Research paper

Studies on final modulus of solid rocket propellants in uni-axial tensile testing curves

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Abstract

Solid rocket propellants are highly filled polymers and exhibit viscoelastic and rubber like elasticity. Concept of unique final modulus (H) for HTPB based solid rocket propellant is proposed and mathematical formulation based on third order polynomial fit for simulation of non-linear section of stress-strain curve is developed. Propellants are tested at different strain rates and temperature. It was observed that final modulus is independent of both strain rate and temperature. This indicates that after dewetting, mechanical behavior is not governed by fillers, strain rate or temperature. Additionally, with the help of proposed final modulus, complete stress-strain curve for propellant can be simulated at any temperature and strain rate. Non-linear portion of tensile testing curve is modeled using third order polynomial fit. Using a single additional parameter, simulation of complete stress-strain curves and dewetting strain is uniqueness and power of approach. Conventional mechanical properties parameters like initial modulus, tensile stress and percentage elongation at tensile strength changes with strain rate and temperature, but final modulus remain fixed and constant. It is in true sense an invariant material property.

Keywords : solid rocket propellants, filled polymers, mechanical characterization, tensile test, elastic modulus.

Symbols used :

Bn : Constants for mathematical formulation, n=1,2,3 and4.
E : Initial modulus (MPa)
H : Final modulus (MPa)
σ_1 : Dewetting Stress (MPa)
σ_m : Tensile strength (MPa)
ε_1 : Dewetting Strain
ε_m : Strain at Maximum stress

1. Introduction

Modern rockets, missiles and launch vehicles use HTPB (Hydroxyl Terminated Poly. Butadiene) based composite solid propellants, for propulsion. Main ingredients of solid propellants are polymeric matrix based on HTPB as binder, solid oxidizer particles - AP (Ammonium Perchlorate) and metallic fuel particles - Al (Aluminium) . Main purpose of solid propellants in propulsion system is to impart energy by combustion. But, they are subjected to various types of loading forces at various stages of their manufacture and use. So, solid propellants are supposed to possess sufficient mechanical properties to demonstrate structural integrity throughout processing, handling, transportation, storage and operation.

Importance of proper constitutive equations to predict mechanical properties of solid propellants are discussed in NASA report[1]. The effect of propellant compressibility and mechanical properties on time and temperature are also established. Theoretical stress analysis and failure property generation are also discussed in this report. In another report from AGARD[2] (Advisory Group for Aerospace Research and Development), finite element analysis (FEA) is conducted for solid rocket propellants, shaped in various forms. Mechanical characterizations, elaborated in this report, are stress-relaxation test, uni-axial tensile test (STANAG 4506) and determination of Poisson's ratio and bulk modulus. Similarly structural service life of propellant[3] and effect of environmental conditions on cumulative damage[4] are also points of discussion in various other research papers.

Leaving these advanced techniques aside, in early 60s, solid propellants are characterized as visco-elastic material, simulated best as rubber like filled elastomers[5), 6)]. Time-dependent tensile properties, quasi-equilibrium modulus, temperature dependence of mechanical properties are also illustrated. These generated properties are used for assessing structural margin of safety for actual systems[7)-9)]. Currently, several constitutive models are proposed by different scholars to express governing equations of mechanical properties of propellants[10), 11)].

In recent literature, several attempts are made to explain and practically measure various mechanical property parameters of HTPB based solid propellants. Mechanical properties are measured by Rawley et al[12)] through embedded sensors in solid propellants during mechanical testing. Analysis is conducted using finite element package 'ABAQUS' also. A generalized crosslink point model is also proposed where the relative worth of chemical cross linking, accessional cross linking and tangled chains is established[13)]. At various loading fractions of filler particles, variation of mechanical properties is assessed and filler particle nature as reinforcing or non-reinforcing is quantified. Another attempt is made to propose a three phase (dispersion, interface and continuous) constitutive model of mechanical properties and predict tensile strength of propellants[14)]. Attempt is also made to assess dynamic mechanical behaviour of propellants by image processing[15)].

However, most of the literature available discusses at length the initial linear part of stress-strain curves in tensile testing of solid propellants. The departure from linearity is called dewetting, where debonding between binder and solid filler starts. Beyond this point propellant loses its incompressible nature and poisson's ratio drops from 0.5. This later non-linear part of stress-strain curve is not discussed in the available literature.

