JOURNAL OF APPLIED POLYMER SCIENCE VOL. 14, PP. 953-966 (1970)

Effect of Tensile Strain on the Use of the WLF Equation

ARNOLD ADICOFF and ALBERT H. LEPIE, *Chemistry Division, Research Department, Naval Weapons Center, China Lake, California 93555*

Synopsis

The effect of finite elongation on superposed infinitesimal torsional oscillations has been determined on two propellants, a carbon black-filled rubber and Solithane 113 (Galcit I), as a function of temperature at various fixed frequencies. Torsional storage modulus–temperature data for carbon black-filled rubber and propellant show that the effect of the imposed tensile elongation cannot be explained by any simple temperature–elongation shift relationship. The shift factors for the torsional moduli of these two polymeric systems have been calculated as a function of temperature at various tensile elongations. The WLF constants C_1 and C_2 have been computed for these systems as a function of the elongation. The constants decrease with increasing elongation. The values of the constants at 0% elongation are larger than those commonly found in unfilled materials. The temperature dependence of the shift factor of the torsional storage modulus was found to differ from that of the loss modulus in the cases of carbon black-filled rubber and propellant. This difference is slight for the rubber and large for the propellant. The effect of increased elongation is to increase the difference in the shift behavior of the moduli for each of these filled polymers. The shape of the loss tangent curve of the propellants examined indicates that these propellants are not thermorheologically simple.

INTRODUCTION

In describing the mechanical behavior of polymeric systems, more particularly that of propellants, and in propellant stress analysis, much use is made of characteristic material functions such as moduli, temperature coefficients, and time–temperature shift factors. It is generally assumed that the small deformation mechanical behavior in shear and simple tension is independent of a simultaneous finite tensile strain. This paper examines the effect of such a strain on the torsional dynamic shear moduli of a carbon black-filled rubber, two propellants, and Solithane 113 (Galcit I).

The experiments were carried out in the torsional pendulum described earlier,[1] except that the pendulum was converted from free to forced oscillation to avoid the limitations of the freely oscillating pendulum.[2] It is now possible to obtain the dynamic tensile and shear modulus over three decades of frequencies from 0.01 to 10 Hz over a temperature range from −90°C to 200°C after the specimen has been subjected to a finite strain of 0% to 100% elongation.

In the analysis of the data, the sample was regarded as a new specimen at each level of the finite elongation. The strained sample is effectively probed at each elongation with the small superposed torsional oscillation. In this way the complications arising from a proper stress analysis are avoided. It is recognized that this approach can only be regarded as a first approximation justified by the complexity of the problem. Under a finite deformation, a specimen (particularly when filled) may become anisotropic. A uniaxially strained specimen would then become transversely isotropic or axisymmetric. A material of this symmetry requires five material functions to characterize its behavior even in infinitesimal deformation. Experiments currently under way at this Center point to the possibility that a uniaxially stretched specimen may acquire anisotropic properties. Further work, however, is needed to clarify this point.

EXPERIMENTAL

The filled rubber used in these experiments was a carbon black-filled blend of natural and synthetic rubbers (Ratcliff Rubber Co., Gardena, California) and was cured in cylindrical molds according to the manufacturer's specification.

The propellants were Naval Weapons Center formulations designated as propellants A and B, have similar compositions, and are prepared from carboxy-terminated polybutadiene. They differ in that propellant A demonstrates a greater aging effect than does propellant B. Rectangular specimens were milled from the propellant. The A propellant had been aged 2 years before machining. The B propellant was recently prepared. Cylindrical specimens of Solithane 113 (Galcit I) were obtained from Professor Nicholas Tschoegl of the California Institute of Technology, Pasadena, California, and prepared in his laboratory. Galcit I has been adopted as interim standard in the Air Force Rocket Propulsion Laboratory's Standardized Rubber Program.[3] It is a highly crosslinked polyurethane rubber prepared from equal volumes of castor oil and Thiokol Solithane 113 (castor oil capped with tolylene triisocyanate).

All specimens were placed in a suitable aligning jig and were cemented into barrel-shaped aluminum end pieces.

The specimens were protected from the bath liquid (methanol) by slipping thin, lay-flat polyethylene tubing over the specimen and the end pieces. The diameters of the end pieces were large enough so that the polyethylene tubing was slightly stretched over the barrel. This arrangement protected the specimen adequately during the test, although some methanol vapor (but no liquid methanol) was detected inside the tubing upon prolonged exposure to the methanol bath at room temperature.

The temperature of the bath was controlled from −40°C to +30°C by a thermostated circulating bath. Measurements at the lower temperatures were obtained by circulating liquid nitrogen through the coils. The bath container was a Dewar flask with copper tubing for cooling and heating and contained suitable temperature-measuring devices.

The specimens were subjected to finite strains of up to 10% elongation at a crosshead speed of 2 in./min. The small deformation shear moduli were measured in torsion using a maximum angular deflection of 1 degree of arc over a length of 3 in. Torsional measurements were taken after the stress in the axial direction had sensibly relaxed. The lateral contraction of the specimen upon elongation was taken into account in the calculation of the torsional moduli, assuming a Poisson ratio for an ideal elastomer according to the classical Cauchy definition.

