

The Strain Dependence of Rubber Viscoelasticity Part II. The Influence of Carbon Black

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In Part I of this series it was shown how variations in the dynamic Young's modulus with extension could be represented by linear relations for gum rubbers in the region of 0 to 100% extension.¹ The present work uses a similar treatment to examine how the viscoelastic behavior of natural rubber within this extension region is affected by the incorporation of two carbon blacks of widely differing colloidal activity. One of these materials, MT black, consists substantially of spherical particles with a mean diameter of about 0.4 microns: electron microscopy of cut surfaces of the black-rubber compound showed that the individual particles were well-dispersed. The finer material, HAF black, has a mean particle diameter of about 0.04 microns but exists in the rubber compound in a flocculated condition with aggregates up to about 0.3 microns in diameter.

The rubber containing the coarse, MT black yielded linear strain relations enabling a direct comparison to be made with the behavior of the gum: the HAF material did not give linear relations for either the dynamic or the equilibrium Young's modulus. To facilitate discussion of this behavior it is desirable to set out more explicitly than in Part I the model underlying the analysis.

Figure 1 shows the model used to formalize the

dependence of dynamic behavior upon extension. The series modulus E_∞ represents the normal Hookean elasticity of a solid. This will be a slowly decreasing function of temperature and probably a slowly increasing function of strain,² but its magnitude will generally be well in excess of 10^{10} dyne/cm.², so that the deformation in this element will be relatively small under conditions where there is an appreciable rubberlike contribution to the elasticity. The rest of the model comprises an equilibrium modulus E_0 in parallel with a number of Maxwellian elements typified by the modulus E_i damped by the series viscosity $\tau_i E_i$, τ_i being the relaxation time of the element.

It is now supposed that the system is stretched to a finite extension ratio λ and allowed to relax at this extension so that E_∞ , E_0 , E_i , and τ_i all take up equilibrium values dependent on λ and, in general, differing from their values in the unstrained state. In the present work the frequency and temperature are such that the dynamic Young's modulus $E^*(=E' + iE'')$ is always much smaller than E_∞ , and under this condition

$$E' = E_0 + \sum_i [\omega^2 \tau_i^2 / (1 + \omega^2 \tau_i^2)] E_i$$

and

$$E'' = \sum_i [\omega \tau_i / (1 + \omega^2 \tau_i^2)] E_i \tag{1}$$

where $\omega/2\pi$ is the frequency and the other variables all relate to the extension ratio λ .

In amorphous viscoelasticity theory the moduli E_0 and E_i are treated as rubberlike moduli, being directly proportional to the absolute temperature and to the density. If it is now assumed that these moduli all have the same strain dependence, viz:

$$\begin{aligned} E_0(\lambda) &= E_0(1)f(\lambda) \\ E_i(\lambda) &= E_i(1)f(\lambda) \text{ for all } i \end{aligned} \tag{2}$$

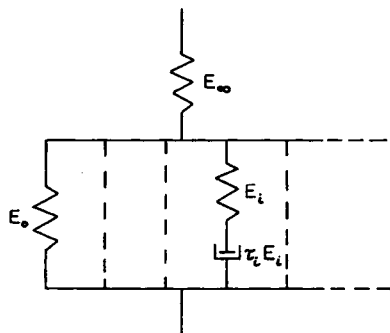


Fig. 1. Equivalent mechanical circuit for stretched rubber.

then the strain dependence of both components of the elastic modulus will also be given by $f(\lambda)$. This function can be obtained directly from the equilibrium modulus E_0 measured at different extensions, or it may be expressed in terms of various empirical stress-strain relations such as that of Mooney³ or that of Martin, Roth, and Stiehler,⁴ in the ranges where these equations are valid. The Mooney equation offers a particularly attractive approach, because it separates the strain dependence into two terms, one deriving from the statistical theory of high elasticity and the other representing departures from that theory: the strain-dependence function in this case is

$$f(\lambda) = (C_1 + F_2 C_2) / 6F_1(C_1 + C_2) \quad (3)$$

where C_1 and C_2 are the Mooney constants (C_1 being the term given by statistical theory) and

$$F_1 = \lambda[2(2\lambda^3 + 1)]$$

and

$$F_2 = (\lambda^3 + 2) / [\lambda(2\lambda^3 + 1)]$$

Using eq. (1) the complex modulus components can be written in the form

$$\begin{aligned} F_1 E' &= C_1' + F_2 C_2' \\ F_1 E'' &= C_1'' + F_2 C_2'' \end{aligned} \quad (4)$$

