1712	100.0
Vulcan 6 (ISAF)	69.0
Stearic acid	1.5
Zinc oxide	3.0
Santoflex AW	1.0
	174.5
Stage II[b]	
Masterbatch from stage I	174.5
SBR 1712	37.5
Sulfur	2.0
CBS	1.1

[a] Stage I: 0 min., 1/2 black, ZnO, stearic acid, etc., polymer on top; 2 min., rest of black; 4 min., dump and sheet out.

[b] Stage II: 0 min., Masterbatch and rubber, sulfur and CBS. 2 min., dump pass through mill 3 times, no remill.

Boonstra and Medalia have shown that a two-stage mix can give excellent dispersion owing to the high viscosity of the first stage, and in fact this procedure has been recommended[3] for dispersion of hard-to-disperse blacks of low structure.   On the other hand, it is known from latex masterbatching studies that rubber mixtures of too high a loading are very difficult to dilute with more rubber.[4]   Boonstra and Medalia, however, studied carefully the effect of too high a loading of black on a two-stage mix, and demonstrated very convincingly the disastrous effect on rubber properties which can be caused by agglomerates of large size.   For a 69 phr black loading in masterbatch the dispersion was excellent, loadings of 95 phr or more gave poor results.   The study discussed in this paper is concerned with a 50 phr final mix, so therefore a two-stage mix process was adopted. Stock was then prepared by a two-stage high viscosity mix with 69 phr in the first stage.   The details of the two-stage process are given in Table II.

Experimental

Since it was desired to make observations particularly at small deformations as well as to apply moderately large strains, sinusoidal straining by shear stress was selected as the experimental procedure.

Vulcanized test specimens as cylinders 1.6 cm. in diameter and 2.54 cm. in length were prepared in a multicavity mold lubricated with silicone oil. The cured specimens were removed from the mold and handled with the minimum deforming.

The sinusoidal strain tester has been described previously.[5]   The test specimens were bonded one on either side to a central metal plate which applied the oscillating force and to restraining static plates.[6,7]   It was convenient[6] to apply a chosen stress and record the strain produced for displacements of 0.1–100 μ and to select the strain and observe the stress of greater displacements up to 1.25 cm.   The frequency was 0.1 cycle/sec.

After setting up and resting overnight, the specimens were tested first at the lowest strains and measurements continued to successively higher strains.   The stress–strain readings became steady within the first few cycles and were reproducible after a resting period subsequent to deformation within the range covered.   The experimental measurements were of the maximum straining force, the resulting amplitude of strain and the phase angle between the sinusoidal stress and strain oscillation.[5]   From these measurements, the components of the modulus in-phase with the strain G', and out-of-phase with the strain G'', were readily calculated from the relationships $\tan \delta = G''/G'$ and $G^* = G' + iG''$, where δ is the phase angle in degrees and G^* is the complex shear modulus.

Dynamic Results

Figure 1 shows the variation in G' for the range of rubbers studied. There is obviously a systematic decrease in the dynamic shear modulus with increased mixing time, the results for the two-stage process (compound H)
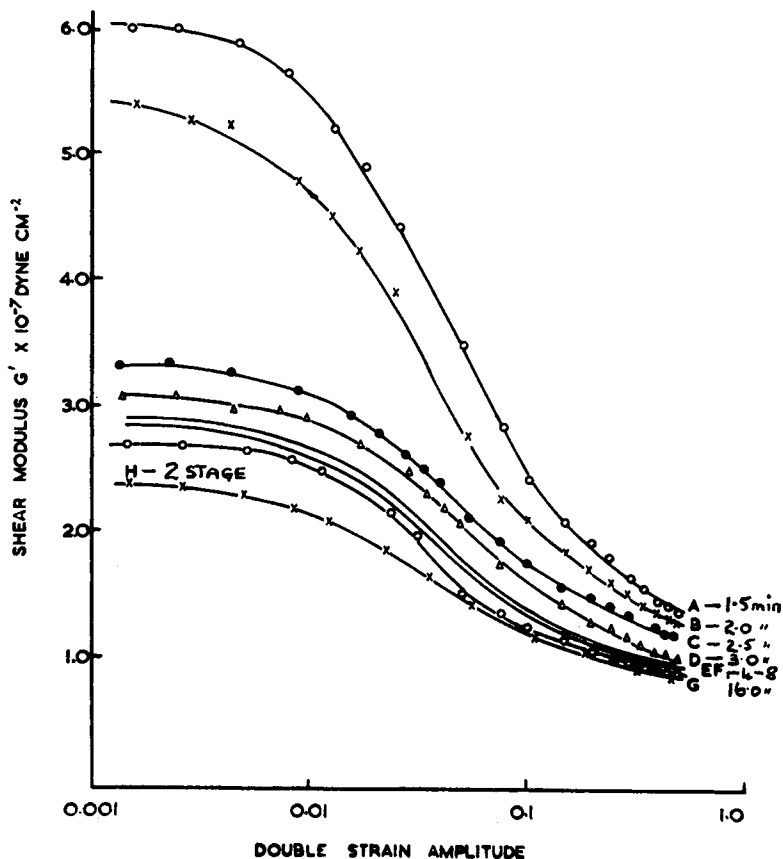
Fig. 1. Variation of G' with the dynamic amplitude of straining (double amplitude).

