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Dynamic Mechanical Properties of Neoprene Type W*

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INTRODUCTION

In this paper we present measurements on the dynamic mechanical properties of cured Neoprene Type W, a commercial poly-2-chloro-1,3-butadiene elastomer,[1] under small shear deformations. Such time-temperature dependent studies provide a powerful means to ascertain the linear viscoelastic behavior of a polymer over a wide range of conditions. The results may further be related to the molecular origin of the various segmental motions in terms of their relaxation mechanisms. The theories and techniques involved have been described in the recent book of Ferry.[2]

EXPERIMENTAL

The material studied was a gum stock having the composition in parts by weight of 100 Neoprene Type W/5 ZnO/4 MgO/1 phenyl-α-naphthylamine (Neozone A)/0.35 2-mercaptoimidazoline (NA 22). The synthetic elastomer was a commercial sample whose structural characteristics had been reported elsewhere.[1] This commonly used gum recipe[3] was cured at 153°C. for 30 min. Sample discs were then cut out from a $^3/_{16}$ in. sheet with a knife blade tool mounted on a drill press. The material had a density of 1.25 g./cm.^{3} at room temperature; the glass transition temperature, T_g, and its thermal expansion coefficient above T_g were estimated to be -46 ± 2°C. and 6.5×10^{-4} cm.^{3}/cm.^{3}°C., respectively, by linear expansion measurements. Previous work in this laboratory[4] indicated the sample to have 14% crystallinity which did not change appreciably between $-15°$ to the crystalline melting point of about 45°C. The crosslink density of such a vulcanizate had been measured to be 5.05×10^{-5} mole/g.[3]

Measurements of the complex shear compliance ($J^* = J' - iJ''$) were made with a Fitzgerald Transducer[5] at frequencies between 30 to 3000 cycles/sec. The instrument was tested after calibration by measurements on two pairs of the National Bureau of Standards polyisobutylene sample[6] at 25.0 and -4.7°C. The results were in good agreement with the published values of Fitzgerald, Grandine, and Ferry.[7] Figure 1 is a plot of loss tangent (J''/J') vs. log frequency reduced to 25°C. from the two

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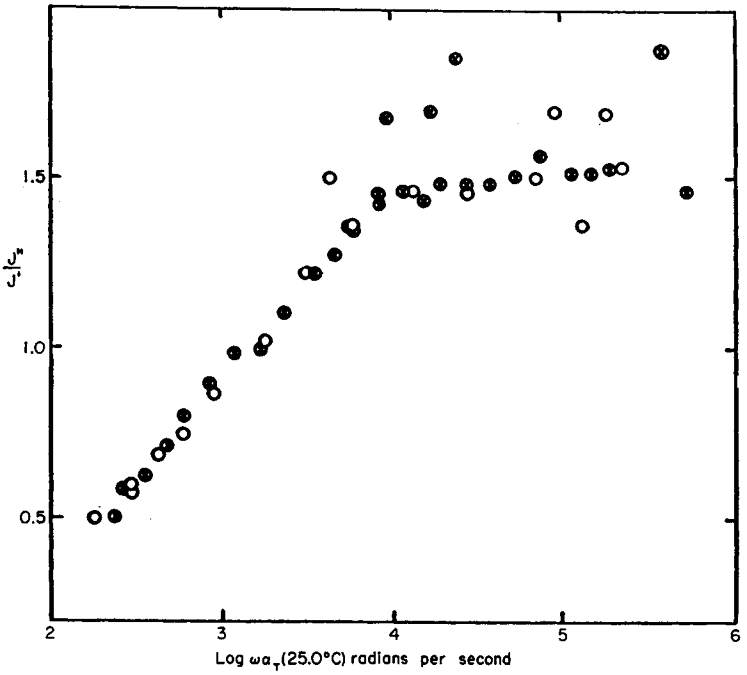

Fig. 1. Mechanical loss tangent (J''/J') vs. reduced frequency of NBS polyisobutylene. (⊗) From ref. 7 at 25.0 and 5.0°C.; (○) from this work.

sources. The quotient was chosen since it is more sensitive to discrepancies and is independent of sample coefficients.

