

The Tensile Properties of Highly Filled Polymers. Effect of Filler Concentrations

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I. INTRODUCTION

The mechanical behavior of highly loaded polymer systems is of interest in a number of applications. However, few well-defined studies have been made in an effort to fully explain the mechanical behavior in polymer systems containing a large proportion of solid, nonreacting, filler.

The mechanical behavior of loaded solids is very complex. In general, the response characteristics of nonloaded elastomeric materials can be represented in terms of the operations of mechanical models which involve the actions of Hookean springs and Newtonian dashpots.¹ However, in the case of elastomers highly filled with solids, the inclusion of particles further complicates the mechanical behavior. Since any deformation of a polymeric matrix results in nonuniform straining in the vicinity of a filler particle, the localized behavior is nonhomogeneous. Therefore, models analogous to those used by unfilled polymers would be expected to yield only approximate correlations. In addition, physical interaction between particles amplifies the complexity of the already intricate response behavior of the filled polymer at high loading.

Because of the interest shown in highly filled rubbers, an investigation was undertaken to characterize the response behavior of systems loaded with uniform glass spheres. The primary objective of this paper is to present some of the more significant findings of this program by describing typical behavior of filled rubbers when tested in uniaxial tension. The effects of temperature, rate-of-strain, and filler concentration were noted. Wide ranges of these variables were employed; the utility of high-rate testing in establishing the fundamental behavior of the loaded polymer systems was therefore shown.

II. EXPERIMENTAL

A. Limitations of Test Data

The behavior of highly filled elastomers may vary greatly with changes in bond strength between the filler particles and polymeric matrix. For very weak (or zero) bond strength, the filler-polymer bond fails immediately upon straining, and small holes (or vacuoles) are created next to a particle. Since there is no physical reinforcement, the material is weak and highly extensible. Alternatively, if the bonds are strong, the filled material exhibits a relatively high modulus with considerable reduction in the ultimate elongation.

It is in those systems where the adhesive bond is of intermediate value, however, that the problem of localized failure appears. As the specimen undergoes tensile loading, the weakest bond strengths are first exceeded. The filler particles are then released, transmitting a higher stress to the neighboring polymer-particle bonds. The effect observed is that of a line of released particle perpendicular to the direction of strain. If the applied load occurring after this phenomenon does not exceed the bond strength of the remaining intact bonds, the polymer along this line experiences very high strains and eventually fails. The extremes of tensile properties (those exhibited by high and low bond strengths) in filled materials are approached depending on the width of the localized yield band. The width of this yield band is inversely related to the comparative bond-strength values.

The implication of the above behavior is apparent: the stress-strain data (in simple tension) obtained after localized yielding occurs may no longer be related to the overall behavior of the material. In addition, localized yielding appears to be sensitive to temperature and strain rate. There-

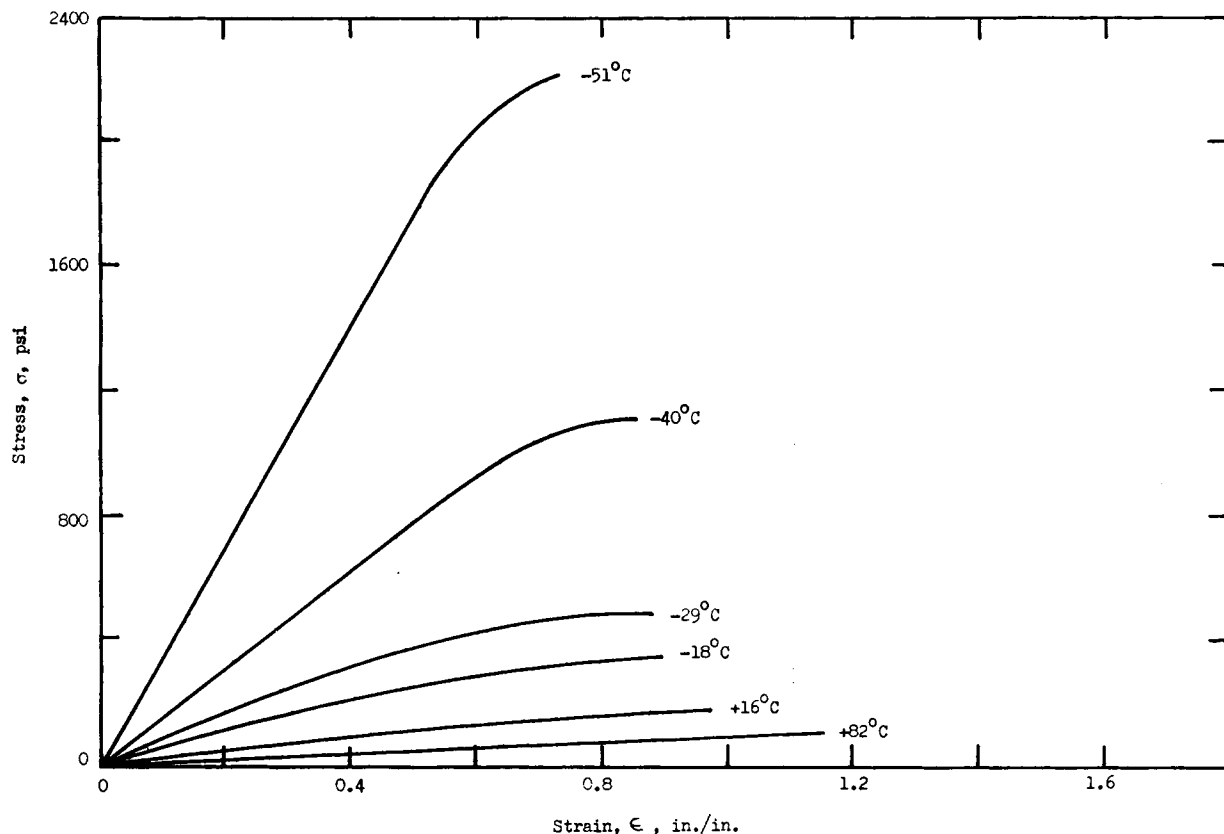


Fig. 1. Effect of temperature on the stress-strain properties of a filled polyurethan rubber. Volume fraction of filler $v_2 = 0.625$; strain rate $\dot{\epsilon} = 0.74 \text{ min.}^{-1}$.

fore, the data presented in this study have been confined to moderately low strains where localized yielding apparently is minimal.

