The Viscoelastic Behavior of Rubber in Extension

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I. INTRODUCTION

Analysis of the viscoelastic behavior of polymers in the rubberlike state is commonly based on the existence of a wide range, or spectrum, of relaxation times.[1-3] The material is formally replaced by an assembly of relaxing elements, each associated with a single relaxation time. Thus, if simple extensional properties are being considered, the ith element will be a spring of Young's modulus E_i damped by a viscosity $\tau_i E_i$. To determine the response of this system to sinusoidal vibrations, the real and imaginary parts E' and E'' of the complex dynamic Young's modulus E^* may be obtained by summing the contributions over the relaxing elements thus

$$E' = \sum_i \frac{\omega^2 \tau_i^2}{(1 + \omega^2 \tau_i^2)} E_o \qquad (1)$$

and

$$E'' = \sum_i \frac{\omega \tau_i}{(1 + \omega^2 \tau_i^2)} E_i \qquad (2)$$

where ω is the circular frequency of the vibration. If desired, this discrete spectrum may be treated as continuous and the summations replaced by integrals.

The general applicability of Ferry's method of reduced variables[2] supports the usefulness of the above model with the added feature that the moduli E_i are proportional to the absolute temperature; in other words, the individual "spring" elements must be considered to possess rubberlike elasticity, even though they are not identified directly with molecular mechanisms as in some recent theories.[4-6]

From eqs. (1) and (2) it is evident that the components of the dynamic Young's modulus will depend upon strain in just the same way that the rubberlike moduli E_i depend upon strain, providing, of course, that the deformations are sufficiently small for the strain to be homogeneous. This dependence can therefore be calculated from the equilibrium stress-strain relations for rubber in simple extension, which have been found to be derivable for moderate strains[7,8] from a Mooney form of strain-energy function,[9] viz.,

$$W = C_1(I_1 - 3) + C_2(I_2 - 3) \qquad (3)$$

where W is the strain-energy density, $I_1 = \sum_i \lambda_i^2$ and $I_2 = \sum_i \lambda_i^{-2}$, the λ_i being principal extension ratios, and C_1 and C_2 are elastic constants.

It is the main purpose of the present paper to compare the measured strain-dependence of the components of the dynamic Young's modulus with the dependence calculated on the basis of eq. (3).

Consider now a strip of rubber stretched in simple extension to a major principal extension ratio λ. If incompressibility is assumed, the minor principal extension ratios are each $\lambda^{-1/2}$, so that I_1 is $(\lambda^2 + 2\lambda^{-1})$ and I_2 is $(\lambda^{-2} + 2\lambda)$. Differentiation of eq. (3) then yields the stress-strain relationship:

$$\sigma = 2\lambda(C_1 + \lambda^{-1}C_2)(\lambda - \lambda^{-2}) \qquad (4)$$

where σ is the (actual) tensile stress. Experimentally it has been found that eq. (4) is valid for rubbers at moderate extensions as shown, for example, by Figure 1, in which equilibrium or "static" stress-strain data are presented for the natural rubber used in the present work. The departure from linearity at a strain of about 140% has been shown[8] to arise from the rapidly increasing proportion of network chains which are fully extended.

The Young's modulus E of the stretched rubber may be defined as the slope of the tensile stress-strain curve, both stress and strain being calculated on the actual dimensions of the specimen in the stretched state. This modulus is then directly comparable with the measured real and imaginary parts of the dynamic Young's modulus.

