

Effect of Temperature on Mechanical Properties of Solid Rocket Propellants

Himanshu Shekhar

High Energy Materials Research Laboratory, Pune-411 021, India
E-mail: himanshudrdo@rediffmail.com

ABSTRACT

Mechanical properties of solid rocket propellants are dependent on temperature. Any change in temperature brings significant change in the tensile strength, percentage elongation, and elastic modulus of the propellant. Different classes of operational solid rocket propellants namely extruded double-base propellants, composite, extruded composite and nitrate ester polyester propellants were evaluated at different temperatures in the operating range of the rockets and missiles preferably in the range of -50°C to $+55^{\circ}\text{C}$. It was observed that for each class of propellant, as temperature reduces, propellant becomes hard. This is depicted by increase in elastic modulus and tensile strength of the material. However, trend of percentage elongation is not very uniform. Extruded double-base propellants show less percentage elongation (around 1 per cent) at reduced temperature (-50°C) probably due to brittleness. So is the trend with case-bonded composite propellants. However, reverse trend is exhibited by cartridge-loaded composite propellants and nitrate ester polyester propellants. Such propellants show higher percentage elongation (6 per cent for CLCP and 35 per cent for NEPE) at reduced temperature (-50°C). This makes such propellants tough and more area under stress-strain curve at reduced temperature is observed.

Keywords: Solid propellants, mechanical properties, temperature, stress, strain

1. INTRODUCTION

Development of solid propellants for missiles and launch vehicle operations has undergone several modifications in last one century. Starting from the conventional extruded double base propellants based on nitrocellulose and nitroglycerin, propellant development has seen tremendous growth in due course of time due to the development of new polymeric binders. Right from poly vinyl chloride (PVC) and poly propylene glycol (PPG) to the workhorse binder for modern solid rocket propellants carboxyl-terminated poly butadiene (CTPB) and hydroxyl-terminated poly butadiene (HTPB), propellant development has touched the extremes of performance in terms of energy¹⁻³. Chemical cross-linking was introduced in propellant manufacture with advent of many new classes of polymers. HTPB is currently being used as polymeric binder in many operational propulsion systems of the world, and at present, most of the composite propellants are made of HTPB as binder. They are chemically cured at elevated temperature using isocyanate as the curing agent. Composite propellants are developed in two varieties on the basis of loading in the rocket motor chamber. One is cartridge-loaded composite propellants (CLCP), where high strength and low modulus is desirable for better strength. Other is case-bonded composite propellants (CBCP), where high elongation and high modulus is desirable for better structural integrity. Later, cross-linked double base propellants are developed in the form of nitrate ester poly-ester (NEPE) propellants. Another remarkable development is use of elastic thermoplastic elastomers in the solid propellants for better density, strength, and recycling ability. This class of

propellants is called extruded composite propellants (ECP).

Since propellant development for a mission is always associated with assessment of margin of safety through structural integrity analysis, mechanical properties requirement forms a part of research, development, evaluation, and production phases of solid propellants. Since mechanical properties of solid rocket propellants are dependent on rate of straining, temperature, ageing, it is worth exploration to assess effects of these parameters on tensile properties of selected class of propellants. The simulation of propellant as nonlinear elastic, rubber like elastic or viscoelastic⁴⁻⁷ materials is available in open literature. Temperature affects performance parameters of propellants⁸ and its effect on mechanical properties is also significant. In the present study, effect of temperature on tensile properties namely tensile strength, percentage elongation, and elastic modulus has been consolidated and analysed for different classes of propellants—extruded double base propellants (EDBP), CLCP, CBCP, ECP, and NEPE propellants. No doubt, all propellants are basically filled polymers and dependence of mechanical properties on temperature is an outcome of basic nature of the polymer. However, at elevated temperatures, pure polymers use to soften, resulting in reduction of strength and modulus and increment in elongation. However, for filled polymers like propellants, this behaviour is worth exploration.