B. Materials and Test Instruments

All of these tests were conducted on a crosslinked polyurethan rubber containing from 0 to 62.5 vol.-% glass spheres. The glass beads were closely sieved fractions having a uniform particle size ranging from 60 to 90 μ in diameter. The polymer system was chosen for comparatively high reproducibility, while the glass beads offered a relatively low filler-polymer bond strength (15 psi tensile at 80°F.).

Tensile testing was performed with an Instron tensile tester (Model TTC) for low rates of straining (0.074 to 7.4 min.^{-1}) and an Alinco high rate tester (Model 625A) for testing in excess of 7.4 min.^{-1} strain rate (7.4–1850 min.^{-1}). The test specimens were measured at 11 temperatures over the range -51 to $+82^\circ\text{C}$. The samples employed had a dumbbell shape and had an overall length of 6 in. The effective gage length determined from

photographic grids was 2.7 in. The samples containing up to 40 vol.-% glass beads were cast to size. The more highly loaded samples were milled to size from bulk-cast material. Each specimen received 3 hr. temperature conditioning prior to testing.

C. Typical Tensile Behavior of Filled Rubbers

Representative data for the filled polymer system (below the localized yield point) are shown in Figures 1, 2, and 3. The stress-strain behavior of filled rubbers under tensile loading is affected by decreasing temperature (Fig. 1), increasing strain rate (Fig. 2), and increasing solids content (Fig. 3).

In addition, the nature of the tensile curve is directly affected by the localized yielding behavior. Local yielding (at 0.01 in. strain) is shown in Figure 2 at 1850 min.^{-1} strain rate. In low-temperature, high-strain-rate tensile testing an abrupt change is seen at low strain values. The localized yielding appears to occur in a wider section of the specimen than it does either at higher tempera-

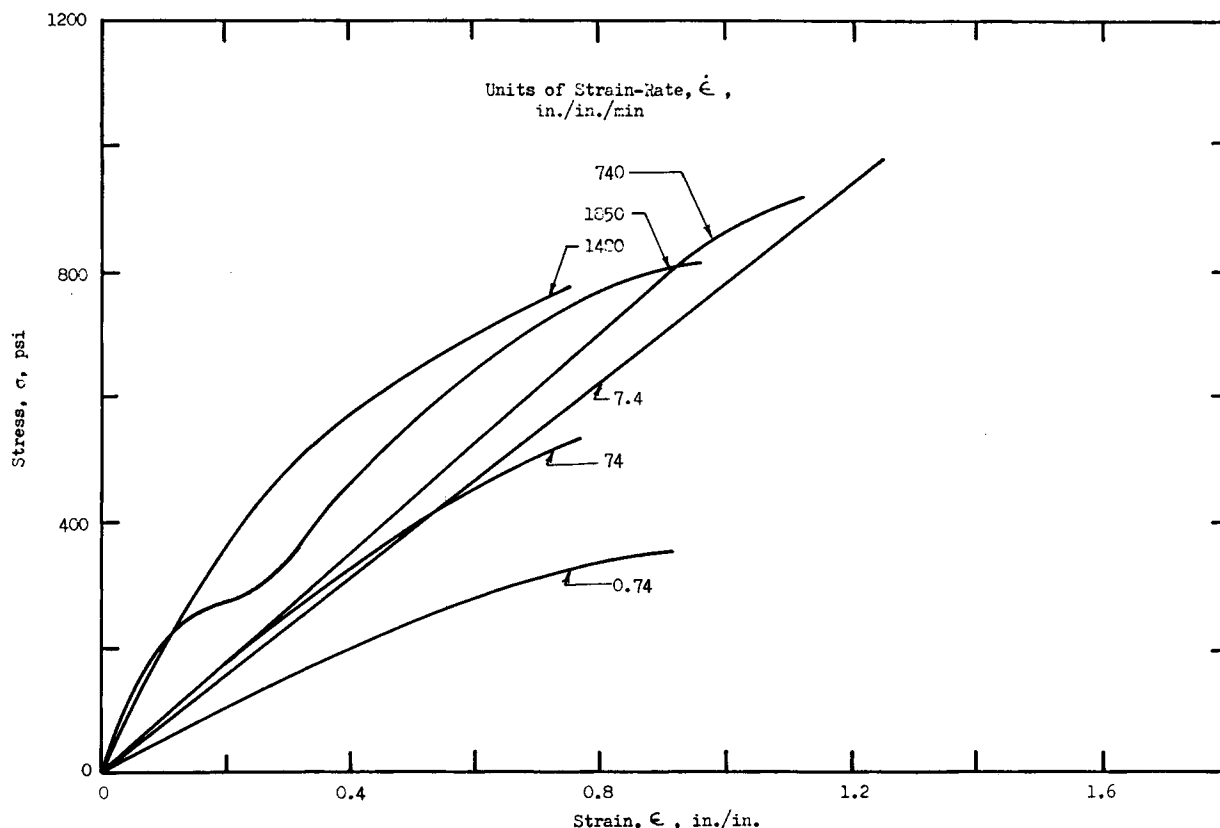


Fig. 2. Effect of strain rate on the stress-strain properties of a filled polyurethane rubber. Test temperature -29°C .; volume fraction of filler $v_2 = 0.625$.

tures or at lower strain rates. This produces a greatly yielded, weak specimen which then qualitatively shows the same behavior exhibited by a specimen tested at a lower strain rate. This behavior tends to increase the ultimate elongation values as well.