The C parameters are functions both of the Mooney constants of the elemental moduli and of the relaxation times, thus

$$\begin{aligned} C_1' &= C_{10} + \sum_i [\omega^2 \tau_i^2 / (1 + \omega^2 \tau_i^2)] C_{1i} \\ C_2' &= C_{20} + \sum_i [\omega^2 \tau_i^2 / (1 + \omega^2 \tau_i^2)] C_{2i} \\ C_1'' &= \sum_i [\omega \tau_i / (1 + \omega^2 \tau_i^2)] C_{1i} \\ C_2'' &= \sum_i [\omega \tau_i / (1 + \omega^2 \tau_i^2)] C_{2i} \end{aligned} \quad (5)$$

In the regions where the Mooney strain-energy function is applicable, the results for black-filled rubbers are analyzed in terms of eqs. (4) and (5); otherwise the analysis is based on the more general eqs. (2).

EXPERIMENTAL

From unpublished work by Mullins and Tobin it was expected that a rubber containing the coarser carbon black would show Mooney-type behavior at moderate strains for concentrations of black up

to about 20% by volume. The present test materials were therefore prepared at concentrations just below this value by incorporating 50 parts by weight of carbon black in 100 parts of the natural rubber described in Part I. Taking the density of the coarser (MT) black as 1.9 g./cc. and that of the finer (HAF) black as 2.0 g./cc., analysis of the compounds showed that the volume concentration of black in each material was 18%.

First, the pseudo-equilibrium behavior of the materials was characterized by measurements of their stress-strain relations in simple extension at 20°C. by means of essentially the technique of Gumbrell, Mullins, and Rivlin.⁵ Load increments were added at intervals of 4 min., so that each stress-strain curve took about 2 hr. to complete. Strips of cross section approximately 3 mm. \times 3 mm. were used both for these tests and for the dynamic measurements, and all specimens were conditioned by stretching six times to an extension of 200%, followed by immersion for 2 min. in boiling water. This was intended to bring the materials into a reproducible condition and avoid some of the marked structural hysteresis which Mullins⁶ has shown to be associated with the first stretching of black-filled rubber.

Glass-transition temperatures of the filled rubbers were determined as in Part I from observations of the density-temperature relationships, ethanol being used as the immersion fluid and the temperature being increased at a rate of approximately 10°C./hr.

Measurements of the real and imaginary components of the complex Young's modulus were obtained at extensions between 0 and 100% by use of the wave-propagation technique described in Part I and references therein. The specimens were immersed during test in a bath of ethanol which was controlled at the desired temperatures within a range of approximately -30°C. to +25°C. All measurements were made at a frequency of 1 kcycle/sec.

RESULTS

Equilibrium Elastic Behavior

Conventional plots of $\sigma/2\lambda(\lambda - \lambda^{-2})$ against λ^{-1} , σ being the tensile traction, were linear over a range of at least 5-80% for the MT and gum rubbers: the HAF material showed very nonlinear behavior, except for a linear section between about 30 and 60%. Thus the former two materials could be characterized by a Mooney strain-energy