2. EXPERIMENTS

Universal testing machine is generally used for evaluation of mechanical properties. With different types of grips, the same system is used for tensile, compressive flexural and other

specialised tests for various specimens. The machine used for generation of mechanical properties of solid rocket propellant specimen is a constant rate of travel universal testing machine with a conditioning chamber for testing specimen at different temperatures. For harder specimen like EDBP, sturdy wedge grip was used, while for softer specimens spring-loaded grip was used. Harder specimens were tested at 5 mm/min speed, while other specimens were tested at 50 mm/min test speed.

Propellant specimens were prepared in double-dumbbell form as per ASTM D638 type IV⁹. Specimen thickness and width were maintained around 4 mm and 6 mm, respectively as per the standard. The grip distance was maintained during tensile testing as 60 mm and crosshead displacement was taken as displacement. For calculation of strain, gauge length of 45 mm was considered. Cross-sectional area at the central portion of the specimen was measured by digital vernier and initial cross-section was used for calculation of stress. Specimens of propellants of various classes namely EDBP, CLCP, CBCP, ECP, NEPE were conditioned at different temperatures for at least 4 h and tested in conditioning chamber maintained at stipulated temperatures. Stress-strain curves were obtained and analysed for trend. For each test condition, minimum 5 specimens was tested and average values have been reported in graphical form under results and discussion.

In the tensile testing curve, which is essentially a plot between recorded stress and strain, maximum value on stress axis is called tensile strength of the material. Initial slope of the stress-strain curve is called elastic modulus or initial modulus of the material. The propellant exhibit yielding in some case and elongation at this point is important. Sometimes strain at break is also reported. At yield point, linearity of stress-strain curve is lost and the curve curls down, indicating a reduction in elastic modulus or slope of the curve.

For all five classes of propellants mentioned above, stress-strain curves were generated in uni-axial tensile mode using constant rate of travel universal testing machine. At nominal temperatures of 27 °C and cross-head speed of 50 mm/min (EDBP tested at 5 mm/min), the curves were plotted in Fig. 1. It is clear from the figure that EDBP is hard, as it has highest tensile strength. For this reason, this is plotted on secondary axis. The nature of the curve is also quite different from other

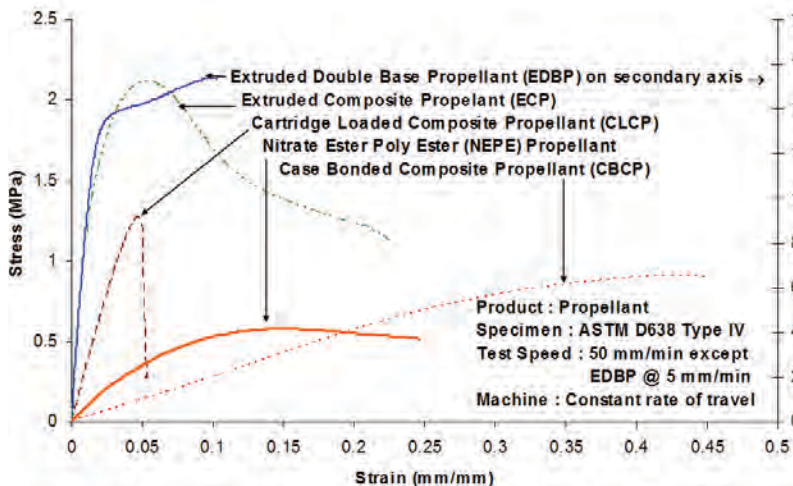


Figure 1. Tensile testing curve of all propellants at 27 °C.

classes of propellants. It was found to have a very steep rise indicating a higher elastic modulus. Yielding was followed by further enhancement in stress at a lower pace showing strain hardening type of effect. The behaviour matches that of a metallic sample.

Cartridge-loaded composite propellant and extruded composite propellants exhibit similar behaviours. The stress-strain curves attain a maximum at tensile strength and then the curve curls down. It reduces strength of the material rapidly. The strain at maximum stress and that at break are almost coincident in the case of CLCP and ECP. The breaking stress is much lower than tensile strength of the material.

