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The Dynamic Mechanical Properties of Hypalon-20 Synthetic Rubber at Small Strains

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INTRODUCTION

During the past several years, considerable effort has been expended towards the determination of the viscoelastic properties of high polymers. Particularly, polyisobutylene has been studied to a large extent.[1] The techniques developed in these studies provide a powerful means for a rather complete characterization of the dynamic mechanical properties of elastomers at small strains. In this work, a double electromagnetic transducer has been used to determine the viscoelastic properties of Hypalon-20, a commercial elastomer.[2]

EXPERIMENTAL

A. Materials

Hypalon-20 synthetic rubber is a chlorosulfonated poly-ethylene elastomer.[2] The sample used in the present experiments contained 27.77% Cl, 1.24% S, and 0.05% H_2O. The material was prepared from a polyethylene having a number-average molecular weight of about 20,000.[2] A value of $[\eta] = 0.79$ dl./g. in chloroform at 30°C. was obtained for the intrinsic viscosity of the Hypalon-20.

Dilatometric measurements on this material gave the density as 1.13 g./cm.^{3} at 25°C. and a value of $\beta = 7.3 \times 10^{-4}$ deg.$^{-1}$ for the thermal expansion coefficient of the specific volume above the glass transition temperature. Below the glass transition temperature ($T_g = -28 \pm 1$°C.), $\beta = 4.4 \times 10^{-4}$ deg.$^{-1}$, which is considerably higher than for most polymers.

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B. Apparatus

The double electromagnetic transducer which was employed for these measurements is the same which had previously been used for the determination of the dynamic mechanical properties of polyhexene-1.[3] This transducer is a modification of the one constructed by Marvin, Fitzgerald, and Ferry,[4] and it is designed to be used for measuring the real and imaginary components of the complex shear modulus in the 25 to 2500 cycle/sec. frequency range, from +80 to −70°C. Shear moduli from about 10^6 to 10^{10} dyne/cm.^{2} can be obtained with an accuracy of 5%.

The transducer is constructed for a tube of square cross section. A sketch of the tube with attached coil forms is shown in Figure 1. The coil forms are made of polystyrene and attached to the tube by aluminum inserts. Each coil consists of a $^1/_2$-inch layer of No. 30 magnet wire dipped in coil varnish. The combined weight of the

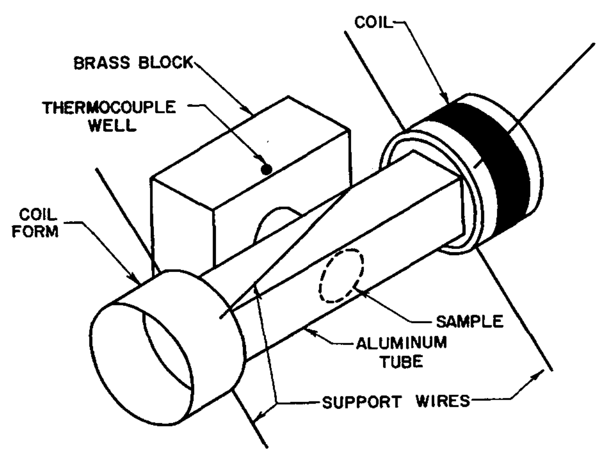

Fig. 1. Details of the transducer tube and method of mounting samples.

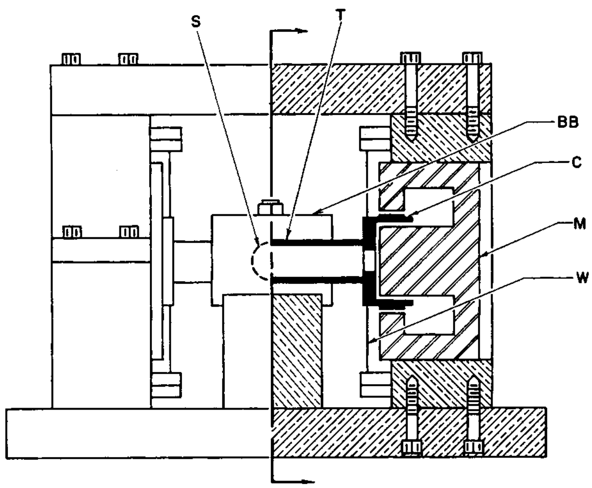

Fig. 2. Detail drawing of the transducer showing transducer tube T, sample position S, support wires W, permanent magnet M, coil C, and brass block BB.

