CONSTITUTIVE MODELLING OF HIGH-ELONGATION SOLID PROPELLANTS

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Abstract

A phenomenological approach is used to represent the nonlinear viscoelastic behavior of solid propellants. A three dimensional finite strain viscoelastic model, modified by a strain softening function that accounts for damage effects, is considered in the research. Some of the significant aspects of high-elongation propellants are incorporated into the constitutive model. The resulting stress-strain relation is applied to a particular high-elongation propellant by means of the related material characterization. The response predicted by the model is compared with the experimental data for different loading conditions. The model predicts the propellant behavior quite well at uniaxial strain magnitudes up to 50%. Numerical analysis of very general geometries and loadings are possible, since a fully general model is calibrated.

Nomenclature

$\mathbf{A}'$ $= \mathbf{A} - 1/3tr(\mathbf{A})\mathbf{I}$

$\mathbf{C}$ = right Cauchy-Green deformation tensor

$DEV(\mathbf{A}) = \mathbf{A} - 1/3(\mathbf{A}:\mathbf{C})\mathbf{C}^{-1}$

$\mathbf{E}$ = Green strain tensor

$\mathbf{F}$ = deformation gradient

G_{rel} = shear relaxation modulus

G_{eq} = equilibrium value of relaxation modulus

G_i = relaxation coefficients

g = strain softening function

J = det $\mathbf{F}$, volume change

p = pressure

$\mathbf{S}$ = second Piola-Kirchhoff stress tensor

$\mathbf{T}$ = Cauchy stress tensor

λ = stretch

τ_i = relaxation times

Ξ = equivalent strain

1 Introduction

Solid propellants are considered as lightly cross-linked, long-chain polymers filled with solid particles and they are classified as highly nonlinear viscoelastic materials. The mathematical description of their behavior is quite complex, since it has to take into account the physical and geometric nonlinearities existing in the propellant. On the other hand, the description must be reasonable for computational purposes, such as having the ability of being implemented in a finite element code, without any major difficulty and yet preserving its predictive capabilities. These two aspects lead to two main approaches in the development of constitutive laws: micromechanics and phenomenological approaches. While the former considers different mechanisms in the microstructure of the material to model its macroscopic behavior, the latter uses internal state variables which are a measure of the physical state of the material.

The approach used in this research is concerned with the prediction of the mechanical behavior of high-elongation[1] solid propellants from a phenomenological point of view. Basically two nonlinear constitutive models are considered : Simo's [12] three dimensional finite strain viscoelastic model and a generalized linear constitutive relation, modified by a strain softening function, developed by Swanson [13]. An altered model based on these two models is used to represent the behavior of a high-elongation PEG/NG[2] solid propellant. The motivation for considering Swanson's model is its simplicity in incorporating damage into the constitutive law. The model uses a stress correction approach to assess damage, i. e. it considers a strain softening function multiplying the stress response. This function is easily determined by means of little experimental data. The selection of Simo's model is motivated by its ability to be applicable over any range of deformations, the general anisotropy and recovery of finite elasticity incorporated in it. The altered model combines the 'finite strain viscoelastic' formulation of Simo and the 'stress correction approach to damage' of Swanson.

The objectives of this research are (1) to determine the strain softening data from simple loading experiments, (2) to determine a suitable function to fit these data, (3) to make necessary modifications to the strain softening function in order to account for the effect of different loading variables such as temperature, strain rate, decreasing stress, etc. , and (4) to compare the response predicted by the model with complex loading experiments.

The numerical procedures necessary to achieve these objectives are carried out through the finite element code TEXPAC [1].

The remainder of this paper is organized as follows. The *second section* consists of the description of solid propellants in general and the typical properties of high-elongation propellants. The *third section* describes the two constitutive models considered to represent the behavior of

[1] Greater than 100% uniaxial strain capability.
[2] Polyethyleneglycol/nitroglycerin.

high-elongation solid propellants. The *fourth section* consists of the description of the constitutive model applied to PEG/NG propellant and the related material characterization. The response predicted by the model is compared with the experimental data for different loading conditions. Finally, some observations regarding the model used in the research are discussed in *conclusions*.