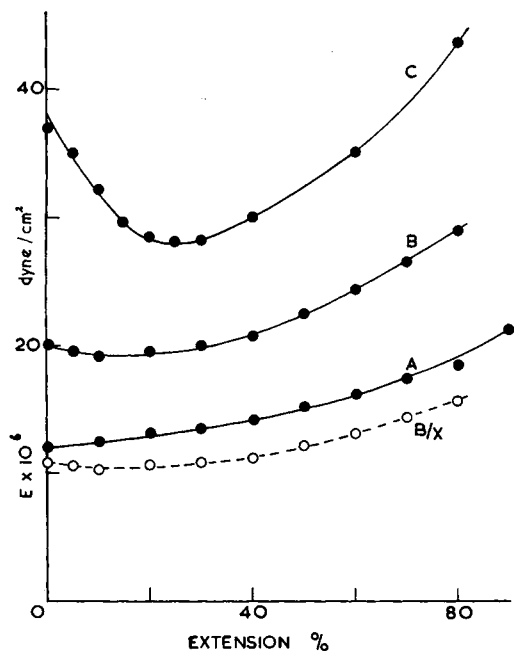


Fig. 2. Strain dependence of equilibrium Young's modulus at 20°C.; (A) gum rubber; (B) MT black-filled rubber; (C) HAF black-filled rubber.

function and their dynamic behavior analyzed according to eqs. (4) and (5).

Values of the equilibrium Young's modulus at different extensions, obtained by graphical differentiation of the stress-strain curves, are given in Figure 2. This shows the qualitative similarity of the behavior of the gum and the MT black rubbers as well as the contrasting behavior of the HAF black rubber, in particular the striking decrease in modulus during the early stages of extension. The dotted curve represents the modulus of the MT material divided by a factor X representing the stiffening effect of a volume fraction ϕ of monodisperse, rigid spherical particles. For the unstrained state, the problem of stiffening is formally identical with that of the increase in viscosity of a liquid produced by the suspension of the same fraction of particles, so that X at $\lambda = 1$ may be identified with the relative viscosity of the analogous liquid system. For concentrations in the present range, above the level up to which the Einstein expression ($X = 1 + 2.5\phi$) is valid, there are several theoretical expressions available, mostly well-attested by experimental data, and there is no way at present of discriminating between them.⁷ In particular there is the relation of Vand⁸ ($X = 1 + 2.5\phi + 7.17\phi^2 + 16.2\phi^3$) and that developed successively by Guth,

Simha, and Gold ($X = 1 + 2.5\phi + 14.1\phi^2$) which has been used for the analogous elastic problem in filled polymers, notably by Guth,⁹ Smallwood,¹⁰ and Landel.¹¹ Simha¹² has discussed improvements in the Guth-Simha-Gold expression leading to the form $X = 1 + 2.5\phi + 12.6\phi^2$ which will be adopted in the present work: it may be observed that the value given by this relation at the relevant volume concentration of 18%, viz, $X = 1.78$, is within 5% of the values given by the other two expressions.

Figure 2 shows that in the unstrained state the factor X accounts approximately for the difference in modulus of the MT rubber and the gum; the residual difference is within the normal modulus variation between different preparations of nominally the same rubber. Furthermore, the empirical use of the same factor X to reduce the modulus of the MT rubber in the *strained* state increases this residual difference by at the most another 10%. Hence, this reduction procedure will be used for comparative purposes in analyzing the variations in dynamic modulus which extend over several decades.

Glass-Transition Temperatures

No significant difference was found between the glass-transition temperatures of the three test materials. As this result was unexpected, two further preparations were examined, one for each filler, at a volume concentration of approximately 9%. There was no trend in the scatter of the results, all transition points lying within 0.7°C. of the value of -65.7°C . measured for the gum rubber.

Dynamic Measurements

Analysis of the real and imaginary parts of the complex Young's modulus was made for the gum and MT rubbers on the basis of eqs. (4), and the results for the MT material at selected temperatures are shown in Figure 3. The data shown are all inside the strain region of 5 to 80% for which the equilibrium Mooney plots were linear, and it is seen that substantially linear results were obtained at temperatures from 25°C. to -20°C . Furthermore, the intercepts are generally very small in comparison with the slopes, as was found in Part I for the gum rubber.