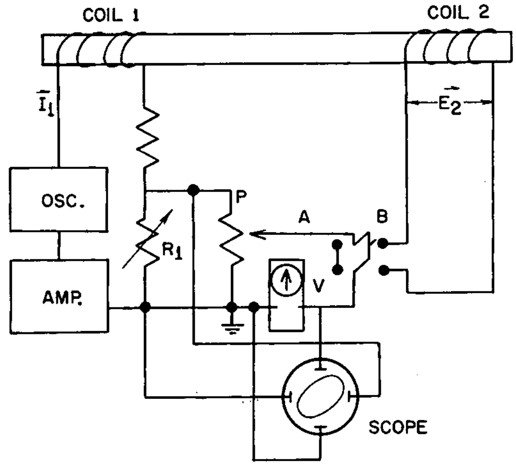

Fig. 3. Electrical circuit for the transducer showing the transducer coils, oscillator, amplifier, oscilloscope, voltmeter, and potential divider.

aluminum tube plus coils is 44.2 grams. The tube is suspended between two Alnico V permanent speaker magnets (Jensen Manufacturing Co.); the pole pieces were built in our shop with a gap width of 0.100 in. (see Figure 2). The magnets were assembled, demagnetized and magnetized in a 500-oersted field. The transducer tube suspension is made by means of four 0.005-inch diameter steel wires at each end.

The details of the transducer construction are shown in Figure 2. The samples to be measured are sheared between the transducer tube and the brass blocks mounted on a slide fastened to the transducer base. These blocks are constructed so as to move by means of a micrometer screw (not shown), which permits lateral positioning of the tube-sample system. The blocks are then firmly clamped in place by a bolt as shown. The thickness of the samples is determined by means of a 3-inch micrometer caliper placed across the sample blocks and a knowledge of the tube and block thickness. The flat plate across the top of the two magnet supports eliminates support vibrations which would otherwise occur when thin samples of high modulus are measured.

When in use, the transducer is mounted on a heavy felt pad in a Tenney[5] controlled-atmosphere chamber where temperatures from −70 to +80°C. may be obtained.

The electrical circuit for the transducer is shown in Figure 3. Except for the oscilloscope, this is essentially the circuit used by Marvin, Fitzgerald, and Ferry.[4] The current for the driving coil, coil 1, is supplied by means of a 30-watt Sonex audio amplifier which in turn is driven by a Hewlett-Packard model 200I audio oscillator. Resistance R_1 (25 ohm) is a precision resistor, and the potential divider P (input impedance 10,000 ohm) is an Electro-Measurements precision decade box. The voltmeter V (input impedance of 0.5 megohm) is a Ballantine model 300 vacuum tube voltmeter.

The mechanical impedance Z of a double transducer is related to the driving current I_1, and the resulting open circuit voltage E_2 by the following equation:

$$Z = K^2 I_1/E_2 \tag{1}$$

where K^2, the transducer constant, is given by (B_1l_1) (B_2l_2), B and l being the magnetic field and coil length, respectively. The quantity I_1/E_2 is the electrical transfer admittance. If Z_0 represents the impedance of the free transducer tube and Z_L the impedance of the transducer when shearing a polymer sample, the polymer impedance, Z_p, will be given by $Z_L - Z_0$. The complex shear modulus, G^*, of the polymer may now be calculated from the dimensions of the polymer sample and the measured impedance by means of the equation,

$$G^* = i\omega Z_p(h/A) \tag{2}$$

where h is the thickness of the polymer sample, A its area, and ω the angular frequency.

The real and imaginary components of the transfer admittance are determined as follows: With the switch in position B (see Fig. 3) the potential divider is adjusted so that a circle is observed on the oscilloscope. At this point a fraction α_1 of the potential drop across R_1 is just equal to the real component of the induced voltage E_2. (The reading on the voltmeter is now a minimum; however, this minimum is quite shallow, and balancing by means of the circle on the oscilloscope proved to be considerably more sensitive.) The reading of the voltmeter is noted, the switch is set in position A, and the potential divider is readjusted to a new value α_2 such that the previous voltmeter reading is reproduced. An analysis of the circuit yields the mechanical impedance of the tube in terms of potential divider readings. Equation (1) may then be rewritten as

$$Z = \frac{K^2}{R_1}\left(\frac{\alpha_1}{\alpha_1^2 + \alpha_2^2}\right) - i\,\frac{K^2}{R_1}\left(\frac{\alpha_2}{\alpha_1^2 + \alpha_2^2}\right) \quad (3)$$

Calibration of the transducer was carried out by two methods. If m is the mass of the transducer tube, k, the elastance of the supporting wires, and f represents a small, viscous factor, chiefly that attributable to air resistance, eq. (1) becomes

$$f + i\,(\omega m - k/\omega) = K^2\, I_1/E_2 \quad (4)$$

There will be a resonance when the imaginary part of the expression vanishes. For the present transducer, this occurs at 9 cycles/sec. At frequencies well above this resonance, k/ω becomes small, and, since f is also very small,

$$I_1/E_2 \cong im\omega/K^2 \quad (5)$$

Thus, a plot of the measured transfer admittance against the frequency ν should give a straight line of slope $2\pi m/K^2$. Such a plot is shown in Figure 4. The straight line is an indication that no resonances are occurring, and the value of K^2 determined from the slope of this line is $(5.10 \pm 0.04) \times 10^4$ ohm dyne sec. cm.$^{-1}$.