Two pairs of neoprene samples were used. Samples 1, $^{11}/_{16}$ in. diameter by $^{3}/_{16}$ in. thick, were measured successively at 61.0, 71.1, 50.0, 40.4, 29.6, 19.5, 9.3, 5.3, −2.0, and −7.1°C., followed by a check run at 19.5°C. which agreed well with the initial one. Samples 2, $^{5}/_{16}$ in. by $^{3}/_{16}$ in., were studied in chronological order at 5.3, −0.8, −6.4, −29.5, −23.0, −16.9, and −10.6°C. Results from the two pairs of samples at 5.3°C. checked within 4% and no empirical corrections on the sample coefficients were applied. However, at temperatures below −10°C., the sample crystallinity increased with cooling as indicated by sharp stepwise compliance decrements; hence the dynamic results were difficult to interpret and are not included here.

RESULTS AND DISCUSSION

The Superposition Principle

The mechanical properties of a polymer may be characterized over a wide time scale at some reference temperature, T_0, by the Method of Reduced Variables[8] which is derived from the assumption that all relaxation mechanisms have the same temperature dependence. The Method in-

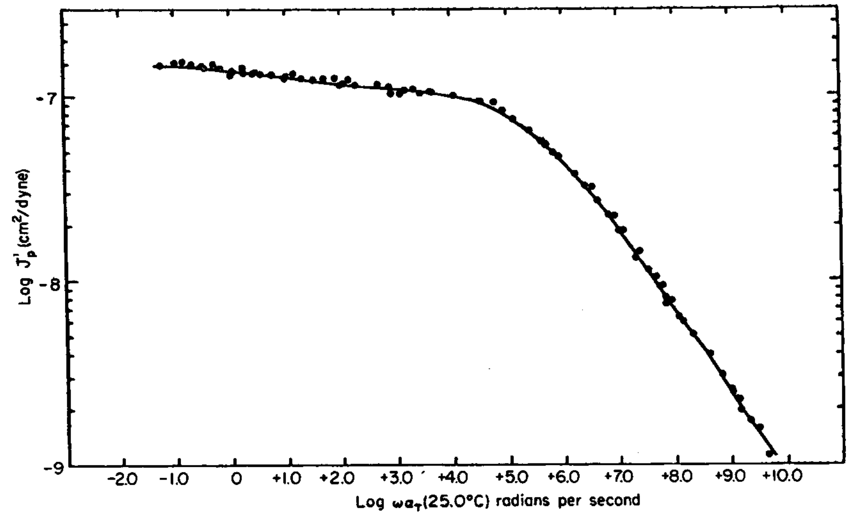

Fig. 2. Real part of complex compliance (J') plotted logarithmically vs. frequency after reduction to 25.0°C. Pip up at left, 71.1°C., successive 45° rotations clockwise correspond to 61.0, 50.0, 40.4, 29.6, 19.5, 9.3, 5.3° (averaged), −0.8, 2.0, −6.4, −7.1°C.

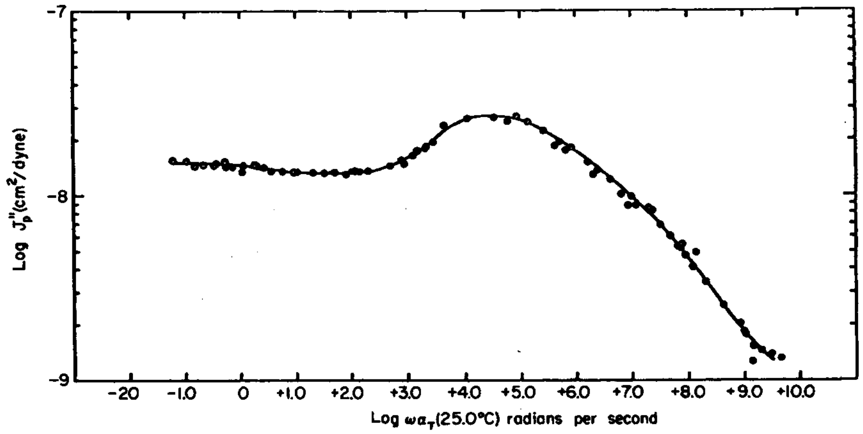

Fig. 3. Imaginary part of complex compliance (J'') plotted as in Fig. 2.

volves slight adjustments of J' and J'' by a multiplication factor of $(T\rho/T_0\rho_0)$ for temperature and density corrections; and an empirical shift on the frequency scale to achieve superposition.