For the HAF material the function $f(\lambda)$ of eqs. (2) was obtained from Curve C in Figure 2, and the real and imaginary modulus components were divided by f to give moduli formally analo-

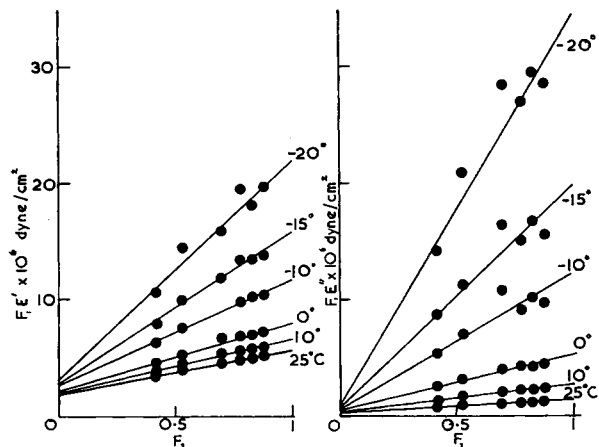


Fig. 3. Strain dependence of modulus components for MT rubber at 1 keycycle/sec.

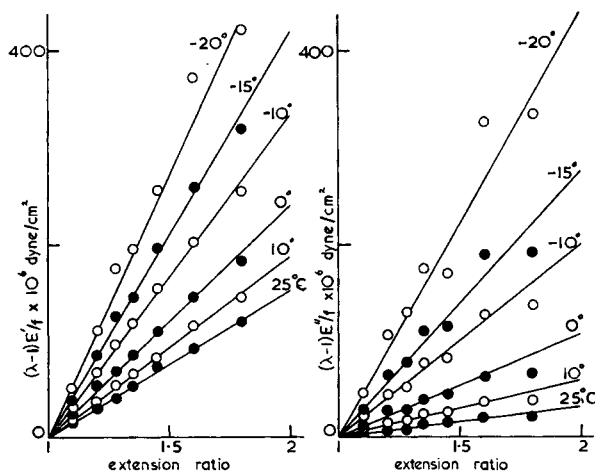


Fig. 4. Strain dependence of modulus components for HAF rubber at 1 keycycle/sec.

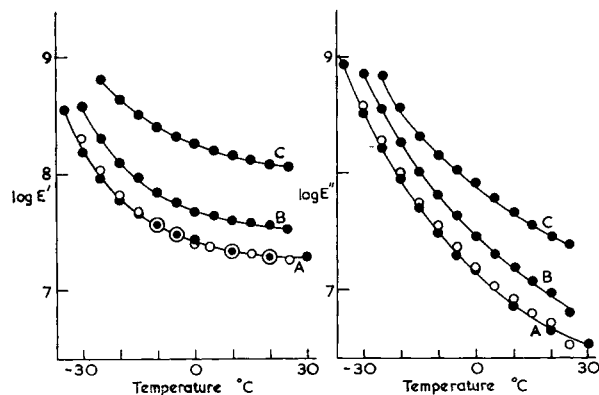


Fig. 5. Temperature dependence of modulus components at zero strain and 1 keycycle/sec.: (A) gum rubber; (B) MT black-filled rubber; (C) HAF black-filled rubber; (O) = B/X.

gous to $6(C_1' + C_2')$ and $6(C_1''$ and $C_2'')$, respectively. To examine the strain dependence of the dynamic behavior these quantities were then multiplied by $(\lambda - 1)$ and plotted against λ : to the extent that the dynamic strain dependence can be represented by the equilibrium parameter f this should give at any one temperature a straight line passing through the origin. Results at selected temperatures are shown in Figure 4. It can be seen that both components can be represented by linear relations although, in contrast to the behavior of the gum, there is considerably more scatter of the points for the imaginary component.