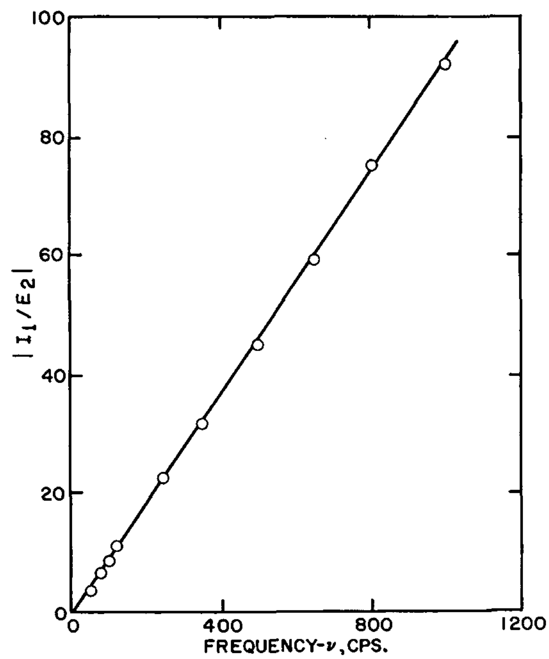

Fig. 4. Transfer admittance as a function of frequency. The slope of this curve, $2\pi/K^2$, is used to determine the transducer constant K^2.

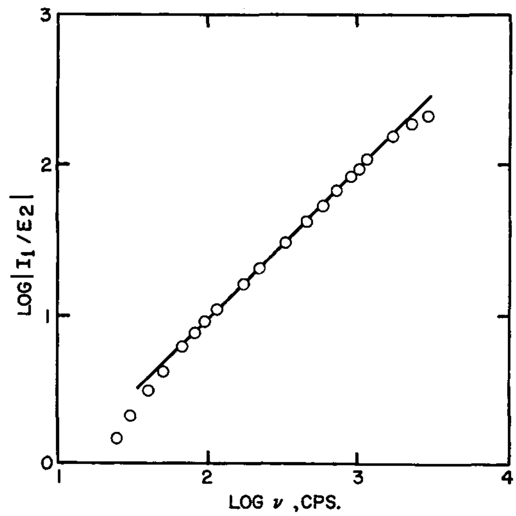

Fig. 5. Log transfer admittance vs. log frequency, showing the effects of the resonances at 9 cycles/sec. and somewhat over 6,000 cycles/sec. The straight line is drawn with a slope of 1.

Another and more general method is due to H. M. Trent.[6] If a mass m' is added to the transducer, the impedance becomes

$$Z = f + i[(m + m') - k/\omega] \quad (6)$$

The difference between this impedance and the impedance without the added mass is

$$i\omega m' = K^2\left[\left(\frac{I_1}{E_2}\right)_1 - \left(\frac{I_1}{E_2}\right)_2\right] \quad (7)$$

and K^2 may be determined directly from the measured admittances in the two cases. The value of K^2 was determined in this manner for m' ranging from 10 to 30 grams and gave $K^2 = (5.16 \pm 0.09) \times 10^4$ ohm dyne sec. cm.$^{-1}$, which is the same, within experimental error, as that obtained from Figure 4. The value of f was unmeasurably small over the whole frequency range.

A plot of log I_2/E_2 against log ν should be a line with a slope of unity as long as the tube is acting as a stiff rod. Such a plot is shown in Figure 5. It will be seen that some bending is occurring at about 2500 cycles/sec. This appears to be the onset of a resonance which occurs at somewhat over 6000 cycles/sec., which was the upper frequency limit of the audio oscillator used. In spite of this bending, K^2 was found to be constant up to 2500 cycles/sec. as measured by the Trent method.

