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Studies on Stress-Strain Curves of Aged Composite Solid Rocket Propellants

Himanshu Shekhar

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

ABSTRACT

Mechanical property evaluation of composite solid rocket propellants is used as a quick quality control tool for propellant development and production. However, stress-strain curves from uni-axial tensile testing can be utilised to assess the shelf-life of propellants also. Composite propellants (CP) of two varieties cartridge-loaded (CLCP) and case-bonded (CBCP) are utilized in rocket and missile applications. Both classes of propellants were evaluated for mechanical properties namely tensile strength, modulus and percentage elongation using specimens conforming to ASTM D638 type IV at different ageing time. Both classes of propellants show almost identical variation in various mechanical properties with time. Tensile strength increases with time for both classes of propellants and percentage elongation reduces. Initial modulus is also found to decrease with time. Tensile strength is taken as degradation criteria and it is observed that CLCP has slower degradation rate than CBCP. This is because of two facts–(i) higher initial tensile strength of CLCP (1.39 MPa) compared to CBCP (0.665 MPa) and (ii) lower degradation rate of CLCP (0.0014 MPa/day) with respect to CBCP (0.0025 MPa/day). For the studied composite propellants, a degradation criterion in the form of percentage change in tensile strength is evaluated and shelf life for different degradation criteria is tabulated for quick reference.

Keywords: Composite propellants, mechanical properties, ageing, degradation, tensile testing

1. INTRODUCTION

Ageing of composite solid rocket propellants results in deterioration in performance. The significant effect of environmental conditions, exposure duration and performance variation are studied by various researchers under ageing studies with an aim to predict shelf life or operational life of various propulsion systems. Since solid rocket propellants, used in rockets and missiles is the fastest degrading component of the complete system, shelf life of the system is mainly governed by the life of the propellants. The main variety of composite solid rocket propellants for rockets and missile application is composite propellant, based on hydroxyl terminated polybutadiene (HTPB), ammonium perchlorate (AP), and aluminium (Al) powder. Since they are used in both cartridge loaded and case bonded modes in actual applications, several attempts are made to study their shelf life under elevated temperature ageing[1-3]. However, earlier attempts were made to study the shelf life of conventional nitrocellulose and nitroglycerin based double base propellants and other classes of propellants[4,5]. Methodologies, practical results, modeling and analysis of ageing and service life predictions for all classes of the propellants is illustrated in advisory group for aerospace research and development (AGARD) report[6].

For ageing study, the first part is the selection of a measurable parameter, which changes appreciably with time. Plasticizer content, gas evolution, thermal and vacuum stability, mass loss on heating, autoignition, mechanical properties degradation, change in ballistic performance, etc are invariably used for assessment of shelf life of double base propellants[7]. Molecular weight reduction of nitrocellulose and diffusion of surface coating agents to propellant are studied for prediction of shelf life of the double base propellants[8]. However, due to chemical cross-linking in composite propellants, it is difficult to apply the same criteria to the composite propellants. Failure of Arrehenius type degradation equations to predict ageing behaviour of composite propellants is deliberated in open literature[9]. Modeling for ageing of HTPB based composite propellants using different activation energy is carried out and effect on shelf-life is established[10]. In addition to selection of parameter, the deterioration criteria should be well defined also. In general uni-axial tensile testing results are easily measurable and the results vary with time significantly for the composite propellants. In fact, raising temperature can further enhance the variation of mechanical properties under uni-axial tensile loading. Generally, 30 per cent variation in properties is taken as end of useful shelf life of the propellant. However, this criterion is derived from structural analysis of propellants for adequacy of margin of safety for subjecting mechanical loads. In fact mechanical processes in composite propellants may initiate micro-failures of propellants, subsequently resulting in an acceptable degradation of propellant properties. Mechanical loads introduced in composite propellant may be primarily due thermal cool down. Inner bore, grain termination areas and the propellant bond lines are highly stressed portion of the propellant grains[11]. Dynamic mechanical analyser (DMA) is used to characterise damaged propellants and service life of more than 15 years is predicted, but is treated as only indicative of a trend during ageing[12]. Using DMA, increase