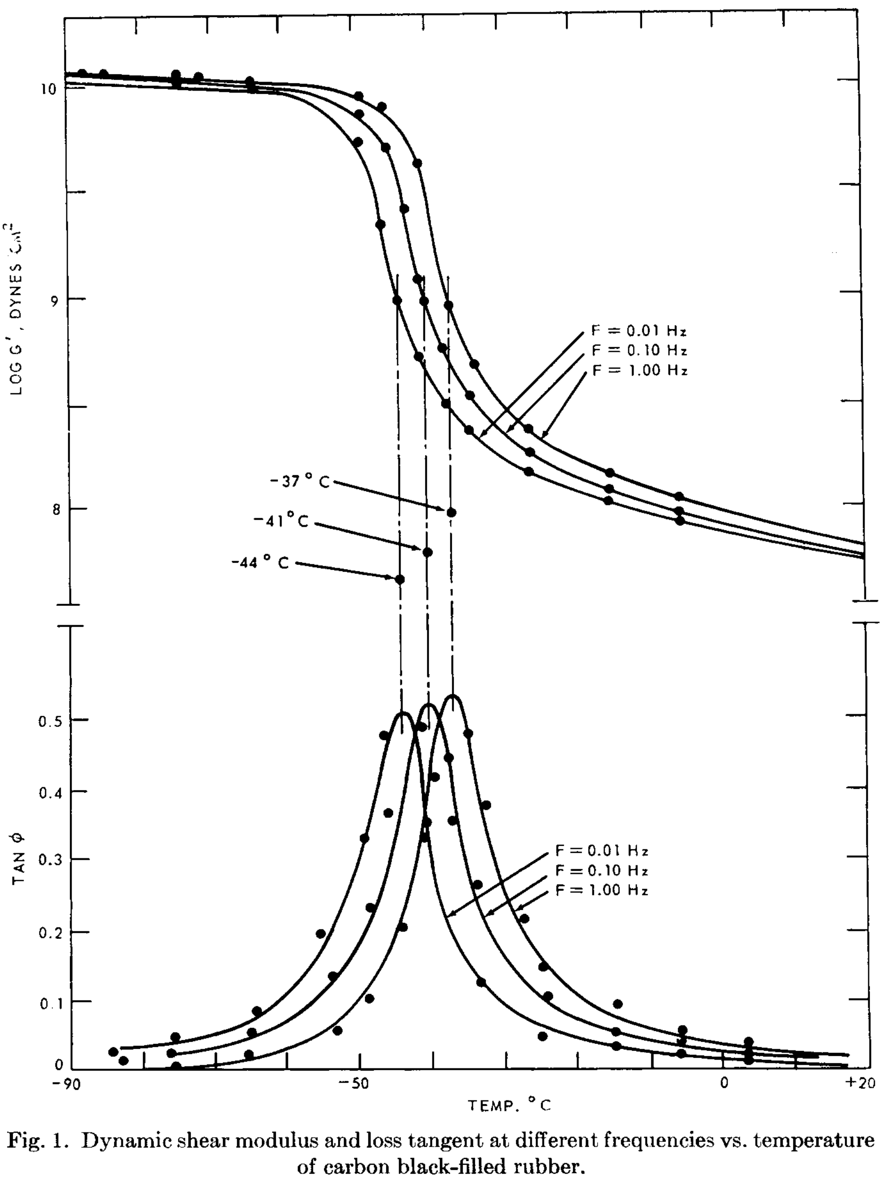

Fig. 1. Dynamic shear modulus and loss tangent at different frequencies vs. temperature of carbon black-filled rubber.

RESULTS AND DISCUSSION

To obtain background information on the torsional dynamic behavior of propellants under finite strain, the behavior of the B binder and propellant was compared with that of the carbon black-filled rubber in the absence of finite strain. Figure 1 presents the shear storage modulus and loss tangent of the carbon black-filled rubber as a function of temperature at the three frequencies of 0.01, 0.1, and 1.0 Hz. The figure clearly shows the usual shift of the damping maximum with frequency. The extent of the shift is approximately the expected 3°C per decade of frequency. From Figure 1 the location of the damping peak on the temperature scale at a given frequency can be obtained much more precisely than from data obtained in