D. Application of Theory of Linear Viscoelasticity

1. Relations Employed. Considerable success has been obtained in this laboratory in the application of the linear viscoelastic theory (generalized Maxwell model) to the low- and high-rate tensile data of filled rubbers. This model is shown schematically in Figure 4. In this treatment a master curve may be calculated by combining the data obtained at different temperatures and at different strain rates. This is accomplished through relations suggested by Smith² by plotting $\log \lambda \sigma T_s / \dot{\epsilon} T a_T$ versus $\log \epsilon / \dot{\epsilon} a_T$ where σ is the nominal load per unit initial cross-sectional area (psi), ϵ is strain, (inches per inch), λ is an extension ratio equal to $(1 + \epsilon)$ (inches per inch), $\dot{\epsilon}$ is the strain rate (inches per inch per minute), T is the

test temperature (absolute), T_g is the glass transition temperature, T_s is a standard reference temperature, where

$$T_s = T_g + 50 \quad (1)$$

and a_T is a dimensionless shift factor dependent only on temperature.

The shift factors, a_T , may be obtained from the Williams, Landel, and Ferry (WLF) equation³ from the experimentally measured glass-transition temperatures and the relation

$$\log a_T = C_1(T - T_s) / [C_2 + (T - T_s)] \quad (2)$$

where C_1 and C_2 are nearly universal constants equal, respectively, to 8.86 and 101.6.

For the filled polymer systems presented here, the a_T and T_s values were obtained by superposing the test data which were obtained at different rates and temperatures. This method of data reduction allowed for an independent test of the validity of the WLF relation for a_T , in addition to an experimental determination of the values of T_s for the filled polymer systems.

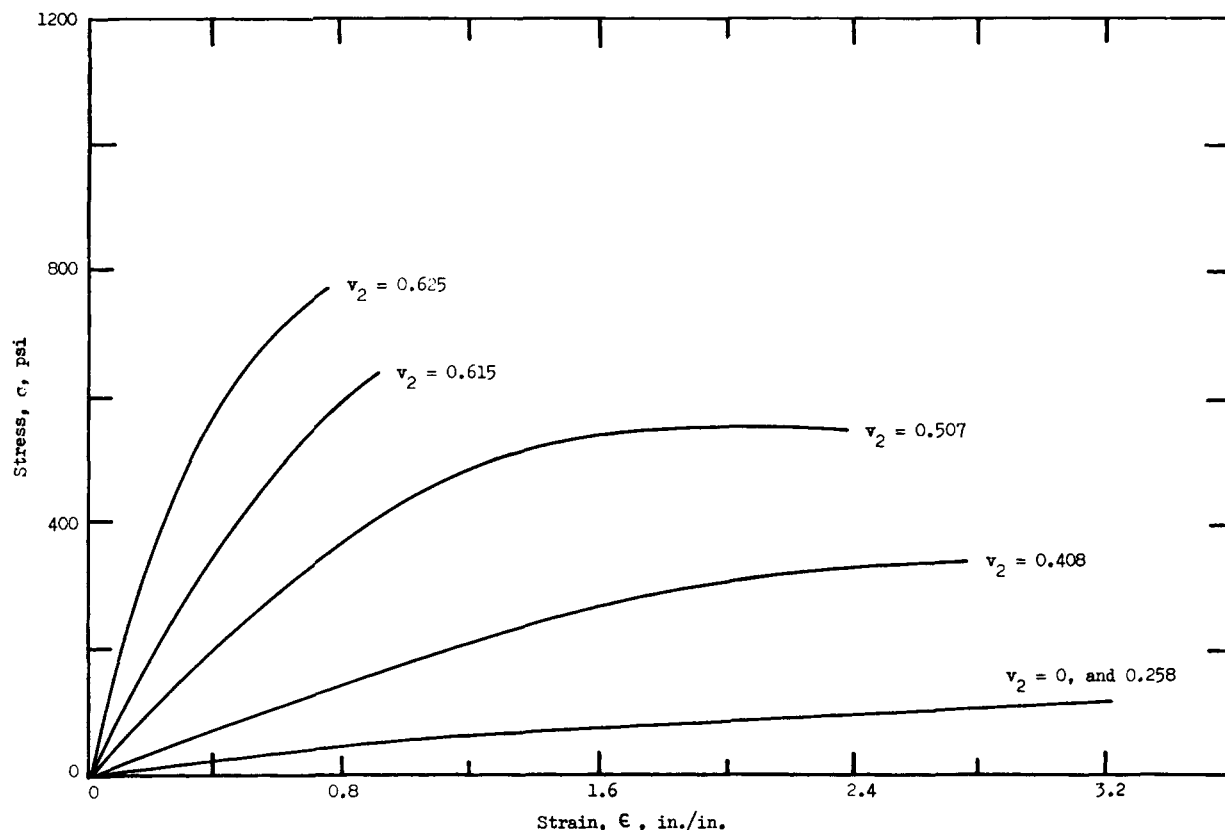


Fig. 3. Effect of filler concentration on the stress-strain properties of a polyurethan rubber. Test temperature -7°C ; strain rate $\dot{\epsilon} = 740 \text{ min.}^{-1}$.

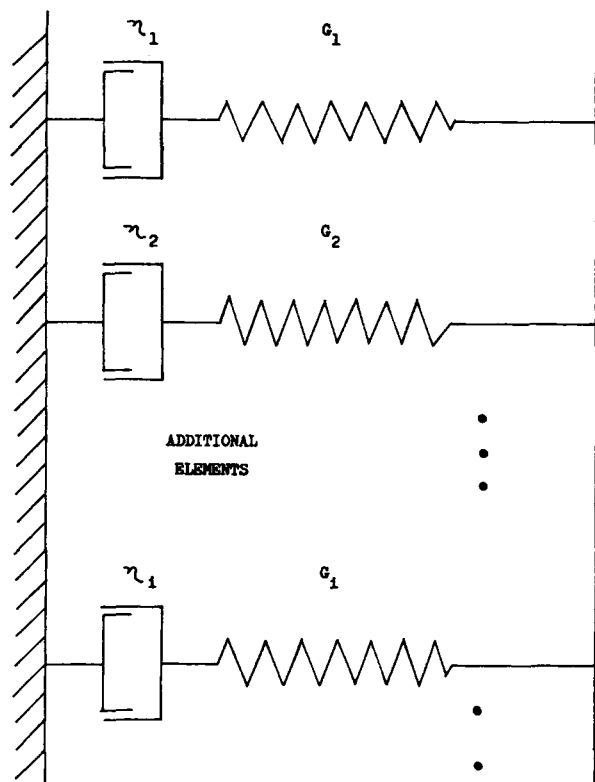


Fig. 4. Generalized Maxwell model characterized by a distribution function of relaxation times $N(t)$.