are lower than for the rubbers obtained by a continuous mixing by a single-stage process (compounds A to G).

Figure 2 shows the large change in the out-of-phase modulus G'' that occurs with increased mixing time. Again, the two-stage process (compound H) gives a lower result than even the 16-min. extended mixing time by the single-stage process (compound G).

Figure 3 shows the change of phase angle that occurs with the mixing time, and the systematic decrease in the phase angles at high amplitudes with increased mixing time is apparent. The two-stage process shows lower phase angle values at high strains as compared to the single-stage mixing results.

Some micrographs of section of compounds mixed between 1.5 and 8 min. were obtained. The difference in the optical dispersion of the stocks was very apparent. Very little evidence of any agglomerates was seen in the 8-min. compound which compares markedly with a short-time mix such as the 1.5-min. mix, where the black was seen to occur in streaks. The
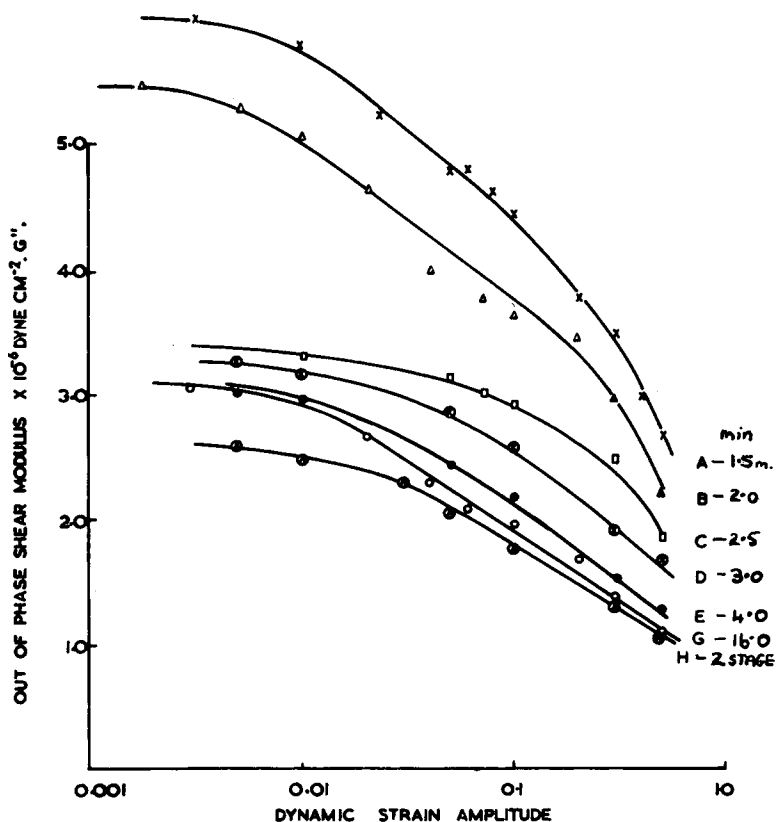
Fig. 2. Variation of the out-of-phase modulus G'' with the dynamic amplitude of straining (double amplitude).