2. Experimental work

To ascertain stress-strain behaviour after dewetting and to generate total stress-strain curve for HTPB/AP/Al based composite solid propellant, propellants are processed by vacuum casting followed by elevated temperature curing. The propellant formulations used for analysis has 86% solid loading. Ammonium perchlorate (AP) is used as oxidizer and tri-modal particle size distribution is used in the formulation. Aluminium (Al) is used as metallic fuel. Hydroxy terminated polybutadiene (HTPB) is used as binder and Di-octyl adipate (DOA) is used as plasticizer. Toluene di-isocyanate (TDI) is used as curing agent. Ballistic modifiers are used in small quantities to modify ballistic parameters, but they do not alter mechanical properties of propellants significantly.

For processing of solid propellant formulations, all liquid ingredients (HTPB, DOA) except curing agent (TDI) are mixed in a vertical planetary mixer and minor solid ingredients (Ballistic modifiers) are added. Metallic fuel (Al) and installments of multi-modal oxidizer (AP) in pre-defined sequence is added and mixing is carried out after each addition at pre-specified speed for5minutes. Mix temperature is raised to 40°C and curing agent (TDI) is added. Final mixing is carried out for 30 minutes and thick viscous propellant slurry with viscosity of the order of 5000 poise is discharged under vacuum (3torr) in molds. Solid propellant slurry in molds is placed in ovens for curing at 50°C for 5 days. Propellant slurry becomes solid due to cross-linking and formation of poly-urethane linkages. Propellant grains are demolded and propellant specimens are prepared for evaluation of mechanical properties.

Mechanical properties of propellants are evaluated using ASTM D638 Type IV specimen in uni-axial tensile mode with a constant strain rate of loading machine. Propellant specimens are tested at a nominal strain rate of 0.0185185 s^{-1}. Nominal test temperature of +27°C is maintained. Testing is carried out at four more strain rates. For testing at different temperatures (high at +55°C and low at -20°C), propellant dumbbells are prepared as per specification and kept in ovens at set temperatures for soaking for a period of6hrs. The universal testing machine is equipped with chamber which is heated to pre-set high temperature by electric heater-banks. Similarly for low temperature testing, cryogenic nitrogen gas is used to maintain the temperature of test chamber at pre-set levels during testing. So, propellant at pre-soaked temperature is tested in chambers maintained at test-temperature by suitable means (heaters or nitrogen). The machine has provision to set different rate of loading also.

From each test condition, minimum5samples are tested under uni-axial tensile loading and initial modulus (E), tensile strength (σ_m) and elongation (ε_m) at maximum stress are recorded for each sample. Each of the reported values is average of 5 samples from one single batch.

Stress-strain curves for uni-axial tensile testing at different strain rates and at +27°C temperature are given in Fig. 1. It is clear that with increasing strain rate of testing, initial modulus of the propellant increases. However, initial modulus can characterize the linear portion of the stress-strain curve only. The departure from linearity takes place at dewetting point, where bond between binder and solid filler breaks. Since fillers act as reinforcement, after dewetting, a marked decrease in modulus is expected. As depicted in insert of Fig. 1, it is clear that non-linear portion at different strain rates, if shifted properly with coincident dewetting points, may lead to almost same nature of curve. If non-linear portion of the stress-strain curve is characterized by another hypothetical modulus called final

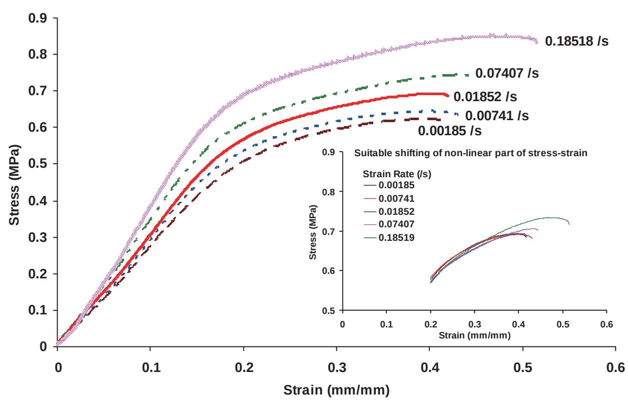


Fig. 1 Stress−strain curves for solid propellants at different strain rates.