A stress increment $d\sigma$ will correspond to a strain increment of $\lambda^{-1}d\lambda$ so that

$$E = \lambda \frac{d\sigma}{d\lambda}$$

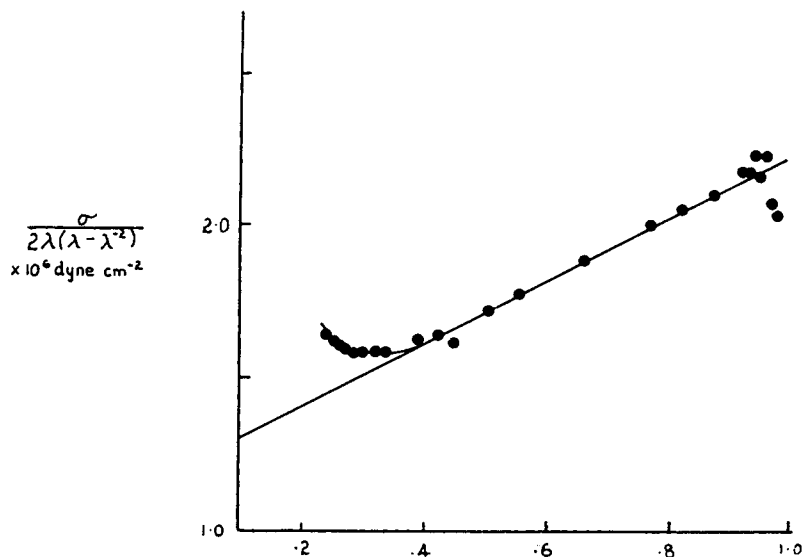With the value of σ given by eq. (4), on re-

Fig. 1. "Static" stress-strain relation for natural rubber, temperature 50°C.   Abscissa: λ^{-1}.

arrangement, the strain dependence of E is found to take the form

$$F_1 E = C_1 + F_2 C_2 \qquad (5)$$

where

$$F_1 = \lambda \, [2(2\lambda^3 + 1)]^{-1}$$

and

$$F_2 = (\lambda^3 + 2)[\lambda(2\lambda^3 + 1)]^{-1} \qquad (6)$$

Each of the elements E_i may therefore be represented by a relation similar to eq. (5), with the elastic constants C_{1i} and C_{2i} appropriate to that element.

Thus

$$F_1 E_i = C_{1i} + F_2 C_{2i}$$

so that, from eqs. (1) and (2)

$$
\left.
\begin{aligned}
F_1 E' &= \\
&\sum_i \frac{\omega^2 \tau_i^2}{(1 + \omega^2 \tau_i^2)} C_{1i} + F_2 \sum_i \frac{\omega^2 \tau_i^2}{(1 + \omega^2 \tau_i^2)} C_{2i} \\
\text{and} & \\
F_1 E'' &= \\
&\sum_i \frac{\omega \tau_i}{(1 + \omega^2 \tau_i^2)} C_{1i} + F_2 \sum_i \frac{\omega \tau_i}{(1 + \omega^2 \tau_i^2)} C_{2i}
\end{aligned}
\right\} \quad (7)
$$

$$
\left.
\begin{aligned}
C_1' &= \sum_i \frac{\omega^2 \tau_i^2}{(1 + \omega^2 \tau_i^2)} C_{1i} \\
C_2' &= \sum_i \frac{\omega^2 \tau_i^2}{(1 + \omega^2 \tau_i^2)} C_{2i} \\
C_1'' &= \sum_i \frac{\omega \tau_i}{(1 + \omega^2 \tau_i^2)} C_{1i} \\
C_2'' &= \sum_i \frac{\omega \tau_i}{(1 + \omega^2 \tau_i^2)} C_{2i}
\end{aligned}
\right\} \quad (8)
$$

eqs. (7) become

$$
\left.
\begin{aligned}
F_1 E' &= C_1' + F_2 C_2' \\
F_1 E'' &= C_1'' + F_2 C_2''
\end{aligned}
\right\} \quad (9)
$$

and C_1', C_2'; C_1'', C_2'' are evidently the dynamic counterparts of the C_1- and C_2-parameters of equilibrium theory.

As discussed above, C_1 and C_2 (and therefore C_{1i} and C_{2i}) are known to be substantially constant up to moderate strains, and eqs. (8) show that, if the relaxation spectrum does not vary significantly with strain in this region, the dynamic C-parameters should also be independent of strain.