The dynamic strain dependence of all three materials has thus been represented by a series of linear plots: F_1E^* versus F_2 for the gum and for the MT black and $(\lambda - 1)E^*/f$ versus λ for the HAF black. Comparison of the dynamic behavior of the materials at any point in the moderate strain range may then be made in terms of the slopes of these lines and their intercepts. For the unstrained state in particular the moduli can be read off as the intercepts on $\lambda = 1$ for the HAF plots and as six times these intercepts for the other materials (since $F_1^{-1} = 6$ at $\lambda = 1$): the resulting moduli are shown in Figure 5 as a function of temperature and the open circles show the values of modulus of the MT black divided by the factor X .

DISCUSSION

These results may be most profitably discussed in relation to the work of Landel,¹¹ who used a model system of glass beads in polyisobutylene at volume concentrations up to 37%. The MT black may be taken as essentially a similar, though less well-defined system with a particle diameter of about one-tenth that of Landel's beads; the HAF black is an order of magnitude finer still, but differs primarily from the other systems in the existence of strong particle flocculation and, possibly, particle-rubber interaction.

The first point of difference which may be noted refers to Landel's finding that the presence of the filler increases the glass-transition temperature T_g . At the present volume loading of 18% this increase would amount to 4.5°C., but the direct observation of T_g described above showed no significant effect either of the MT or of the HAF black. Landel's observation was derived by application of the Williams-Landel-Ferry equation¹³ to the dynamic data for different loadings, and indicates in the first place changes in the reference

temperature T_s , which is a parameter of this equation. An increase in T_s , however, does not necessarily imply the same or even any increase in T_g , since the value of $(T_s - T_g)$ can vary between systems.¹⁴ Thus, an increase of 5°C. in T_s could be taken up, without any change in T_g , by decreases of about 3% in f_g , the free volume at T_g , and in α_f , the thermal expansion coefficient of that free volume; neither of these changes would be readily detected directly. The present measurements do not provide an estimate of T_s , but increases of a few degrees centigrade have been reported^{15,16} for the comparison of compounds similar to the HAF black rubber and the gum so that there was probably no difference between them in T_g .

Over the dispersion range covered by the present work, viz., about one decade change in E' and two decades in E'' , Landel found that the presence of the filler could be almost completely accounted for by the (unmodified) Guth-Simha-Gold loading factor, together with the changes in T_s . Figure 5 shows similar agreement for both real and imaginary modulus components for the unstrained gum and MT black rubbers, for the modified loading factor X and with assumption of no difference in T_s . The moduli of the HAF black rubber, however, are much greater than can be accounted for by X , and furthermore the variation with temperature is less than that for the other materials.

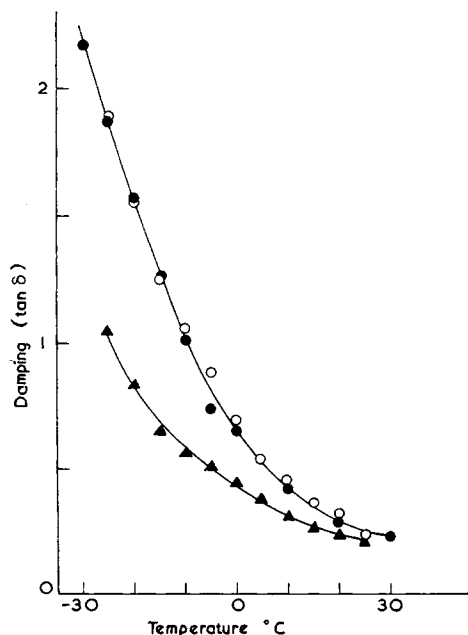


Fig. 6. Temperature dependence of damping at 1 kcycle/sec.: (—●—) gum rubber; (—○—) MT black-filled rubber; (—▲—) HAF black-filled rubber.