2 Solid Propellants

Solid propellant is a highly-filled elastomeric material composed mainly of solid particles, such as oxidizer crystals and fuel, suspended in a matrix of syntetic rubber binder. These particles constitute 85% of the mass and have sizes in the $10 - 100$ micron range. Some ingredients, such as curing agents and burn-rate catalysts are added to the propellant to improve the rheological and physical properties, to optimize the burn rate and to improve bonding.

A common classification of solid propellants is done according to their maximum uniaxial strain capability. Propellants with approximately 50% maximum strain capability are considered to be medium-elongation propellants. The propellant type that this research deals with is called high-elongation and has greater than 100% maximum strain capability. A typical stress-strain curve for high-elongation propellant in uniaxial tension is shown in Figure 1. High-elongation propellants typically exhibit some or all of the following phenomena :

- Large deformations and large strains
- Strain softening
- Rapid decrease of stress during unloading
- Large hysteresis during cyclic loading
- Thermorheologically complex behavior
- Elevation of stress due to the stiffening under pressure

- Transition from incompressible behavior at small strains to compressible behavior at large strains
- Dewetting, i. e. void formation in the binder or filler-binder interface.

3 Constitutive Models

The model used to represent stress-strain behavior of high-elongation PEG/NG propellant, is based on the formulations developed by Swanson [13] and by Simo [12].

3.1 Swanson's Model

The basic idea of Swanson's model is the representation of the propellant behavior as the generalization of the convolution integral of linear viscoelasticity using Lagrangian formulation as

$$\mathbf{S}' = g(E) \int_0^t 2G_{rel}(t-\tau) \frac{\partial \mathbf{E}'}{\partial \tau} d\tau \tag{1}$$

for deviatoric part of the response. The volumetric stress-strain relation is given in terms of mean Cauchy stress T_{kk} and volume change J as,

$$\frac{T_{kk}}{3} = f(J-1) \tag{2}$$

where f is a nonlinear relation reducing to bulk modulus times $(J-1)$ for elastic bulk response. The use of the softening function g is motivated by the similar nonlinearity observed in stress relaxation and constant strain rate tests. This function is determined from the ratio of measured to calculated Cauchy stresses for uniaxial constant strain rate loading.

Swanson's model is not suitable for representing large deformations in solid propellants, since the definitions of strain and stress deviators have physical significance only for small strains. The advantage of the model is the relatively easy determination of the softening function. Motivated by this and by the fact that the model has been, with some success, applied to medium-elongation propellants, Swanson's strain-softening approach is incorporated into the constitutive relation used to model the behavior of high-elongation propellants.

3.2 Simo's Model

The three-dimensional viscoelastic model developed by Simo is mainly characterized by the uncoupled bulk and deviatoric responses over any range of deformations. The proper decomposition in the nonlinear range is accomplished by the kinematic split of the deformation gradient $\mathbf{F}$ into volume-preserving and deviatoric components as

$$\mathbf{F} = J^{1/3}\overline{\mathbf{F}} \tag{3}$$

where $\overline{\mathbf{F}}$ is referred to as the volume–preserving part of $\mathbf{F}$.

Simo's model is based on a definition of an uncoupled free energy function $\mathbf{\Psi}$ of the form

$$\mathbf{\Psi}(\mathbf{E},\mathbf{Q}) = U_0(J) + \overline{\mathbf{\Psi}}^0(\overline{\mathbf{E}}) - tr(\mathbf{Q}\overline{\mathbf{E}}^T) + \mathbf{\Psi}_{\mathbf{I}}(\mathbf{Q}) \tag{4}$$

where U^0 and $\overline{\mathbf{\Psi}}^0$ are the uncoupled volumetric and deviatoric parts of the initial elastic stored energy $\mathbf{\Psi}^0$, $\mathbf{Q}$ is an internal variable, and $\mathbf{\Psi}_I$ is a function to be determined from the conditions of thermodynamic equilibrium. For the isothermal case the stress tensor $\mathbf{S}$ is obtained from

$$\mathbf{S} = \frac{\partial\mathbf{\Psi}(\mathbf{E},\mathbf{Q})}{\partial\mathbf{E}} \tag{5}$$

The viscoleastic behavior is introduced through the evolution equation of the internal variable $\mathbf{Q}$. The resulting constitutive equation is of the following form

$$\mathbf{S} = Jp\mathbf{C}^{-1} + \quad J^{-2/3}DEV\int_0^t \{[\beta + (1-\beta)e^{-\frac{t-s}{\nu}}]$$

$$\frac{d}{ds}DEV[\frac{\partial\overline{\Psi}^0(\overline{\mathbf{E}}(s))}{\partial\overline{\mathbf{E}}}]\}ds \tag{6}$$

where $\beta + (1-\beta)e^{-t/\nu}$ represents the shear modulus.