It should be noted that measured moduli curves (e.g., Fig. 6) generally do not extend over the full 25 to 2500 cycle/sec. frequency range. There are two reasons for this. The sample impedance is determined by subtracting the impedance of the free transducer tube from the impedance of the polymer-tube system. According to eq. (4), the imaginary portion of the tube impedance increases as ωm while the imaginary portion of the polymer impedance varies as G'/ω. At high frequency and low moduli the impedance of the tube will tend to mask the impedance of the polymer. Measured moduli curves are therefore terminated when the error in impedance differences becomes greater than 5%.

When samples of high impedance are measured, the coupling between the tube-polymer system and the shearing weights becomes important. To use electrical analogies, the latter forms a circuit in parallel with the tube-polymer circuit. The exact impedance of the weight circuit will depend on the elastance of the weight supports and on the effective mass M of the weights. If these factors were known, exact allowance could be made for this shunting impedance. However, the elastance here is difficult to ascertain. Nevertheless, the impedance of the shearing weight system will increase essentially as ωM, so that its effect will disappear at high frequencies. In the present measurements, high moduli values are therefore terminated below 200 cycles/sec., that is, where the motion of the supports interfered with the measurement of sample impedance.

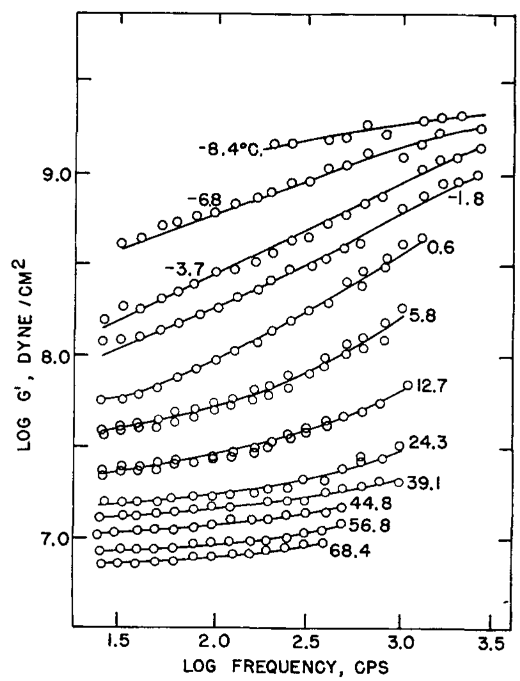

Fig. 6. Real component of the complex shear modulus as a function of frequency for Hypalon-20 synthetic rubber.

C. Procedure

Samples of Hypalon-20 were prepared by molding at 200°F. for 12 minutes. Three different size samples were used in order to carry measurements into the glass transition region. In general, the samples lacked sufficient adhesion at room temperature to yield good bonding between the transducer tube and the polymer samples. However, by raising the temperature to 60°C. and then cooling to room temperature it was possible to obtain satisfactory bonding.

In taking measurements on thick samples, it was necessary to apply considerable compressive force to the sample and as a result some bulging of the sample was observed; a correction was applied to compensate for this effect.[7]

DISCUSSION

The complex dynamic shear modulus G^* is defined in terms of its components through the relation $G^* = G' + iG''$. The real portion G' of the complex shear modulus is shown in Figure 6 for temperatures from -8.4 to $+68.4$°C. Values of G' range from 7×10^6 dynes/cm.^{2} = 101.5 lb./in.^{2} in the rubbery region to 2.1×10^9 dynes/cm.^{2} = 30,450 lb./in.^{2} in the glassy region. The corresponding values for the imaginary component G'' of the complex shear modulus are 2.1×10^6 dynes/cm.^{2} = 30.45 lb./in.^{2} in the rubbery region to 9×10^8 dynes/cm.^{2} = 13,000 lb./in.^{2} in the glassy region.

The method of reduced variables[8,9] may frequently be used to obtain modulus curves which extend over many decades of frequency. This

