



Viscoelastic Characterization of Different Solid Rocket Propellants Using the Maxwell Spring-Dashpot Model

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Abstract: A single spring and a single dashpot in series was utilized to simulate the stress-strain curve for different classes of solid rocket propellants, namely extruded double base propellants (EDBP) and composite propellants (CP), in the uniaxial tensile mode in a constant rate of travel machine. The propellant behaves as a viscoelastic material and invariably exhibits stress relaxation, which cannot be simulated by elastic mechanical property parameters. In order to generate a complete stress-strain curve of a solid rocket propellant under tensile testing, different classes of solid rocket propellants were evaluated and the stress-strain curve generated was modelled using the single spring-single dashpot Maxwell fluid model. Using two constants, called the spring constant (K) and the damping factor (D), it was possible to generate a complete stress-strain curve. Mathematical formulation gives the stress (σ) – strain (ϵ) relation as $\sigma = D \cdot (d\epsilon / dt) \cdot (1 - e^{-K \cdot \epsilon / (D \cdot (d\epsilon / dt))})$. Additionally the physical nature of the spring constant resembles that of the elastic constant and the damping coefficient gives the contribution of the viscous part of the load bearing capacity of solid rocket propellants. The development of a general mathematical formulation, the calculation of constants for different classes of propellants and insight into the viscoelastic nature of propellants are the main themes of this article.

For all classes of propellants, two ratios are defined. The first is a dimensionless parameter 'H', which is the ratio of the spring constant to the initial elastic modulus. The second is the ratio of the damping coefficient to the spring constant depicted by parameter 'S'. The spring constant is higher than the initial elastic modulus and the value of 'H' is always higher than 1. For brittle propellants (extruded double base propellants, EDBPs, with a high elastic modulus), the spring constant is numerically very close to the spring constant (H is around 1.75). As the ductility (percentage elongation) of the solid rocket propellants increases (from cartridge loaded composite propellants, CLCPs, to case-bonded composite propellants, CBCPs), the value of parameter 'H' also increases (H \simeq 10 for CP). For EDBPs

the parameter 'S' is smaller (~ 1.24), but for CLCPs and CBCPs, it is high ($S \sim 5$ to 8). Both of these ratios are basic properties of the polymeric matrix. The first ratio depicts the departure of the actual stress-strain curve from linearity, while the second ratio is another way of expressing the relaxation time. A higher 'H' indicates a softer and more ductile propellant, while a higher 'S' indicates a shorter relaxation time for the propellant. A lower 'S' indicates that the propellant recovers faster on removal of strain.

Keywords: damping coefficient, Maxwell model, rocket propellants, spring constant, tensile test, viscoelastic properties

Introduction

Rocket and missiles for short range and tactical purposes are propelled by solid rocket propellants. Simple design, absence of moving parts, safety concerns, no sloshing in transportation, higher density, preconceived thrust time profile etc. are some of the advantages of using solid rocket propellants, especially in missile applications. Solid rocket propellants are available in a large variety and each variety has different utility, performance and advantages. In the course of time, extruded double base propellants (EDBP), cartridge-loaded composite propellants (CLCP), case-bonded composite propellants (CBCP) and nitramine-based propellants have all been used for missile applications. A brief summary of the development of propellants in many countries may be found in the open literature [1-6]. Almost all followed the same trend and all classes of propellants are developed by all countries. India has also followed the same trend and has expertise to develop propellants of all varieties [7].

The mechanical properties of solid rocket propellants are important for structural integrity considerations and propellants must possess sufficient strength and elongation to absorb various handling, processing, transportation, storage and operational loads. To ascertain the mechanical properties of propellants, specimens are generally prepared as per ASTM D638 Type IV [8] and tested in a constant strain rate of loading machine at a nominal strain rate of 0.0185 per second in the uniaxial tensile mode. A stress-strain curve is generated, which is non-linear in nature and salient mechanical parameters such as the initial modulus, tensile strength, elongation at peak stress and elongation at breakpoint are ascertained from the generated curves. However, these parameters alone are not able to completely represent the nature of solid propellants.

