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A NONLINEAR CONSTITUTIVE RELATIONSHIP FOR COMPOSITE PROPELLANTS

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INTRODUCTION

The mechanical response and the failure of composite solid propellants are known to be related to the formation and growth of vacuoles on the microscopic or macroscopic scale. Failures in composite materials such as composite propellants originate at the filler particle or binder molecular level. These microscopic failures, whether adhesive failures between the binder and filler particles or cohesive failures in the binder, result in vacuole formation. The cumulative effect on all vacuole formation and growth is observed on the macroscopic scale as strain dilatation. The strain dilatation in composite propellants varies with binder type, binder formulation, filler particles, and presumably filler particle size distribution. The strain dilatation caused by vacuole growth and formation results in a nonlinear stress-strain behavior for these materials.

The experimental investigations of Leeming et al. (1), Bornstein (2), and Martin (3) emphasize the fact that the state-of-the-art linear viscoelastic theory does not predict propellant grain stresses and strains under realistic loading conditions. The most significant portion of the error is due to the constitutive nonlinearity of the material. Linear thermorheological simple viscoelastic theory has certain important limitations; however, it is still the only constitutive theory currently used in most analyses because no other constitutive equations previously existed that are as easily incorporated in the analyses.

There has been considerable progress in the development of nonlinear constitutive theories and methods of approximating specific nonlinear viscoelastic behavior in the last few years. There will be no attempt in this paper to review the extensive literature on the general theories of nonlinear viscoelasticity.

BACKGROUND AND THEORY

Farris (4) demonstrated that the mechanical response and the failure in solid propellants are related to the formation and growth of vacuoles within the composite material and that this phenomenon is directly related to the macroscopically observed strain dilatation. The mechanical properties, particularly Poisson's ratio, are strongly dependent on the dilatational behavior of these materials. Strain dilatation measurements, even for the uniaxial tensile tests, are cumbersome, tedious, and time consuming. Therefore, a relationship that would permit the determination of strain dilatation and Poisson's ratio as a function of strain utilizing only the stress-strain data would be most desirable. Insight into the factors which govern the nonlinear response and failure of composite propellants can be obtained utilizing a model for dewetting, vacuole formation, and growth of vacuoles which is based on assumptions regarding the microstructural behavior of the system. The model can then be used to develop an expression for dilatation as a function of stress and strain and to compare the predicted dilatation with experimental measurements of dilatation. The degree of agreement between the predicted and experimental values of dilatation gives an indication of the validity of the model. This approach was used by Farris (5,6), Fedors and Landel (7), and others (8,9).

The present state of the art of predicting dilatation as a function of strain is limited because there is very little quantitative information available on the experimentally determined dilatation under conditions similar to those encountered with solid propellant rocket motors. Various models describing this phenomenon have appeared in the literature. In developing such a model, attention is focused on a rigid filler particle contained in an elastomeric matrix. As the material is strained above some critical value, a vacuole is formed about the filler particle due to the internal failure of the composite. The source of vacuole formation may be either adhesive failure of the filler-binder bond or cohesive failure in the binder near the filler particle (10,11). As the strain in the material increases, the vacuoles continue to increase in size and number. The shape and instantaneous behavior of these vacuoles seem to follow these assumptions:

1) Vacuoles from arbitrarily at any magnitude of strain above the critical value.

2) Each vacuole behaves as an ellipsoid of revolution with the minor axis determined by the diameter of the enclosed filler particle.

3) The major axis of the ellipsoidal vacuole increases linearly with strain at a rate proportional to the size of the filler particle it contains.

Various constitutive theories exist and experimental investigations can be designed to produce specific stress-strain equations. In this section a constitutive relationship for uniaxial tensile data is discussed and the similarity with Farris' equation is noted (4).

Martin (12) used the constitutive relationship

$$\sigma(\epsilon,T,t) = \left\{F(\epsilon,T,t)e^{-\ell n f(\epsilon)}\right\}\epsilon \quad . \tag{1}$$

Equation (1) has been verified experimentally.