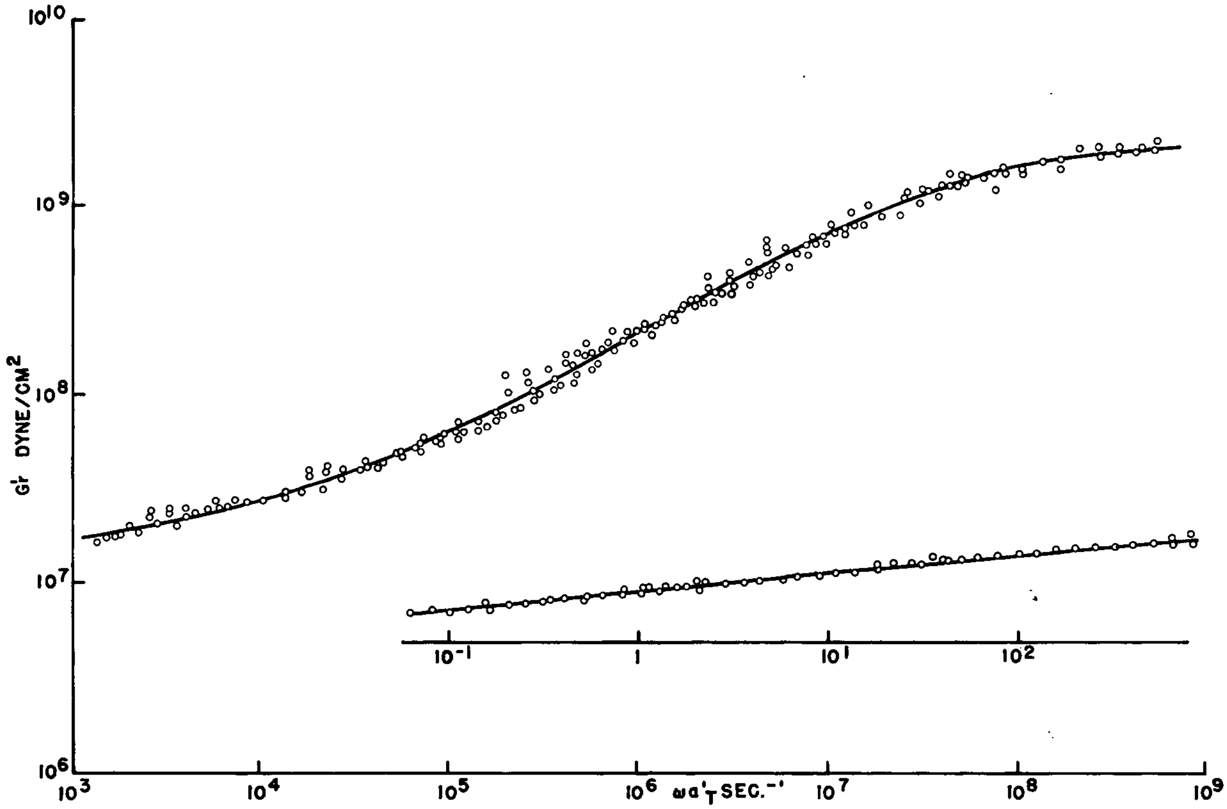

Fig. 7. Real component G_r' of the reduced complex shear modulus (25°C.) for Hypalon-20.

