

The Strain Dependence of Rubber Viscoelasticity. Part III. Natural and Butyl Rubber at High Extensions

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I. INTRODUCTION

In previous papers in this series^{1,2} the linear viscoelastic behavior of gum and filled rubbers has been studied at mean extensions up to 100%. Linearity was assured by allowing each specimen to relax at the required extension to its equilibrium state and then measuring the complex Young's modulus for very small strains superimposed upon this equilibrium extension. Analysis of the data was made either in terms of a Mooney strain-energy function or, more generally, by relation to the experimentally determined equilibrium stress-strain curve of the material. At much higher strains, however, the use of a strain-energy function is invalidated by the hysteretic behavior of the rubber, and the determination of a stress-strain curve at anything resembling equilibrium becomes increasingly difficult. Consequently in the region of high strain it is preferable to examine the strain dependence of the viscoelasticity without involving a direct comparison with the equilibrium behavior.

In principle, the most significant analysis would be obtained from a study of the strain dependence of the relaxation or retardation spectrum. The long-time end of the spectrum could perhaps be measured using a refined creep or stress relaxation technique, although considerable care would be required to separate the effects from the residual behavior resulting from the initial large elongation. In the rubber-glass transition region, with which this work is primarily concerned, the difficulty lies in making measurements over a sufficiently wide frequency range. Normally the Williams-Landel-Ferry (WLF) equation³ would be used to transform constant-frequency data from a wide temperature range to the equivalent isothermal spectrum over a wide frequency range; however, the validity of this equation has been confirmed only for amorphous polymers, and its application to highly stretched, anisotropic rubber involves several untested assumptions as discussed further below.

The main object of the present paper is to describe the observed variations in the viscoelasticity of natural and butyl rubber over a wide range of extension and temperature, although, of necessity, over a limited range of frequency. In addition, a tentative indication of the influence of strain upon the relaxation spectra is given, and the implications of this are examined.

II. EXPERIMENTAL PROCEDURE

Real and imaginary parts of the complex Young's modulus of stretched natural and butyl rubbers were calculated from measurements of the propagation constants of longitudinal waves in stretched rubber filaments. Details of the wave-propagation technique have been given in Part I (and references therein), together with the composition and preparative details of the rubbers.

At very high extensions it becomes particularly important to make allowance, in calculating the modulus components, for the equilibrium tensile traction in the material. The appropriate equations were stated in Part I, and their derivation from the relevant equation of motion has been given elsewhere.⁴ Tensile traction-extension curves sufficiently close to equilibrium for the present purposes were therefore obtained using the method described by Gumbrell, Mullins, and Rivlin,⁵ the load increments being added at 3-min. intervals. Before making these measurements the test pieces were stretched six times to a high elongation, i.e., 700% for the natural rubber and 800% for the butyl, and then placed for 2 min. in boiling water. This conditioning procedure was intended to reduce the hysteretic behavior shown by vulcanized rubber in its first extension.

For wave-propagation measurements a similar conditioning procedure was followed. The specimen was then clamped in the test position at the required extension and allowed to relax for 1/2 hr. at 20°C. before measurements were made. Each

specimen was tested over the whole of the appropriate temperature and frequency range, but at one extension only.

The natural rubber was tested at extensions up to about 650% and the butyl rubber, which was considerably softer, at extensions up to about 750%. Ethanol was used as the confining fluid by which the temperature was controlled within the working range of -45°C . to $+50^{\circ}\text{C}$. Under these conditions the velocity of propagation ranged from about 40 to 1800 m./sec.

III. EXPERIMENTAL RESULTS

Measurements of E' and E'' , the real and imaginary parts respectively, of the complex Young's modulus, were made between -45°C . and $+50^{\circ}\text{C}$. for the natural rubber and between -10°C . and $+50^{\circ}\text{C}$. for the butyl. As discussed above, the possible frequencies of measurement were determined by the wavelength at any particular temperature and extension. The observed propagation characteristics—velocity and attenuation—were therefore plotted against frequency and