Starting with Farris' equation and defining $F = \sigma/\epsilon$ as the secant modulus, as was used by Martin, the following relationship is obtained:

$$F(\epsilon) = \frac{\sigma}{\epsilon} = E_1 \, e^{-\beta\left(\frac{\Delta V}{V_o}\right)1/\epsilon} \quad , \tag{2}$$

where E_1 is the initial modulus and $F(\epsilon)$ is meant to indicate F at a given strain. This value will be indicated simply by F in the remainder of this work. After rearrangement one obtains:

$$\frac{F}{E_1} = e^{-\beta(\Delta V/V)1/\epsilon} \quad . \tag{3}$$

Equation (3) indicates that the nonlinearity of the stress-strain curve (of which the vacuole formation and growth is considered to be the major contributor) should be described by the ratio of F/E_1. Taking the natural logarithm of both sides of Equation (3) results in Equation (4):

$$\beta\left(\frac{\Delta V}{V}\right)\frac{1}{\epsilon} = \ell n\left(\frac{E_1}{F}\right) \quad . \tag{4}$$

Since β is assumed to be independent of strain magnitude, Equation (3) suggests that a plot of $\{\epsilon \ell n(E_1/F)\}$ versus strain should have a similar shape to the dilatation-strain curve. Figure 1 shows plots of $\{\epsilon \ell n(E_1/F)\}$ and $(\Delta V/V)$ versus strain. The similarity in the shapes of

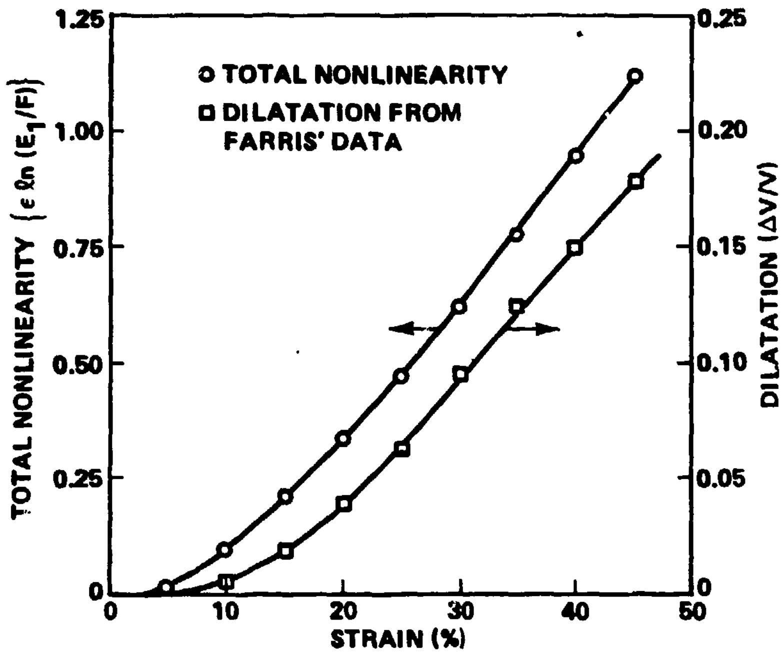

Figure 1. Total Nonlinearity and Dilatation Versus Strain for a Granular Filled Elastomer.

the two curves indicates that the total nonlinearity, $\{\epsilon \ell n(E_1/F)\}$, in the materials' behavior may be calculated from an equation similar to that used by Farris (4). The same reasoning used by Farris results in the expression

$$f(\epsilon) = S\gamma_{max} \int_{-\infty}^{n} \int_{-\infty}^{n} \frac{e^{-n2/2}}{\sqrt{2\Pi}} \, dndn + \gamma_o \epsilon \quad , \qquad (5)$$

where

$f(\epsilon)$ = total nonlinearity of the materials' behavior

$S = (A - B)\sqrt{2\Pi}/\gamma_{max}$

γ_o = initial slope of the $\{\epsilon \ell n(E_1/F)\}$ versus strain curve

γ_{max} = final slope of the $\{\epsilon \ell n(E_1/F)\}$ versus strain curve

$\bar{\epsilon}$ = the strain magnitude at the intersection of the initial asymptote of slope γ_o and the final asymptote of slope γ_{max}

A = the magnitude of $\{\epsilon \ell n(E_1/F)\}$ at $\bar{\epsilon}$

B = the magnitude of the ordinate at the intersection of the two asymptotes

$n = (\epsilon - \bar{\epsilon})/S.$

Equation (5) then would permit one to estimate the total nonlinearity of the propellant once the parameters have been determined. It would be more useful, however, to obtain a quantity representing the propellant's nonlinear behavior that could be readily utilized in the current linear viscoelastic programs to account for the nonlinear response of the material. With this in mind, consider Equation (3), which after rearranging becomes

$$\beta\left(\frac{\Delta V}{V}\right) = \epsilon \ell n\left(\frac{E_1}{F}\right) \quad . \tag{6}$$