1.5- and 2.5-min. mixes would be rated as very poor dispersions and the 8-min. mix as very good. The two-stage mix gave very similar results to the 8-min. mix. Boonstra and Medalia[1] have published some excellent

TABLE III
Tensile Stress, Strength, and Elongation Results

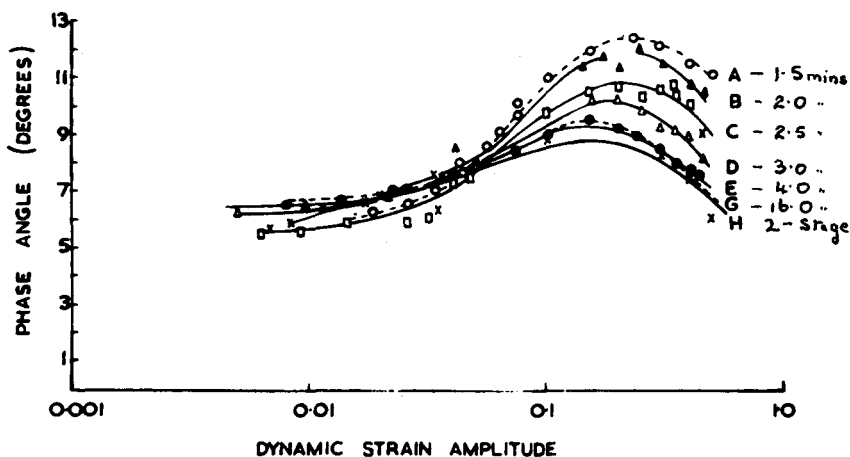| Mix desig- nation	Mixing time, min.	Stress at various elongations, psi				Tensile strength, psi	Elongation at break, %
		50%	100%	200%	300%		
A	1	360	640	1000		1300	250
B	2	300	520	1250		1840	300
C	2.5	250	480	1080	1950	2400	360
D	3.0	220	350	850	1500	2350	480
E	4.0	200	280	830	1470	3000	480
F	8.0	150	260	800	1450	3000	500
G	16.0	150	260	760	1450	3400	540
H	Two-stage mix	150	260	770	1500	3200	520

Fig. 3. Variation of phase angle δ with the dynamic amplitude of straining (double amplitude).

color photographs of exactly similar compounds obtained with exactly similar mixing schedules, and the reader is referred to their publication[1] to confirm the nature of the change of optical dispersions with increased mixing time.

Tensile Measurements

Previous studies on the dynamic properties of filler-loaded rubbers indicate that a decrease in G' with the amplitude of oscillation is paralleled with a decrease in the low extension modulus, even though the high extension modulus increases. The effect of increased mixing time produces a similar effect, as a drastic decrease is apparent in the tensile modulus values at low strain. Table III gives the relevant details, showing the effect of mixing in the Banbury on the tensile modulus. These results parallel the results of a similar study by Boonstra and Medalia.[1] Figure 4 is a graphical interpretation of the stress elongation results for some of the compounds and shows up clearly the effect on these properties of the increased mixing time. An inspection of the tensile measurement for compounds G and H in Table III reveals that the 16-min. Banbury compound yields very similar results to the two-stage mixing compound (H).

Normalization of the Modulus Data

The various empirical relationships suggested by different authors for the dependence of the dynamic modulus on the strain amplitude have been discussed,[7,9] 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 modulus breakdown curves. The method proposed here involves "normalizing"
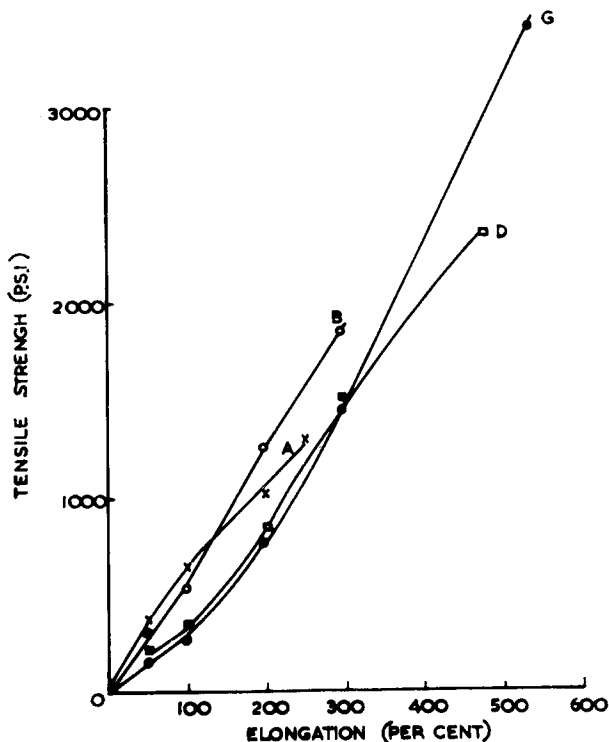
Fig. 4. Tensile stress–strain curves for compounds A, B, D, and G.