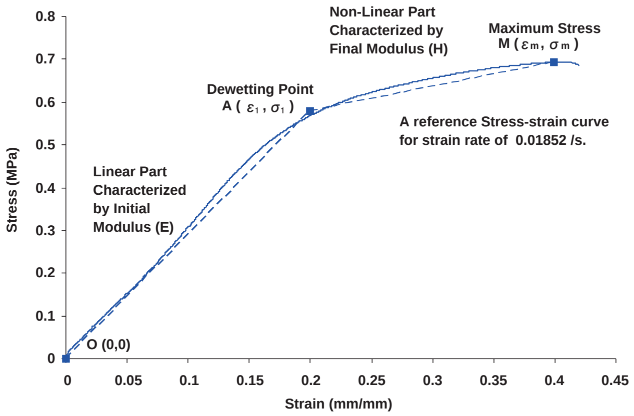


Fig. 2 Salient parameters of reference stress−strain curve.

modulus (symbolized as H), complete stress-strain curve can be simulated. Mathematical formulation describes importance and approach for generation of stress-strain curve using final modulus (H).

3. Mathematical formulation

Stress-strain curve of solid rocket propellant at a reference strain rate is depicted in Fig. 2. It is clear that curve has end of linear section at point 'A' (ε_1, σ_1), known as dewetting. Slope of linear section is known as initial modulus. As curve is linear, dewetting stress can also be obtained from dewetting strain, if initial modulus is known by using Hook's law. Point 'M' (ε_m, σ_m), of Fig. 2, which corresponds to maximum stress on stress-strain curve is also indicative of tensile strength of the material and is completely defined for a given stress-strain curve. Final modulus (H) is defined as slope of line joining points 'A' and 'M' and can describe non-linear section of stress-strain curves. As nature of the curves in non-linear section is almost similar, final modulus is found to be independent of strain rates. Mathematical formulation is devised to generate stress-strain curve for solid rocket propellants using the concept of final modulus.

First part of stress-strain curve is linear and slope is given by initial modulus (E). This is valid for the curve in Fig. 2 from point 'O' to point 'A'. Proportionality of stress-strain holds for this section as given in Eq. 1. It is possible to get stress at point 'A' in Fig. 2 by introducing strain at A as 'ε_1' in the Eq. 1.

$$\sigma = Ex\varepsilon \tag{1}$$

Cubic (third order) curve is fitted for non-linear phase of stress-strain curve between point 'A' to point 'M'. Stress values in this domain are thought to follow a cubic variation in strain with governing relation given as Eq. 2.

$$\sigma = B1x\varepsilon^3 + B2x\varepsilon^2 + B3x\varepsilon + B4 \tag{2}$$

Here B's are constants to be evaluated from boundary conditions. In the stress-strain curve for solid propellant, point 'M' is completely defined as (ε_m, σ_m). By implementing hypothetical final modulus concept, strain values at point 'A' can be generated using Eq. 3.

$$\varepsilon_1 = (\sigma_m - Hx\varepsilon_m)/(E - H) \tag{3}$$

Strain at point 'A' (ε_1), is dependent on three measured parameter and the proposed final modulus. It can be determined for a stress-strain curve. Using Eq.1,stress at point 'A' (σ_1) can also be evaluated, thus defining point 'A' completely on stress-strain curve.

Since Eq. 2 has four independent constants (B's) , four boundary conditions are needed to evaluate them. After evaluation of *Bdash* 1s, stress-strain curve from point 'A' to point 'M' can be generated using Eq. 2. These four boundary conditions are given below : -

1. Stress-strain curve must pass through 'A'.
2. Stress-strain curve must pass through 'M'.
3. Slope of stress-strain curve at 'A' is same as slope of line joining 'O' and 'M'.
4. Slope of stress-strain curve at 'M' is zero.

With these four boundary conditions, the four equations can be written in matrix form as Eq. 4.

$$\begin{Bmatrix} \sigma_1 \\ \sigma_m \\ \sigma_m/\varepsilon_m \\ 0 \end{Bmatrix} = \begin{pmatrix} \varepsilon_1^3 & \varepsilon_1^2 & \varepsilon_1 & 1 \\ \varepsilon_m^3 & \varepsilon_m^2 & \varepsilon_m & 1 \\ 3\varepsilon_1^2 & 2\varepsilon_1 & 1 & 0 \\ 3\varepsilon_m^2 & 2\varepsilon_m & 1 & 0 \end{pmatrix} \begin{Bmatrix} B1 \\ B2 \\ B3 \\ B4 \end{Bmatrix} \tag{4}$$

By inverting 4 x 4 square matrix in strains (ε) , values of B's can be obtained and then non-linear section of stress-strain curve can be simulated using Eq. 2.