The tensile testing curve of NEPE and CBCP exhibit a maximum on stress axis indicating tensile strength. They have lowest initial slope or elastic modulus. The variation is relatively nonlinear in initial zones of straining also. In case of CBCP, strain at maximum stress and that at break are almost the same. In fact, point indicating tensile stress and break of specimen almost coincides in this case. However, for NEPE, after attaining maximum stress, the tensile testing curve continues to grow on strain axis at almost constant stress. This is creep behaviour where materials flow (elongates) at almost constant stress. So this class of propellants exhibit coincident stress at break and tensile strength. However, strains at maximum stress and that at break are different. This behaviour is opposite to that of CLCP.

Propellant specimen of each class of propellants were subjected to tensile testing after conditioning propellant specimen at a given temperature for a minimum duration of 4 h and variation of stress with strain was observed.

3. RESULTS AND DISCUSSION

Extruded double-base propellants (EDBP) use nitrocellulose (NC) and nitroglycerin (NG) as main ingredients. The manufacturing process starts with manufacturing of double-base paste in a process called impregnation, where NG is poured slowly in the agitated solution of NC in water. NC absorbs NG, resulting in formation of paste. The paste is dried to reduce water content. This is followed by kneading, rolling, and extrusion of propellant grains in required dimensions. The process of manufacture of EDBP is the same as explained by

Davenas¹⁰. Propellant specimens of extruded double-base propellant as per ASTM D638 type IV are tested at 5 mm/min test speed at different temperatures ranging from -50 °C to +55 °C. The superimposed stress-strain curves are shown in Fig. 2.

At low temperature (-55 °C), EDBP behaves as brittle material and breaks without much elongation. The variation of stress and strain is a straightline and yield point matches with break point. As temperature is raised to -20 °C, initial modulus of the propellant (initial slope) reduces and percentage elongation increases. Increasing temperature further, results in introduction of necking region and elongation at yield and break are different. Propellant shows substantial ductility at high temperature region. At +55 °C, the propellant stretches more, at almost constant stress and exhibit creep type of behaviour. Although numerical

values are different, the trend is similar as given by Davenas¹⁰. This behaviour of double-base propellants is derived from its matrix, which softens on heating. At sub-zero temperatures, the propellant matrix (mainly NG) is brittle due to presence of weak secondary bonds in the matrix. At elevated temperatures, these bonds disappears or breaks and propellant behaviour becomes solely dependent on primary covalent bonds, which stretches more to impart sufficient elongation at low stress.

Composite propellants based on hydroxy terminated polybutadiene (HTPB) as binder, ammonium perchlorate (AP) as oxidiser and aluminium (Al) as metallic fuel are generally used in many operational rockets and missiles. The propellant is obtained by vacuum casting followed by elevated temperature curing of mixed slurry of ingredient. This class of propellants has two modes of loadings in rocket motors and first variant is cartridge-loaded composite propellant (CLCP), which is fed to the rocket motor casing like bullet is fed to guns. Tensile testing of CLCP is carried out at 50 mm/min test speed at different temperatures and superimposed stress-strain curves are shown in Fig. 3. From the curves depicted in Fig. 3, it is clear that nature of the curve does not change with temperature. However with increase in temperature, tensile strength, elastic modulus and percentage elongation come down in a linear fashion. Since more strength is needed in cartridge-loaded propellants, the departure from normal polymeric behaviour is clearly visible and reduction in percentage elongation by increase of temperature shows dominant effect of reinforcement or solid loading and cross-linking. Brittleness at low temperature can be attributed as one of the reasons for a reduction in elongation. Another significant finding is the increased area under stress-strain curve at reduced temperature. This gives tough propellant at reduced temperature and propellant can take more load at reduced temperatures. The behaviour of propellant is affected by cross-linking and interface strength of binder and solid reinforcement plays a major role in observed mechanical behaviour relegating polymer mechanical properties to secondary status.