the data between the limits at very high and very low strains. Consider the shear modulus G'; let G_0 represent its value at strains approaching zero, and G_∞ its value at very high strains, where there is no further change in G' with increase of strain. The normalized modulus is given by

$$Z = (G' - G_\infty)/(G_0 - G_\infty)$$

and is shown in Figure 5 plotted on probability paper against the energy of oscillation or strainwork for three of the rubbers (B, D, and G) as typical examples of this type of plot. The G_0 and G_∞ values used in this normalization of these rubbers and the other compounds are given in Table IV. It will be appreciated that there is some, but very small latitude in fixing a value for G_∞, but the variation is too small to influence the position of the plot on probability paper.

It has been shown in previous papers[8–10] that neither stress nor strain is the independent parameter which governs the variation of the dynamic modulus with strain, but the product of stress and strain, which will be referred to as strain work and is used in preference.

It is useful to consider the strain work corresponding to $Z = 0.5$, and Table IV lists these values for the different rubbers. It is apparent that these values are very similar, although there is a small increase in the value
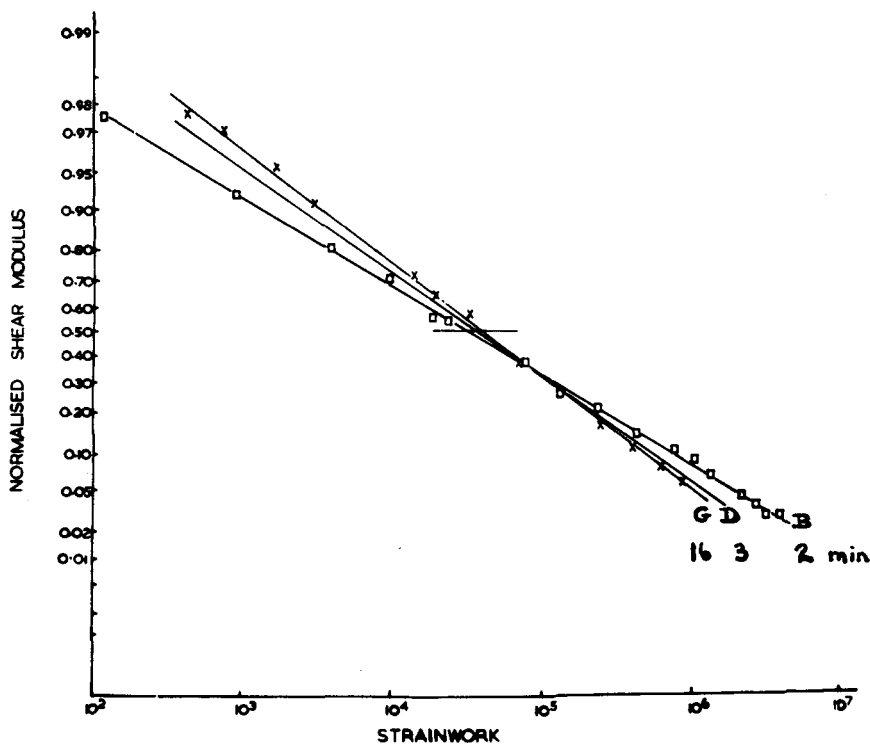
Fig. 5. Normalized modulus Z vs. strain work for compounds B, D, and G. (Strain work = double stress amplitude $\times$ double strain amplitude of test, in dyne/cm.^{2}).

with the degree of dispersion. These values are very similar to values quoted in the literature from previous studies.[8,10]