4. Result and discussion

Stress-strain curve for solid rocket propellant tested at ambient temperature and different strain rate is depicted in Fig. 1. Salient conventional mechanical property parameters like initial modulus (MPa), tensile strength (MPa) and percentage elongation at maximum stress are extracted from the curve. End of linearity (shown as point 'A' in Fig. 2) is also derived from the curves and depicted for each strain rate in table 1.

Final modulus is calculated for each test case using Eq. 3 in modified form. With all numerical values available, as

Table 1 Calculation of final modulus (H) at different strain rates.

Strain rate (s^{-1})	E (MPa)	σ_m (MPa)	ε_m (mm/mm)	σ_1 (MPa)	ε_1 (mm/mm)	H (MPa)
0.00185	2.66	0.623	0.397	0.437	0.164	0.804
0.00741	2.80	0.645	0.392	0.464	0.166	0.792
0.01852	2.89	0.693	0.399	0.517	0.178	0.796
0.07407	3.34	0.745	0.428	0.529	0.158	0.800
0.18518	3.99	0.851	0.466	0.598	0.150	0.797

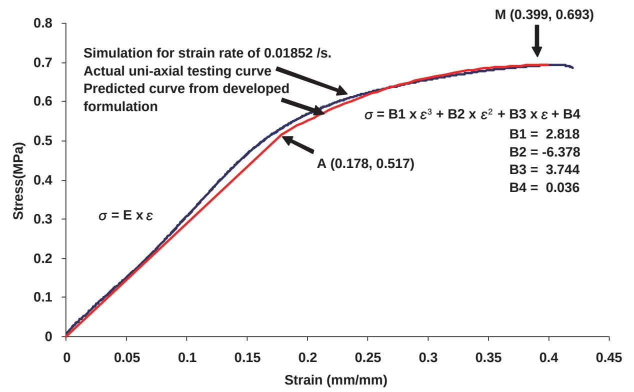
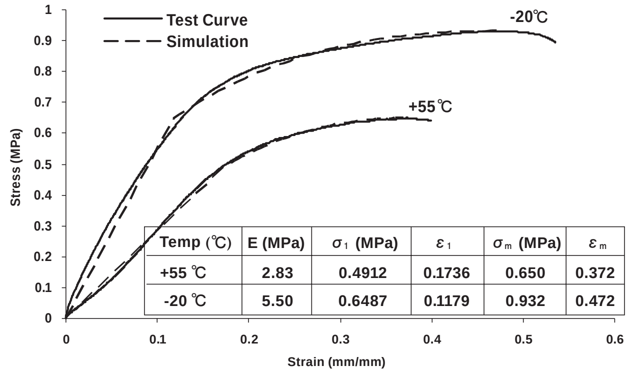


Fig. 3 Simulated and actual tensile testing curves at ambient temperatrue.



Temp (℃)	E (MPa)	σ_1 (MPa)	ε_1	σ_m (MPa)	ε_m
+55 ℃	2.83	0.4912	0.1736	0.650	0.372
-20 ℃	5.50	0.6487	0.1179	0.932	0.472

Fig. 4 Simulation of stress-strain curves at different temperatures.

depicted in last column of table 1, it is clear that value of final modulus is constant. Although initial modulus changes with strain rate but final modulus remain fixed. Same final modulus can be adopted for a propellant formulation at different strain rates at a given temperature of testing.

From least square fit for errors, final modulus for the given propellant formulation is taken as 0.8 MPa. Assuming cubic variation of stress with respect to strain as per Eq. 2, nonlinear section of stress-strain curve is modeled. For the nominal strain rate of 0.01852 per second, initial modulus (2.89 MPa), percentage elongation (39.9%) at maximum stress (0.693 MPa) is extracted from table 1. With final modulus of 0.8 MPa, dewetting stress and strain are calculated using Eq. 3. With the help of Eq. 4, values of constant parameters, B's are calculated. Linear section is plotted on stress-strain plane as a straight line with slope equal to initial modulus as per Eq. 1. Non-linear section is plotted using Eq. 2. Actual tensile testing curve is superimposed over generated stress-strain curve and is reproduced as Fig. 3. Close matching of both the curves indicate that the mathematical formulation developed in previous section is suitable for generation of stress-strain curve for uni-axial-tensile testing of solid rocket propellant.