Eqs. (9) are therefore used in the subsequent analysis of the measured strain-dependence of E' and E''.

II. EXPERIMENTAL TECHNIQUE

Measurements of the dynamic modulus were made over a wide range of temperatures by the wave propagation method employed by Nolle[10] and other workers. Details of the present technique have been given elsewhere,[11] but it may be remarked that the valve voltmeter has now been replaced by direct observation of the oscillogram amplitude, so that the essential apparatus is reduced to a power oscillator, a vibrator, a gramophone pick-up, and an oscilloscope.

In essence, the method consists in vibrating one end of a stretched rubber filament along its length. A steady-state condition is set up in which continuous waves are propagated along the filament being progressively attenuated by virtue of the internal viscosity and undergoing a progressive re-
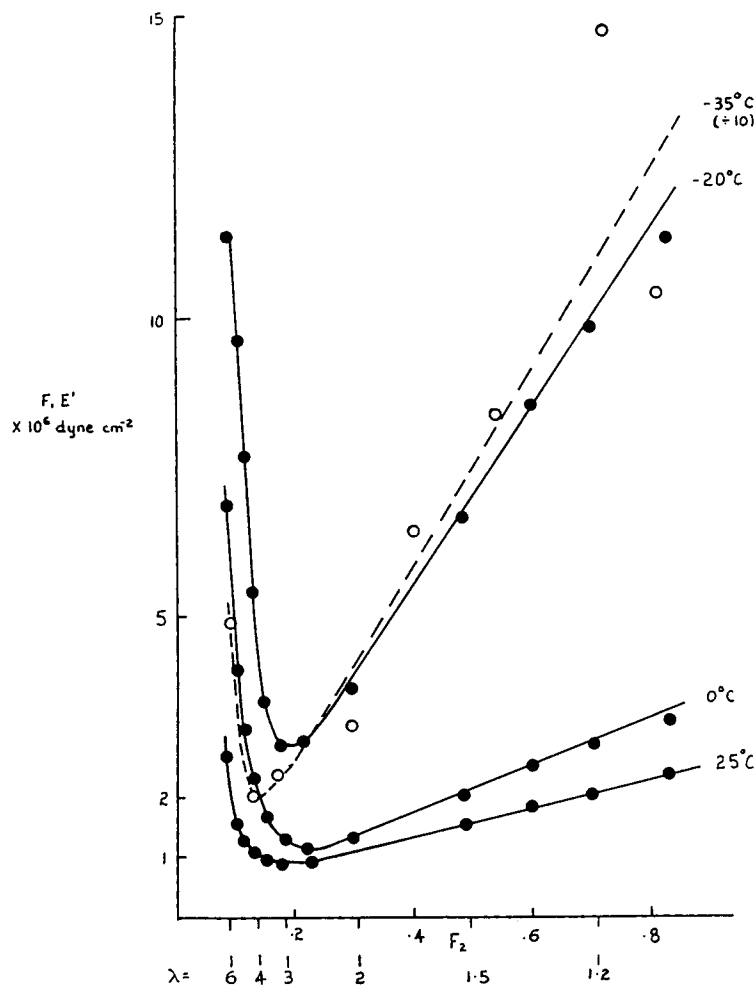
Fig. 2. Dependence of E' on strains up to 600%, frequency 1 kcycle/sec.

tardation of phase by virtue of the Young's modulus. Measurements of the attenuation and phase change per unit length are obtained from observations of the signal from a pick-up pressed into contact with the specimen at different points along its length. From these two quantities the components E' and E'' of the dynamic modulus are readily calculated. It is noteworthy that the graphs of log (amplitude) against distance and of phase against distance, which must be drawn for every experiment, provide built-in checks of the linearity of the viscoelastic behavior.

For most of the work discussed below (viz., the data for extensions up to 100%) measurements were made at a frequency of 1 kcycle/sec. This was experimentally convenient and gave wavelengths ranging from about 4 cm., a value sufficiently greater than the transverse specimen dimensions to apply the theory, to about 100 cm., at which value the phase change per centimeter was still sufficiently large for reliable measurement. For the work at

higher extensions frequencies ranging from 250 cycles/sec to 20 kcycles/sec. were used.