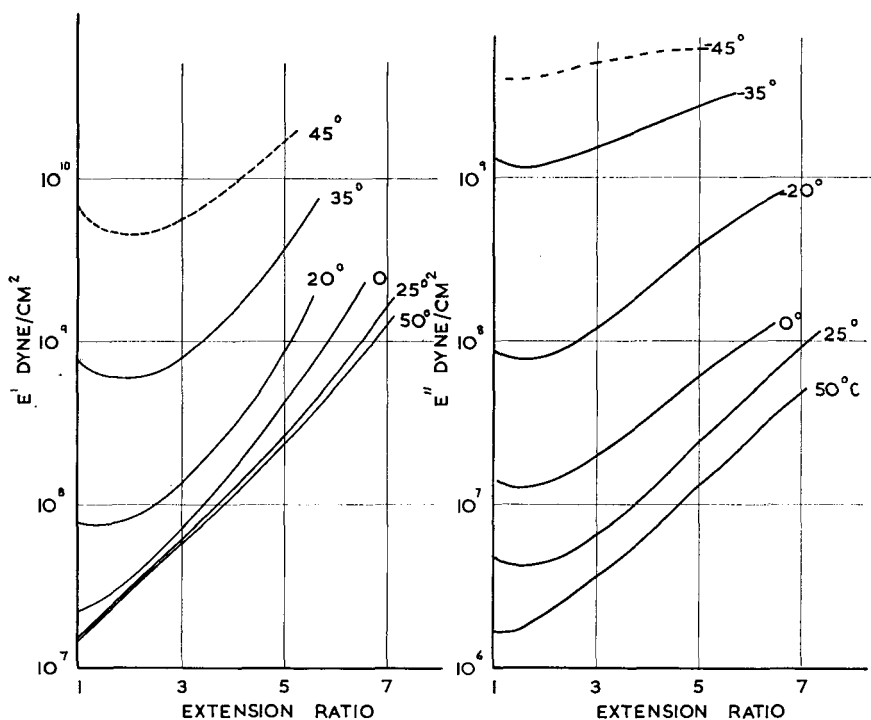


Fig. 1. Dynamic Young's moduli of stretched natural rubber at 1 kc/sec.

There is a theoretical lower limit to the wavelength which can be measured by this technique, as well as a practical upper limit: for plane-wave propagation the wavelength must be considerably greater than the lateral dimensions of the specimen, and for a reasonable experimental accuracy the wavelength should not greatly exceed the length of the specimen. These conditions restricted the wavelengths to values between about 3 and 100 cm. Thus, although a total frequency of 200 cycles/sec. to 20 kcycles/sec. could be used in the experiments, the maximum frequency variation for any one extension and temperature was only about 30:1. The narrowness of this range made it impossible to use the data for testing the applicability of the WLF equation to stretched rubber.

extrapolated where necessary to obtain a set of data relevant to the single frequency of 1 kcycle/sec. Modulus components were then calculated from the 1 kcycle/sec. data for each extension and smoothed by plotting against temperature.

The variation with extension of the resulting moduli is shown for selected temperatures in Figures 1 and 2. A range of over three decades is covered by the natural rubber data, but only two decades by the butyl data, for which the temperature variation was smaller.

In addition it is evident that the moduli of the natural rubber increase more rapidly with extension than do the moduli of the butyl rubber. A similar relation exists between the equilibrium values as shown by the stress-strain curves in Figure 3.