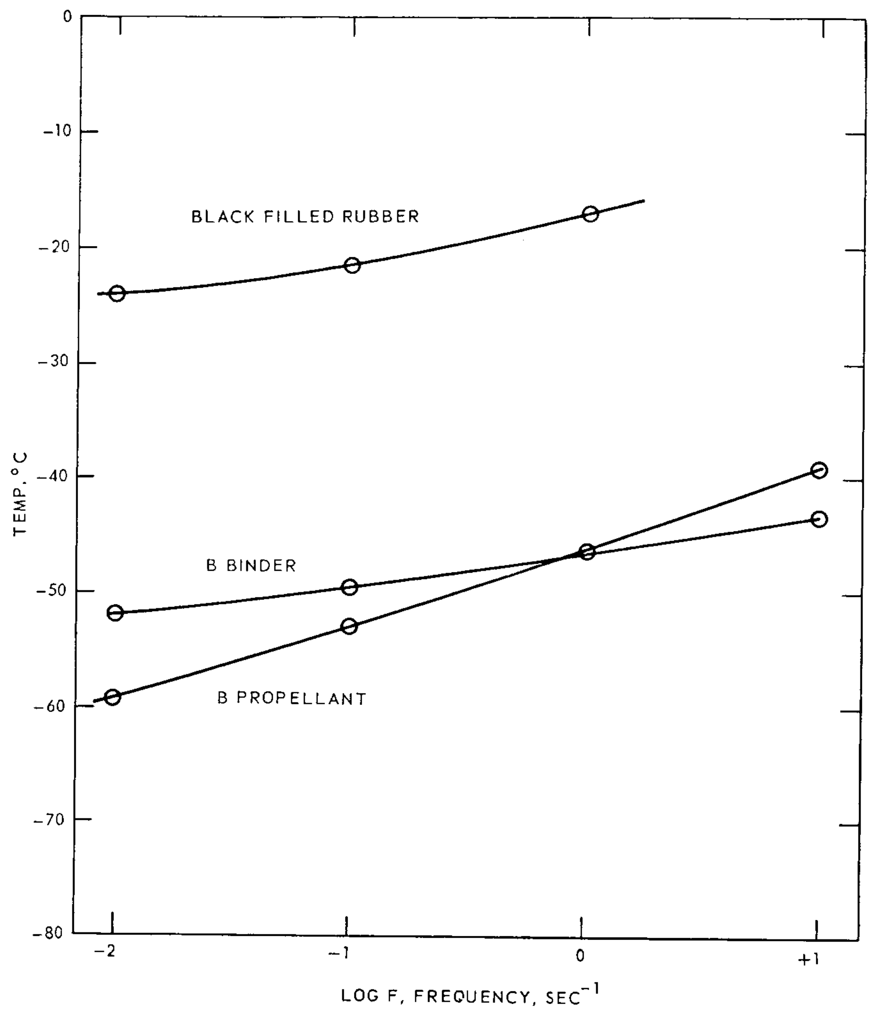

Fig. 2. Variation of temperature of maxima of loss tangent as a function of frequency.

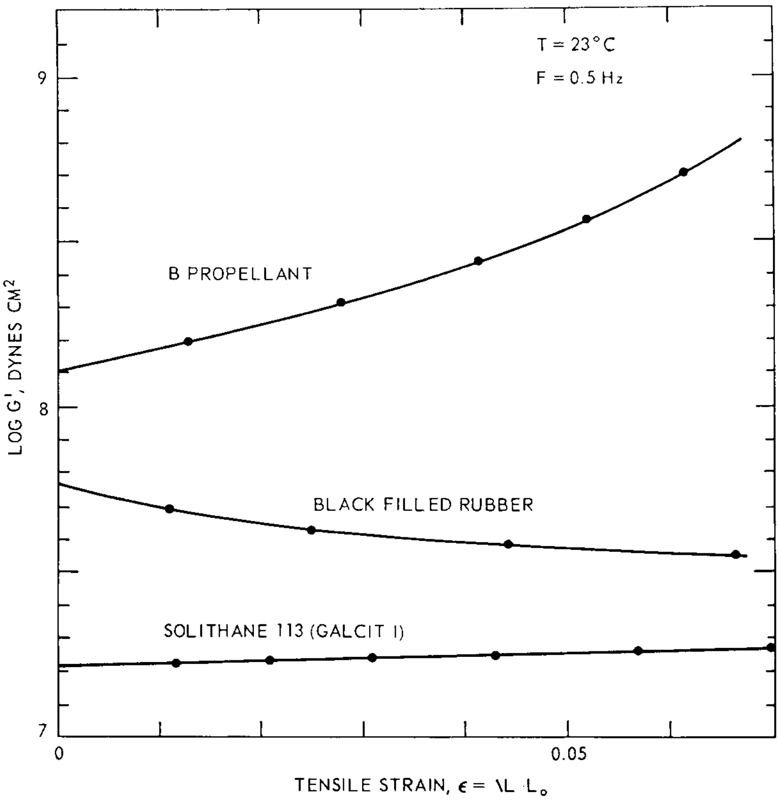

Fig. 3. Effect of tensile strain on storage shear modulus of different materials.

free oscillation. As shown by Platzek et al.,[4] the freely oscillating pendulum tends to be completely damped (i.e., tan $\phi \rightarrow \infty$) near the inflection point of the modulus-versus-temperature curve.

Similar determinations of the damping peaks were also made on the B binder and propellant. The maximum damping temperatures (*MDT*) are plotted as a function of frequency in Figure 2.

The variation of the *MDT* with frequency has been found to be characteristic for the materials examined. The variation for the carbon black-filled rubber is approximately 3.5°C per frequency decade; it is 3°C per frequency decade for the B binder, and about 6.5°C per frequency decade for the propellant. Ferry[5] has shown that the change in the glass temperature per decade of shift along the time axis is given by

$$\frac{d\Delta T_g}{d \log a_T} \cong \frac{C_2^g}{C_1^g} \cong 3°\mathrm{C}$$

for amorphous polymers. In this equation, C_1^g and C_2^g are the universal constants of the WLF (Williams, Landel, Ferry) equation referred to the glass transition temperature (T_g) as the reference temperature. The value of C_1^g is 17.44 and that of C_2^g is 51.6°C. Since the variation of the *MDT* of the propellant per decade of frequency is roughly equivalent to $d\Delta T_g/d \log a_T$, the data indicate that the effect of the filler in the propellant is reflected in a change of the ratio C_2^g/C_1^g toward higher values.

The effect of the finite strain (up to about 7% elongation) on the torsional storage shear modulus of the B propellant, the carbon black-filled rubber, and Solithane 113 (Galcit I) at a constant temperature of 23°C and a constant frequency of 0.5 Hz is shown in Figure 3. The three materials exhibit very different behavior. There is a small but definite linear rise in the modulus of Solithane 113. The propellant modulus increases about tenfold in the same range while the carbon black-filled rubber decreases moderately.