The material used throughout was a natural rubber vulcanizate prepared from 100 parts by weight of natural rubber:3 parts of sulfur:5 parts of zinc oxide:1 part of stearic acid:0.5 part of mercaptobenzothiazole:1 part of antioxidant. This mix was vulcanized for 45 min. at 140°C.

III. EXPERIMENTAL RESULTS

The first application of eqs. (9) was made to data which had already been obtained in an examination of the variations in dynamic modulus over a wide extension range.[11] Figure 2 shows the relation between E', the real part of the dynamic modulus, and the appropriate strain functions. It is apparent first that the relation is approximately linear for moderate strains over the whole temperature range. Just as for the equilibrium stress-strain measurements represented in Figure 1, the curves show an abrupt departure at about 140% extension in the
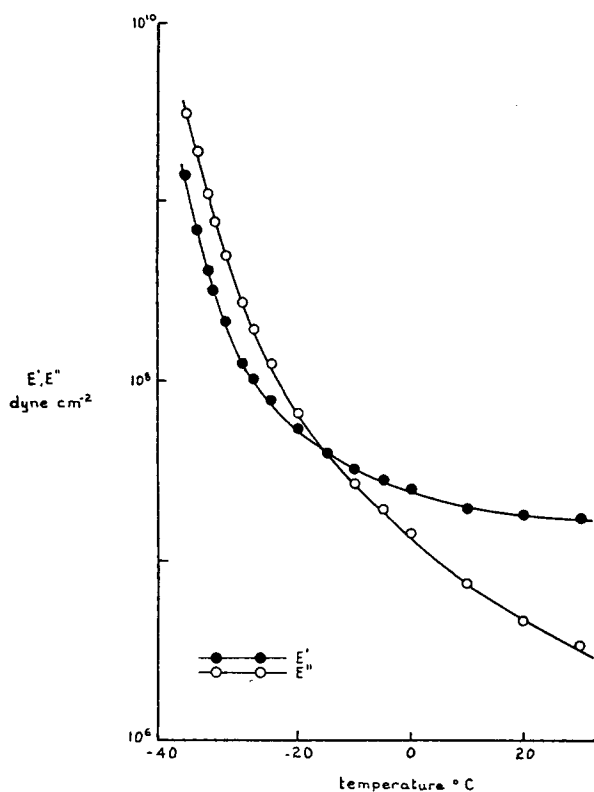
Fig. 3. Temperature-dependence of dynamic modulus components: extension 60%; frequency 1 kcycle/sec.

perature is associated almost entirely with an increase in the slope of the line (C_2') rather than with changes in the intercept (C_1').

In view of the apparent linearity in the range where normal statistical theory is applicable, a more detailed study was made on specimens strained by amounts up to 100%. Figure 3 shows a typical set of measurements of the dynamic modulus components over a range of temperatures and at 1 kcycle/sec. The derived strain-relations for the real and imaginary components are given in Figures 4 and 5, respectively. Approximately linear relations are obtained for both components, and the significance of this is discussed further below. The increasing experimental scatter at low temperature may be attributed to the high rate of change of damping with temperature in this region.

IV. DISCUSSION

From Figures 4 and 5 it can be said that the dynamic behavior in the statistical theory region of moderate strains can be characterized by four parameters: C_1' and C_2', which define the strain dependence of the real part of the elastic modulus, and C_1'' and C_2'' which define that of the imaginary part. The limitations imposed on making this statement by experimental scatter are largely offset by the wide range of the variables covered.