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in modulus on ageing is established for composite propellant and the suggested mechanism is the disappearance of gel fraction by cross-linking to the main network due to oxidation of HTPB molecules during ageing[13]. The ageing of composite solid propellants becomes interesting but complex due to four common material non-linearity: (i) strain sensitivity, (ii) volume change or dewetting, (iii) thermo-mechanical coupling, and (iv) damage and reheating effects[14]. For plateau burning composite propellants, burning rate, and thermal decomposition are established as major degradation criteria, relegating mechanical properties degradation as significant over the tested period of 32 weeks[15].

For the current study, HTPB based composite solid rocket propellants-based on toluene diisocyanate (TDI) cured HTPB/AP/Al system is taken. Propellant specimens are tested in uni-axial tensile mode at different time steps and variation of tensile strength with ageing time is measured. The rate of variation of tensile strength is established for different classes of composite solid rocket propellants-based on regression analysis. Degradation criteria are selected arbitrarily to numerically illustrate shelf-life prediction approach.

2. EXPERIMENTAL RESULTS

Propellant blocks are kept for prolonged duration at 27 °C ± 5 °C and at different lapsed time double dumbbell propellants specimens conforming to ASTM D638 type IV[16] dimensions are prepared. They are tested using a constant rate of travel universal testing machine at a speed of 50 mm/min. The environmental conditions during test are maintained as 27 ^{o}C ± 2 ^{o}C and 50 ± 5 per cent relative humidity. The specimens are gripped at a grip distance of 60 mm and gage length is taken 45 mm for the propellant specimen. The initial cross-sectional area is measured using vernier. Minimum five specimens are tested at each condition and reported results are consistent average results. The standard deviation over mean value for all the curves is maintained less than 1 per cent.

For the analysis two classes of composite propellants are considered. Cartridge loaded composite propellants (CLCP) have high strength and low elongation and are stored in ambient environment for prolonged duration. The propellant is an aluminised composite propellant (HTPB/AP/Al–15/67/18) cured by TDI with an NCO/OH ratio of 0.7. Mechanical properties are evaluated at regular intervals and resulting stress-strain curves under uni-axial tensile testing is depicted in Fig. 1. At the end of curing cycle, propellant exhibited high elongation, which continues to reduce with time. The initial modulus or slope of stress-train curve at zero strain continues to increase with time. The tensile strength is found to increase with time.

Another class of propellants used in rockets and missiles is called a case-bonded composite propellants (CBCP). They are cast directly in insulated rocket motors and are cured along with the casing to form integral part of the casing. This type of propellants has high elongation and moderate strength. HTPB-based aluminised propellant (HTPB/AP/Al – 16/68/16) with TDI as curing agent with an NCO/OH ratio of 0.6 is taken. The propellant is not case-bonded, but cast and cured in stand alone mode. Ageing studies are carried out for CBCP using similar test conditions and specimen sizes as depicted above. The variation of stress-strain curve at different ageing time for a CBCP is shown in Fig. 2. All three parameters namely modulus, elongation and tensile strength showed the same trend with time as shown by CLCP.

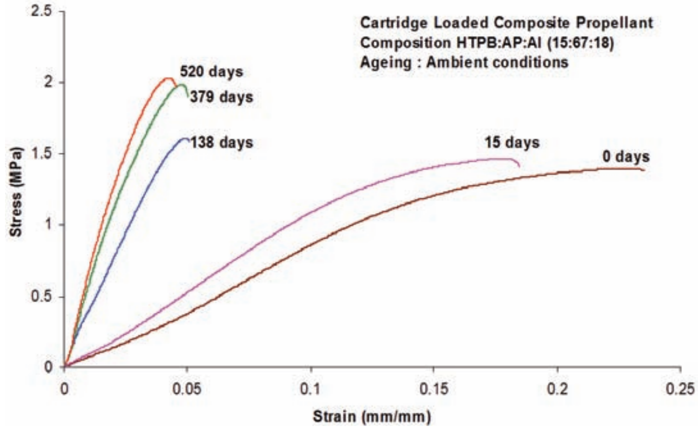

Figure 1. Stress-strain curves for CLCP at different ageing time.