This difference between the materials is emphasized by the temperature dependence of the loss tangent shown in Figure 6: as this is a ratio of the moduli ($\tan \delta = E''/E'$) it reduces the possibility of distorting the comparisons by use of an incorrect loading factor. It is clear that the gum and MT black rubbers show substantially the same loss but that the HAF black rubber is less damped and shows less dispersion. The gum-MT comparison is in agreement with Landel's results which showed no change in the relaxation spectrum up to a loading of 20%. At a loading of 37% of glass beads Landel found that the relaxation spectrum (in this time-temperature region) was transposed parallel to itself along the frequency axis by an amount equivalent to a threefold increase in the monomeric friction coefficient ζ_0 of the polymer. It is evident from Figures 5 and 6 that the HAF relaxation spectrum is not parallel to that of the gum in this region, and therefore that the effect of the HAF cannot solely be explained in terms of an increased ζ_0 . This emphasizes the view suggested by the absence of a change in T_g , that the effect of the HAF black is to be sought in physical terms, such as the stress distribution under a variable degree of aggregation, rather than in physico-chemical terms, such as adsorption and variable degrees of crosslinking.

The foregoing discussion may be applied equally to strained material within the moderate strain range examined. The modulus variation may be derived from the linear relations given in Figures 3 and 4 and the corresponding relations for the gum, and Figure 7 shows the results obtained for an extension of 30%. Qualitatively the temperature dependence for the strained materials is the

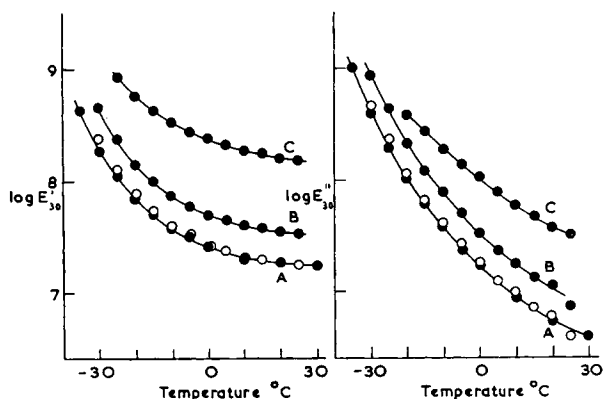


Fig. 7. Temperature dependence of modulus components at 30% extension and 1 kcycle/sec.: (A) gum rubber; (B) MT black-filled rubber; (C) HAF black-filled rubber; (○) = B/X .

same as for the unstrained state shown in Figure 5. Reduction of the MT modulus by X as shown by the open circles again gives reasonable agreement with the values for the gum, in fact, rather better agreement than the equilibrium modulus values shown in Figure 2. Reduction by a loading factor in the strained state, however, must be regarded as essentially empirical, because the state of strain in the rubber matrix is not known, and the viscosity-rigidity analogy is no longer exact.

A remarkable feature of the analysis is the degree of linearity obtained for the strain dependence relations, e.g., in Figures 3 and 4, both for the real and for the imaginary modulus components, over the whole temperature range. This confirms the utility of attributing to the spring elements of a formal model, such as that of Figure 1, the equilibrium modulus-strain dependence which is observed for the material in bulk. It also implies that the relaxation spectrum of these materials is not generally altered by moderate strains, although this may not be true for the HAF material at the higher temperatures where there are indications of curvature in the E'' curves (Fig. 4).

For the MT and gum rubbers which show Mooney-type behavior, C_1' is relatively small and C_1'' is zero, so that the marked variations in complex modulus with temperature can be associated almost entirely with C_2' and C_2'' . Bearing in mind that C_{10} is only linearly proportional to the absolute temperature and that C_{20} is also not strongly temperature-dependent,¹⁷ inspection of eqs. (5) shows that the C_{2i} terms are mainly responsible for the temperature variation and that they must be much greater than the corresponding C_{1i} coefficients.