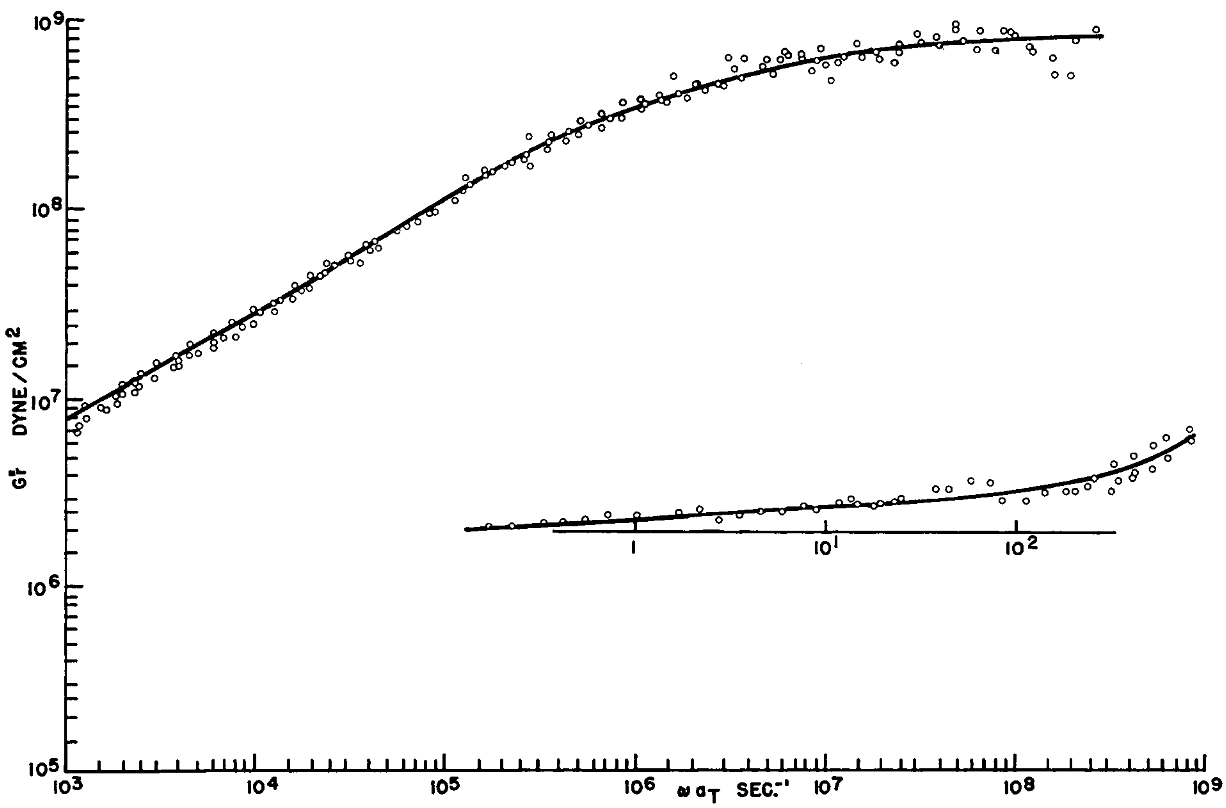

Fig. 8. Imaginary component G_r'' of the reduced complex shear modulus (25°C.) for Hypalon-20

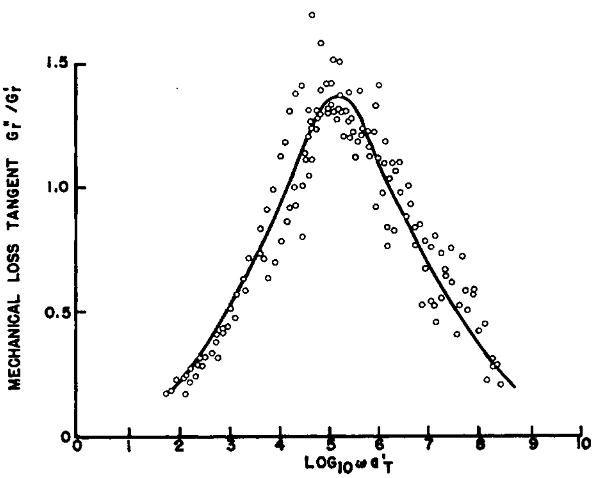

Fig. 9. Reduced mechanical loss tangent for Hypalon-20, reduced to 25°C.

method appears to be applicable for Hypalon-20. Composite curves for the reduced real and imaginary components of the modulus G_r' and G_r'', respectively, are shown in Figures 7 and 8, respectively. The curves are reduced to the *reference temperature, 25°C.* They extend over the reduced frequency $\omega a_T'$ from 10^{-1} to 10^9 radians/sec.; ω is the angular frequency, and a_T' is a function of the temperature alone:

$$a_T' = \frac{a_T}{a_{25°\mathrm{C.}}} \tag{8}$$

where a_T is given in Figure 10. The function a_T is discussed more fully below.

The mechanical loss tangent G_r''/G_r' as given by the method of reduced variables at 25°C. is shown in Figure 9. It is evident that Hypalon-20 reaches its maximum loss at $\omega a_T' \cong 10^5$ radians/sec. From this relation in combination with Figure 10 and eq. (8) it is evident that, for example, at 200 cycles/sec. the maximum loss of $G''/G' = 1.3$ occurs at about 10°C. A similar calculation for 2 cycles/sec. gives the maximum loss temperature of about −5°C. This may be compared with a maximum loss temperature of −7°C. at 2 cycles/sec. for chlorinated polyethylene (28.2% Cl).[10]

The function a_T is obtained experimentally from the shift along the frequency axis necessary to give the composite curve for either G_r' or G_r''; a_T is thus the temperature dependence of the relaxation times of the polymer, the temperature dependence of all relaxation times being taken as equal. Since the method of reduced variables appears to be operable for Hypalon-20, a_T seems indeed independent of the relaxation time.

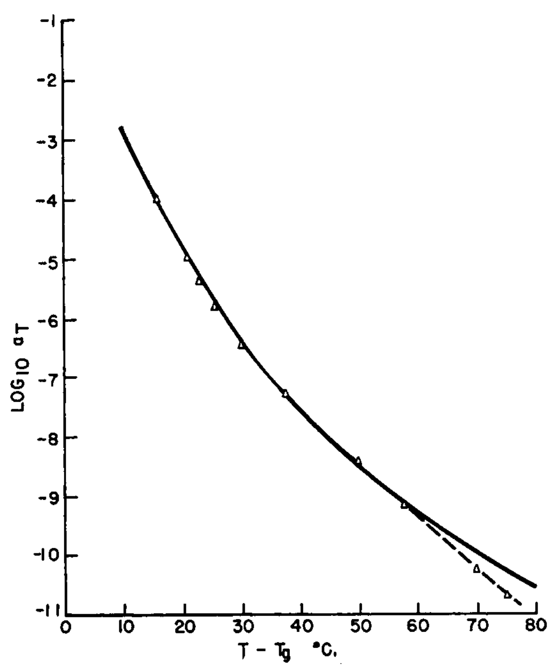

Fig. 10. Temperature reduction factors for Hypalon-20 reduced to −24.5°C. The triangles are experimental points; the line is a plot of eq. (9).