Another class of composite propellants is directly cast in insulated rocket motors and forms integral part of the propulsion system. This class of propellants is called case-bonded composite propellants (CBCP). It has high elongation and moderate tensile strength. Variation of stress-strain curve in uni-axial tensile mode with temperature is depicted for CBCP in Fig. 4. It is clear that as temperature reduces, tensile strength and modulus of the propellant increases, while percentage elongation reduces. This is the normal tendency exhibited by any polymeric material and CBCP in true sense represents polymeric nature of the propellants. High temperature induces softening of polymers resulting in more elongation and lowering of tensile strength.

Extruded composite propellant is one of the important

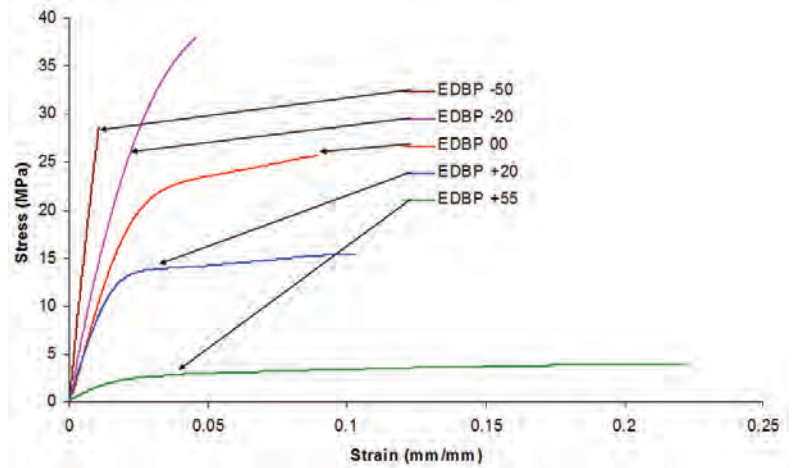


Figure 2. Tensile testing curve of EDBP.

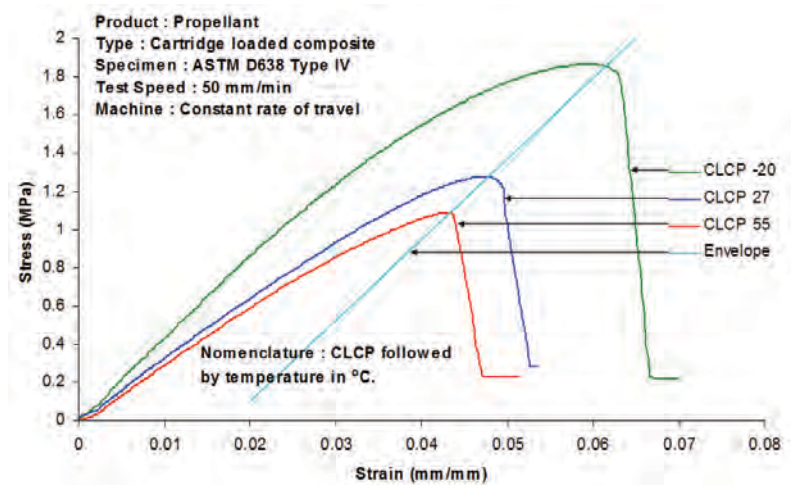


Figure 3. Stress strain curve of CLCP.

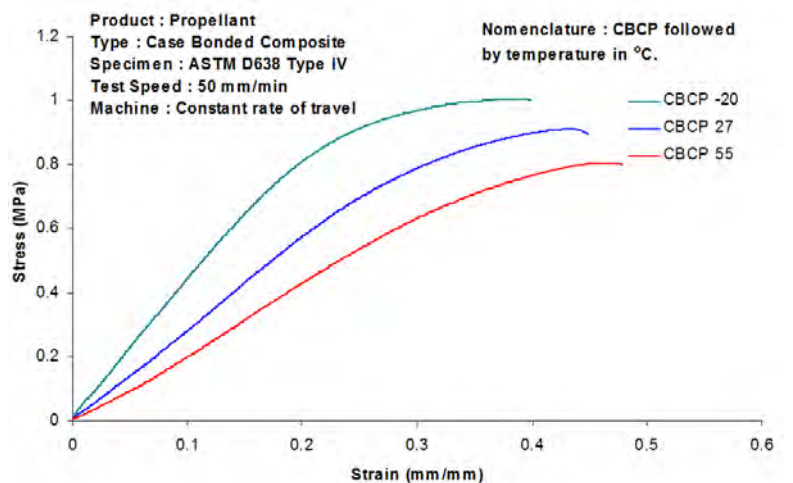


Figure 4. Stress strain curve of CBCP.

