Title: A VISCOELASTIC MODEL FOR PBX BINDERS

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Abstract. Stress-strain measurements done at different rates and temperatures along with measurements of the rate- and temperature-dependent dynamic storage modulus have allowed us to construct a generalized Maxwell model for the linear viscoelastic response of plasticized estane. A theoretical analysis is presented to include effects of impurities.

INTRODUCTION

Complete knowledge of the thermo-mechanical behavior of the constituents of PBX-9501 is required for any micromechanics method to be a useful tool for modeling its behavior. The primary constituents of PBX 9501 are the explosive cyclotetramethylene-tetranitramine (HMX) crystals and the inert plasticized estane binder matrix. Estane 5703 is a polyester polyurethane elastomer manufactured by the B.F. Goodrich Company with a density of 1.19 gm/cm$^3$. The polymeric binder shows dramatic sensitivity to changes in strain rates and temperatures. For example, a change in the temperature from -50°C to 50°C will have an associated change in the shear modulus of five orders of magnitude. Obviously, a successful theory for PBX 9501 must account for this behavior. Because of recent experimental effort, much high-quality stress-strain data has become available for the plasticised binder. A primary goal was to use this data to formulate a generalized Maxwell model (GMM) thermo-mechanical constitutive law for the binder. While a GMM constitutive law has immediate applications for PBX 9501, our theoretical analysis used to obtain the constitutive law has interest to the general community involved with plastic bonded high explosives.

The aforementioned stress-strain data was measured by the LANL’s Material Structure/Property Group (MST-8) and was obtained by several different experimental methods. An Intron 5567 testing machine was used for measuring uniaxial stress-strain data for rates in the range of $10^{-4}$ s$^{-1}$ to 1 s$^{-1}$. A hydraulic MTS 810 material testing machine was used for rates between $10^{-1}$ s$^{-1}$ and 10 s$^{-1}$, while Split-Hopkinson Pressure Bar (SHPB) was used for rates around $10^{3}$ s$^{-1}$. Our approach is to use the torsion pendulum experiments of G. Flowers$^1$ to construct the GMM. Upon determining the GMM we then use the Boltzmann Superposition Principle (BSP) to calculate the stress-strain response predicted by our GMM for the binder. By comparing our stress-strain predictions with experiments involving Instron, MTS, and SHPB, which are uniaxial stress experiments, we can “fine tune” our GMM. Flowers’ torsion pendulum data are functions of sinusoidal rather uniaxial loading strains. Consequently, a theoretical analysis is required to convert his data into a form useful for our micromechanics work.

THEORETICAL ANALYSIS

When the deformation is small, the theory of linear viscoelasticity assumes that the dynamic behavior of any viscoelastic material can be described in terms of
various relaxation processes. These dynamic processes originate from the motions that occur in any complicated entangled molecular network comprising the viscoelastic material. Since the number of relaxation processes are typically huge, a continuous distribution of relaxation times is required to fully describe the dynamic behavior of the material. The corresponding transient shear moduli can be expressed in terms of this relaxation time distribution as:

\[
G(t) = G_e + \int_{-\infty}^{+\infty} H(\tau) e^{-t/\tau} d(\ln \tau),
\]

where \(H(\tau)d(ln \tau)\) represents the relaxation times in the range \(ln \tau\) to \(ln \tau + d(ln \tau)\), and \(G_e\), if different from zero, is called the equilibrium modulus.

The Generalized Maxwell Model of viscoelasticity replaces the spectrum of relaxation times with a discrete spectrum labeled by \(\tau_i\)

\[
H(\tau) = \sum_{i=1}^{n} G_i \tau_i \delta(\tau - \tau_i),
\]

where \(G_i\) is the strength of the \(i^{th}\) mode. In this approximation, the shear modulus becomes:

\[
G(t) = G_e + \sum_{i=1}^{n} G_i e^{-t/\tau_i}.
\]

Flowers has determined the storage and loss moduli, \(G'(\omega)\) and \(G''(\omega)\), respectively, for the binder over a temperature range of -150 C to 75 C, and driving frequencies from 0.6 radians s\(^{-1}\) to 60 radians s\(^{-1}\). To extend the effective frequency range, Flowers invoked the well-known time-temperature superposition theory of Williams, Landel and Ferry (WLF), by introducing a time-temperature shift factor \(a_T\). Figure 1 shows a numerical fit to Flowers’ measurements of \(Log G'\) as a function of \(Log(\omega)\), at a reduced temperature \(T_0\) of 19 C.