Several assumptions are made by researchers about the nature of a solid propellant as a mechanical, load bearing material. The mechanical characterization

of solid propellants began with the development of the classical theory of physics. Sometimes it is preferred to possess rubber-like elasticity [9], sometimes viscoelasticity [10, 11], sometimes time-temperature superposition [12, 13]. Many researchers in recent years have simulated the mechanical properties of hydroxyl terminated polybutadiene (HTPB) based, composite, solid propellants by using empirical relations [14-17]. Invariably the propellant exhibits stress-relaxation behavior and at constant strain, the stress generated in the propellant specimen reduces with time. As stress-relaxation behavior can be best represented by the Maxwell fluid model, an attempt is made in this paper to simulate the complete stress-strain curve of a propellant during uniaxial tensile testing as a Maxwell fluid. A Maxwell fluid is represented by a spring and a dashpot arranged in series and is the best way to represent the stress-relaxation shown by propellants. For HTPB/AP/Al based, case-bonded, composite propellants, the utility of the Maxwell fluid model in the evolution of the stress-strain curve in the uniaxial tensile mode has already been reported [18, 19]. In the present article, the Maxwell fluid model is extended to other classes of solid rocket propellants.

Mathematical formulation

All models of viscoelasticity are a simplification of the mechanical behaviour of the material in terms of some combination of spring and dashpot systems. A spring represents the elastic behaviour of the material and depends on the normal Hook's law. It is specified by a spring constant (K) and the stress developed in the material is assumed to be proportional to the strain. On the other hand, a dash-pot works on Newton's law of viscosity, where the shear stress is proportional to the rate of straining. In this case, the element is represented by a damping coefficient (D) and is a constant of proportionality for stress and strain-rate.

The simplest model requires a spring and a dash-pot. If these two are arranged in series, the material behaviour is said to be as a Maxwell fluid, while a parallel arrangement of these two elements results in a Kelvin-Voigt Solid behaviour. A Maxwell fluid (Figure 1) depicts the stress-relaxation behaviour correctly. The mechanical behaviour of the material is depicted by two constants, the Spring constant (K) and the Damping coefficient (D). The formulation for tensile testing of a solid rocket propellant can be generated from this model.

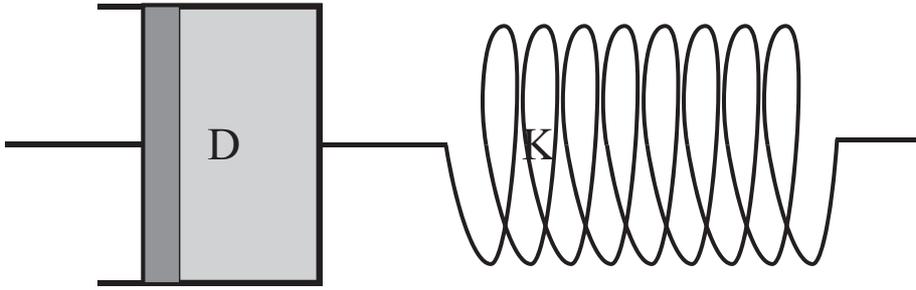


Figure 1. Schematic representation of a Maxwell fluid.

Normally tensile testing is conducted at a constant strain rate. Let stress, σ be applied at the ends of this model. Both of the elements of the model will experience the same stress, σ . However, they will elongate to different extents. Let the strain in the spring be ε_1 and the strain in the dash-pot be ε_2 .

From the element properties, the stress in the spring is proportional to the strain in the spring.

$$\sigma = K \cdot \varepsilon_1 \quad (1)$$

For the dash-pot, the stress is proportional to the strain rate. So the mechanical property relation is given by equation 2:

$$\sigma = D \cdot d\varepsilon_1 / dt \quad (2)$$

The total strain (ε) is the sum of the strain in both elements:

$$\varepsilon = \varepsilon_1 + \varepsilon_2 \quad (3)$$

Putting values from equations 1 and 2 into equation 3 and simplifying, equation 4 can be obtained:

$$d\sigma / dt + K \cdot \sigma / D = K \cdot d\varepsilon / dt \quad (4)$$

This is a linear differential equation with constant coefficient, which can be solved using initial conditions. Initially, no stress is produced at zero strain. The solution of the differential equation is obtained as in equation 5:

$$\sigma = D \cdot (d\varepsilon / dt) \cdot \left(1 - e^{-K \cdot \varepsilon / (D \cdot (d\varepsilon / dt))}\right) \quad (5)$$

Normally, tensile testing for solid rocket propellants is conducted at a constant rate of travel depicted by a constant strain rate ($d\varepsilon/dt = 0$). From the equation developed above, it is also possible to find out the initial modulus of the propellant specimen. For that purpose equation 5 is differentiated with respect to strain, as depicted by equation 6:

$$d\sigma / d\varepsilon = K \cdot e^{-K \cdot \varepsilon / D(d\varepsilon / dt)} \quad (6)$$

To determine the initial modulus, strain (ε) is equated to zero, which gives the initial modulus as equal to the spring constant (K). The damping coefficient only gives an indication of the non-linearity of the stress-strain curves. The mechanical properties of the different classes of propellants were modelled as Maxwell fluids as per equation 5 and the results are compiled in the next section.