classes of propellants, where elastic thermoplastic elastomers are used as binders. The ingredients and processing methods are discussed elsewhere^{11,12}. The propellant, used for study has viton as binder and is loaded with ammonium perchlorate. This gives higher density, recycling ability and higher density impulse of the propellants. These are suitable for high energy power cartridge application and are good for bulk production

in smaller dimensions. This class of solid rocket propellants is also tested in uni-axial tensile mode at different temperatures and resulting variations are shown in Fig. 5.

It is clear that because of thermosetting nature, the variation of tensile testing curves with temperature follows a different trend altogether. At elevated temperatures, ECP becomes soft. Lowering of tensile strength and percentage elongation in Fig. 4 depicts this. As temperature is reduced, propellant consolidates in a better way and polymer chains are more coiled, resulting in higher strength. Rise of elastic modulus with reduction in temperature is observed due to stiffening of thermoplastic elastomeric polymer used. Percentage elongation is the highest for medium temperature (27 °C). The characteristic properties of polymeric binder are reflected in propellants also. Since polymer is brittle at low temperature and at high temperatures, they become ductile; the same properties are depicted by propellants. At low temperature brittleness of propellant reduces percentage elongation and at high temperature induced ductility increases percentage elongation.

To take advantage of high strength of double-base propellants and flexibility offered by chemical cross-linking, nitrate ester polyester propellants are developed, which are referred by Davenas¹ as XLDB (cross-linked double base) propellants. Mechanical properties are evaluated for propellant specimen of this class of propellant at different temperatures. The stress-strain curves in uni-axial tensile mode are given in Fig. 6. It is observed that there is no change in nature of the curves at lower strains, making mechanical properties of propellant virtually independent of temperature. Cross-linking makes propellants almost invariant to temperature. Reduction of temperature results in minor increase in tensile strength. One of the peculiar behaviours is increase in elongation at break at reduced temperature. This may be anomaly as stress-strain curve cannot depict exact nature of such materials after yield point. The behaviour may not be exactly representing the behaviour of propellants. However strain induced crystallization of polymers may be considered as a possible mechanism for such behaviour of NEPE propellants. Rise in temperature generally promotes strain induced crystallization. At elevated temperature, more strain induced crystallization reduces elongation and at low temperature, such crystallizations are not supported well and elongation is on higher side. However, the initial modulus independent of temperature is a significant feature of this class of propellant.

The use of the tensile testing curve at different temperature can be exploited by generating failure envelopes for the propellants. By joining break point at different temperatures on the tensile testing curve for a given type of propellant, failure envelopes can be generated. For a given temperature at a given strain, value of stress generated in the material should not

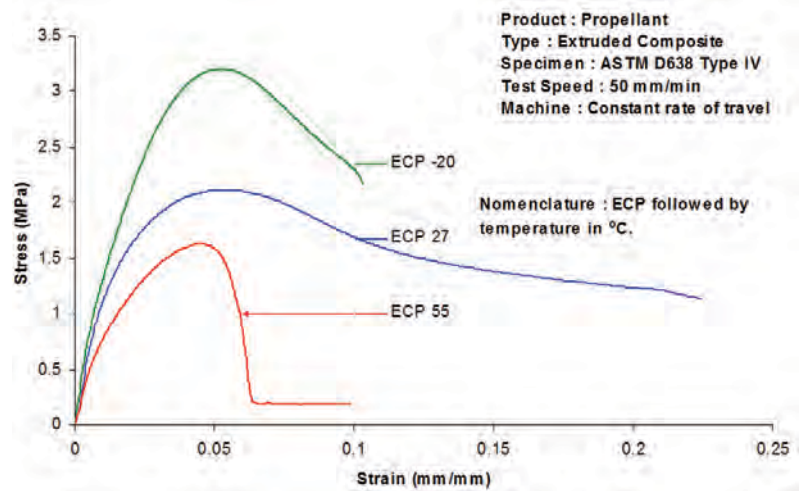


Figure 5. Tensile testing curves of ECP.