The most significant feature of the constitutive model developed by Simo is the uncoupling of volumetric and deviatoric responses over any range of deformations. However, the determination of the functions and parameters in the model, such as the internal variable $\mathbf{Q}$ and the function $\mathbf{\Psi}_I$ of the free energy, does not appear to be straightforward. Therefore, the model does not have the advantage of easy parameter determination as does Swanson's model.

4 Application of Constitutive Model to Solid Propellant

4.1 Altered Model

The constitutive model used to represent the behavior of PEG/NG solid propellant is obtained from the relation (6) by modifying the deviatoric components of stress by a multiplicative strain softening function introduced in equation (1). The resulting constitutive law is of the form

$$\begin{aligned}\mathbf{S} = Jp\mathbf{C}^{-1} + \quad & g(\Xi)J^{-2/3}DEV\int_0^t [G(t-\tau) \\ & \frac{d}{d\tau}DEV(\overline{\mathbf{C}})]d\tau\end{aligned} \tag{7}$$

where g is the strain softening function. The argument of g, called equivalent strain, is assumed to be associated with the distortional behavior of the material and is defined as

$$\Xi = \sqrt{tr(\overline{\mathbf{C}}\overline{\mathbf{C}}^T)} \tag{8}$$

where $\overline{\mathbf{C}}$ is the Cauchy-Green tensor associated with $\overline{\mathbf{F}}$, the volume preserving part of the deformation gradient, and is given as

$$\overline{\mathbf{C}} = \overline{\mathbf{F}}^T \overline{\mathbf{F}} = J^{-2/3}\mathbf{C} \tag{9}$$

The constitutive law given in equation (7) accounts for two of the typical properties of high-elongation propellants, large deformations and strain softening, through a suitable definition of deviatoric components and uncoupling of volumetric and distortional responses, and a strain softening function representing damage effects. Further modifications to include some other effects introduced in Section 2 are as follows:

- *Mullins' effect*

Solid propellants subject to deformation undergo irreversible microstructural changes, called damage, which influence the current state of the material. In particular, it is experimentally observed that the stress response depends on the past maximum strain, the so-called Mullins' effect [9]. To account for this effect, the softening function g is considered to depend on the maximum equivalent strain achieved by the propellant up to the present time, i. e.

$$g = g(\Xi_{max}) \tag{10}$$

where

$$\Xi_{\max} = \max_{\tau \in (\infty, t]} \sqrt{tr(\overline{\mathbf{C}}\overline{\mathbf{C}}^T)} \tag{11}$$

- *Hysteresis in cyclic loading*

The Mullins' effect described above causes a large amount of hysteresis when solid propellant is subjected to cyclic loading. This effect is represented in part by the hysteresis inherent in viscoelasticity, but primarily through the softening function g. This is accomplished by giving the softening function a different value when the current equivalent strain has a value less than its maximum during the loading history. For unloading the softening function is given as

$$g = g(\Xi_{max})[1 - \kappa(1 - \frac{\Xi(t)}{\Xi_{max}})] \tag{12}$$

where Ξ_{max} is the maximum equivalent strain previously attained, $\Xi(t)$ is the current value of equivalent strain, and κ is a constant to be determined from experimental data at an intermediate strain level.

- *Temperature effect*

The temperature effect upon the behavior of high-elongation PEG/NG solid propellant is included in the constitutive model through the conventional approach and allowing the softening function to depend on temperature. The conventional approach is the assumption of thermorheologically simple behavior, and it is incorporated into the constitutive model by replacing the real time with the so-called reduced time, ξ, defined in terms of some temperature shift factor, a_T, as

$$\xi = \int_0^t \frac{d\eta}{a_T(\eta)} \quad \text{and} \quad a_T = a_T[T(\tau)] \tag{13}$$

Several analytical representations of the shift factor a_T have been developed for viscoelastic materials. The one frequently used for solid propellants is called the WLF equation [3] and is of the form

$$\log a_T = -\frac{c_1(T - T_0)}{c_2 + T - T_0} \tag{14}$$

where c_1 and c_2 are material constants, and T_0 and T are the reference and current temperatures, respectively.