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Synopsis

Elastic and viscous components of the dynamic Young's modulus were measured at strains up to 80% and over a temperature range of -30°C . to $+30^{\circ}\text{C}$. for natural rubber containing 18% by volume of carbon black. These components were derived from the velocity and attenuation of 1 kcycle/sec. longitudinal waves in stretched filaments. Two types of carbon black were examined, with mean particle diameters of about 0.4 microns (MT black) and 0.04 microns (HAF black). It was possible to represent the strain dependence of the modulus components of the MT-filled material by the linear relations previously developed for the gum rubber; division by a volume loading factor derived from the Guth-Simha-Gold equation gave close agreement with the corresponding values for the gum at the same strain and temperature. The strain dependence of the HAF-filled rubber was analyzed with reference to the equilibrium modulus-extension curve. This material showed increases in modulus components much greater than indicated by the volume loading factor and the temperature coefficients of these components were much less than for the gum rubber. The glass-transition temperature of -65.7°C . for the gum rubber was not significantly affected by the presence of either carbon black.

Résumé

On a mesuré les constituants de l'élasticité et de la viscosité des modules dynamiques de Young des caoutchoucs naturels, contenant 18% an volume de noir animal, à des tensions s'élevant de 80% sur une échelle de température de -30°C . à $+30^{\circ}\text{C}$. On a obtenu ces constituants à partir de la vitesse et du ralentissement des ondes longitudinales de 1 kilocycle/sec dans des filaments tendus. On a examiné deux types de noir animal, l'un dont le diamètre moyen des grains est de 0,4 microns (noir M.T.), l'autre de 0,04 microns (noir H.A.F.). Il nous a été possible de rendre compte de la dépendance de la tension sur les constituants du module de l'échantillon contenant du noir M.T., par une relation linéaire développée au préalable pour les caoutchoucs gommeux: la division par un facteur correctif de volume, obtenu a partir de l'équation de Guth-Simha-Gold, nous donne un très bon accord avec les valeurs correspondantes pour les gommés à la même tension et température. On a analysé la dépendance de la tension sur les caoutchoucs contenant du noir H.A.F. en nous basant sur la courbe d'extension du module à l'équilibre. Cet échantillon montre un accroissement beaucoup plus élevé des constituants du module que celui indiqué par le facteur

correctif de volume et les coefficients de température de ces constituants sont beaucoup plus faibles que pour les caoutchoucs gommeux. La présence de deux sortes de noir animal n'a pas d'influence significative sur la température de transition vitreuse de $-65,7^{\circ}\text{C}$ pour les caoutchoucs gommeux.

Zusammenfassung

Die elastische und viskose Komponente des dynamischen Youngmoduls wurden bei Verformungen bis zu 80% und in einem Temperaturbereich von -30°C bis $+30^{\circ}\text{C}$ an Naturkautschuk mit einem Russgehalt von 18 Volumsprozent gemessen. Diese Komponenten wurden aus der Fortpflanzungsgeschwindigkeit und Dämpfung von Longitudinalwellen mit 1 kHz/sek in gestreckten Fäden abgeleitet. Zwei Russtypen, mit mittlerem Partikeldurchmesser von etwa 0,4 Mikron (MT-Russ) and 0,04 Mikron (HAF-Russ), wurden untersucht. Die Verformungsabhängigkeit der

Modulkomponenten des MT-gefüllten Materials konnte durch die früher für den "Gum"-Kautschuk entwickelten linearen Beziehungen dargestellt werden: Division durch einen aus der Guth-Simha-Gold-Gleichung abgeleiteten Volum-Beladungsfaktor lieferte eine gute Übereinstimmung mit den entsprechenden Werten für das "Gum" bei gleicher Verformung und Temperatur. Die Verformungsabhängigkeit des HAF-gefüllten Kautschuks wurde an Hand der Kurve Gleichgewichtsmodul-Dehnung analysiert. Dieses Material zeigte eine viel grössere Zunahme der Modulkomponenten als nach dem Volumsbeladungsfaktor zu erwarten und der Temperaturkoeffizient dieser Komponenten war viel geringer als beim Gum-Kautschuk. Die Glasumwandlungstemperatur des "Gum"-Kautschuks von $-65,7^{\circ}\text{C}$ wurde durch die Gegenwart keines der beiden Russe wesentlich beeinflusst.

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