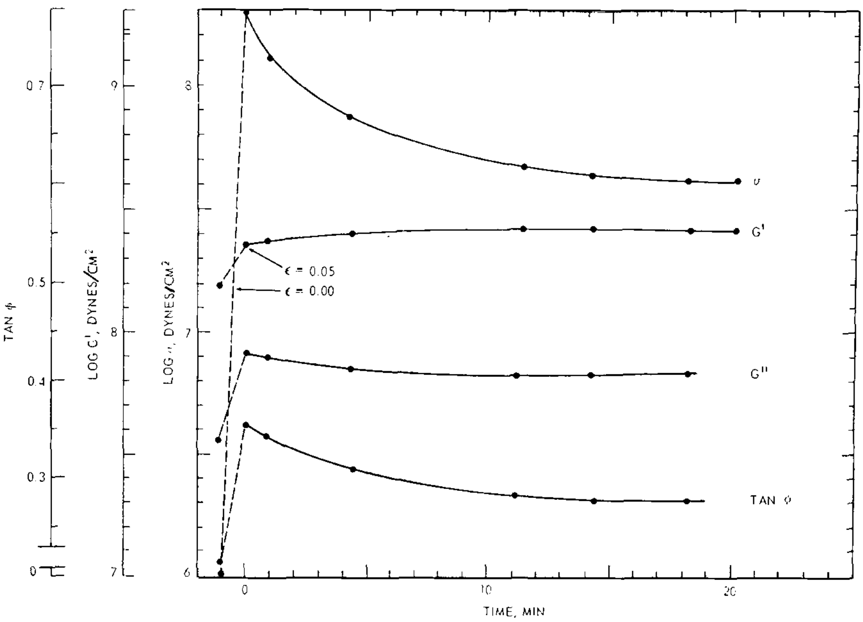

Fig. 4. Effect of tensile strain and stress relaxation on shear properties of propellant A at constant frequency.

The effect of finite elongation on the torsional storage modulus of Solithane 113 (Galcit I) is similar to that observed by Kuhn and Künzle[6] on natural rubber under even larger elongations, and to the effect of lateral compression on the storage modulus of styrene–butadiene rubber (SBR) in simple shear reported by Tschoegl and Smith,[7] except that the small increase of the modulus with strain was not observed in the natural rubber and the SBR. Mason[8] reported an increase in the tensile storage modulus of natural rubber with superposed elongation at 1 kHz. Tschoegl and Smith[7] observed increases of the storage and loss moduli of a polyurethane propellant in simple shear as a function of the lateral compression.

To ascertain whether the effect of elongation on the torsional shear modulus could be ascribed to relaxation of the tensile stress, torsional measurements were made on A propellant as a function of time after a 5% elongation. The results are shown in Figure 4. There is an immediate increase

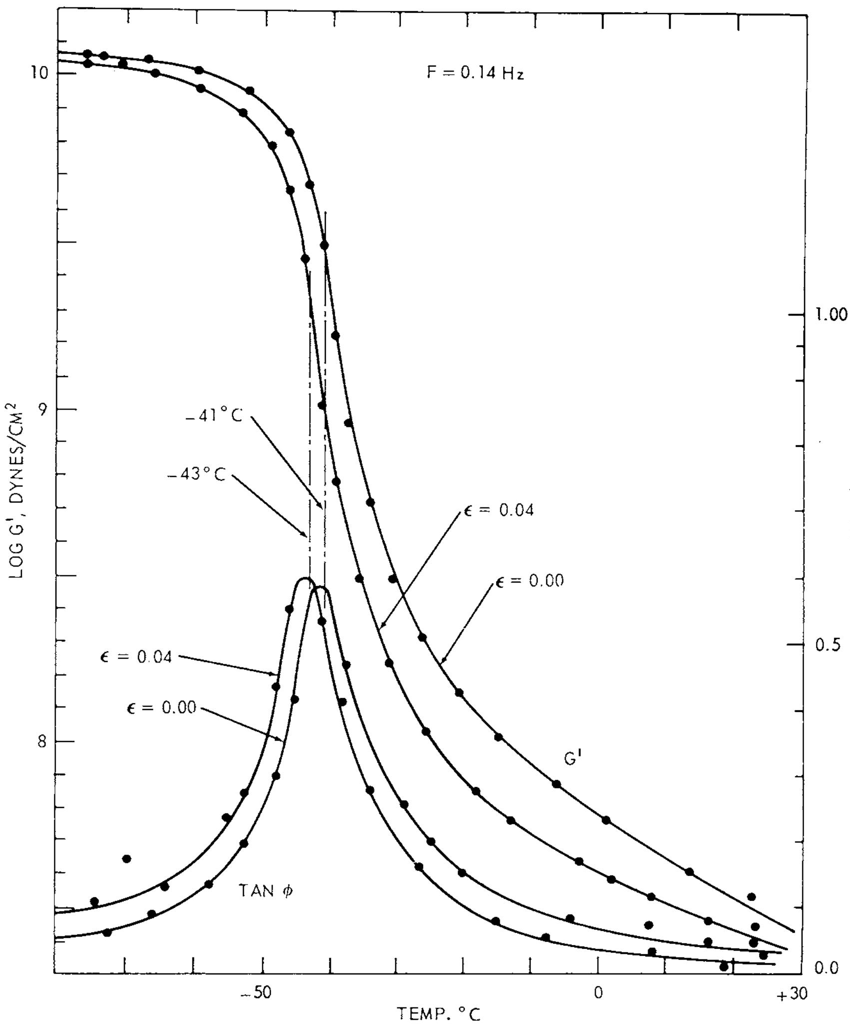

Fig. 5. Effect of tensile strain on torsional shear properties of carbon black-filled rubber.

in the moduli and loss tangents on stretching. As the tensile stress relaxes, the torsional storage modulus slightly rises while the loss modulus and loss tangent slightly decrease. The torsional properties become sensibly constant after about 10 min and it may be concluded that the relaxation of the tensile stress did not influence the measurements reported in this paper.