The statistical theories of viscoelasticity suggest a vertical shift of the relaxation modulus in addition to the horizontal shift [3]. Furthermore, experimental data indicate that stress predictions for solid propellants based on the assumption of thermorheologically simple behavior underpredict the observed stress response by a factor of two or more when applied to the combined thermal and mechanical load histories [5]. Motivated by these observations, the softening function is considered to depend on temperature as

$$g(T, \Xi) = g(\Xi)\kappa_T \frac{T_o}{T} \tag{15}$$

where κ_T is a constant to be determined as a best fit to the experimental data, and T_0 and T are the reference and current temperatures in Kelvin.

- *Effect of volume change and dewetting*

It is experimentally observed that, although solid propellants are nearly incompressible under compressive states of stress, their compressibility increases with increasing extensions. This increase is primarily due to the onset of dewetting, i. e. vacuole formation and void coalescence in the microstructure of the material. The effect of dilatation caused by dewetting is included by assuming the function f in equation (2) to be of the form

$$f(J-1, \overline{\mathbf{C}}) = K\left(\frac{\overline{I}_1}{\overline{I}_2}\right)^n (J-1) \tag{16}$$

where n is the compressibility exponent, and $\overline{I}_1$ and $\overline{I}_2$ are the first and second invariants of $\overline{\mathbf{C}}$. The term $K(\overline{I}_1/\overline{I}_2)^n$ can be interpreted as the effective bulk modulus and it reduces to K for uniform dilatation. The above form of the function f has been considered due to its success in characterizing uniaxial and biaxial volume change data for some solid propellants.

- *Effect of superimposed pressure*

It is experimentally observed that the effect of the increasing pressure on the relaxation modulus, is similar to the effect of decreasing temperature. This observation suggests a time-pressure superposition in a similar way to time-temperature superposition. A general time-temperature-pressure shift function $a_{T,P}$ is introduced for this purpose [4], which is of the form

$$\log a_{T,P} = -\frac{c_1[T - T_0 - \Theta(P)]}{c_2 + T - T_0 - \Theta(P)} \tag{17}$$

where

$$\Theta(P) = c_3 \ln[\frac{1 + c_4 P}{1 + c_4 P_0}] - \ln c_5[\frac{1 + c_6 P}{1 + c_6 P_0}] \tag{18}$$

and c_i are material constants to be determined from experimental data.

4.2 Material Characterization

The constitutive law given in equation (7) requires two material functions; the shear relaxation modulus G and the softening function g. The bulk modulus K, and the compressibility exponent n also need to be known to incorporate the relation given in equation (16). The available data for a high-elongation PEG/NG propellant used in this research consist of the master relaxation curve and the time-temperature shift function a_T given in Figure 2 and a set of stress-strain curves [6]. The bulk modulus and the coefficient of thermal expansion are given as $K = 3447\, MPa$ $(5.E5\, psi)$ and $\alpha = 55.E - 6\, F^{-1}$, respectively. The compressibility exponent n is taken as unity due to lack of experimental volume change data.

- *Shear Relaxation Modulus*

The master modulus curve given in Figure 2 is represented mathematically by a Prony series expansion as

$$G_{rel}(\xi) = G_{eq} + \sum_{i=1}^{N} G_i e^{-\frac{\xi}{\tau_i}} \tag{19}$$

where G_{eq} is the equilibrium value of modulus, G_i are the relaxation coefficients, τ_i are the relaxation times and ξ is the reduced time introduced in equation (13). An eight term Prony series is fitted to the master curve.

- *Evaluation of Softening Function*

The softening function g of the constitutive equation (7) is determined through uniaxial constant strain rate tests ranging from $0.00025 min^{-1}$ to $105 min^{-1}$. For this purpose the assumption of incompressibility is made, since g is associated only with the distortional responce of the material. The incompressible uniaxial formulation results in

$$g = \frac{2}{3} \frac{\lambda \sigma_{exp}}{T'_1} \tag{20}$$

where λ denotes the uniaxial stretch in the direction of the applied load, and T'_1 is a deviatoric component of the Cauchy stress tensor.