The assembled data on Neoprene Type W were treated accordingly to yield two master curves reduced to 25°C. as shown in Figures 2 and 3. The shift factors, log a_T, were found to obey the following WLF equation[9]

$$\log a_T = -10.6\ (T - T_0)/(93.6 + T - T_0);\quad T_0 = 25.0°\text{C.}$$

It is interesting to note that if the *Universal Constant* of 51.6 were used in the denominator, the estimated T_g would be −17°C., which is about 30°

higher than that observed dilatometrically. However, the two derived molecular parameters, f_g, the fractional free volume at T_g, and α_f, the thermal expansion coefficient of the fractional free volume, were calculated to be 0.023 and 4.4 × 10^{-4}/°C., respectively, and were in good agreement with the *Universal* values of 0.025 and 4.8 × 10^{-4}.

Mechanical Properties

The two components of the reduced dynamic compliance, J'_p and J''_p, were converted to the corresponding reduced moduli, G'_p and G''_p, by the well-known reciprocal relationship of $G^*_p = 1/J^*_p = G'_p + iG''_p$. They are shown in Figure 4. The equilibrium shear modulus, G_E, of this permanently crosslinked system may be estimated from the limiting value of G'_p at low frequencies to be $10^{6.82}$ dynes/cm.². Since the present state of cure gives optimum tensile properties, the calculated G_E should be of general interest.

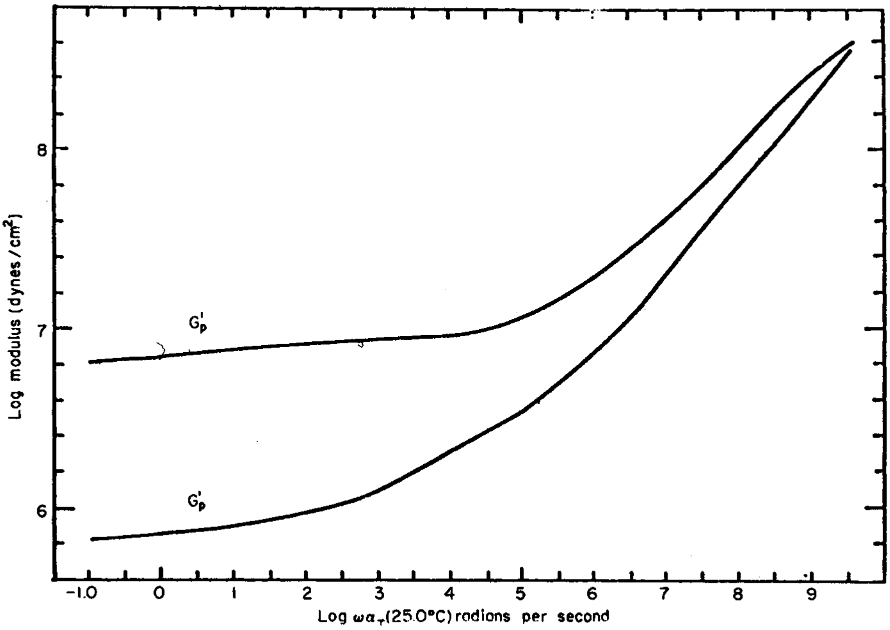

Fig. 4. Real (G') and imaginary parts (G'') of complex modulus vs. reduced frequency.

The average degree of polymerization per network strand, Z_c, can be calculated from the present data in two ways;[2] from the height of the maximum in J'' and from the location of the maximum in J'' on the frequency scale, ω_m. They are estimated to be 23 and 104, respectively, whereas from crosslink density the estimate is 112.