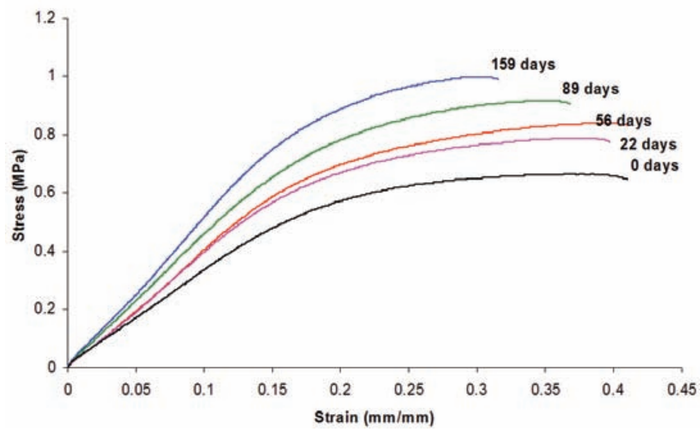

Figure 2. Stress-strain curves for CBCP at different ageing time.

For comparison of both the types of propellants, stress-strain curve under standard condition at the beginning of ageing cycle for both classes of propellants is shown in Fig. 3 on the same scale. Relative values of their strength, modulus and elongation are clearly depicted in the Fig. 3. Case bonded propellants exhibited low strength, high elongation and low modulus than cartridge loaded propellants.

As far as stress-strain curves are concerned, three main parameters are present for assessment of ageing–modulus, percentage elongation and tensile strength. Any one of the three can be taken as degradation criteria. In fact degradation mechanism brings down percentage elongation and increases modulus and tensile strength of both the classes of propellants. Composite propellants are chemically cured solid masses with an NCO/OH ratio of around 0.7-0.8. At the beginning of curing cycle, the propellant has low strength, which builds up during curing at elevated temperature. In the initial days, property changes are significant, which dies down in the course of time. When there is no appreciable change in properties, the propellant is said to have cured and is taken

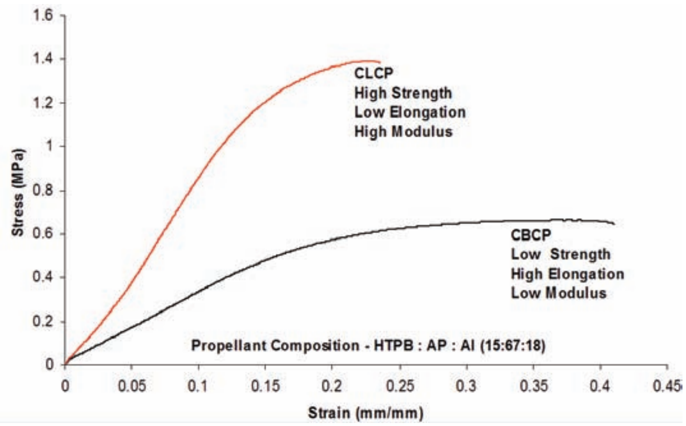

Figure 3. Reference stress-strain curves for CLCP and CBCP.

out for further testing or use. However, the chemical cross-linking reaction continues but at a slower pace and hardening of composite propellants is attributed to more cross-linking at prolonged storage. Since composite propellant manufacture is well established, the curing cycle and duration for cure-completion time is established by trials, cross-linking density is not assessed. However, degradation mechanisms for composite propellants is stated in the literature to be chemical cross-linking rather than plasticiser migration or evolution of gases (stability criteria), as used for double base propellants. It is ease of measurement and appreciable changes in the properties, which governs the selection of control parameters.