The linearity of the plot of the normalized modulus against the logarithm of the strain work implies a relationship of the type:

$$Z = (G' - G_\infty)/(G_0 - G_\infty)$$

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

where Z is the normalized modulus and $x = \log X$, where X is the strain work. The strain work is the normalizing measure, which has a normally distributed tolerance; μ is the median effective strain work. As the normalizing transformation is logarithmic, μ is $\log X_{0.50}$, where $X_{0.50}$ is the value of the strain work at $Z = 0.5$; it can also be shown that

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

Therefore the difference in log units between the strain work at $Z = 0.10$ and $Z = 0.90$ is directly related to σ and therefore to σ^2. Table IV lists the spread or "width" of the normalized curves in log units, as the difference in log units between $Z = 0.10$ and 0.90. It can be seen that the spread

TABLE IV
G_0, G_∞, Strain Work, and "Width" Values

Mix designa-tion	Time of mixing, min.	G_0 $\times$ 10^{-7}, dyne/cm.^{2}	G_∞ $\times$ 10^{-7}, dyne/cm.^{2}	"Width," log-arithmic units	Strain work $\times$ 10^{-4}, dyne/cm.^{2} at $Z = 0.5$
A	1.5	6.08	1.0	2.9	3.5
B	2.0	5.50	1.0	2.9	3.5
C	2.5	3.33	0.95	2.8	3.5
D	3.0	3.12	0.95	2.5	3.9
E	4.0	2.92	0.95	2.5	3.9
F	8.0	2.86	0.90	2.3	3.9
G	16.0	2.70	0.90	2.25	3.9
H	Two-stage mix	2.40	0.90	2.3	3.9

decreases with increasing time of mixing, i.e., increasing dispersion. The values quoted are again very similar to previously published values.[8,10]

It must be concluded that there is a decrease in the spread of the modulus changes, although the change is small as is also the effect of increased mixing time on the medium effective strain work μ, or the strain work at $Z = 0.5$. It is to be expected that the effect of increasing mixing time would tend to reduce the contribution to the modulus enhancement at very low strains by reducing the very weak structures. This reduction in the amount of the weak structure would have the effect of reducing the spread of the modulus changes and increasing the mean energy required to break down the remaining structure or agglomerates.

The similarity of the values of G_∞ is interesting: they are indeed very similar, although there is an apparent decrease with increased mixing time. The differences between G_∞, for instance, for compound A and compound G is really very small compared to the difference in the G_0 values. It was earlier assumed that G_∞ could be regarded as a compounded function of two parameters; (1) the modulus of the rubber network and (2) the effect of particles acting in a hydrodynamic sense. As G_∞ is similar, then we

TABLE V
Percentage Swelling of Compounds A to H

Mix designation	. Linear swelling, %
A	40
B	40
C	47
D	47
E	53
F	53
G	53
H	53

would expect no difference on swelling in a solvent. Table V lists the linear swelling in n-decane after 48 hr.

This was unexpected, and there is obviously an effect of the degree of dispersion on these results; in fact, if the usual analysis of swelling was carried out in an attempt to evaluate the effective degree of crosslink formation, it would predict higher crosslinking for compound A than for compound G. This is highly improbable but must reflect some restrictive effect on swelling of agglomerate formations which are probably due to the shape factor effects of the agglomerate. It is thought unlikely that the small difference in G_∞ can be attributed to extra linkages between the rubber and black in the case of compounds A and G, in spite of the evidence of reduced swelling, but more probably reflects the change in shape factor of the agglomerates which must alter considerably with the time of mixing, if the evidence suggested by the micrographs on the agglomerate pattern is to be believed. Boonstra and Medalia measured, in an exactly similar experimental compound mixed by an identical schedule, the percentage bound rubber content, and these values are quoted in Table VI.

TABLE VI
Bound Ratio and Swelling Ratios as Related to Mixing Time and $(G_0 - G_\infty)$

Mixing time, min.	Bound rubber, %[a]	Swelling ratio of bound rubber	$(G_0 - G_\infty)$ $\times 10^{-7}$, dyne/cm.^{2} [b]
1.0	16.2	30.9	—
1.5	16.4	31.5	5.08
2.0	18.3	27.6	4.50
3.0	22.2	30.9	3.17
4.0	27.8	27.9	2.97
8.0	30.2	27.2	2.96

[a] Data of Boonstra and Medalia.[1]
[b] From Table IV.