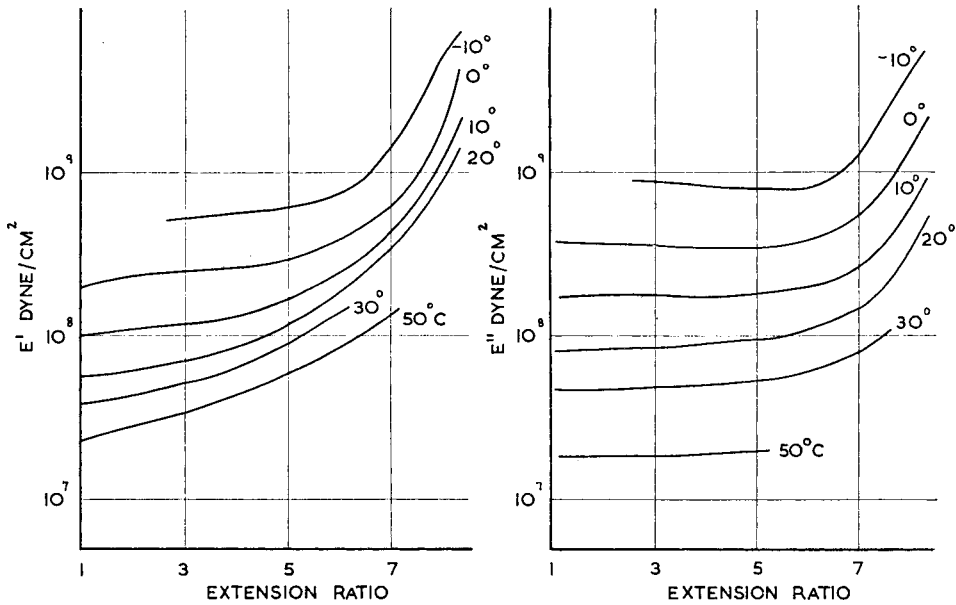


Fig. 2. Dynamic Young's moduli of stretched butyl rubber at 1 kcycle/sec.

at moderate extensions each curve follows the normal Mooney behavior [cf. Part I, Figure 1 and eq. (2)], but a turning point is reached after which the slope increases with increasing extension. This behavior results from the finite extensibility of the network, and Mullins⁶ has used this fact to

obtain a quantitative characterization of the network in terms of the extension ratio λ^* , at which the departures from the Mooney form reach a certain level.

Mullins' theory is evaluated in terms of a network parameter, M_c (physical), which is the number-average molecular weight of the chain segments constituting the effective network from the viewpoint of mechanical deformation. These chain segments may be terminated either by a chemical crosslink or by a physical constraint or entanglement; they may thus be considerably shorter than the segments of ideal statistical theory, which are the chain lengths between crosslinks.⁶

From the curves in Figure 1 of Part I λ^* is obtained as 2.82 for the natural rubber and 4.17 for the butyl rubber. The value for butyl is well outside the calibration range given by Mullins,⁶ but for the present purposes a considerable extrapolation is acceptable, and values of M_c (physical) of 10,000 and approximately 22,000 are obtained for the natural and butyl rubbers respectively.

Although both of the complex modulus components tend in general to increase with extension, the real component E' increases more rapidly than the imaginary component E'' . Thus the mechanical damping (defined as $\tan \delta = E''/E'$) tends to decrease with increasing extension. The bivariate dependence of damping upon extension and temperature is illustrated by the projections given in Figures 4 and 5. It is apparent that at 50°C.

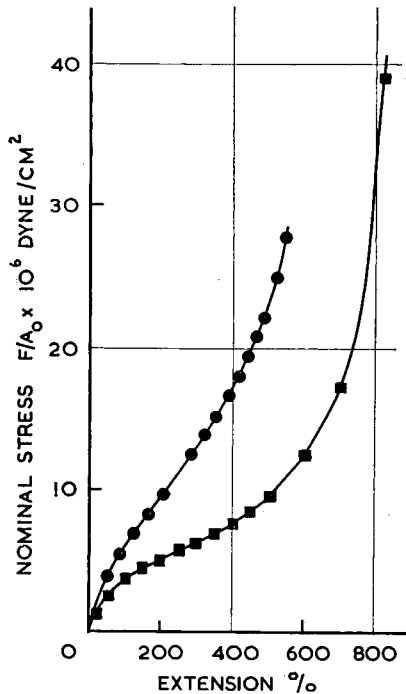


Fig. 3. Equilibrium stress-strain relations at 20°C.: (●) natural rubber; (■) butyl rubber.