Furthermore it appears that $C_1'' \doteqdot 0$ (more exactly, $C_1'' \ll C_2''$), and that C_1' does not vary by more than about a factor of three over the whole temperature range investigated. On the other hand, C_2' varies by more than a hundredfold and C_2'' by
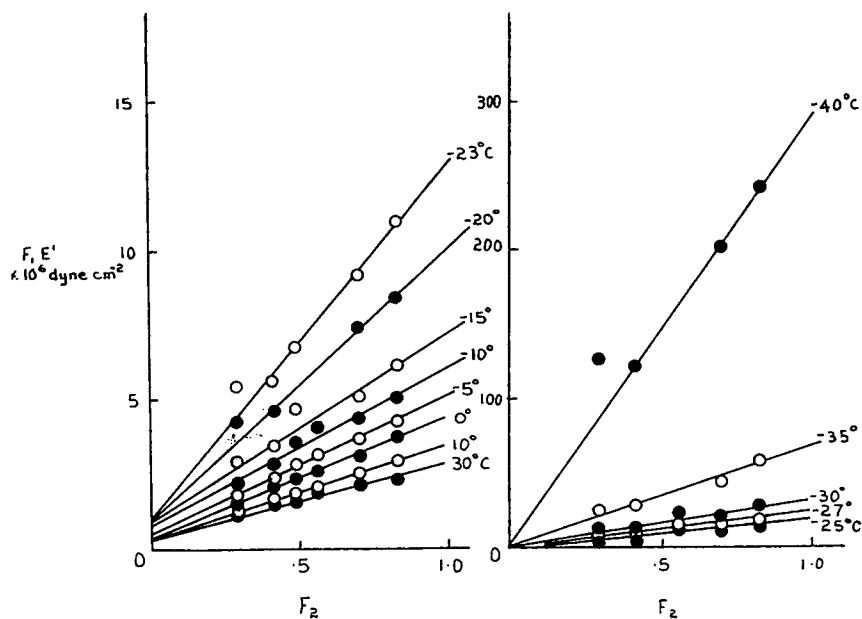
direction of increasing stiffness; by analogy this effect may be attributed to the finite extensibility of parts of the network. Secondly, it is evident that, inside this linear region, the great increase in dynamic stiffness produced by lowering the tem-

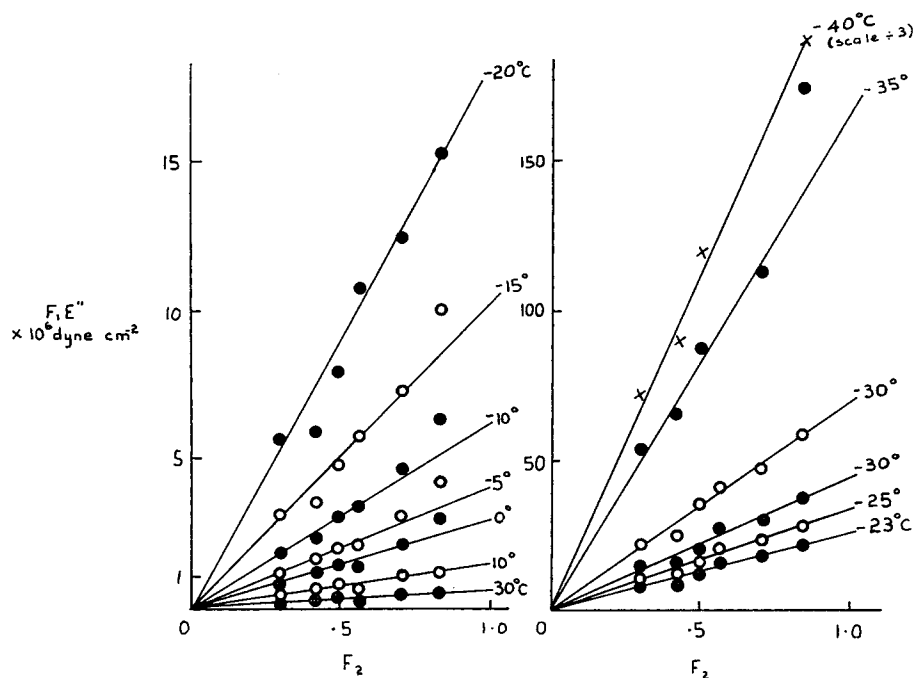Fig. 4. Strain-dependence of E': frequency 1 kcycle/sec.