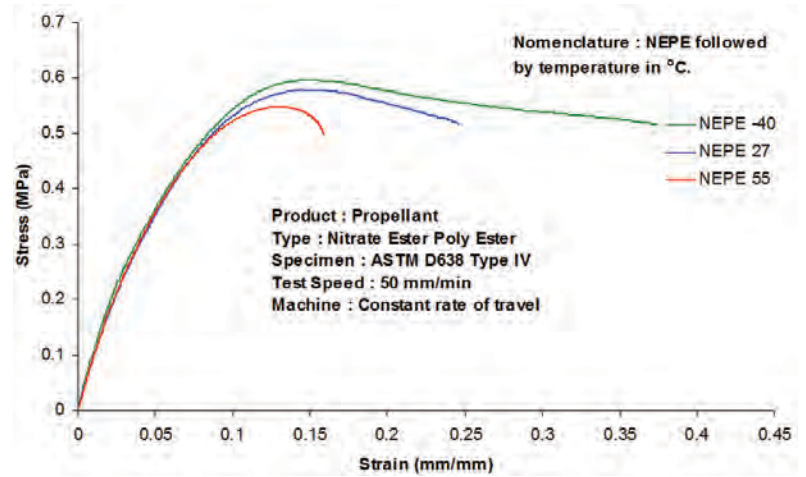


Figure 6. Tensile testing curves of NEPE propellant.

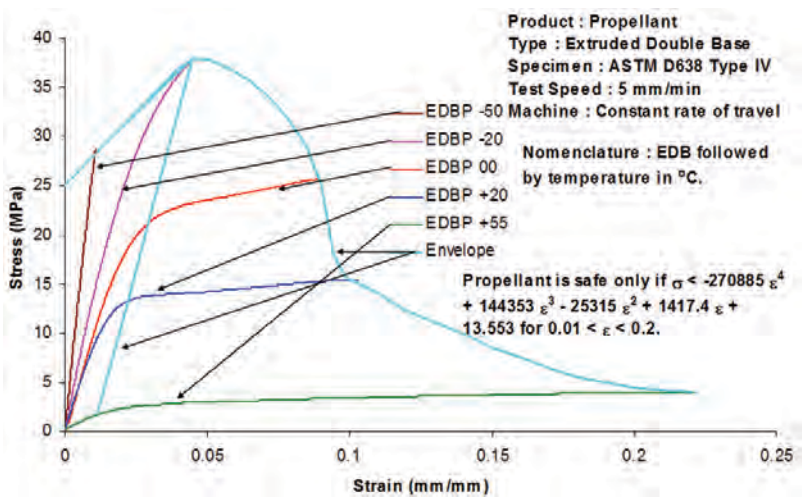


Figure 7. Failure envelop for EDBP.

exceed quartic equation (given in Fig. 7) for certain margin of safety. If stress applied is more and calculation by the equation, the propellant will fail. For example the variation of stress-strain for EDBP with temperature is plotted again in Fig. 7 along with the failure envelope. For the tested propellant, the equation of failure envelop is also generated along with range of strain for validity of developed equation. At strain level of

0.05, the value of limiting stress from equation in Fig. 7 is 37.48 MPa. This indicates that if stress associated with strain of 0.05 exceeds 37.48 MPa at any temperature, the propellant is stressed beyond its capabilities and will fail. However, value of stress < 37.48 MPa does not indicate that propellant is safe. For assuring safety, operating temperature must be considered. If stress generated in the propellant at a strain of 0.05 is 30 MPa, then for temperatures above 0 °C, the propellant will fail but below -10 °C, it may be safe provided it is capable of taking the mentioned strain levels at lower temperatures.