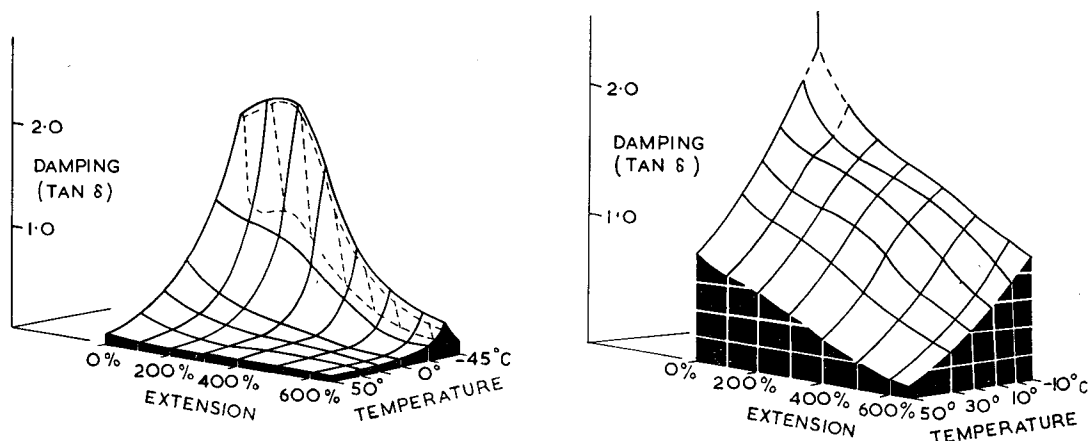


Fig. 4. Damping of stretched rubber at 1 cycle/sec.: (left) natural rubber; (right) butyl rubber.

the decrease in damping with increasing extension is more pronounced for the butyl rubber, although at lower temperatures the position may be reversed over part of the extension range. This behavior would appear to depend more upon the chemical nature of the polymer than upon the network structure, as there is no indication of any singularity in the neighborhood of the respective critical extension ratios λ^* . It is well known that the relaxation characteristics of the two rubbers are quite different

in the amorphous state,⁸ but extension produces still further differences between them.

IV. DISCUSSION

If the above measurements of the complex modulus components had been obtained for an amorphous polymer they could be reduced to isothermal values at a reference temperature T_s by use of the WLF transform

$$\log a_T = -C_1(T - T_s)/(C_2 + T - T_s)$$

where a_T is the change in frequency required to compensate for the change in temperature from T to T_s , and C_1 and C_2 are constants. If the glass-transition temperature T_g is taken as the reference temperature, a simple geometrical interpretation of this equation can be obtained³ in which C_1 is determined by f_g , the free volume at T_g , and C_2 is determined both by f_g and by $\Delta\alpha$, the difference between the thermal expansivities in the glassy and rubberlike states.

It has been found that the dynamic properties of a wide range of amorphous polymers and other glass-forming liquids may be transformed by the WLF equation using constant values for C_1 and C_2 together with a reference temperature appropriate to the material in question. No experimental test has yet been made of the applicability to stretched polymers, so before applying the equation to the present data it is necessary to consider separately the effects of orientation and crystallization upon C_1 , C_2 , and T_g .

1a. Constancy of the free volume at T_g forms the basis of the Fox-Flory treatment of the glass-transition point.^{9,10} This approach has been successful¹¹ for polymers of molecular weight above

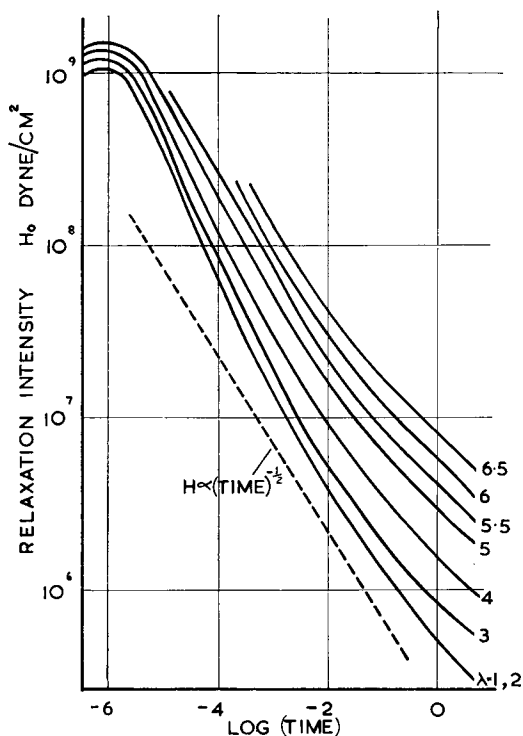


Fig. 5. Approximate shear relaxation spectra of stretched natural rubber. Reduced temperature -17°C .

about 3,000 and of differing chemical types. There seems no reason to suppose that orientation would alter the situation so that C_1 may be provisionally taken at its normal value as found for amorphous materials.