The arbitrariness of selection criteria for degradation of propellant ageing is clear from the fact that even shore a hardness of propellant, which is a surface property and is a non-destructive test method is used for assessment of degradation of composite propellants[17]. Cross linking density and mechanical properties are correlated during ageing of composite propellants using sol fraction assessment[18]. Modulus is slope of the stress-strain curve at initial stage and it cannot be reliably measured due to the initial kink formation and continuous variation in values with strain. The percentage elongation at break varies with the extent of necking exhibited by the propellants. At high temperature, some propellants have tendency to neck and elongate more after attaining a maximum stress. However this behaviour is not very consistent. Clearly, maximum stress in the stress-strain curve or tensile strength is the left parameter to be considered, which changes significantly during ageing and changes can be measured easily.

Although any of the selection parameter indicates the same degradation mechanism of propellant, it is ease of measurement, adequate representation of ageing and appreciable change in properties, for which tensile strength is taken as degradation criteria. Appreciably it seems to represent an enhancement in strength of propellants, but it is also indication of reduction in percentage elongation, which is adverse for structural integrity of the propellants. So, tensile strength is selected as degradation criteria and not the end requirement. In fact many degradation mechanisms are possible for composite propellants and it cannot be attributed to any single reason[9].

3. ANALYSIS AND DISCUSSION

The mechanical properties of CLCP at the start of the ageing period (immediately after curing) has percentage elongation of around 23.33 per cent and has a tensile strength of 1.39 MPa. The elastic modulus is depicted in Fig. 4 as 9.30 MPa. The point of maximum stress (tensile strength) has slightly higher value on stress axis and lower value on strain axis than break point.

As time progresses, tensile strength increases and percentage elongation reduces (Fig. 2). This makes propellant brittle due to more cross-linking and oxidation and makes it unsuitable for further use. Variation of tensile strength with time (t in days) can be represented by a polynomial fit as given by Eqn (1).

$$\text{Tensile strength (MPa)} = 0.0014 \times (\text{time in days}) + 1.39 \qquad (1)$$

This equation gives a continuous rise in tensile strength with respect to time. If tensile strength of 2 MPa denotes degraded propellant, then it is achievable in 433 days from the Eqn (1), derived from the practical prolonged storage data for as class of typical CLCP. For CLCP, variation of percentage elongation is very significant and is the main mechanical parameter to be observed. A marked variation is observed between 15 days and 138 days, after which variation is sluggish. Investigation on percentage elongation needs further studies.

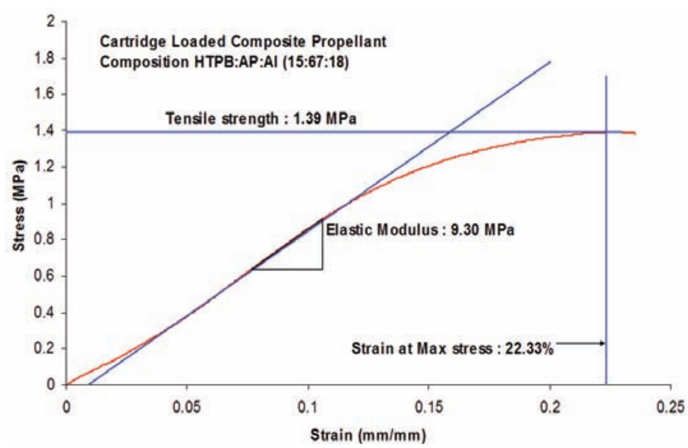

Figure 4. Reference stress-strain curves for CLCP.