2. Application to Tensile Data. The reduced stress-strain curve for the pure polyurethan rubber is presented in Figure 5. These results indicate the typical range of experimental error obtained with the use of the above method of calculation. The experimentally obtained shift factors, a_T , are plotted in Figure 6, where they are compared with the theoretical values calculated from eq. (2). In this comparison, a value of 267°K . was used for T_s . This value was obtained from the reduced tensile curves. A very good agreement is noted, verifying the applicability of the WLF relation to this polyurethan system.

The reduced stress-strain curves for the filled polymers did not superpose but were displaced a small amount related to the volume loading. These data are shown in Figure 7. In each case, the experimental values of a_T correspond closely to those calculated by eq. (2).

The values of T_s for the filled polymers were found to increase with filler content. This relation is shown in Figure 8. It should be noted that this increase is essentially linear, following the relation

$$T_{sf} = T_s + mv_2 \quad (3)$$

where T_{sf} and T_s are the values of the reference temperature for the filled and unfilled polymer,

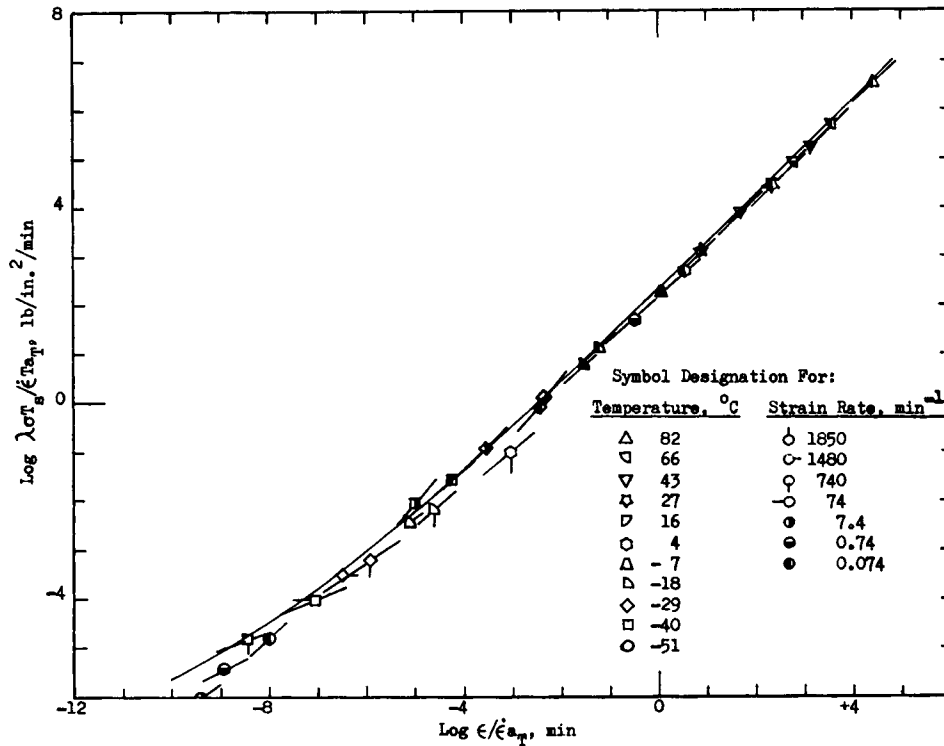


Fig. 5. Reduced stress-strain curve for a polyurethan rubber.

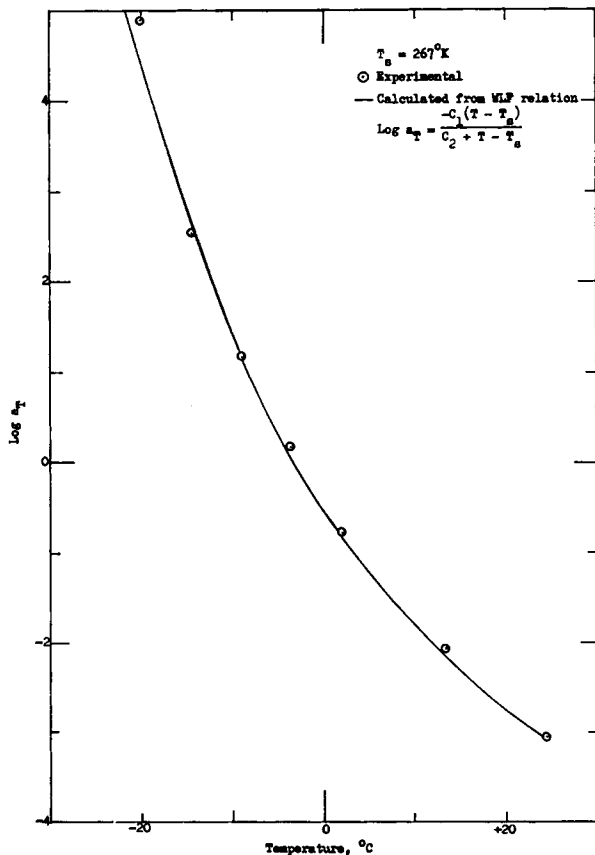


Fig. 6. Temperature dependence of shift factor a_T at $T_s = 267^\circ\text{K}$: (○) experimental; (—) calculated from WLF relation, $\log a_T = -C_1(T - T_s) / [C_2 + (T - T_s)]$.

respectively, v_2 is the volume fraction of filler, and m is an empirical constant. The value of m was found to be 22.5°K , which compares favorably with data obtained in other filled-rubber systems.