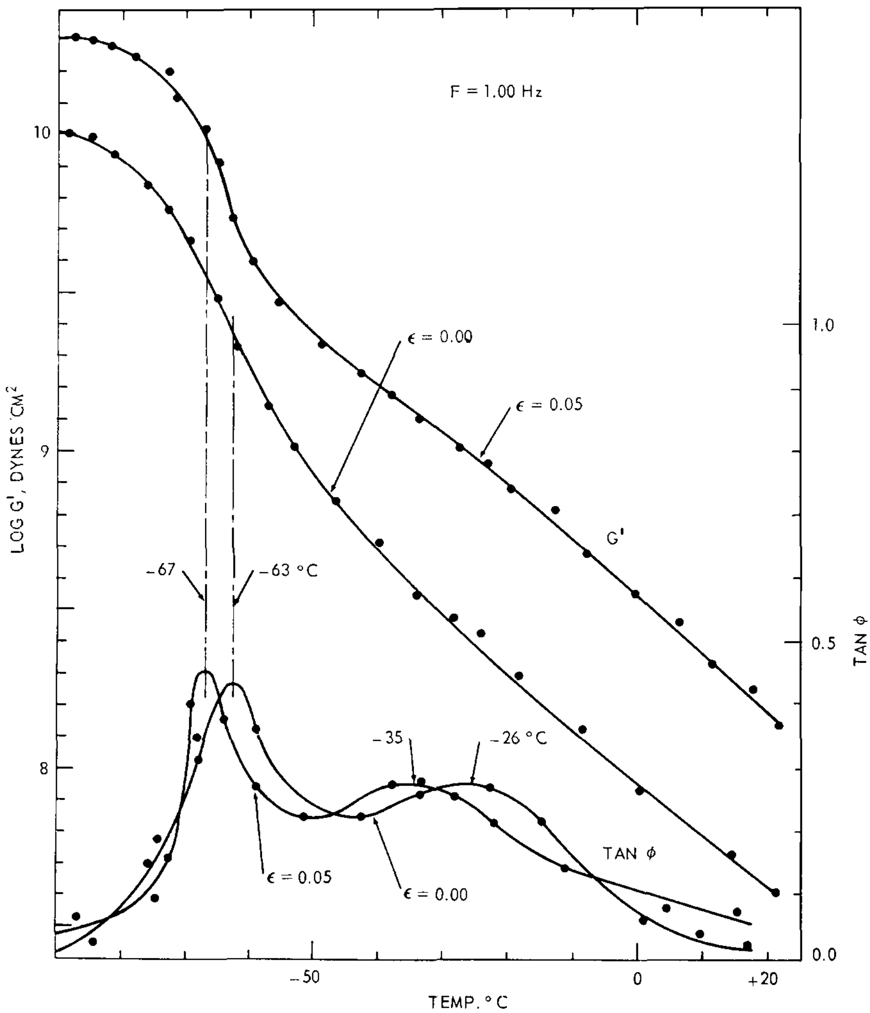

Fig. 6. Effect of tensile strain on torsional shear properties of propellant A.

Isochronal curves covering a temperature range of −75°C to 20°C are shown for the carbon black-filled rubber in Figure 5 and for the A propellant in Figure 6. The data in Figure 5 show the effect of 4% elongation on the storage modulus and loss tangent of the carbon black-filled rubber at the frequency of 0.14 Hz. The torsional storage modulus decreases with increasing elongation over the entire temperature range. The maximum damping temperature is reduced from −41°C to −43°C as a result of the elongation. The data are not sufficient to permit the prediction of the shift according to the Stratton-Ferry equation.[9] The modulus data shown in Figure 5 indicate that the curves obtained at 0% and 4% elongation cannot be superposed by simple horizontal and vertical shifts.