For the other class of propellant CBCP, with lapse of time, tensile strength and percentage elongation show similar trends. Because the main matrix is same and cross-linking mechanism and effect of temperature is also same, a similar trend of variation of properties is expected. Stress-strain curve of a typical CBCP at a reference ageing time is given in Fig. 5. It has a lower tensile strength of 0.665 MPa and strain at maximum stress is higher (36.35 per cent). The value of elastic modulus (3.4 MPa) is much lower than a typical CLCP (9.30 MPa) depicted in Fig. 4. One major difference is in the fact that maximum stress point is separated from break point. Stress at break point is lower than tensile strength and strain at break is higher than that at maximum stress point. However, ageing characteristics are similar but the rate of change of various properties is different. Here also tensile strength changes at a faster pace in the beginning and later on

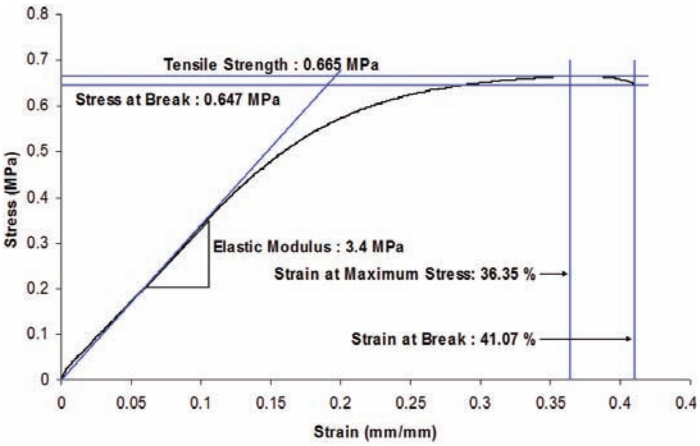

Figure 5. Reference stress-strain curves for CBCP.

it becomes sluggish. Variation of tensile strength with lapse of time can be depicted by Eqn (2) as a linear curve.

Tensile strength (MPa) = 0.0025 x (time in days) + 0.665 (2)

However, this variation again depicts a monotonically increasing tensile strength with time, which is not the fact. However, it is clear from the Eqn (2) that the rate of change of tensile strength with time is faster for CBCP. This is represented by the higher value of slope (0.0025) in Eqn (2) wrt (0.0014) in Eqn (1). If strength enhancement to 1 MPa is taken as degradation criteria of the propellant, then this propellant degrades in 144 days only.

For both the classes of propellants, degradation criteria can be given as some percentage change in the initial value of the tensile strength. Predicted life for both types of propellants are given in Table 1. It is clear that CLCP has higher shelf life than CBCP. This is because both higher tensile strength and lower degradation rate (slope) are in favor of CLCP. For comparison a trial property and slope is also added as one column in Table 1. Comparison of data of CLCP and trial indicates that trial has lower shelf life. This is due to lower value of initial tensile strength of the trial. Comparison of CBCP and trial indicates that trial has higher shelf life because it has a slower degradation rate.

Table 1. Comparison of shelf life for different degradation criteria

Type	CLCP	CBCP	Trial
Initial TS (MPa)	1.39	0.665	0.665
Slope (MPa/day)	0.0014	0.0025	0.0014
Degradation criteria (percentage)	**Predicted life (days)**		
10	99.28571	26.6	47.5
20	198.5714	53.2	95
30	297.8571	79.8	142.5
40	397.1429	106.4	190
50	496.4286	133	237.5
60	595.7143	159.6	285
70	695	186.2	332.5
80	794.2857	212.8	380
90	893.5714	239.4	427.5
100	992.8571	266	475

4. CONCLUSIONS

Tensile testing specimens of two classes of composite solid rocket propellants namely cartridge loaded (CLCP) and case-bonded (CBCP) are evaluated at different ageing time in uni-axial tension using a constant rate of travel universal testing machine. Tensile strength of both classes of propellants increase with time and percentage elongation reduces. It is observed that CLCP has slower degradation rate and has a higher shelf life as compared to CBCP. This is because of higher initial strength and lower degradation rate of CLCP. Shelf life for different degradation criteria is also predicted using linear degradation criteria.

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Contributor

Dr Himanshu Shekhar received PhD from University of Pune and MTech (Mechanical Engineering) from IIT, Kanpur. Prsently he is working as Joint Director at High Energy Materials Research Laboratory, 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.