Testing parameters

Material

The EDBP class of solid propellants contain NC (nitrocellulose) and NG (nitroglycerin), along with a stabilizer. The final composition has 60-65% NC and 30-40% NG. The remaining parts may consist of plasticizer, stabilizer and opacifier at low percentages, each less than 1%. The process of manufacture starts with wet mixing followed by sheet making. This is left for maturation and drying before blending. The actual manufacturing concludes with hot rolling, carpet rolling, extrusion and machining. The propellant grains are generally obtained in tubular form. The specimen for mechanical testing of double base propellants has dimensions conforming to ASTM D638 type IV and was obtained by punching. CLCP and CBCP are basically composite propellants containing solid oxidizer (ammonium perchlorate), solid fuel (aluminum) and binder (prepolymer HTPB and plasticizer). The propellants were processed by gravity with vacuum casting and the specimen for mechanical testing was obtained by punching. Since the mechanical behaviour of solid rocket propellants should not change significantly during their shelf-life, the stress-strain curve of the propellants must not change over time. It is immaterial whether the propellant specimen is taken from a fresh lot or from an old lot, the mechanical behaviour of the propellant should remain constant and unchanged and must not alter or degrade with time. All of the propellant specimens were taken from lots which had been processed 1-3 years before testing and all had sufficient shelf-life remaining.

Method

Uniaxial tensile testing using a constant rate of travel machine assesses the mechanical properties of propellant of different varieties. As per ASTM D638 type IV specification, dumbbells were prepared and tested at 50 mm/min speed. The specimen was gripped with a grip distance of 60 mm and the gauge length for the calculation of the strain was taken as 45 mm in a constant rate of travel uniaxial tensile test. A minimum of five specimen were taken for each type of propellant and consistent results are reported. Upon straining, the grip distance increases and the propellant specimen placed between the grips is stretched. As one grip is fixed, the movement of the second grip is taken as the extension of the specimen. Simultaneously, the grip experiences some force, which increases with increase in extension. The engineering strain is taken as the ratio of extension and gauge length and the stress is the force divided by the initial cross-sectional area (width \times thickness of the specimen). The stress-strain diagram was plotted for each propellant specimen until they broke.

Parameters

Most of the stress-strain diagrams are linear in nature at low strains. The slope of the stress-strain diagram at low strain is called the elastic modulus of the propellant. As the strain increases, the rate of increase of the stress reduces and the stress-strain curves tend downwards. The stress attains a maximum value called the tensile stress. The strain corresponding to this maximum is also significant for analysis. Further stretching of the propellant leads to a reduction of stress and finally to breaking of the specimen. The strain at the breakpoint is important for those propellant specimens where significant stretching after attaining the maximum stress is not observed. It is clear that four main parameters are specified in the tensile testing curve of a propellant specimen, namely Elastic modulus (E-Mod), tensile stress, strain at maximum stress and strain at breakpoint.

However, it is obvious that a propellant follows linear elastic behaviour for only a very small part of the strain axis ($\sim 30\%$). The tensile testing curve tends downwards and the slope of the stress-strain curve at higher strain decreases, indicating loss of strength of the specimen. So, the mechanical behaviour of an HTPB-based solid rocket propellant is dependent upon strain as well as the rate of straining. It is a viscoelastic material. In addition, it also shows stress-relaxation. Various classes of propellants, including EDB propellants, CLCP, and CBCP, were tested in the tensile mode using a universal testing machine at a nominal strain rate of 0.0185 per second. The stress-strain curve was modelled using the mathematical formulation developed in the previous section.

Results and Discussion

The tensile testing curves generated for the various classes of propellants in the uniaxial mode on a constant rate of travel machine were simulated using the Maxwell fluid model developed in the earlier section. The propellants were basically highly filled polymers and their behaviour is governed by three factors, namely polymer strength, reinforcement contribution and the polymer/solid filler interface. It is clear that at low strain the mechanical properties of the propellants are a strong function of the interface and the role of the polymer alone slowly becomes dominant, as strain increases in the course of the tensile test.