Recalling that β and E_1 are independent of strain and differentiating both sides with respect to strain, one has

$$\beta \frac{d\left(\frac{\Delta V}{V_o}\right)}{d\epsilon} = \ell n \frac{E_1}{F} + \left(1 - \frac{E}{F}\right) \quad , \tag{7}$$

where E = the instantaneous slope of the stress-strain curve. Equation (7) now contains two unknowns, β and $d/d\epsilon(\Delta V/V_o)$. Now, consider the change of dilatation with respect to strain. According to Farris' data (5), the quantity $d/d\epsilon(\Delta V/V_o)$ obtains a maximum somewhere between the points of maximum stress and rupture stress and remains constant until failure occurs. Farris proposed the relationship

$$\frac{d}{d\epsilon}\left(\frac{\Delta V}{V_o}\right) = c\ V_{fd} \quad , \tag{8}$$

where V_{fd} = volume fraction of dewetted solids. Experimental data were presented for systems that tend to dewet completely. These data gave excellent agreement with the model represented by Equation (8). The maximum slope of the dilatation-strain curve is shown to be directly proportional to the volume fraction of filler particles in the material. For materials that tend to dewet completely, the proportionality factor is unity (c = 1); therefore,

$$\left[\frac{d}{d\epsilon}\left(\frac{\Delta V}{V_o}\right)\right]_{max} = \phi_f \quad , \tag{9}$$

where ϕ_f is the total volume fraction of filler particles in the system.

With these observations noted, the following simplifying assumptions will be made that will enable the determination of the factor β without having to conduct the dilatation-strain measurements:

1) The maximum slope of the dilatation-strain curve is obtained at a strain magnitude equal to halfway between the point of maximum stress and breaking stress.

2) All composite propellants are totally dewetted in the region of the sample where failure occurs.

The assumption that all filler particles in composite propellants are totally dewetted in the region of failure is not too unrealistic for the following reasons. In composite propellants where the bond between the filler particles and the binder is stronger than the cohesive strength of the binder, vacuoles initiate in the binder and propagate to the surface of the filler particle prior to failure. In these materials there is probably a large strain gradient in the region of failure and there would be a high probability of totally dewetted filler particles in this region. One reason that Equation (9) does not appear to be true for all propellants is that the measured dilatation, whether localized or not, is averaged over the total volume of the sample. If the localized band of dewetted filler particles is narrow, the measured dilatation would appear to be much smaller than the actual dilatation in the region of failure. The maximum slope of the dilatation-strain curve is related to the dewetted filler particles, but the dewetted filler particles may be contained in a narrow band around the failure region.

The assumption that the maximum slope of the dilatation-strain curve is obtained at a strain magnitude halfway between the points of maximum stress and breaking stress is approximately correct according to Farris' data. The purpose of this assumption is to fix the point on the stress-strain curve for the calculation of the coefficient β. One reason that failure points are not recommended for this calculation is the variation in ways of selecting failure points. The use of the stress and strain values at $\epsilon = (\epsilon_m + \epsilon_b)/2$ should minimize the variations in methods of selecting failure points as a source of error in the calculation of β.

Substituting Equation (9) into Equation (7) yields the following results after rearranging:

$$\beta = \frac{1}{\Phi_f}\left\{\ell n \frac{E_1}{F} + 1 - \frac{E}{F}\right\} , \tag{10}$$

to be evaluated at $\epsilon = (\epsilon_m + \epsilon_b)/2$.

With β known, one can then utilize Equation (6) to determine the dilatation as a function of stress and strain. The resulting expression is as follows:

$$\left(\frac{\Delta V}{V_o}\right) = \frac{\epsilon}{\beta}\,\ell n \frac{E_1}{F} \quad . \tag{11}$$

This equation was utilized to calculate the apparent volume change for two composite materials where the experimental dilatation-strain data were available. The calculated and experimentally measured dilatation-strain data were in excellent agreement.

To more readily utilize the volume change data obtained in this way for a nonlinear viscoelastic stress analysis, the following method is proposed. It would be more desirable to reflect the propellant nonlinearity in an equivalent Poisson's ratio, which would be allowed to vary with strain magnitude, strain rate, and temperature. The variable Poisson's ratio could then be incorporated into the current linear viscoelastic stress analysis program to reflect the propellant's nonlinear behavior.