- *Curve-fitting the Softening Data*

The strain softening function g is curve-fitted by means of a Weibull distribution of the form

$$g = A + Be^{-\left(\frac{\epsilon^M(t) - C}{D}\right)^E} \tag{21}$$

where ϵ^M is the Murnaghan strain given as

$$\epsilon^M = \frac{1 - \lambda^{-2}}{2} \tag{22}$$

for the incompressible uniaxial case. The dependence of the softening function on the strain rate is incorporated allowing the parameters to depend on the strain rate as shown in Figure 3.

4.3 Results

The constitutive model described up to this point is used to predict the response of a high-elongation PEG/NG solid propellant for different types of loading conditions. The predicted responses and their comparison with the experimental data are discussed for the following test types :

Constant strain rate: The sample is loaded at constant elongation rate to a certain strain level. The comparison between the predicted and measured responses demonstrates the success of the

Weibull representation of the softening function, as shown in Figure 4.

Stress relaxation: The sample is loaded at a constant strain rate to a certain level of strain at a constant temperature and then allowed to relax at that level of strain. The model predicts the response quite well for small strain levels at different temperatures and moderate loading rates. However, as the loading rate becomes larger the response is underpredicted for small strain levels and overpredicted for large strain levels. An example is shown in Figure 5.

Complex loading: These tests consist of subsequent loading and unloading at different strain rates, and relaxation at different strain levels. While the loading portion is well represented by the model, the response for relaxation and unloading portions is overpredicted, as shown in Figure 6.

Straining and cooling: The sample is loaded at a constant strain level while, simultaneously, the temperature is lowered at a constant rate. The use of a softening function modified according to changing temperature, resulted in better predicted response, as shown in Figure 7.

Creep and recovery: A ramp load is applied to the sample and then its response under constant load is calculated. The recovery response is obtained by decreasing the load to zero. The response predicted by the model seem to be reasonable, although no experimental creep and recovery tests were available for comparison.

5 Conclusions

The prediction of the mechanical behavior of high–elongation solid propellants has been the subject of this paper. A phenomenological approach has been used to represent the nonlinear viscoelastic behavior of solid propellants. A three dimensional finite strain viscoelastic model has been considered along with a strain softening approach accounting for damage effects, and some modifications accounting for the effect of some loading variables such as temperature, strain rate, pressure, volume change, unloading and dewetting.

The response predicted by the model has been compared with the available experimental data for different loading conditions. Based on the obtained results, the following comments and recommendations related to this reserach and future work can be made.

• Although only uniaxial test data were available, a fully general three dimensional model has been calibrated. Thus numerical analysis of very general geometries and loadings are possible.

• The effect of thermorheological complexity, as exemplified by the vertical shifting of the relaxation modulus, has been included in an ad-hoc manner through the temperature dependence of the softening function, giving the model the advantages of being easy to calibrate, and of fitting within existing computational schemes of viscoelastic analysis.

• The strain rate dependence of the softening function has been incorporated into the model by allowing its parameters to vary with strain rate. The undesirable effects that might be caused due to shifting from one curve to another are not expected to occur when the rate dependence of the convolution integral is considered together with that of the softening function.

• The softening function has been considered to be a function of strain, strain rate and temperature. In more general cases, stresses may also have to be considered in this function for a better representation of internal damage.

• More experimental data are necessary to check and/or to modify the model for multiaxial effects, strain rate dependence of the softening function and the effects of pressure on the rate of damage.

• A better understanding of microstructural changes along with a more complete experimental data is necessary for a more realistic model of dewetting.

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Figure 1: Stress-strain curves for high-elongation propellant in uniaxial tension at different strain rates.

Figure 2: Master modulus curve and experimental shift function for high-elongation PEG/NG solid propellant.

Figure 3: Comparison of softening function vs. Murnaghan Strain at different strain rates.

Figure 4: Constant strain rate at 70^0F and $0.25min^{-1}$

Figure 5: Stress relaxation at 3% and 50% strain and 70^0F

Figure 6: Complex loading at 70^0F

Figure 7: Straining and cooling at $0.0025min^{-1}$