1b. Orientation leads to a high degree of anisotropy in thermal expansion¹² and tends to reduce the expansivity term $\Delta\alpha$. The value of C_2 is thereby affected, but from Boyer and Spencer's data the change is probably not very great, particularly under conditions well removed from the glass transition when the contribution of $(T - T_g)$ exceeds that of C_2 .

1c. The influence of orientation upon T_g is the hardest contribution to evaluate because it depends critically upon the boundary conditions. Gee et al.¹³ have shown that under strictly constant stress conditions T_g increases with the extension (by as much as 7.6°C. at 260% elongation for natural rubber); however, when the specimens were allowed to relax their stress in the glassy state the effect was reversed, the glass-transition temperature tending to decrease with increasing extension. In the present experiments the boundary conditions are indeterminate as a result of differential thermal expansion between the specimen and its supports, but will probably lie somewhere between these two extremes. It seems reasonable, therefore, to suppose, as a first approximation, that the effective value of T_g in the present circumstances is unaltered by elongation. This supposition is supported by the observation that the temperature at which the maximum damping ($\tan \delta$) occurred at 2 kcycles/sec. did not vary by more than about $\pm 4^\circ\text{C}$. for extensions in natural rubber up to 600%.

2. As suggested by Landel,¹⁴ the effects of crystallization *per se* upon mechanical dispersion may be attributed simply to the action of the crystals as a filler. This is reasonable because there will be relatively little dispersion in the crystalline phase, which will therefore act mechanically as a diluent, affecting the distribution of the relaxation times but not their temperature dependence. In particular, the value of T_g is not dependent upon equilibrium crystallization.¹⁵ Provided, then, that the proportion of crystalline material remains constant for a given extension, the WLF transform should be directly applicable. There is some evidence from dielectric measurements¹⁶ that the transform may be applied to partially crystalline polymers which have been adequately annealed.

As a tentative investigation, therefore, the WLF

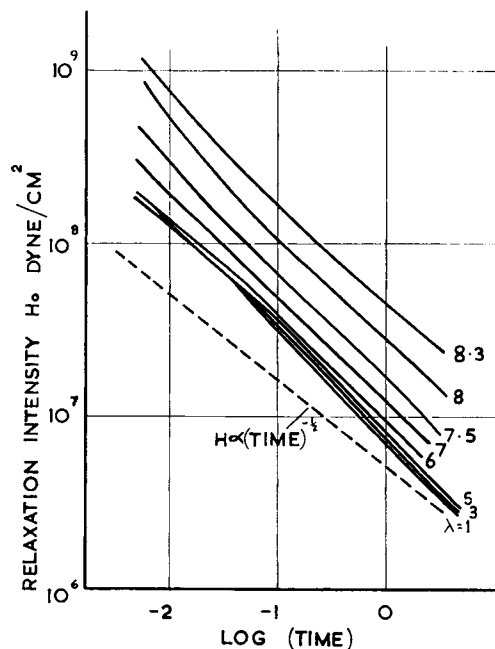


Fig. 6. Approximate shear relaxation spectra of stretched butyl rubber. Reduced temperature -20°C .

equation was used to transform the present measurements to reference temperatures of -17°C . for the natural rubber and -20°C . for the butyl, these being 50°C . greater than the respective glass-transition temperatures measured in the amorphous state. Specifically the procedure adopted was first to divide the imaginary Young's modulus E'' by 3 to obtain the equivalent shear modulus, then to multiply by $(T_g + 50^\circ)/T$ to reduce to the reference temperature, and finally to multiply by $2/\pi$ to obtain the shear relaxation intensity H . This gives a measure of the relaxation spectrum which is only very approximate¹⁷ but nevertheless sufficient in view of the limitations outlined above.

The resulting spectra are shown in Figures 5 and 6. There is seen to be little effect at moderate extensions, but at higher extensions the curves are displaced progressively in the direction of longer times. In the lower part of the rubber-glass transition region, where $10^7 > H > 10^6$, the spectra approximate to straight lines with a common slope of $-1/2$. This is the behavior predicted for amorphous polymers by theories independently due to Blizard, Rouse, and Bueche, and differences and differences in location on the time scale can be directly interpreted in terms of changes in the internal friction.⁸