From the reduced compliance or modulus curves, the loss tangent spectrum of Neoprene W can be constructed as shown in Figure 5. The corresponding curves for polyisobutylene,[10] vulcanized natural rubber,[2] and

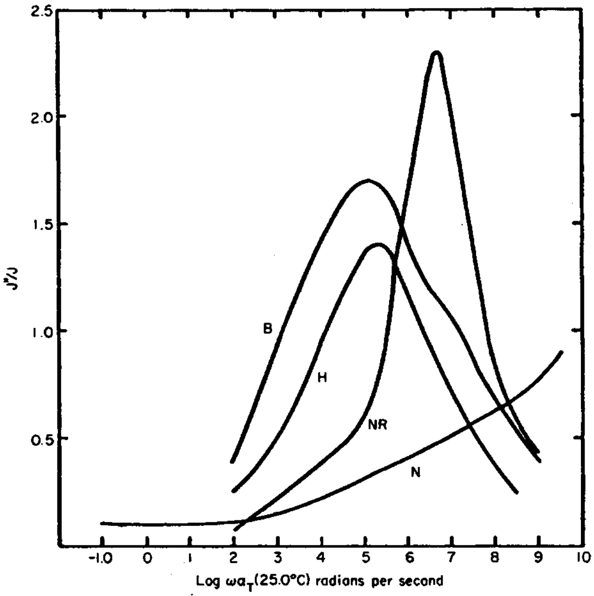

Fig. 5. Mechanical loss tangent of Neoprene W (N) Hypalon-20 (H), polyisobutylene (B), and vulcanized natural rubber (NR) all reduced to 25°C.

Hypalon-20[11] are also shown for comparison. Although our present Neoprene W data does not extend far enough to cover its loss peak, nevertheless it is obvious that it occurs at a much higher frequency region than for the other elastomers. This appears to be an unusual feature and was not expected by us.

Relaxation and Retardation Spectra

Distribution functions of mechanical relaxation and retardation times at 25°C. were calculated from the corresponding reduced moduli and compliance curves according to the Second Approximations of Williams and Ferry;[12] they are presented in Figure 6. The general agreement between the results from the real and imaginary components is satisfactory except at the onset of the dispersion region ($-4.5 < \log \tau < -30$). Both spectra exhibit general features common to crosslinked systems, that is, the existence of a rubbery plateau at $\log \tau > -3.0$ and a transition zone at shorter times.

The modified Rouse theory[13] predicts a slope of -0.50 for a double logarithmic plot of H vs. τ at the onset of the transition region. The present slope is -0.43 over an extended time scale of at least four decades. Such deviation is not uncommon in various polymers.[2] The monomeric friction coefficient, ζ_0, estimated[13] from the relaxation spectrum at $\log H = 6.0$, is found to be 1.8×10^{-6} dynes-sec./cm. at 25°C. using a value of 4.6 A. for the average root-mean-square end-to-end distance per square

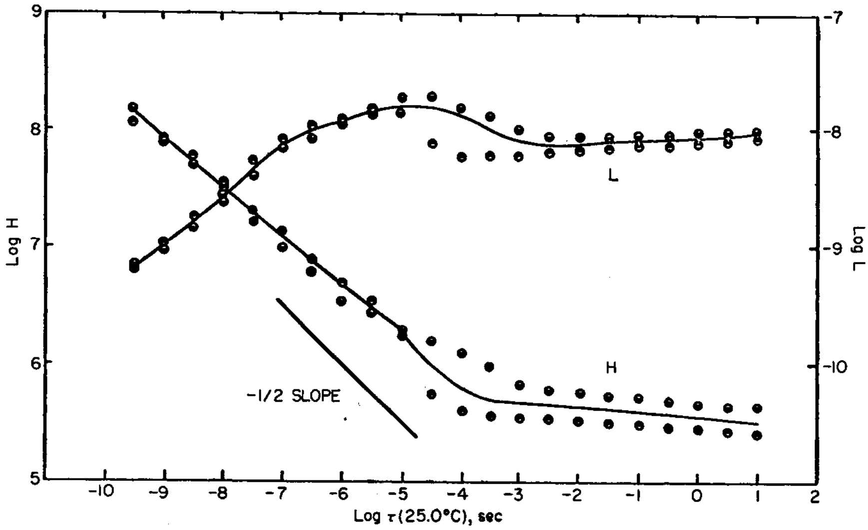

Fig. 6. Retardation spectrum (L) and relaxation spectrum (H). (●) From J'_p or G'_p; (◒) from J''_p or G''_p.

root monomer unit,[14] as compared to polyisobutylene (4.5×10^{-5}) and vulcanized natural rubber (1.8×10^{-6}). The magnitude of ζ_0 and the position of its loss peak both reflect an unusually high degree of local flexibility for Neoprene Type W in the vicinity of room temperature and audiofrequency.