To derive an expression of Poisson's ratio as a function of stress and strain, the volume change is approximated by the first strain invariant neglecting higher order terms involving strain.

$$\left(\frac{\Delta V}{V_o}\right) = e_1 + e_2 + e_3 \quad , \tag{12}$$

where e_1, e_2, and e_3 are the strains in the principal directions and are related as follows in the uniaxial condition:

$$e_1 = \epsilon$$

$$e_2 = e_3 = -\nu e_1 = -\nu\epsilon \quad , \tag{13}$$

where ν is Poisson's ratio. Substituting these relationships into Equation (11) results in the following

$$\left(\frac{\Delta V}{V_o}\right)\frac{1}{\epsilon} = (1 - 2\nu) \quad . \tag{14}$$

Substituting Equation (14) into Equation (6) and rearranging, one obtains the relationship:

$$\nu = \frac{1}{2}\left\{1 - \frac{1}{\beta}\,\ell n\left(\frac{E_1}{F}\right)\right\} \quad . \tag{15}$$

Also, substituting Equation (14) into Farris' equation yields the following constitutive relationship for the uniaxial nonlinear behavior:

$$\sigma = E_1 \epsilon e^{-\beta(1-2\nu)} \quad . \tag{16}$$

For the nonlinear viscoelastic treatment, the initial slope modulus, E_1, is allowed to vary with strain rate and temperature; the nonlinearity coefficient, β, is allowed to vary with strain rate and temperature; and the Poisson's ratio, ν, is allowed to vary with strain rate, temperature, and strain magnitude.

EXPERIMENTAL VERIFICATION

The model used in deriving the expressions for dilatation and Poisson's ratio as a function of stress and strain was based on certain assumptions regarding the microstructural behavior of composite materials such as composite propellants. The validity of the assumptions and the model is indicated by good agreement of calculated and experimental stress and dilatation data.

Figures 2, 3, and 4 are plots of stress and dilatation versus strain for a granular filled elastomer. The experimental data were obtained from Farris'work (5). The experimental data in these figures were obtained at 25°C (75°F) and at strain rates of 6.66, 66.6, and 666%/min. The plotted points represent the data read from Figure 6 in Farris' paper. The solid lines indicate the values calculated using Equation (16) for stress and Equation (11) for dilatation. Figures 2, 3, and 4 indicate good agreement between calculated and experimental values of stress and dilatation at all strain rates. The dilatation-strain data appear to be shifted by a constant factor along the strain axis in some cases. This would indicate a slight error in the dilatation measurements, which could be attributed to localized dewetting or vacuole formation as discussed previously. Equation (16) is shown to yield excellent agreement with experimental stress values at all strain rates. In Figure 4, Equation (11) is shown to also give excellent agreement with the dilatation experimental data at a strain rate of 666%/min up to a strain magnitude of 35%. At strain magnitudes in excess of 35%, the experimental dilatation data fall below the predicted values. While vacuoles may form arbitrarily at all strain magnitudes above a critical value, it is reasonable to assume that the weakest point in the composite material will be more susceptible to vacuole formations and should contain a larger population of vacuoles than the remainder of the material. The formation of vacuoles to relieve the large strain gradient that would be present at the weakest point in the composite requires a finite time in which to react. If the composite material is strained at a rate faster than the material can respond through microstructural failure and vacuole formation, the dilatation would appear to be uniform throughout the material until conditions were such that the rate of dilatation at the weakest point in the material became large enough to promote the formation of a localized band of a large population of vacuoles. The data presented in Figure 4 indicate that at a strain rate of 666%/min, near uniform dilatation is present up to a strain magnitude of approximately 35%. At this strain a localized band of a large population of vacuoles developed at the weakest point in the composite material, which then began to have a strong influence on the material's behavior. As the material is strained in excess of 35%, the volume increase in the vacuoles within the established localized failure region is more than the measured average dilatation. This would explain why the experimental dilatation data presented in Figure 4 became less than the calculated values as the strain magnitude increased to exceed 35%. At the lower strain rates of 6.66 and 66.6%/min, the localized failure region was established in the initial portion of the test ($\epsilon < 0.10$), thus explaining why experimental dilatation deviated slightly from the calculated dilatation for the duration of the test.