The values of T_{sf} as obtained from the reduced stress-strain plots were compared with those obtained by a differential thermal analysis (DTA) method for the measurement of glass transition temperature. These are presented in Table I. Here, the values of T_{sf} were obtained by use of eq. (1) from the experimentally measured T_g values. A very good agreement is observed.

TABLE I

v_2	$T_{sf}, ^\circ\text{K}$.	
	From reduced stress-strain plots	From DTA measurement of T_g
0	267	264
0.258	273	272
0.408	273	276
0.507	278	281
0.615	281	282
0.625	281.5	283

E. Effect of Filler Concentration

In tensile testing, an important effect of adding the filler to a rubber is to increase the value of T_s . This observation suggested that the relative ratios

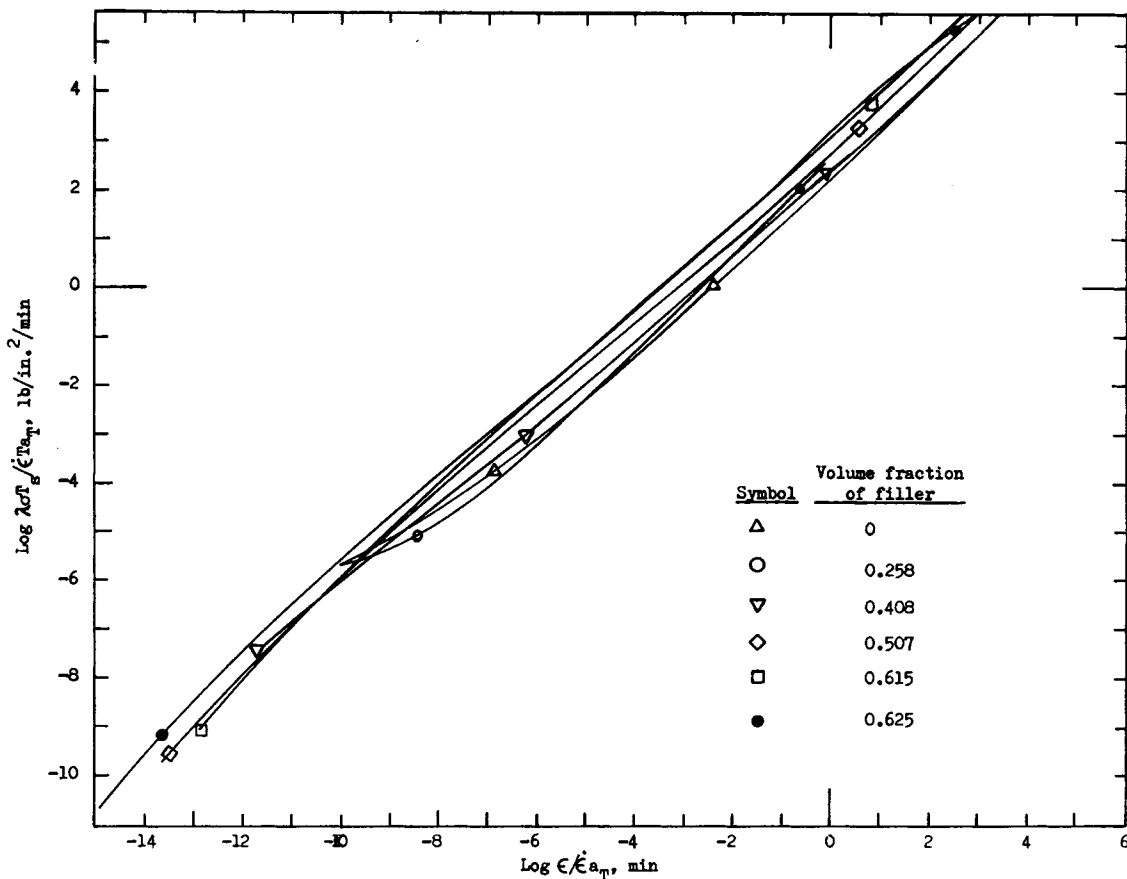


Fig. 7. Effect of filler concentration v_2 on the reduced stress-strain curve for a polyurethane rubber.

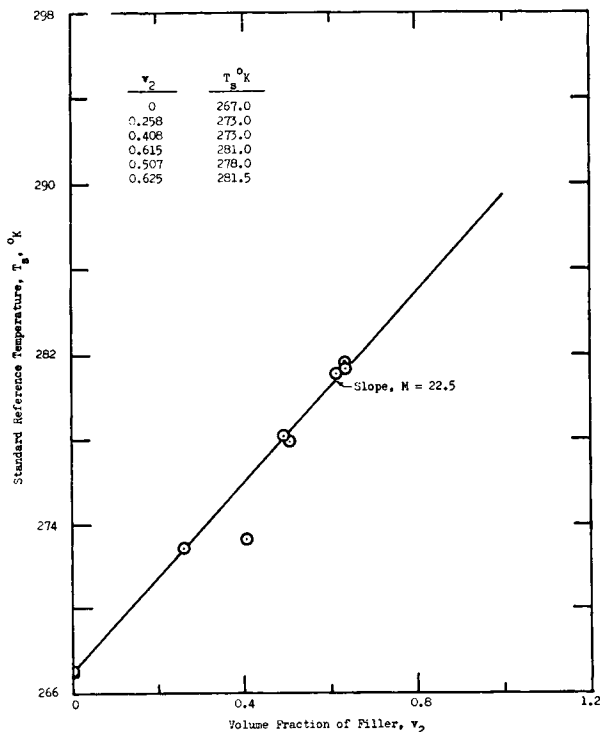


Fig. 8. Effect of volume filler loading v_2 on the standard reference temperature T_s .