Test results

Extruded double base (EDB) propellant is one class of propellant, where the propellant is made of a matrix of mainly nitrocellulose and nitroglycerin and the method of manufacture is gelatinization. Because of the very large molecular weight of the polymer, the behaviour of the propellant is linearly elastic and the stress-strain curve resembles a straight line. The propellant exhibits a very high elastic modulus and has a very low strain (percentage elongation). The tensile strength of EDB propellants is also very high as depicted in Figure 2. The curve has an initial modulus of 1600 MPa. However on simulation of the stress-strain curve using the Maxwell fluid model, the values of the spring constant and the damping coefficient are 2800 MPa and 3400 MPa·s, respectively. The curve can be simulated well as a Maxwell fluid model. Since the propellant is made by chemical gelatinization, formation of hard segments in the propellant formulations occurs, thus raising both the elastic and the viscous components. The value of the spring constant is higher than the initial modulus of the propellant and the ratio of the spring constant and the initial elastic modulus is 1.75. The ratio of the damping coefficient to the spring constant is 1.214 s.

A similar simulation was carried out for a TDI-cured, cartridge-loaded, composite propellant (CLCP) containing HTPB/AP/Al (16/67/18) with an NCO:OH ratio of 0.7. The propellant was processed by vacuum assisted, gravity casting and was subsequently cured at an elevated temperature (50 °C) for solidification by cross-linking. The tensile testing curve is depicted in Figure 3. At higher strains, the departure from linearity is clearly visible. The propellant exhibits a lower initial modulus (9.2 MPa) and at higher strains the curve tends downwards, depicting a lowering of the slope of the stress-strain curve. Simulation by the Maxwell fluid model gave a spring constant value and a damping coefficient of 90 MPa and 470 MPa·s, respectively. The value of the spring constant is again higher than the initial modulus of the propellant and the

ratio of the spring constant and the initial elastic modulus is 9.78. The ratio of the spring constant to the damping coefficient is 5.22 s.

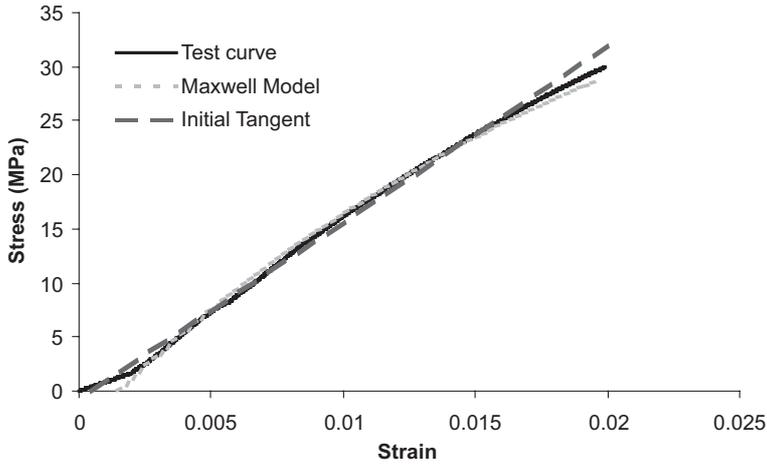


Figure 2. Simulation of the stress-strain curve of EDBP.

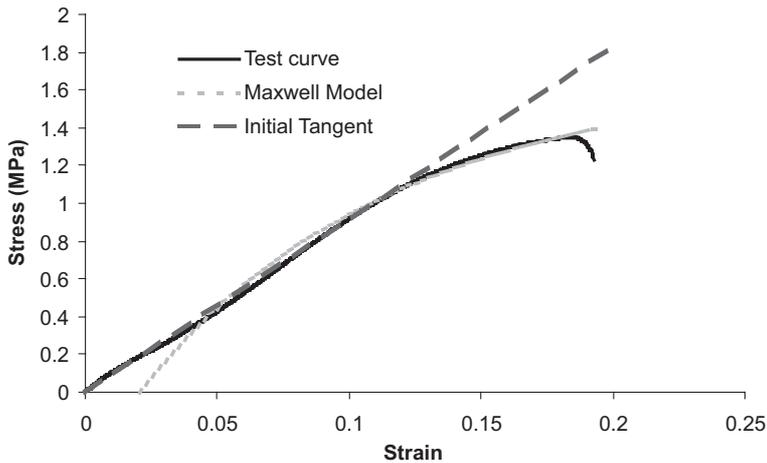


Figure 3. Simulation of the stress-strain curve of CLCP.