The reference temperature for a_T' (i.e., the temperature at which log $a_T' = 1$) may be arbitrarily chosen. This is commonly taken to be 25°C. In this paper the function referred to 25°C. is designated as a_T'. However, recently Williams, Landel and Ferry[11] have demonstrated that it is more natural to choose a reference temperature close to the glass transition temperature, T_g. In such cases the function a_T (referred to T_g) assumes a measure of universal validity for many polymers and even for inorganic glasses. This is expressed by equation

$$\log a_T = -17.44\,(T - T_g)/(51.6 + T - T_g) \tag{9}$$

For Hypalon-20, when one sets $T_g = -24.5$°C. (rather than -28 ± 1°C. which is the value of T_g obtained dilatometrically) in eq. (9), a rather good fit is obtained for a_T, as shown in Figure 10.

The distribution function of mechanical relaxation times τ can be used to describe a wide variety of time-dependent mechanical properties.[12–14] This distribution function for Hypalon-20 was calculated from the real and imaginary components of the reduced complex shear modulus, that is, from Figures 7 and 8, by means of the second approximation formulas of Ferry and Williams.[15] The distribution function, $H(\tau)$, reduced to 25°C. is shown in Figure 11. $H(\tau)$ values computed from

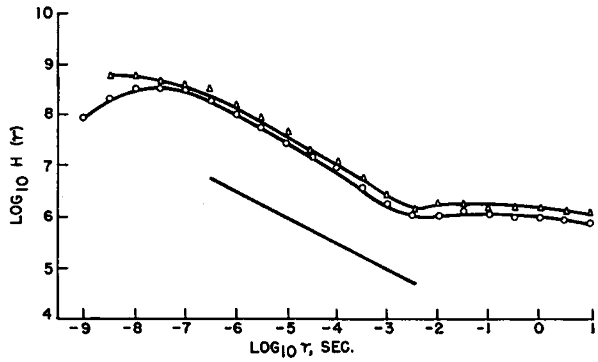

Fig. 11. Relaxation distribution function for Hypalon-20 at 25°C.: (Δ) computed from G_r''; (O) computed from G_r'. The straight line is drawn with slope $-1/2$ as required by theory.

G' and from G'' do not agree precisely; the reason for this difference is not known.

H (τ) appears to have a definite maximum at about 10^{-8} sec. (A broad maximum is indicated at times longer than 10^{-2} sec.) According to molecular theories of relaxation in high polymers in the rubbery state,[16–18] a plot of log $H(\tau)$ versus log τ should give a line having a slope of $-1/2$. This line is also shown in Figure 11. The actual slope for Hypalon-20 is about -0.57 over a large region of relaxation times and is thus in acceptable agreement with theory.

It is noteworthy that these dynamic measurements in conjunction with the method of reduced variables are able to determine H(τ) to as long a time as 10 seconds. Ordinarily a technique such as stress relaxation is required to do this.[1,3] The time range of 10^{-2} seconds to 10 seconds (and beyond) in Figure 11, where $H(\tau)$ is flat, may be termed the "chain entanglement" region. That is, it is the time range where the rate determining processes involve chiefly the disentanglement of polymer chains or the slipping of chains by one another.

In comparison with other polymers, the relaxation distribution function for Hypalon-20 is similar to those for polyisobutylene[1] and for polyhexene-1.[3]

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Synopsis

The dynamic mechanical properties at small strains have been determined for Hypalon-20 synthetic rubber, a commercial elastomer, by means of an electromagnetic transducer which is a modification of one described by Marvin, Fitzgerald, and Ferry. The measurements cover frequencies from 25 to 2500 cycles/sec. at twelve temperatures ranging from -8.4 to 68.4°C. Values of the real portion of the shear modulus (G') vary from 7×10^6 to 2.1×10^9 dynes/cm.^{2}, and those of the imaginary portion (G'') from 2.1×10^6 to 9×10^8 dynes/cm.^{2}. The method of reduced variables (i.e., temperature-frequency superposition) is applicable and is used to extend G' and G'' over the range 10^{-1} to 10^9 radians/sec. At 25°C., $G''/G' = 1.3$ at its maximum at 10^5 radians/sec. The general function for the temperature dependence of mechanical properties proposed by Williams, Landel, and Ferry is valid up to 35°C. if one uses -24.5°C. for the glass transition temperature (T_g); dilatometrically $T_g = -28 \pm 1$°C. The distribution function of relaxation times $H(\tau)$ has a pronounced maximum at about $\tau = 10^{-8}$ sec., decreases with a slope of about -0.57 (for log H versus log τ) to about $\tau = 10^{-3}$ sec., and is nearly flat from $\tau = 10^{-2}$ to 10 sec. H (τ) for Hypalon-20 is similar to those for polyisobutylene and polyhexene-1.