of the initial tangent moduli, E and E_0 , for the filled and unfilled rubber systems respectively, may be temperature-dependent. Therefore, the usually applied expressions of Guth,⁴ Smallwood,⁵ and Eilers⁶ for the effect of concentration of filler on modulus would not be expected to hold over the entire temperature range. The following empirical relation, which is a modification of the Eilers relationship, appeared to be the most useful means for characterizing the effect of filler concentration on modulus:

$$\ln (E/E_0) = Av_2/(1 - Bv_2) \tag{4}$$

where A and B are experimental constants. Rearrangement of eq. (4) gives the relation:

$$1/\ln (E/E_0) = (1/Av_2) - (B/A) \tag{5}$$

The plot of $1/\ln (E/E_0)$ against $1/v_2$ then yields a straight line of slope $1/A$ and intercept B/A . Typical data treated in this manner are shown in Figure 9. It was noted that the test results satisfy the predicted relations over the range 0.74 to 74 min.^{-1} . In addition, the modulus ratio was effectively independent of strain rate. The test for the temperature dependency of E/E_0 was to

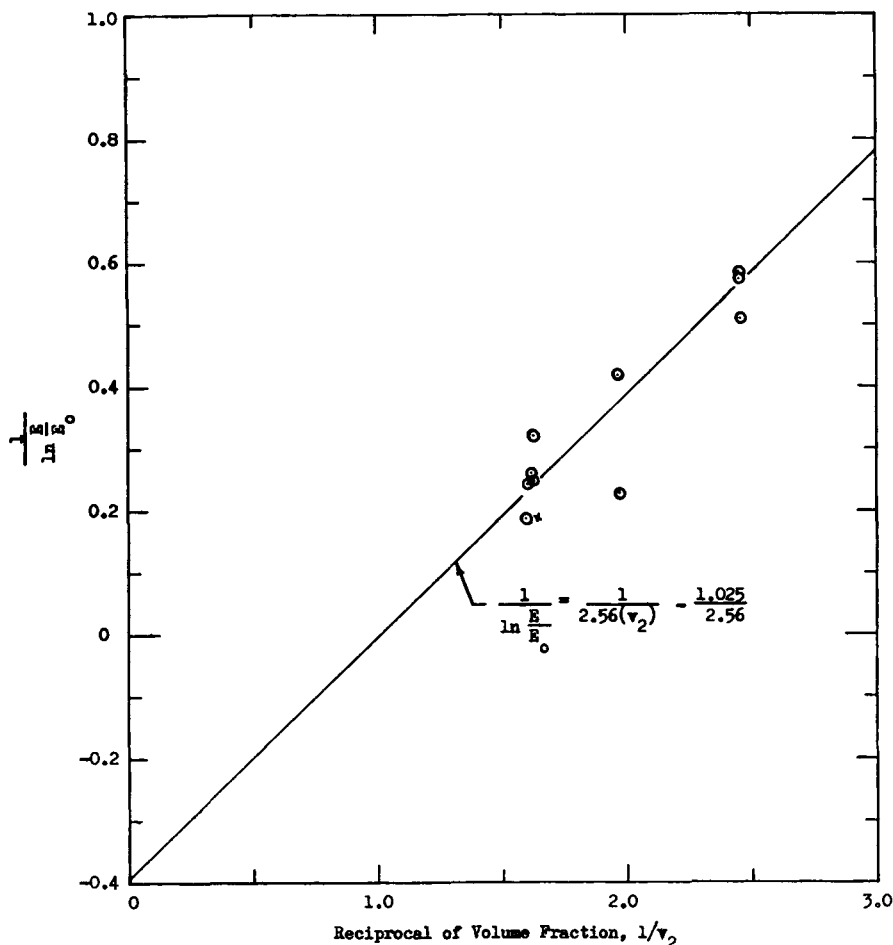


Fig. 9. Effect of filler concentration on the initial modulus of a filled polyurethane rubber. Test temperature -29°C .

determine the manner in which A and B vary with the test temperature. The variation with temperature is shown in Figure 10. It appears to be significant that A is essentially constant and approximately equal to the Einstein constant for rigid spheres, 2.5. The value of B decreases linearly with increasing temperature, yielding the relation:

$$B = -6.4 \times 10^{-3}T + 2.51 \quad (6)$$

The value of B becomes smaller at the higher test temperature and therefore becomes significant only at very high filler loadings. Equations (4) and (6) provide useful relationships for expressing the variation of modulus with filler loading and with temperature. Further, these relations can be shown to be similar in form to the Guth-Smallwood and Eilers functions. On expansion of eq. (4) by an exponential series, the equation becomes

$$E/E_0 = 1 + [2.5v_2/(1 - Bv_2)] + (1/2!)[2.5v_2/(1 - Bv_2)]^2 + \dots \quad (7)$$

Equation (7) can be compared with the Guth-Smallwood relation^{4,5}

$$E/E_0 = 1 + 2.5v_2 + 14.1v_2^2 \quad (8)$$

and the Eilers relation⁶

$$E/E_0 = 1 + [2kv_2/(1 - S'v_2)] + [kv_2/(1 - S'v_2)]^2 \quad (9)$$

Equations (7) and (8) are seen to be of the same form when v_2 is small (or when B is small at larger values of v_2). For small values of v_2 eq. (9) is seen to be of the same form as eq. (7) if $B = S'$. Equation (7) fits the data over a wide range of filler concentration better than either eq. (8) or eq. (9) when reasonable values of the constants are used.