Taking ζ_0 as the monomeric friction coefficient,

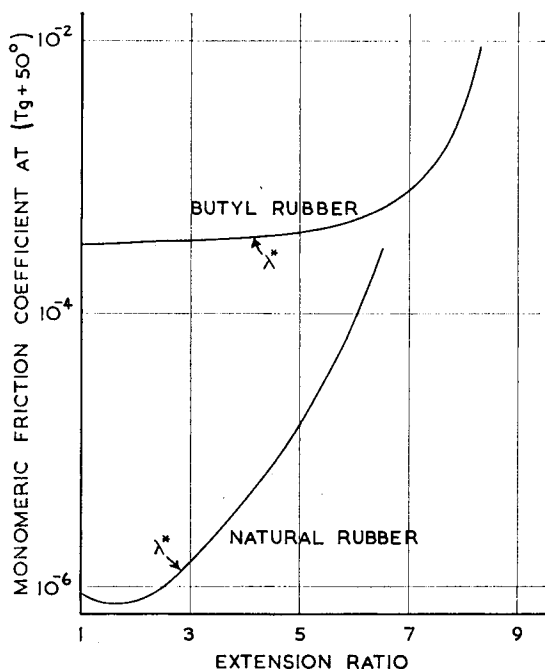


Fig. 7. Monomeric friction coefficients of stretched rubbers at $(T_g + 50^\circ\text{C})$.

i.e., the mean force experienced by a monomer unit moving through the material at unit velocity, the relation between the relaxation intensity H and the time t may be written as

$$\log H = -\frac{1}{2} \log t - \frac{1}{2} \log (6/kT) - \log (2\pi M_0/a\rho L) + \frac{1}{2} \log \zeta_0$$

where k is Boltzmann constant, T the absolute temperature, M_0 the molecular weight of a monomer, ρ the density, L Avogadro's number, and a is a length of the order of the length of a monomer. In this equation the only strain-dependent terms are H and ζ_0 . Figures 5 and 6 show that at constant H the spectra are displaced to longer times with increasing strain; it follows that increasing strain corresponds to increasing ζ_0 . This is shown quantitatively in Figure 7, where the friction coefficients (in units of dyne-sec./cm.) were calculated from the values of $\log t$ at the level $H = 10^7$ dyne/cm.².

In the unstrained state, the friction coefficient of the butyl is seen to be much greater than that of the natural rubber. The ratio of the two is similar to that obtained by Ferry and Landel¹⁸ for these materials at temperatures well above the glass transition. As the strain increases, the friction coefficients also tend to increase, but the form of the strain dependence is quite different for

the two materials. For the natural rubber, the friction coefficient starts to increase rapidly at about 100% extension, while for the butyl the rise is less pronounced and does not become significant below an extension of about 500%. In consequence, the ratio of the friction coefficients falls from several hundred in the unstrained state to about three at 550% extension.

It is tempting to think of this relative behavior in terms of the more compact or "streamlined" envelope of the butyl rubber chain in comparison with that of the natural rubber. However, the detailed distribution of chain segment lengths may be just as important in determining both the value of λ^* (which in Figure 7 is seen to be reasonably close to the upturn in ζ_0) as well as the subsequent distortion of the network; experiments at different degrees of crosslinking would be helpful to test this point. In particular, as the steady-state viscosity is directly proportional to ζ_0 , the viscosities of the unvulcanized polymers would be expected to increase with orientation in the manner shown by Figure 7 (strictly, by the limiting case of this figure as the crosslinking is decreased to zero). This comparison cannot at present be made, as existing experimental measurements of the viscosities of these polymers¹⁹ do not extend to sufficiently high stresses.

Two further remarks may be made on the decrease in damping produced by extension. In the first place Schallamach has found²⁰ recently that the coefficient of friction of natural rubber, measured in the direction of elongation, decreases with increasing elongation. Secondly, a qualitatively similar picture has been found for the case of free retraction of rubber strips from large extensions. The essential difference here is that the energy dissipation occurs in waves whose amplitudes are much greater—typically by a factor of 10^4 —than those of the small amplitude waves used for the above dynamic measurements.

A typical experiment consists in stretching a rubber strip to the required extent, allowing it to relax, and then releasing it abruptly so that it retracts towards its unstrained position. The potential energy in the stretched state is deduced from the known load-extension relation and the kinetic energy on reaching the unstrained position is measured, either by using high-speed cinematography to reveal the velocity distribution²¹ or, more simply, by a ballistic pendulum. The fractional energy loss over the stretching-retraction cycle may then be taken as the finite strain equiv-

alent of the loss factor $\tan \delta$, and preliminary values obtained at room temperature are given in Table I.