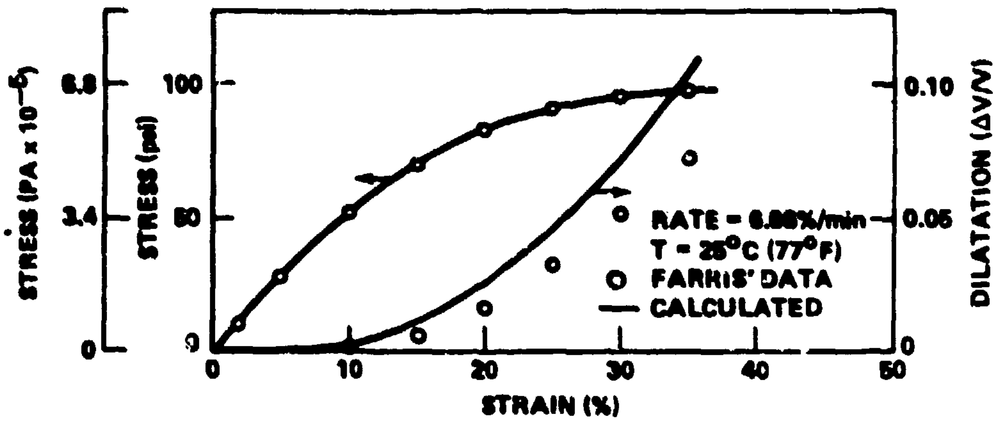

Figure 2. Dilatation and Stress Versus Strain for a Granular Filled Elastomer.

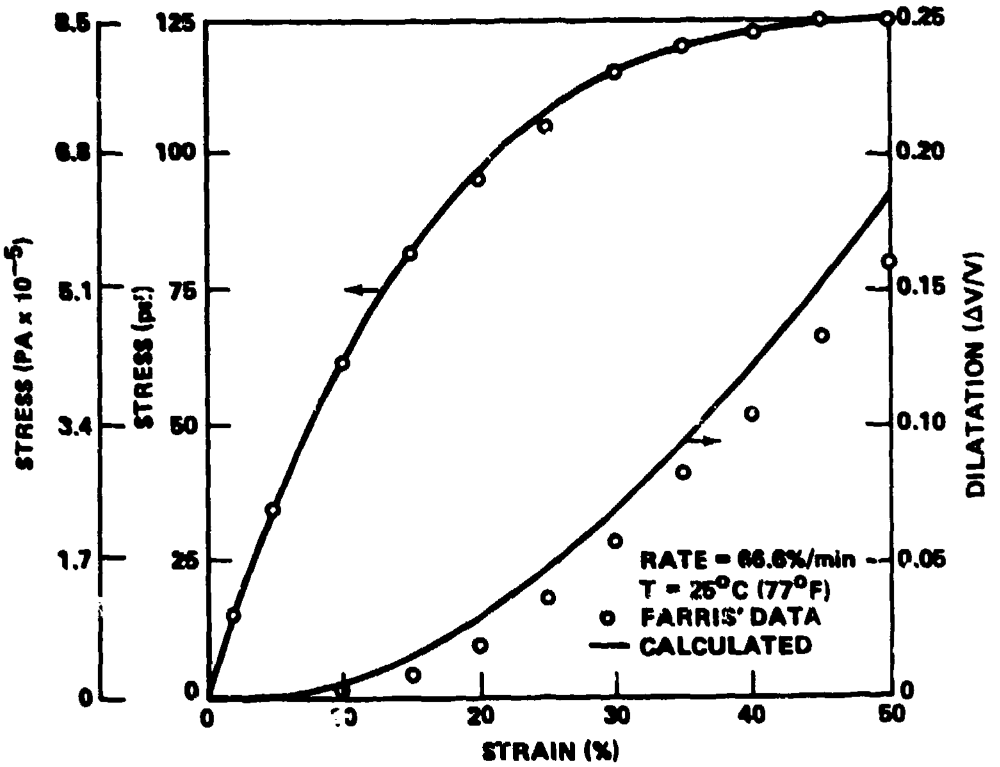

Figure 3. Dilatation and Stress Versus Strain for a Granular Filled Elastomer.