F. Application to Stress Relaxation Data

The theory of linear viscoelasticity has been well characterized through rigorous mathematical treatments.⁷ In these treatments, exact equations have been presented for the interconversion of the

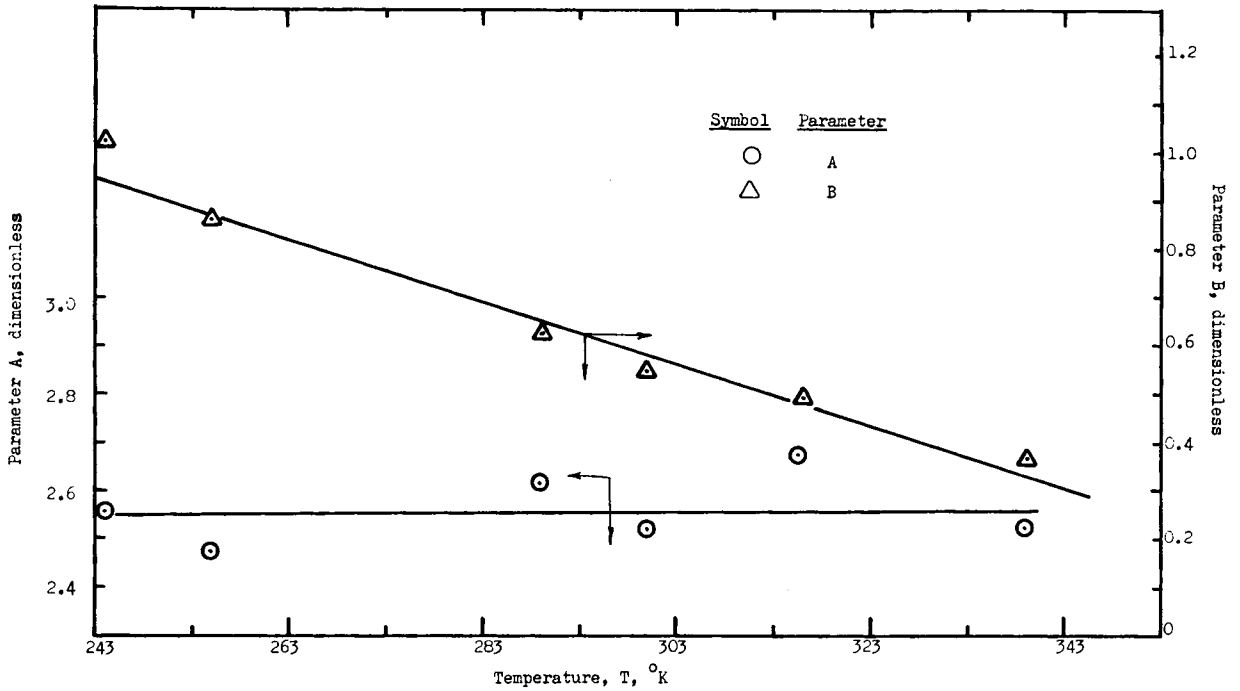


Fig. 10. Effect of test temperature on parameters A and B: (○) parameter A; (△) parameter B.

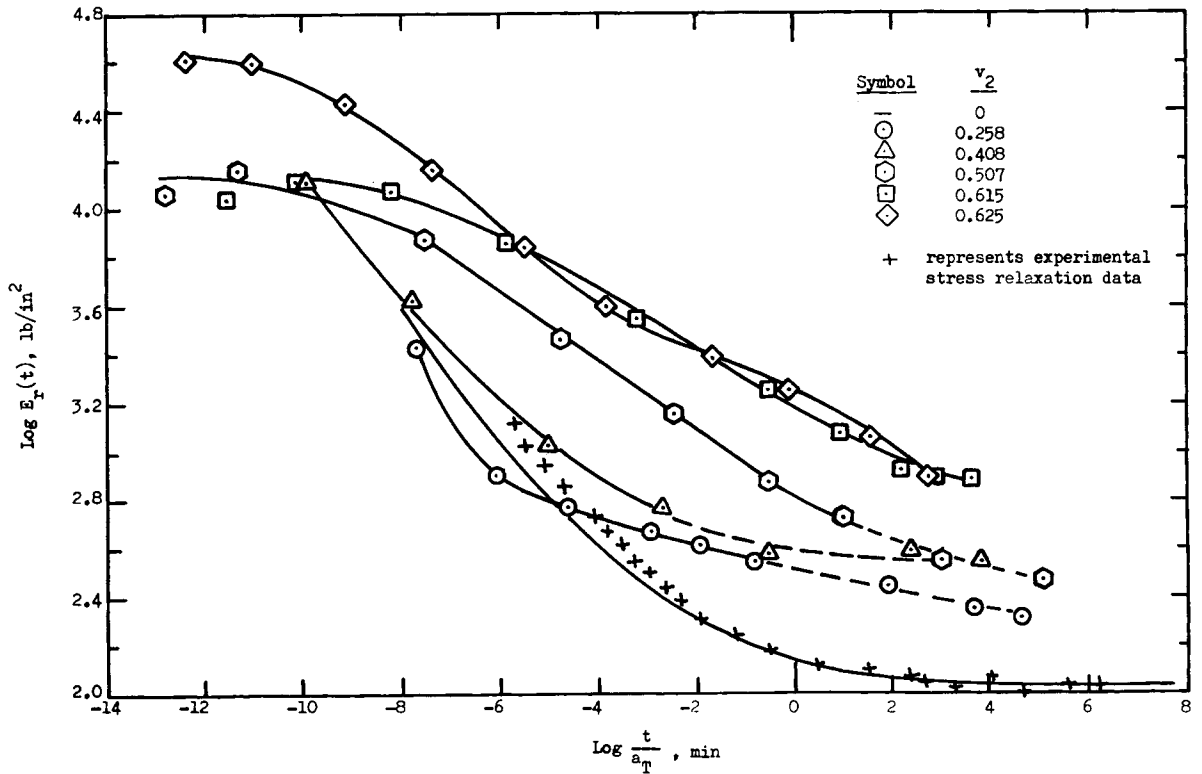


Fig. 11. Effect of filler concentration v_2 on the stress relaxation modulus of a polyurethan rubber (calculated from reduced stress-strain data).

various time-dependent mechanical properties. However, many of these exact relations are difficult and tedious to use, since suitable expressions for the experimental data over an extended time scale are not available. Therefore, graphical or numerical methods are often required. Some approximate relations for the representation and interconversion of time-dependent mechanical properties and derived quantities, such as relaxation and retardation spectra, have been described by Smith.²

The application of the generalized Maxwell model previously employed for the description of the tensile properties of filled rubbers represents the use of one of the approximate relations. The assumption of a limited range of relaxation times has been made in this approximation. Although the relations are approximate, they have proved to be useful, nevertheless.