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Synopsis

The dynamic mechanical properties of cured Neoprene Type W gum stock have been measured on a commercial Fitzgerald Transducer from 30 to 3000 cycles/sec. at twelve temperatures from -7.1 to 71.1°C. The results are reduced to 25°C. by the method of temperature-frequency superposition to obtain master curves for real and imaginary components of complex compliance which encompass over ten logarithmic time scales. The shift factors, log a_T, are found to obey the WLF equation of log $a_T = 10.6\ (T - T_0)/(93.6 + T - T_0)$; $T_0 = 25.0$°C. The equilibrium shear modulus is calculated to be $10^{6.82}$ dynes/cm.^{2}. The relaxation and retardation spectra are presented. The magnitude of its monomeric frictional coefficient (1.8×10^{-6} dynes-sec./cm.) at 25°C. as well as the implied appearance of the loss tangent peak at relatively high frequency reflect a very high degree of local flexibility. This result appears to be unusual when compared with other common elastomers, e.g., polyisobutylene, vulcanized natural rubber, and Hypalon-20.

Résumé

On a mesuré des propriétés dynamiques et mécaniques du néoprène vulcanisé du type W à l'aide d'un transducteur Fitzgerald commercial de 30 à 3000 cps à douze températures de -7.1° à 71.1°C. Les résultats sont rapportés à 25° par le méthode de superposition température-fréquence afin d'obtenir des courbes-type pour des composants réels et imaginaires de compliance complexe qui s'adapte sur les échelles, des logarithmes décimaux-temps. Les facteurs de glissement, log a_T, vérifient l'équation WLF de log $a_T = 10.6\ (T - T_0)/(9.36 + T - T_0)$; $T_0 = 25.0$°C. Le module de cisaillement calculé à l'équilibre est de $10^{5.82}$ dynes/cm.^{2} On présente les spectres de relâchement et de retardement. Aussi bien la grandeur du coefficient de friction du monomère (1.8×10^{-6} dynes-sec/cm) à 25°C que l'apparition implicite du pic de perte à une fréquence relativement élevée. Ces résultats apparaissent comme inhabituels lorsqu'on les compare à d'autres élastomères communs, entr'autres le polyisobutylène, le caoutchouc naturel vulcanisé et l'Hypalon-20.

Zusammenfassung

Die dynamisch-mechanischen Eigenschaften von vulkanisiertem Neopren Type W wurden mit einem käuflichen Fitzgerald-Transducer von 30 bis 3000 Hz bei zwölf Temperaturen im Bereich von $-7{,}1$° bis $71{,}1$°C gemessen. Die Ergebnisse werden nach der Methode der Temperatur-Frequenzsuperposition auf 25°C reduziert und liefern verallgemeinerte Kurven für den Real- und Imaginärteil der komplexen Nachgiebigkeit, welche sich über zehn logarithmische Zeitmasstäbe erstrecken. Die Verschiebungsfaktoren, log a_T, gehorchen der WLF-Gleichung log $a_T = 10{,}6\ (T - T_0)/(93{,}6 + T - T_0)$; $T_0 = 25{,}0$°C. Der Gleichgewichtsschubmodul wird zu $10^{6.82}$ Dyn/cm^2 berechnet. Die Relaxations- und Retardationsspektren werden angegeben. Die Grösse des Monomerreibungskoeffizienten ($1{,}8 \times 10^{-6}$ Dyn. sek/cm) bei 25°C sowie das Auftreten des Maximums des Verlusttangens bei verhältnismässig hohen Frequenzen spricht für einen sehr hohen Grad lokaler Biegsamkeit. Dieses Ergebnisscheint im Vergleich zu anderen üblichen Elastomeren, z.B. Polyisobutylen, vulkanisierter Naturkautschuk und "Hypalon"-20, ungewöhnlich zu sein.

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