Flowers also provided data on the temperature dependence of his shift function. We fit his shift function to a WLF equation:

\[
Log(a_T) = -6.5 \frac{(T - T_0)}{120 + T - T_0}.
\]

Table 1.

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<th>ELEMENT</th>
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<th>ELEMENT</th>
<th>LOG G</th>
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<tr>
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</table>

The storage modulus \(G'(\omega)\) is related to the shear relaxation function by

\[
G'(\omega) = \omega \int_{0}^{\infty} dt' \sin(\omega t') G(t').
\]

Thus

\[
G'(\omega) = G_e + \int_{-\infty}^{+\infty} H(\omega) d(\ln \tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} = G_e + \sum_{i=1}^{n} G_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2}.
\]
We approximate the bulk modulus of the binder as the strain-rate independent value of 3.65 GPa. For the case of uniaxial stress, the relevant modulus is Young’s, given by

\[ E(t) = \frac{9K(t)}{3K + G(t)} = 3G(t). \]  

(7)

Having determined \( G(t) \) from Eq. (3), we then determine the stress-strain behavior from

\[ \sigma(t) = \int_{0}^{t} E(t - t') \dot{\epsilon}(t') dt'. \]  

(8)

Our theoretical stress-strain curves from Eq. (8) are compared to those measured at MST-8. A fine-tuned GMM was then constructed to improve the agreement (Table 1) although only small changes in the original GMM were required. The final stress-strain curves are compared to experiment in Fig. 2.

**RESULTS**

Compressive stress-strain curves measured at MST-8, and those obtained by our theoretical analysis are shown in Fig. 2 for room temperature, low strain rates, and in Figs. 3, and 4 for higher strain rates and colder temperatures.

**FIGURE 2.** Room temperature, low strain-rate compression stress-strain curves for the plasticised binder. At each strain rate, two stress-strain curves are shown, one corresponding to direct stress-strain measurements taken at MST-8, and one corresponding to our theoretical analysis of Flowers’ torsion pendulum measurements.

It is clear, with the exception of Fig. 4, that the agreement between our analysis and the MST-8 data is very good. In these temperature and strain rate regimes our derived constitutive law using the GMM, plus the temperature dependence from the WLF equation (Eq. (4)) provide a good description of the thermo-mechanical behavior of the binder.

At low temperatures and high strain rates, however, the assumptions inherent in the construction of the binder constitutive law begin to fail, and the analysis yields strong discrepancies with the uniaxial SHPB data (Fig. 4). The likely cause of this discrepancy is that, at very low temperatures and high strain rates, the glass-like behavior of the binder has associated yielding which begins to
dominate the stress-strain response, thus invalidating the assumptions of linear viscoelasticity.

The coefficients are now functions of the bulk moduli and concentrations of the binder and the impurities, $K^m$, $c_m$ and $K^f$, $c_i$ respectively. Note, that unlike the pure binder, the composite now has a time-dependent bulk relaxation function. The result of our analysis gives:

$$K^C(t) = K^C_0 + \sum_{i=1}^{M} K^C_i e^{-t/t_i}$$

$$G^C(t) = G^C_0 + \sum_{i=1}^{M} G^C_i e^{-t/t_i},$$

where the coefficients, $K^C_i$ and $G^C_i$, are given by

$$K^C_i = \begin{cases} K^f/K^m (c_i K^m + c_m K^f)^{-1} & i = 0 \\ \frac{4}{3} c_i c_m (K^f - K^m)^2 & i \neq 0 \\ (c_i K^m + c_m K^f)^2 G^m_i & i \neq 0 \end{cases}$$

$$G^C_i = \begin{cases} 0 & i = 0 \\ (1 + 5c_i c_m) G^m_i & i \neq 0 \end{cases}$$

where $G^m_i$ are the coefficients of the GMM for the unfilled binder provided in Table 1. This analysis has be extended to the general case of ellipsoidal shaped impurities.

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