Fig. 5. Strain-dependence of E'': frequency 1 kcycle/sec.

more than a thousandfold over the same temperature range, so that the viscoelastic behavior over most of the temperature range is determined by the dynamic C_2- rather than the C_1- terms. Now Mullins has shown from a detailed study of equilibrium stress-strain behavior[3] that the "static" C_1, after appropriate correction for network defects, is equal to the elastic constant $(1/2)$ ρRTM_c^{-1} predicted by statistical theory, M_c being the number-average molecular weight of the chain segments between cross-

links. The "static" C_2 term represents the deviations from statistical theory behavior. From eqs. (8), it thus appears that C_1' and C_1'' are the terms corresponding to ideal statistical theory behavior of the E_i, while C_2' and C_2'' are the terms corresponding to departures from that theory.

It should be remarked that although C_2' and C_2'', would be expected to increase with increasing crosslinking, the dynamic behavior cannot be attributed directly to the presence of temporary
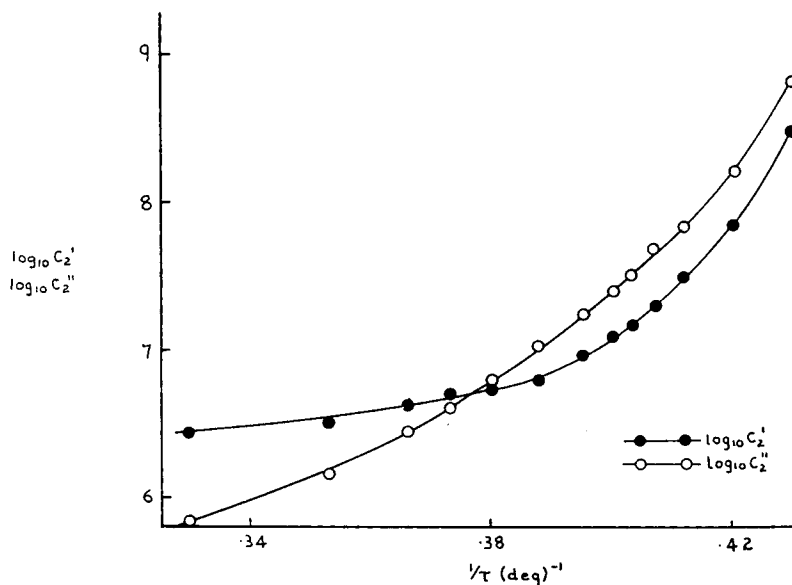
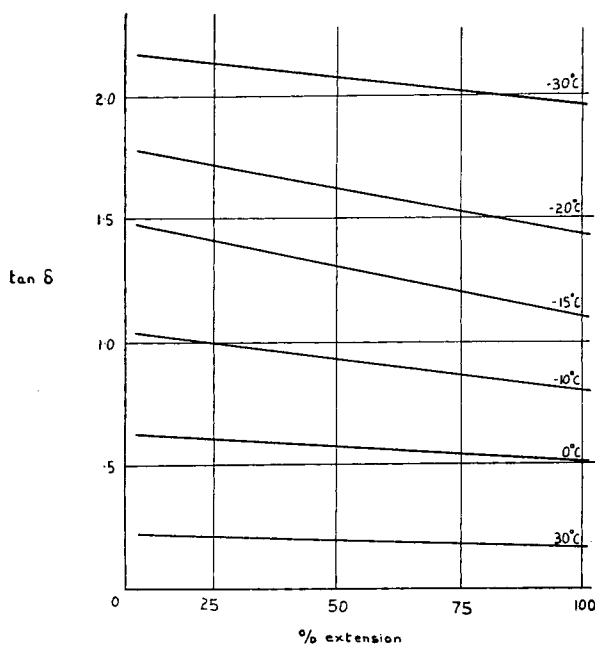Fig. 6. Temperature-dependence of C_2' and C_2'': frequency 1 kcycle/sec.