The successful application of these results to tensile testing suggested further use of the theory for the prediction of the stress relaxation parameters. These were required for two reasons: (1) for comparison between theory and experimental results and (2) for evaluation of the effects of filler loading on the stress-relaxation behavior.

The time-dependent relaxation modulus $E_r(t)$ can be calculated from the slope of the reduced stress-strain curve by use of the relation suggested by Smith.²

$$E_r(t) = (\lambda\sigma/\epsilon)(d \ln \sigma_r/d \ln \epsilon_r)|_{\epsilon=\epsilon_t} \quad (10)$$

where $d \ln \sigma_r/d \ln \epsilon_r$ is the slope taken from the reduced stress-strain plots, while the time t is given by

$$t = \epsilon/\dot{\epsilon} \quad (11)$$

From eqs. (10) and (11), the stress relaxation "reduced" (or "master") curve was calculated for the filled rubber systems. These results are plotted in Figure 11. The calculated curves are compared with a small sampling of experimentally measured stress relaxation test results. The limited test results indicate reasonable agreement with the calculated curves.

The stress relaxation data for the highly filled polymers show a region at very low values of reduced time where the stress is decaying very slowly with time. This plateau corresponds to the glassy modulus of the systems. However, in the case of the pure rubber and the moderately filled systems (v_2 up to 0.408), the glassy state had not been

reached. These observations are in agreement with the previous results which indicated that increasing the filler loading produced a corresponding increase in the temperature at which the system becomes brittle or glassy.

G. Conclusion

Modified viscoelastic relations have been applied satisfactorily to the description of the mechanical behavior at low strain levels of highly-filled polymer systems over a wide range of filler concentrations. The relations were likewise shown to hold over wide ranges of temperature and strain rate. The equation relating the effect of filler concentration on relative modulus contains two constants. The first was found to be equal to the Einstein coefficient for rigid spheres (2.5) and was independent of temperature. The second constant is related to the test temperature.

The interconversion of mechanical properties by the theory of viscoelasticity was employed for the calculation of stress relaxation properties from tensile data. Reasonable agreement is shown.

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Synopsis

The systematic study of the variation in tensile properties with the extent of loading in highly filled systems has received little attention even though it is important to a variety of industries. An investigation was therefore made of the mechanical properties of a polyurethan rubber loaded with uniform glass spheres. Systems containing up to 62.5 vol. % fillers were investigated in tension on a strain rate range of 0.074 to 1850 min.⁻¹ and temperatures of -50 to +80°C. The mechanical behavior at low extensions was found to be represented by the generalized Maxwell model. The Williams-Landel-Ferry relationship was satisfactorily applied to the reduction of the data. Good agreement was obtained between the glassy-state transition temperature calculated from the reduced tensile data and from experimental differential thermal analysis results. The increase in the modulus with increasing filler content was satisfactorily described by an empirical modification of the Eilers relationship. The application of the reduced tensile data to the calculation of the stress relaxation modulus is also

shown. Reasonable agreement was obtained between the calculated and experimental data.

Résumé

On a porté peu d'intérêt à l'étude de la variation des propriétés d'extensibilité en fonction de la charge pour des systèmes fortement chargés bien que cela soit très important pour toute une variété d'industries. Les propriétés mécaniques d'un caoutchouc de polyuréthane chargé au moyen de sphères de verre uniformes ont été examinées. Des systèmes contenant jusqu'à 62,5% en volume d'agent de remplissage ont été étudiés sous tension dans un domaine de vitesse d'étirement de 0,074 à 1850 min.⁻¹ et pour des températures de -50 à +80°C. Le comportement mécanique aux faibles extensions peut être représenté par le modèle généralisé de Maxwell. La relation de Williams-Landel-Ferry a pu être appliquée de façon satisfaisante à la réduction des données. La température de transition vitreuse calculée au départ des données d'extension réduites est en complet accord avec la valeur obtenue au départ des résultats de l'analyse thermique différentielle. L'augmentation du module en fonction de l'accroissement de la teneur en charge peut être interprétée de façon satisfaisante par une modification empirique de la relation de Eiler. L'application des résultats d'extension réduits au calcul du module de tension-relaxation est également donnée. Un accord raisonnable a été obtenu entre les données calculées et expérimentales.

Zusammenfassung

Ungeachtet der Bedeutung für eine Reihe von Industriezweigen hat die systematische Untersuchung der Abhängigkeit der Zugeigenschaften hochgefüllter Systeme vom Füllungsgrad wenig Beachtung gefunden. Es wurden daher die mechanischen Eigenschaften eines mit einheitlichen Glaskugeln gefüllten Polyurethankautschuks untersucht. Systeme mit einem Gehalt von bis zu 62,5 Vol% Füller wurden in bezug auf ihre Spannung in einem Bereich der Verformungsgeschwindigkeit von 0,074 bis 1880 min⁻¹ und der Temperatur von -50 bis +80°C untersucht. Das mechanische Verhalten bei niedriger Dehnung liess sich durch das verallgemeinerte Modell von Maxwell darstellen. Die Williams-Landel-Ferry-Beziehung konnte mit Erfolg zur Reduktion der Ergebnisse verwendet werden. Gute Übereinstimmung wurde zwischen der aus den reduzierten Zugdaten und der aus den Ergebnissen einer experimentellen thermischen Differentialanalyse berechneten Glasumwandlungstemperatur erhalten. Die Zunahme des Moduls mit steigendem Füllergehalt wurde durch eine empirische Modifizierung der Beziehung von Eilers befriedigend wiedergegeben. Weiters wird die Anwendbarkeit der reduzierten Zugdaten zur Berechnung des Spannungsrelaxationsmoduls gezeigt. Eine annehmbare Übereinstimmung zwischen berechneten und experimentellen Grössen wurde erhalten.

Received August 16, 1960