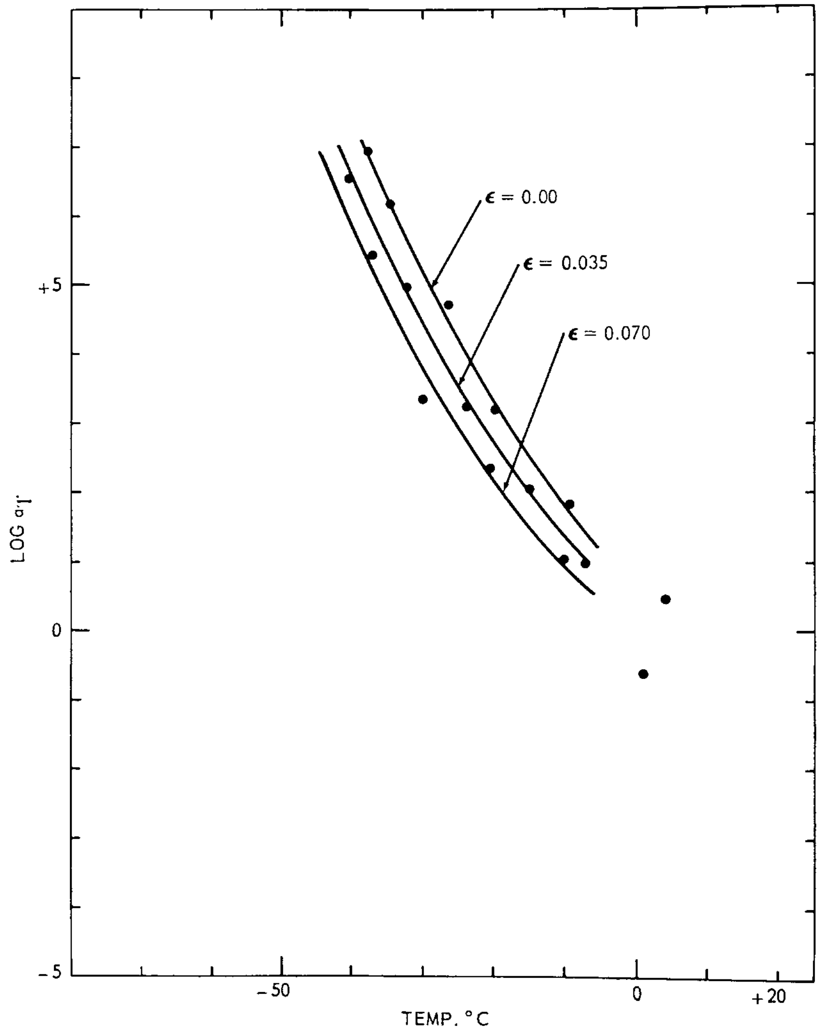

Fig. 7. WLF shift factors for G' as a function of temperature and tensile strain of carbon black-filled rubber.

Figure 6 shows the effect of a 5% elongation on the storage modulus and loss tangent of the A propellant at a frequency of 1.00 Hz. The propellant shows two maximum damping temperatures, one at −26°C and the other at −63°C. These peaks move differently along the temperature axis as a result of the elongation. The peak which is apparently associated with the glass transition temperature is decreased by 4°C for 5% elongation. This shift is similar in magnitude to the shift observed on the carbon black-filled rubber. The molecular origin of the higher temperature peak is unknown. That different relaxation mechanisms must be involved is apparent in the much larger shift, amounting to 9°C for a 5% elongation. As expected

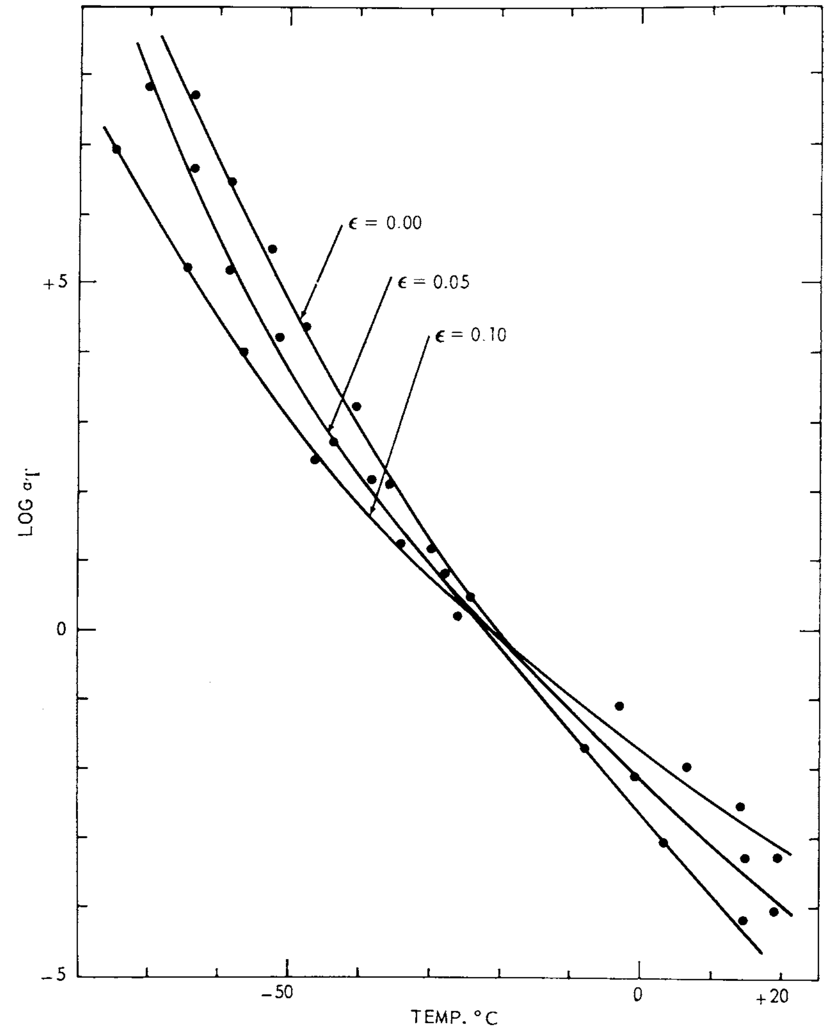

Fig. 8. WLF shift factors for G' as a function of temperature and tensile strain of propellant A.

from the behavior of the loss maxima, the shape of the modulus-temperature curve is different for strained and unstrained specimens. The existence of two loss maxima in the propellant indicates that it is not thermorheologically simple.