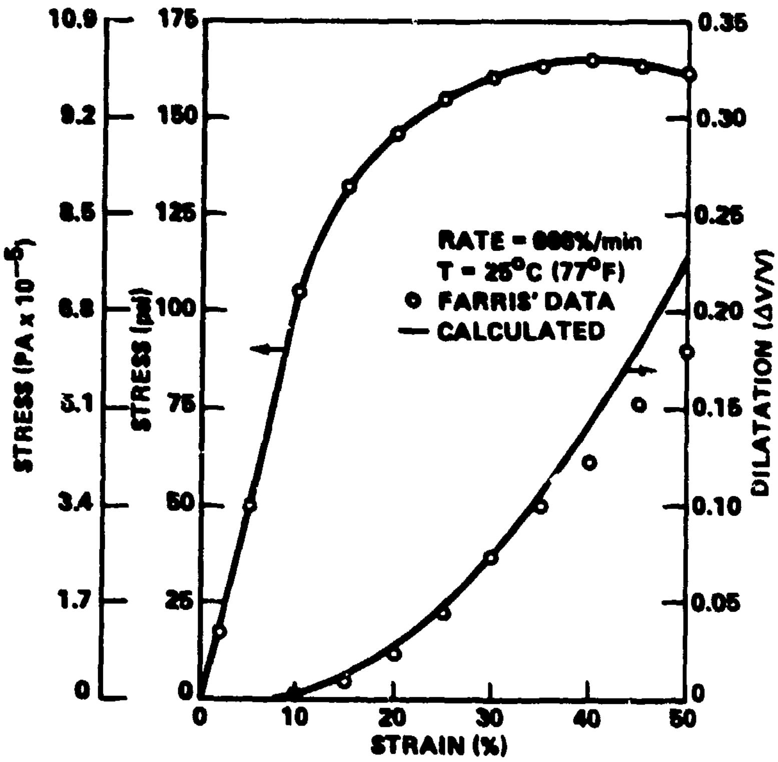

Figure 4. Dilatation and Stress Versus Strain for a Granular Filled Elastomer.

Figures 2, 5, and 6 are plots of stress and dilatation versus strain. The experimental data in these figures were obtained from Figure 3 in Farris' paper (5). These data indicate the stress and dilatation behavior of a typical granular filled elastomer at a strain rate of 6.66%/min at 2 5°, 4.4°, -18°C (77°, 40°, and 0°F). The data shown or Figures 2, 5, and 6 indicate excellent agreement between values of stress calculated by Equation (15) and the experimental values at all temperatures. The behavior of the dilatation strain data is similar to that shown on Figures 2, 3, and 4 with the experimental values deviating slightly from the values calculated by Equation (11). The same reasoning as used previously would also explain the deviation of the experimental dilatation from that calculated by Equation (11), as indicated on Figures 2, 5, and 6.

Normally, nominal stress values were corrected to true stress by multiplying the nominal stress value by the extension ratio, λ_1. This correction was originally derived based on the

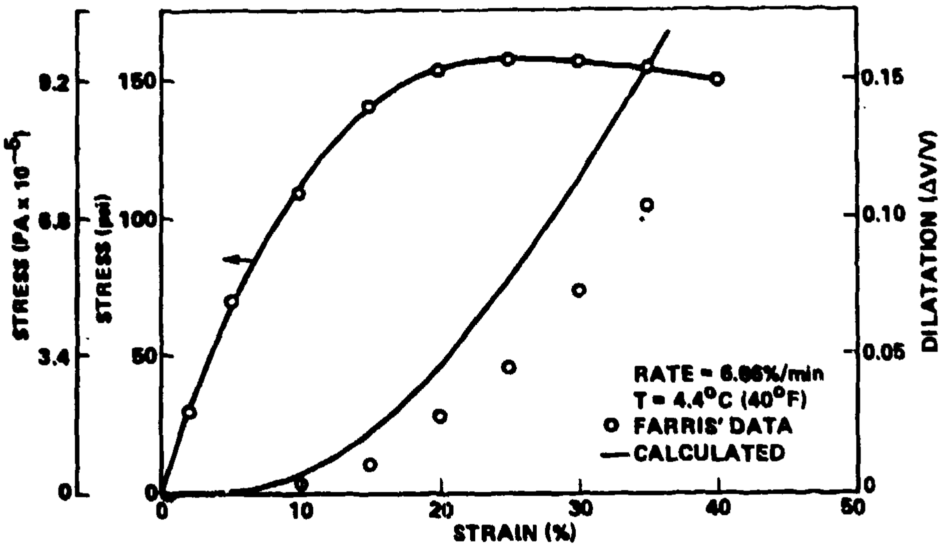

Figure 5. Dilatation and Stress Versus Strain for a Granular Filled Elastomer.