To ascertain versatility of the conceptual final modulus and developed mathematical formulation, propellant specimens from same lot is tested using 0.01852 per second strain rate in uni-axial tensile mode at two different temperatures (-20°C and +55°C). 5 specimens conforming to ASTM D638 type IV are tested at each test condition after soaking at specified temperatures in chambers for 6 hours.

Table 2 Value of B's at strain rate of 0.01852 per second at different temperatures.

Parameters	+55℃	+27℃	−20℃
B1	3.742	2.818	2.988
B2	−7.467	−6.378	−5.433
B3	4.001	3.743	3.132
B4	0.002	0.036	0.350

At low temperatures, initial modulus of propellant improves and so occurs to tensile strength and percentage elongation at maximum stress. At high temperature propellant softens resulting in reduced initial modulus, maximum stress and strain at maximum stress. The curve is depicted in Fig. 4. The salient parameters for both the test condition are also shown.

At low temperature, value of stress and strain at point 'A' and point 'M' is used to calculate slope of non-linear section (using Eq. 3). The value of slope is obtained as 0.8 MPa, which is value of proposed final modulus. Similarly, calculation is carried out for high temperature tensile testing curve. This again results in final modulus of 0.8 MPa. To simulate complete stress-strain curve, the process depicted in section 3 is used and value of parameters B's are calculated. The values of B's are depicted in table 2. Using these values of B's, complete stress-strain curve is generated and superimposed over the tensile testing curves (Fig. 4). Again close matching of observed and simulated stress-strain curve is observed.

It clearly indicates that final modulus is independent of temperature also. Although conventional mechanical properties parameters like initial modulus, tensile strength and percentage elongation at maximum stress changes significantly with temperature and strain rate, final modulus remains invariant and constant.

In the initial phase of stretching during uni-axial tensile testing, bonding of polymeric matrix with solid filler is the governing parameter to decide mechanical properties[14]. As interface bonding plays important role in the initial phases of stretching, polymeric nature of bonding dominates and mechanical parameters as determined by test, vary significantly with temperature. Invariably polymer properties dominate and the values of elastic or initial modulus (E) are significantly affected by minor temperature variation in the range of 30-40°C. But after dewetting, polymeric materials dissociates itself from solid fillers of ammonium perchlorate and aluminum powder. In this later post-dewetting region, fillers as well as interface both do not share any load. Whole applied load is borne by cross-linked matrix of urethane linkage (-NHCO-) of polymer network only. In fact, rheokionetic studies also reveal that for the chemically cross-linked networks, viscous part of material response moves faster. Elastic part begins to rise later indicating delayed formation of structures capable of and responsible for the elastic response[16]. However development of viscous part finishes earlier than elastic part. The post-dewetting region in uni-axial tensile test indicates this period of dominant elastic response of cross-linked polymer network.

In addition to this, high solid loading also affects mechanical properties of cross-linked polymer and restricts final modulus to vary significantly with variation in temperature. These solid fillers in later part of extension behave as obstruction to stress flow and also prevent thinning of polymeric mass. The proposed final modulus is in fact similar to plastic modulus defined for metals showing high elongation during failure. Plastic modulus is slope of stress-strain curve excluding elastic strain region[17]. Composite solid propellants generally behaves as rigid plastic material and when total strain is sufficiently large, elastic strain or dewetting strain is negligible. The behaviour in post dewetting region is defined by this final modulus completely and is sufficient to generate non-linear stress-strain variation by the cubic fit method explained in the paper.

5. Conclusion

Stress-strain curve through uni-axial tensile testing of HTPB/AP/Al based solid rocket propellant is modeled using hypothetical final modulus concept. For the propellant formulation with 86% solid loading, final modulus is calculated to be 0.8 MPa. This is 3-5 times lower than initial modulus values and is found to be independent of strain rates and temperatures. Non-linear section of stress-strain curve is simulated as a third order polynomial fit with suitable boundary conditions. Mathematical formulation is developed for generation of complete stress-strain curves for solid rocket propellants at different strain rates. Contrary to already reported mechanical properties parameters, which changes with strain rate and temperature, an invariant mechanical property parameter called final modulus is introduced and used to simulate even non-linear section of stress-strain curve to a fair amount of accuracy.

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