TABLE I
Fractional Energy Loss in Free Retraction

Extension, %	Fractional energy loss	
	Natural rubber	Butyl rubber
50	0.39	0.51
100	0.32	0.48
200	0.32	0.43
400	0.30	0.40
500	0.11	0.46

It is seen that the loss factor for large strains is higher for butyl than for natural rubber, and that for both rubbers it tends to decrease as the extension increases.

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Synopsis

Dynamic Young's moduli are derived from observations of wave propagation in stretched filaments of natural and butyl rubbers. Extensions up to about 700% are studied within a temperature range of -45 to $+50^\circ\text{C}$. and a frequency range of 0.2 to 20 cycles/sec. At constant temperature and frequency both the real (E') and imaginary (E'') components increase with increasing extension. The loss factor (E''/E') decreases with increasing extension, but the decrease is more pronounced for the butyl rubber so that the large difference in damping between the two polymers in the unstrained state is greatly reduced at high extensions. Approximate relaxation spectra are derived for the strained materials on the basis of several assumptions regarding the applicability of the WLF equation. It is found that the spectra are displaced in the direction of longer times by increasing extension; this is equivalent to an increase in the monomeric friction coefficient with extension. The effect is more pronounced for the natural rubber than for the butyl, and consequently the ratio of the friction coefficients (butyl:natural) falls from several hundred unstrained state to approximately 3 at 550% extension.

Résumé

Les modules dynamiques de Young ont été dérivés d'observations de la propagation d'onde au sein de filaments tendus de caoutchouc naturel et de caoutchouc butylique. Des extensions jusqu'à environ 700% ont été étudiées, dans un intervalle de températures de -45° à 50° et de fréquence de 0,2 à 20 kc/s. À une température et fréquence constantes les composantes réels (E') et imaginaire (E'') augmentent avec l'extension. Le facteur de perte E''/E' diminue avec l'accroissement d'extension mais la diminution est plus prononcée pour le caoutchouc butylique, de sorte que la grande différence d'amortissements des deux polymères à l'état non tendu est principalement réduite sous grandes extensions. Des spectres de relaxation approximative ont été faits pour les matériaux tendus en faisant diverses suppositions quant à l'application de l'équation WLF. On a trouvé que les spectres sont déplacés vers les temps plus longs en augmentant l'extension. L'effet est plus prononcé pour le caoutchouc naturel que pour le caoutchouc butylique de sorte que la relation entre les coefficients de friction (butyl:naturel) tombent de plusieurs centaines à l'état non tendu à environ 3 à une extension de 550%.

Zusammenfassung

Aus der in gedehnten Natur- und Butylkautschukfäden beobachteten Wellenfortpflanzung werden Werte für den dynamischen Youngmodul abgeleitet. Dehnungen bis zu 700% werden in einem Temperaturbereich von -45° bis 50°C und einem Frequenzbereich von 0,2 bis 20 Khz/sec untersucht. Bei konstanter Temperatur und Frequenz nehmen sowohl der reelle (E') als auch Imaginär (E'') Teil

mit steigender Dehnung zu. Der Verlustfaktor (E''/E') nimmt mit steigender Dehnung ab; es ist jedoch die Abnahme beim Butylkautschuk stärker ausgeprägt, so dass der grosse Unterschied in der Dämpfung zwischen den beiden Polymeren im unverformten Zustand bei hoher Dehnung stark reduziert wird. Auf Grundlage einiger Annahmen bezüglich der Anwendbarkeit der WLF-Gleichung werden für das verformte Material angenäherte Relaxationsspektren abgeleitet. Es zeigt sich, dass die Spek-

tren mit zunehmender Dehnung nach längeren Zeiten verschoben werden: das entspricht einer Zunahme des Reibungskoeffizienten der Monomereinheit mit der Dehnung. Dieser Effekt ist bei Naturkautschuk stärker ausgeprägt als bei Butylkautschuk, so dass das Verhältnis der Reibungskoeffizienten (Butyl:Natur) von einigen hundert im unverformten Zustand auf etwa 3 bei 550% Dehnung abfällt.

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