Fig. 7. Derived strain-dependence of tan δ: frequency
1 kcycle/sec.

erties of polymers.[12] The apparent activation energy of the imaginary term C_2'' in the slowly varying region around room temperature is approximately 7 kcal./mole, a reasonable value for the corresponding activation energy for viscous flow of unvulcanized rubber.

From the linear relations developed above it is possible to derive exactly the variation of damping with strain for strains up to 100%, a relation which could not previously be obtained owing to scatter in the measured values of damping (i.e., tan δ). From eqs. (9) the damping factor is obtained as,

$$\tan \delta \equiv E''/E' =$$
$$[C_1'' + F_2 C_2''][C_1' + F_2 C_1']^{-1} \quad (10)$$

With $C_1'' = 0$ and $C_1' =$ the intercept in Figure 4, tan δ may be determined for any extension and temperature using the appropriate values of C_2'' and C_2' from Figure 6. The strain dependence of tan δ calculated in this way for several arbitrary temperatures is shown in Figure 7.

It is of interest to find out how these variations in dynamic properties with strain are reflected in the relaxation spectra. Unfortunately the variations up to 100% strain were not great enough to give significant differences between the spectra at the level of accuracy at which these could be determined. However it was possible to compute the spectra in the range 100 to 600% extension, using Schwarzl's second-order approximation together with a Ferry transform embodying the measured glass-transition temperature of −67°C. and the curves obtained by this procedure are shown in

crosslinks, i.e., contacts between chains which are not chemical crosslinks but which are maintained for at least one vibration cycle, as these would lead to an increase in the C_1-terms which is not observed.

The effects of temperature upon the dynamic behavior shown in Figures 4 and 5 may be summarized by the temperature dependence of C_2' and C_2'' as in Figure 6. It is seen that the apparent activation energies are not constant but increase rapidly as the glass-transition temperature is approached as is usual for the elastic and viscous prop-
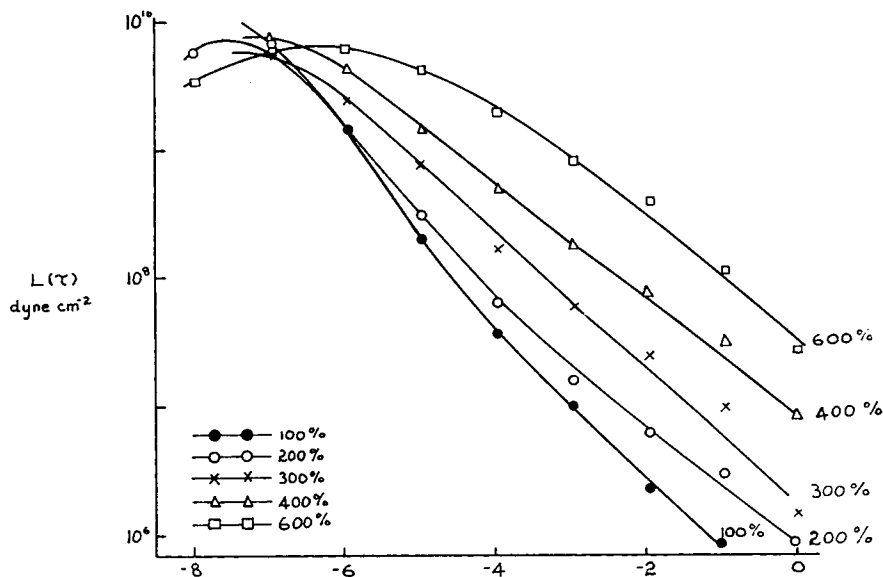

Fig. 8. Relaxation spectra reduced to −20°C. and 1 kcycle/sec.