The amount of bound rubber was determined after 23 days after mixing. The data show an increasing amount of bound rubber as the mixing cycle is increased from 1 to 8 min. It is also noted that the amount of solvent in the bound rubber gel is very large (about 30 times the volume of the polymer) and perhaps decreases slightly as the mixing time increases, presumably indicating tighter bound rubber (more crosslinks) at longer mixing times. This, however, would conflict with the crosslink densities derived from swelling measurements or the G_∞ values, which also decrease with increasing mixing time. Alternatively, we can consider that percentage bound rubber is itself a manifestation of dispersion. If this is so, then the greater the bound rubber content, the lower the dynamic modulus and consequently the smaller the dynamic hysteresis. That this might be so, is suggested by Gessler,[12] who shows that as bound rubber in carbon black-filled butyl rubber is increased the dynamic hysteresis decreases, and in fact

he derived a linear relationship between dynamic hysteresis and percentage bound rubber for a whole range of butyl–black vulcanizates. A significant linear relationship exists also between $(G_0 - G_\infty)$ and the percentage bound rubber content quoted in Table VI, and it can be seen that $(G_0 - G_\infty)$ decreases as the percentage bound rubber increases. As the maximum value of G'' is related to $(G_0 - G_\infty)$,[10] then bound rubber content is related to hysteresis in the manner suggested by Gessler.[12] Further work to establish this relationship more firmly is obviously needed.

Discussion

The effect of increased mixing times, i.e., increased dispersion, is to reduce the dynamic modulus, the viscous modulus (out-of-phase shear modulus) and the phase angle at high strains. The change in properties is reflected in a reduction in the value of G_0, although G_∞ remains substantially constant. The median strain work required to cause a 50% reduction in $(G_0 - G_\infty)$ increases with increased mixing time, there is however a reduction in the spread of the modulus changes with increased mixing time.

In parallel with a reduction in $(G_0 - G_\infty)$, there is an enhancement of the ultimate tensile properties; this is accompanied, as has been shown by Boonstra and Medalia, with improvements in permanent set (reduced), heat build-up (reduced), Mooney viscosity (reduced), d.c. resisitivity, (increased), abrasion loss (reduced), cut growth (improved), hardness (reduced), but with tear resistance and specific gravity remaining substantially the same and with an increase in extrusion shrinkage. Similar observations have been noted on the effect of heat treatment of the rubber compound,[11] attrition of the black,[9] or by use of metal soaps to improve dispersion.[8] It must be remarked on, however, that even after prolonged mixing time (compound G) or by a two-stage mixing process (high viscosity mixing), there is still a lot of "structure" (i.e., $G_0 - G_\infty$) remaining, and only by heat treatment of carbon black compounds by means of nitroso compounds[7,8] or by the use of metal soaps for silica compounds,[10] or by attrition[9,11] and hot temperature mixing is it possible to eliminate $(G_0 - G_\infty)$ almost entirely. It is therefore clear, that conventional mixing techniques cannot completely disperse the black. The two-stage process also does not completely disperse the black, although the stage of adequate dispersion, as judged by technological standards, is reached; however, as remarked above, "adequate" dispersion is still not by any means complete microdispersion of the carbon black.

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Résumé

On a. effectué une étude de l'influence de la prolongation de la durée du mélange de noir de carbone au caoutchouc sur les propriétés dynamiques des vulcanisats caoutchouc-noir de carbone.   Une augmentation de la durée de mélange réduit le module dynamique et la viscosité dynamique aussi bien que l'angle de phase aux faibles amplitudes d'oscillation.   On montre que les changements dans les propriétés dynamiques avec la durée du mélange sont associés à la dispersion du noir de carbone.

Zusammenfassung

Eine Untersuchung des Einflusses einer Erhöhung der Mischdauer für Russ in Kautschuk auf die dynamischen Eigenschaften der Russ–Kautschukvulkanisate wurde ausgeführt.   Erhöhte Mischdauer setzt den dynamischen Modul und die dynamische Viskosität sowie den Phasenwinkel bei mässigen Oszillationsamplituden herab.   Die Abhängigkeit der mechanischen Eigenschaften von der Mischdauer steht in Beziehung zur Dispersion des Russes.