Shift factors were obtained from the storage modulus data and the C_1 and C_2 constants of the WLF equation were determined in the usual way.[4] The reference temperature, T_s, was taken as $T_g + 50°C$, taking T_g as the temperature of the loss peak at 0.01 Hz. The constants, C_1^g and C_2^g, referred to the glass transition temperature, were also calculated[5] for 0% strain. Table I shows these constants for the carbon black-filled rubber.

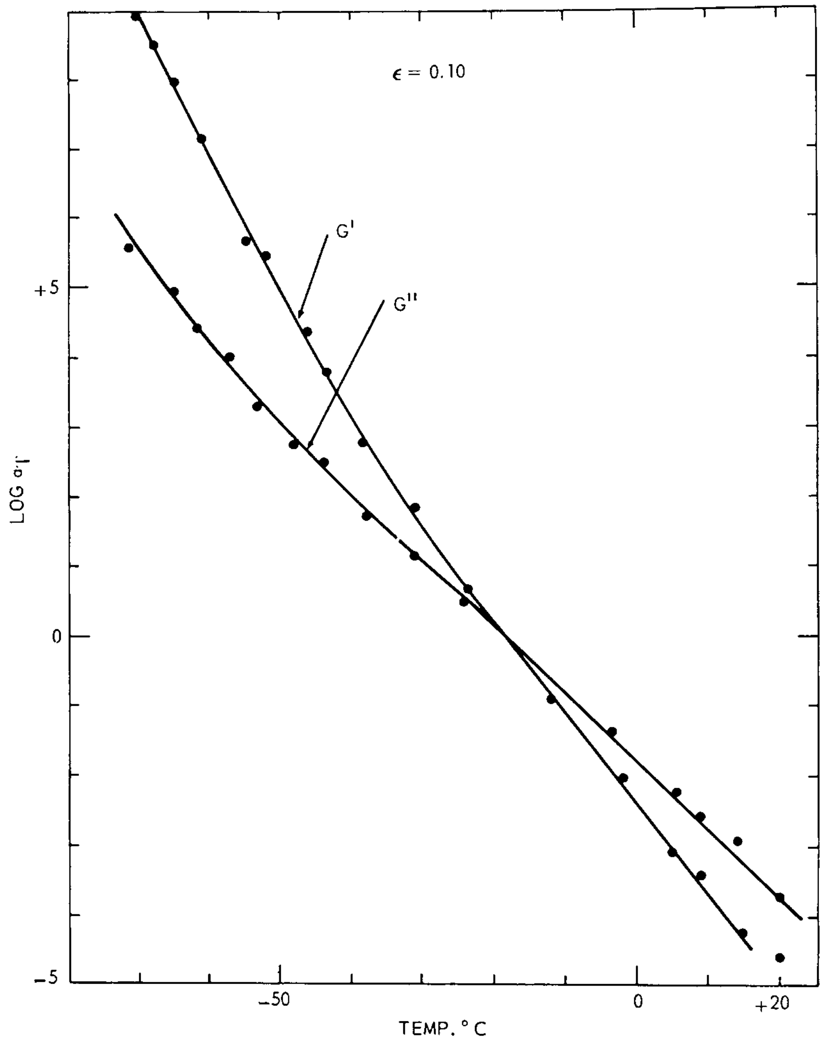

Fig. 9. WLF shift factors for G' and G'' as a function of temperature of propellant A.

The shift factors at different strains are plotted in Figure 7. The constants in Table I have been estimated from these curves. The effect of the elongation on the temperature shift is quite marked. Both C_1 and C_2 decrease

TABLE I
WLF Constants for Carbon Black-Filled Rubber at Different Tensile Strains[a]

Strain, %	C_1	C_2,°C	C_1^g	C_2^g,°C
0.0	21	164	30	115
3.5	15	134	—	—
7.0	10	110	—	—

[a] T_s = 1°C.