A similar simulation was carried out for a TDI-cured, case-bonded, composite propellant (CBCP) containing HTPB/AP/Al (16/67/18) with an NCO:OH ratio of 0.7. The propellant was processed by vacuum assisted, gravity casting and was subsequently cured at an elevated temperature (50 °C) for solidification

by cross-linking. This class of propellants exhibits a relatively lower tensile strength and initial elastic modulus, as compared to CLCPs based on the same binder. However, the percentage elongation, reflected by strain is higher for this class of propellants. The tensile testing curve is depicted in Figure 4. At higher strains, larger departure from linearity is clearly visible. The propellant exhibits a much lower initial modulus (2.8 MPa) and, at higher strains, the curve tends downwards more, reflecting the predominance of the polymeric behaviour at higher strains. Simulation by the Maxwell fluid model gave a spring constant value and a damping coefficient of 30 MPa and 230 MPa·s, respectively. The value of the spring constant is again higher than the initial modulus of the propellant and the ratio of the spring constant and the initial elastic modulus is 10.714. The ratio of the spring constant to the damping coefficient is 7.66 s.

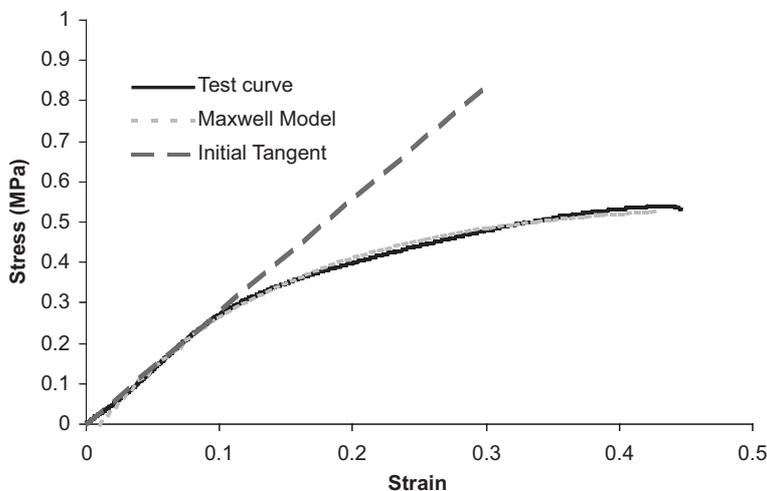


Figure 4. Simulation of the stress-strain curve of CBCP.

Analysis of results

The distinguishing feature of EDBPs, CLCPs and CBCPs are the two ratios. For convenience, two new parameters were introduced. The first is the ratio of the spring constant to the initial elastic modulus, depicted by 'H'. For hard and brittle propellants, the value of 'H' is very close to unity. As the softness and ductility of the propellant increases, the value of parameter 'H' increases. This parameter basically depicts deviation of the stress-strain curve from linearity and if a greater part of the stress-strain curve departs from linearity, the value of this parameter will be high. As CBCPs are soft ductile propellants, the value of 'H' for this class of propellant is high. This is a significant parameter to represent

strain relative to strain at breakpoint, for deviation from linearity.

The second important parameter, evolved out of the simulation by the Maxwell fluid model is parameter 'S', which has unit of time (second). This gives an insight into the viscous tendency of the propellant and represents behaviour of the propellant on removal of stress. In fact, a harder, stronger and brittle propellant exhibits a lower tendency of time-dependent variation of stress with strain. EDBPs have a very small value of this parameter, indicating a lower tendency for viscous behaviour. In fact this parameter represents deviation of the actual stress-strain curve from linearity in the stress axis.

Conclusion

The stress-strain curve for EDBPs, CPCPs and CBCPs can be represented by the Maxwell fluid model with two parameters, the spring constant (K) and the damping coefficient (D). Compared to the initial elastic modulus, the spring constant (K) is always higher and the damping coefficient is numerically higher than the spring constant. For all three classes of propellant, two ratios are defined, namely parameter 'H' and parameter 'S'. Parameter 'H' is a measure of the departure from linearity of the stress-strain curve, while parameter 'S' represents viscous or time dependent variation of the stress-strain curve for solid rocket propellants in uniaxial tensile modes. For soft and ductile propellants, values of both these parameters are on the high side. CBCPs exhibit greater departure from linearity and a major part of the stress-strain curve is non-linear, while for EDBPs linearity is observed in the stress-strain curves until the specimen breaks. The performance of CLCPs is an intermediate case.

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