Figure 8. At long times the curves for all extensions approximate to a linear dependence on $\tau^{-1/2}$, and application of Ferry's extension of the Rouse theory[13] would indicate that the effect of extension in this region is to increase the monomeric friction coefficient.

It may be significant in the present context to draw attention to the location of the maxima in the curves where the intensity is much greater than in the linear region. The effect of increasing extension from about 100% upwards is to move the maximum to longer times, so that the contributions of the elements with the shortest relaxation times are progressively reduced. This may be compared with the observation discussed above that at extensions greater than about 140% the contributions to elastic behavior of the shortest chain segments in the network are progressively eliminated.

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Synopsis

Measurements of the (complex) dynamic Young's modulus of natural rubber have been made by a wave propagation technique on filaments held at mean extensions up to 600%. It is shown that the real and imaginary parts vary with strain in the same way as the equilibrium modulus obtained from "static" stress-strain measurements, the behavior up to about 140% extension being derivable from a Mooney-type stored-energy function and at higher strains being dominated increasingly by the effects of finite extensibility in the network. The viscoelastic behavior in the region up to 140% strain may then be characterized by four parameters, of which one vanishes and another is constant for the rubber studied. It is shown how these parameters may be used to derive the strain-dependence of the damping or loss-factor (tan δ) in this region. The effect of increasing extension upon the relaxation spectra, over the range 100 to 600% extension, is to displace the whole spectrum progressively to longer times.

Résumé

Les mesures du modèle de Young dynamique (complexe) du caoutchouc naturel ont été effectuées par l'utilisation de la technique de la propagation d'onde dans les filaments maintenus à extension moyenne jusque 600%. On a montré que les parties réelles et imaginaires varient avec la tension de la même façon que le module d'équilibre obtenu par des mesures de tension et fatigue "Statique;" le comportement jusqu'à 140% d'extension est dérivable d'une fonction d'énergie emmagasinée du type Mooney et, aux plus hautes tensions, est dominé de façon croissante par les effets d'extensibilité limiteé dans le réseau. La comportement viscoélastique dans la région de 140% peut ainsi être caractérisé par quatres paramètres. Un de ceux-ci disparaît et l'autre reste constant pour le caoutchouc étudié. On a montré, comment ces paramètres peuvent être utilisés pour dériver la dépendance par rapport à l'extension de l'amortissement ou facteur de perte (tan δ) dans cette région. L'effet d'extension croissante sur le spectre de relaxation, dans le domaine de 100 à 600% d'extension, est un déplacement progressif de tout le spectre vers des temps plus longs.

Zusammenfassung

Messungen des (komplexen) dynamischen Young-Moduls von Naturkautschuk wurden mittels einer Wellenfortpflanzungsmethode an Fäden ausgeführt, die bei mittleren Dehnungen bis zu 600% gehalten wurden. Es wird gezeigt, dass der Real- und Imaginärteil die gleiche Abhängigkeit von der Verformung zeigen, wie der aus "statischen" Spannungs-Dehnungsmessungen erhaltene Gleichgewichtsmodul. Das Verhalten bis zu etwa 140% Dehnung kann aus einer Funktion vom Mooney-Typ für die gespeicherte Energie abgeleitet werden; bei höheren Verformungen wird es im steigenden Masse durch die Einflüsse der begrenzten Dehnbarkeit im Netzwerk beherrscht. Das viscoelastische Verhalten im Bereich bis zu 140% Dehnung kann durch vier Parameter charakterisiert werden von denen einer verschwindet und ein zweiter für den untersuchten Kautschuk konstant ist. Es wird gezeigt, wie diese Parameter zur Ableitung der Dehnungsabhängigkeit des Dämpfungs- oder Verlustfaktors (tan δ) in diesem Bereich benützt werden können. Der Einfluss der zunehmenden Dehnung auf die Relaxationsspektra im Bereich von Dehnungen von 100 bis 600% äussert sich in einer zunehmenden Verschiebung des ganzen Spektrums zu längeren Zeiten.