Résumé

On a étudié les propriétés mécaniques dynamiques à faibles tensions dans le cas au caoutchouc synthétique "Hypalon" 20, qui est un élastomère commercial. Les études ont été poursuivies à l'aide d'un transducteur électromagnétique qui est une modification de l'appareil décrit par Marvin, Fitzgerald, et Ferry. Les mesures couvrent les fréquences de 25 à 2500 cycles/sec. à douze températures variant de $-8{,}4$ à 68,4°C. Les valeurs de la partie réelle du module de cisaillement (G') varient de 7×10^6 à $2{,}1 \times 10^9$ dynes/cm^2, et celles de la partie imaginaire (G'') de $2{,}1 \times 10^6$ à 9×10^8 dynes/cm.^{2}. La méthode de réduction des variables (c.a.d., superposition de la température et de la fréquence) est applicable et on l'utilise pour étendre G' et G'' depuis 10^{-1} jusqu'à 10^9 radian/sec. à 25°C $G''/G' = 1{,}3$ et est maximum à 10^5 radian/sec. La fonction générale pour la dépendance de la température des propriétés mécaniques proposées par Williams, Landel, et Ferry est valable à des températures supérieures à 35°C, si l'on prend comme valeur du point de transition vitreuse (T_g) 24,5°C; la valeur dilatométrique de T_g est -28 ± 1°C. La fonction de distribution du temps de relaxation $H(\tau)$ a un maximum prononcée à environ $\tau = 10^{-8}$ sec, décroît avec une perte d'environ $-0{,}57$ (pour un diagramme log H vers log τ) jusqu'à environ $\tau = 10^{-3}$ sec. et reste sensiblement constante depuis $\tau = 10^{-2}$ jusqu'à 10 sec. La valeur de $H(\tau)$ pour l'Hypalon est similaire à celles obtenues pour le polyisobutylène et le polyhexène-1.

Zusammenfassung

Die dynamisch mechanischen Eigenschaften bei kleinen Verformungen wurden mit einem elektromagnetischen Gerät, das eine Modifikation des von Marvin, Fitzgerald, und Ferry beschriebenen ist, an dem synthetischen Kautschuk Hypalon-20, einem handels üblichen Elastomer, bestimmt. Die Messungen erstrecken sich bei zwölf Temperaturen im Gebiet von $-8{,}4$ bis 68,4°C über einen Frequenzbereich von 25 bis 2500 Hertz. Die Werte des Realteiles des Schubmoduls (G') liegen bei 7×10^6 bis $2{,}1 \times 10^9$ Dyn/cm^2, und die des Imaginärteils (G'') bei $2{,}1 \times 10^6$ bis 9×10^8 Dyn/cm^2. Die Methode der reduzierten Variabeln (d.h. Temperatur-Frequenzsuperposition) ist anwendbar und wird benützt, um G' und G'' über den Bereich von 10^{-1} bis 10^9 Radiant/sec zu erstrecken. Bei 25° erreicht G''/G' bei 10^5 Radiant/sec einen Maximalwert von 1,3. Die allgemeine, von Williams, Landel und Ferry vorgeschlagene Funktion für die Temperaturabhängigkeit mechanischer Eigenschaften ist bis zu 35°C gültig, vorausgesetzt, dass für die Glasumwandlungstemperatur (T_g) $-24{,}5$°C eingesetzt wird; dilatometrisch wird $T_g = -28 \pm 1$°C erhalten. Die Verteilungsfunktion der Relaxationszeiten $H(\tau)$ hat ein ausgeprägtes Maximum bei etwa $\tau = 10^{-8}$ sec, fällt mit einer Neigung von etwa $-0{,}57$ (für log H gegen log τ) auf etwa $\tau = 10^{-3}$ sec ab und ist nahezu flach von $\tau = 10^{-2}$ bis 10 sec. $H(\tau)$ hat bei Hypalon-20 einen ähnlichen Verlauf wie bei Polyisobutylen und Polyhexen-1.

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