4. CONCLUSION

Specimens of different classes of propellants have been analysed in uni-axial tensile mode in constant rate of travel universal testing machine. NEPE propellant show virtual invariant stress-strain curve for modulus and tensile strength at different temperatures. For other classes of propellants namely EDBP, CLCP, CBCP and ECP, elastic modulus increase with reduction in temperature. Tensile strength also improves with reduction in temperature. However percentage elongation shows different trends for different propellants. Increase in temperature increases percentage elongation for EDBP (from 0.01 to 0.22 for -50 °C to +55 °C) and CBCP (from 0.39 to 0.48 for -20 °C to +55 °C), while it reduces percentage elongation for CLCP (from 0.06 to 0.04 for -20 °C to +55 °C), and NEPE (from 0.37 to 0.15 for -40 °C to +55 °C) class of propellants. The testing at different temperature can be utilized for generation of failure envelop for all classes of propellant.

ACKNOWLEDGEMENTS

The author expresses gratitude to Director, HEMRL for publication of the article. Author also acknowledges the support given by Propellant Processing Group of HEMRL to make the propellant sample available for testing and analysis of data.

REFERENCES

1. Davenas, Alain. Development of modern solid propellants. *J. Propul. Power*, 2003, **19**(6), 1108-128.
2. Hunley, J.D. The history of solid-propellant rocketry: What we do and do not know. In 35th AIAA, SAE, ASEE Joint Propulsion Conference and Exhibit, Los Angeles, California, 20-24 June 1999. Paper no.-AIAA 99-2925,
3. Singh, Haridwar. Solid rocket propellants technology in India. *South-Asia Def. Strategic Rev.*, 2008, 32-35.
4. Landel, Robert F. & Smith, Thor L. Viscoelastic properties of rubberlike composite propellant and filled elastomers. *ARS Journal*, 1961, 599-608.
5. Jeremic, Radun. Some aspects of time-temperature superposition principle applied for predicting mechanical properties of solid rocket propellants. *Propel., Expl., Pyro.*, 1999, **24**, 221-23.
6. Shekhar, Himanshu & Sahasrabudhe, A.D. Maxwell fluid model for generation of stress-strain curves of viscoelastic solid rocket propellants. *Propel., Expl., Pyro.*, 2010, **35**, 321-25.
7. Shekhar, Himanshu & Sahasrabudhe, A.D. Viscoelastic modelling of solid rocket propellants using Maxwell fluid model. *Def. Sci. J.*, 2010, **60**(4), 423-27.
8. Kershner, R.B. Internal ballistics of rockets. In Book Rocket Fundamentals, edited by B.L. Crawford Jr, George Washington University, 1944. pp. 39-68.
9. American Society for Testing of Materials, ASTM No. ASTM D638-08, ASTM International, USA, 2008.
10. Davenas, Alain. Solid rocket propulsion technology. Pergamon Press, Great Britain, 1993.
11. Varghese, T.L.; Muthiah, R.M.; David, John; Kurian, A.J.; Athithan, S.K.; Krishnamurthy, V.N. & Kurup, M.R. Studies on composite extrudable propellant with varied burning rate pressure index. *Def. Sci. J.*, 1989, **39**(1), 1-12,
12. Haff Jr., C.E. Extruded composite propellant technology development. *Journal of Spacecraft*, 1984, **21**(6), 587-92.

Contributor



Dr Himanshu Shekhar received PhD from University of Pune and MTech (Mechanical Engineering) from IIT, Kanpur. Presently he is working as Joint Director at HEMRL (DRDO), Pune. He has been associated with advanced solid rocket propellants for the last 15 years. It includes development of infrastructure for solid rocket propellant processing, processing of solid rocket propellants, Mechanical properties evaluation, structural analysis and performance prediction of solid rocket propellants. He has 30 papers in peer reviewed journals and an equal number of publications in seminar and conference proceedings.