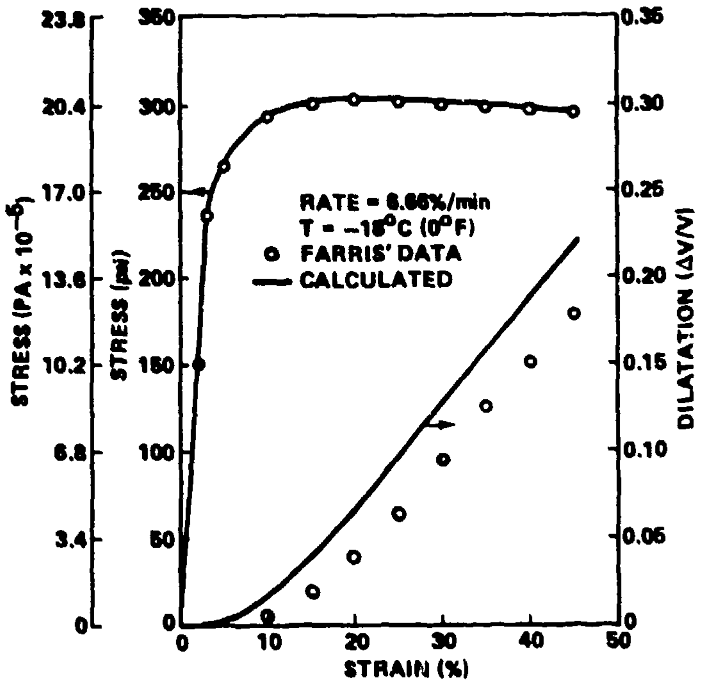

Figure 6. Dilatation and Stress Versus Strain for a Granular Filled Elastomer.

assumption that there is no volume change within the sample for the duration of the test. The relationship considering volume change is derived as follows:

$$\left(\frac{\Delta V}{V_o}\right) = \lambda_1\lambda_2\lambda_3 - 1 \quad , \tag{17}$$

where $\lambda_i = 1 + \epsilon_i$. Therefore, rearranging Equation (17), one obtains

$$\lambda_2\lambda_3 = \frac{1 + \left(\frac{\Delta V}{V_o}\right)}{\lambda_1} = \frac{A}{A_o} \quad . \tag{18}$$

Substituting this expression into the equation $\sigma_c = \sigma_o A_o/A$, one obtains the following:

$$\sigma_c = \frac{\sigma_o \lambda_1}{1 + \frac{\Delta V}{V_o}} \quad . \tag{19}$$

Therefore, the true stress σ_c is lower than would be obtained by the normal correction procedures. Equation (19) reduces to the equation normally used as ΔV approaches zero.

CONCLUSIONS

A nonlinear constitutive relationship is developed for uniaxial stress-strain conditions that are shown to fit experimental data over a wide range of strain rates and temperatures. The total stress-strain nonlinearity of particulate filled composites may be represented by statistical parameters similar to those used by Farris to describe the dilatation-strain behavior. By using Equations (10) and (11), the dilatational behavior of composite propellants may be predicted from the stress-strain data and the total filler content. The relationships derived in this report will enable one to investigate the nonlinear behavior at strain-rates and temperatures where it is very difficult, if not impossible, to obtain measured dilatation data.

The relationship represented by Equation (15) may be utilized, along with experimental stress-strain data obtained at different strain-rates and temperatures, to determine the dependency of an equivalent Poisson's ratio on the strain-rate, temperature, and strain magnitude. The Poisson's ratio thus determined may then be utilized in currently available computer programs to describe transient thermo-viscoelastic behavior with the consideration of the materials' non-linear response.

The relation normally used for obtaining corrected stress data by multiplying the nominal values by the extension ratio would yield values of stress and strain at the maximum corrected stress, which were significantly larger than the true stress-strain values would indicate. These errors could conceivably result in the wrong conclusions as to the structural integrity of marginal designs; i.e., one might predict a safe design utilizing stress-strain allowables based on the normal correction method when, in reality, the true stress-strain allowables would indicate the design would be expected to fail. It is therefore recommended that stress-strain allowables for use in future failure analysis be based on true stress as defined by Equation (18).

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