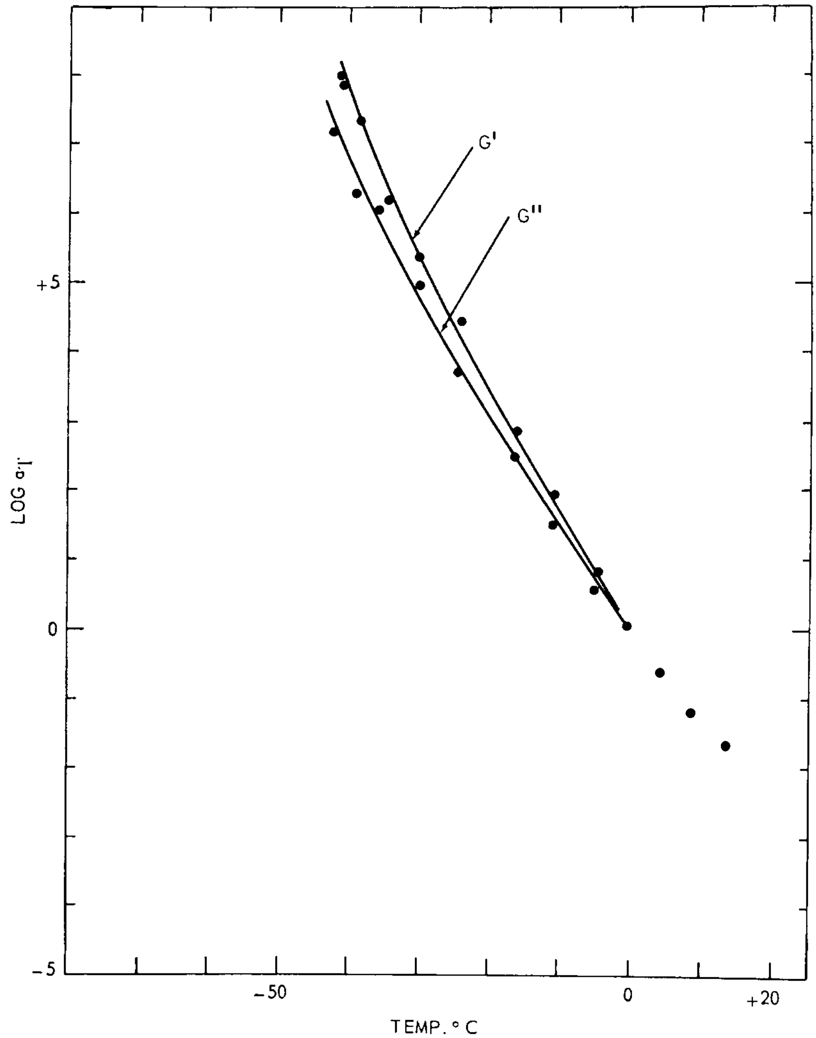

Fig. 10. WLF shift factors for G' and G'' as a function of temperature of carbon black-filled rubber.

with increasing elongation. Comparison with the constants tabulated by Ferry[5] for unfilled amorphous polymers shows that both C_1^g and C_2^g are larger than the values commonly found for unfilled materials.

The shift factors for the A propellant were determined in a similar way and the constants calculated for the WLF equation are shown in Figure 8 and Table II. They show a similar trend to that of the carbon black-filled rubber. Again, C_1^g and C_2^g are considerably larger than the values for unfilled materials. The significance of the large value of C_2^g is not understood, but similar values have been obtained by Moore and Robinson[10] on another propellant system. It should be noted, however, that the

TABLE II
WLF Constants of Propellant A at Different Tensile Strains[a]

Strain, %	C_1	C_2,°C	$C_1{}^g$	$C_2{}^g$,°C
0	21	156	26	126
5	13	131	—	—
10	7	92	—	—

[a] $T_s = -20$°C.

application of the WLF equation to the propellant data is of doubtful validity, since this treatment is applicable only to thermorheologically simple materials.

Figure 9 shows the temperature dependence of the shift factors for the real and imaginary parts of the torsional shear moduli of the A propellant. These data were obtained at 10% elongation. Contrary to the behavior of amorphous unfilled polymers, the storage and loss moduli have different shift factors. This difference in the temperature-dependent behavior was observed for the A propellant even at 0% elongation and increased with increasing elongation.

This behavior of the propellant could be attributed to the fact that it is not thermorheologically simple. However, a similar behavior (although not nearly as severe) was also observed on the carbon black-filled rubber as shown in Figure 10.

CONCLUSIONS

From these investigations the following conclusions are drawn:

(1) The variation of the maximum damping temperature with frequency is dependent on the nature of the material. Unfilled binder shows the smallest variation, carbon black-filled rubber shows a slightly larger variation, and filled binder (propellant) shows the greatest variation.

(2) The effect of increasing tensile strain on the torsional storage modulus is also dependent upon the nature of the material. Solithane 113 (Galcit I) shows a slight increase in the modulus, black-filled rubber shows a moderate decrease, and propellant a marked increase.

(3) The effect of tensile strain on the torsional storage modulus of propellant and black-filled rubber cannot be interpreted in terms of horizontal or vertical shifts of the modulus–temperature curves.

(4) The temperature dependence of the WLF shift factors for the torsional storage modulus of black-filled rubber and propellant also show elongation-dependent behavior. The effect of elongation on the shift factor is small for the black-filled rubber and large for the propellant.

(5) Increasing the elongation tends to decrease the values of the WLF constants C_1 and C_2 calculated from the torsional data.

(6) The WLF shift factors for the torsional storage moduli and torsional loss moduli are found to be different. This difference in behavior is only

slight for the black-filled rubber but large for the propellant. The difference is intensified with increasing tensile deformation.

(7) The existence and finite deformational behavior of the two peaks in the loss tangent–temperature curve of the propellant indicate that the propellant is not thermorheologically simple.

References

1. A. H. Lepie and A. Adicoff, *Rev. Sci. Instrum.*, **38**, 1615 (1967).
2. F. Bueche, *Physical Properties of Polymers*, Wiley, New York, 1961, p. 191.
3. W. G. Knauss and M. K. Müller, *The Mechanical Characterization of Solithane 113 in the Swollen and Unswollen State*, California Institute of Technology, Pasadena, California, CHECIT PL 68-2, AFRPL-TR-125, Dec. 1967.
4. D. J. Plazek, M. N. Vrancken, and J. W. Berge, *Trans. Soc. Rheology*, **2**, 39 (1958).
5. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 252.
6. W. Kuhn and O. Künzle, *Helv. Chim. Acta*, **30**, 849 (1947).
7. N. W. Tschoegl and T. L. Smith, CPIA Publication No. 119, Vol. 1, Silver Spring, Md., Oct. 1966, p. 267.
8. P. Mason, *J. Appl. Polym. Sci.*, **1**, 68 (1959).
9. R. A. Stratton and J. D. Ferry, *Kolloid-Z.*, **171**, 107 (1960).
10. F. Moore and C. N. Robinson, Paper Presented at the 3rd ICRPG-AIAA Solid Propulsion Conference, Atlantic City, N. J., June 4–6, 1968.

Received December 4, 1969