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Prediction of Storage Life of Propellants having different Burning Rates using Dynamic Mechanical Analysis

V.S. Wani, Mehilal*, Sunil Jain, P.P. Singh, and B. Bhattacharya

High Energy Materials Research Laboratory, Pune - 411 021, India
**E-mail: drmehilal@yahoo.co.in*

ABSTRACT

Propellants, visco-elastic in nature, show time and temperature dependent behaviour on deformation. Hence, the time–temperature superposition principle may be applied to the visco-elastic properties of propellants. In the present study, dynamic mechanical analyser (DMA) was used to evaluate the dynamic mechanical properties and quantify the storage life of four different propellants based on hydroxyl terminated polybutadiene, aluminium and ammonium perchlorate having different burning rates ranging from 5 mm/s to 25 mm/s. Each sample was given a multi-frequency strain of 0.01 per cent at three discrete frequencies (3.5 Hz, 11 Hz, 35 Hz) in the temperature range - 80 °C to + 80 °C. The storage modulus, loss modulus, tan delta and glass transition temperature (*Tg*) for each propellant samples have been evaluated and it is observed that all the propellants have shown time (frequency) and temperature dependent behaviour on deformation. A comparison of the log a_T versus temperature curves (where a_T is horizontal (or time) shift factor) for all four propellants indicate conformance to the Williams–Landel–Ferry (WLF) equation. The master curves of storage modulus (log E′ versus log ω plots) were generated for each propellant. A plot of E′ versus time for all propellants was generated up to 3 years, 6 years, and 10 years of time, respectively. The drop in the storage modulus below the acceptable limit with time may be used to predict the shelf life of the propellant.

Keywords: Glass transition temperature, mechanical properties, storage modulus, loss modulus, hydroxyl terminated polybutadiene, visco-elastic properties

NOMENCLATURE

E′	Storage modulus
E′′	Loss modulus
tan δ	Tan delta
T_g	Glass transition temperature
T	Temperature
t	Time

1. INTRODUCTION

Composite propellants are heterogeneous mixtures of a binder such as hydroxyl terminated polybutadiene (*HTPB*), a metallic fuel such as aluminium powder (*Al*), an inorganic oxidiser such as ammonium perchlorate (*AP*), and isocyanates based curatives, toluene diisocyanate (*TDI*) along with various other additives being generally used in different missile programmes as well as space applications[1]. Due to presence of polymeric binder, propellants are viscoelastic by nature. The concept of viscoelasticity[2] arises from the fact that most materials do not exhibit purely elastic (ideal solids) or purely viscous (ideal liquids) behavior but a combination of both. When a stress is applied to a viscoelastic material, it shows a time-dependent deformation. Any viscoelastic material, given enough time, flows under an applied stress and when the stress is removed the material does not fully recover. The portion of strain that is recovered represents the energy stored or the elastic portion of the material's response. The portion of the strain that is not recovered represents the energy dissipated or viscous portion of the material's response. Solid rocket propellants exhibit mechanical responses that are a mixture of viscous and elastic behavior, hence are viscoelastic. It is well known that the viscoelastic properties of propellant systems are dependent on various factors like nature of polymer, curative type and level, filler loading, additives, etc. On storage, various chemical reactions and physical processes take place in composite rocket propellant grains (a propellant charge with a definite solid geometrical configuration) which affect their physical, chemical, thermal, ballistic, mechanical properties and propellant's performance.

Due to increase in the use of viscoelastic solid fuels in rocket motors, there is an increasing importance of the viscoelastic analysis in evaluating the structural integrity of solid propellant rocket motors. Moreover, it is essential to quantify the storage life of propellants for their safe use. One methodology in common use is based on the chemical kinetics models using Arrhenius relationship. Dynamic mechanical analysis is a rather new technique which can be used to determine the service life of propellants. Since the viscoelastic materials show time and temperature dependent behaviour on deformation, the time–temperature superposition (TTS) principle may be applied to the viscoelastic properties of such materials[3]. Different researchers have opined that the superposition is due to molecular behaviour and therefore, formulated equations based on the activation energy (*E*), as:

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$$\ln a_T = E/R \ln (1/T - 1/T_0) \quad (1)$$

where, a_T is the horizontal (or time) shift factor, R is the universal gas constant, T_0 is the reference temperature (K), and T is the temperature at which a_T is desired. The shift (shifting of curve to reference temperature curve) follows an Arrhenius temperature dependence, with an apparent energy of activation (E). Another commonly used empirical equation for TTS is Williams–Landel–Ferry (WLF) equation[4-5], which relates a shift in temperature with a shift in time. The WLF equation can be expressed as:

$$\log a_T = C_1 (T-T_0)/(C_2+T-T_0) \quad (2)$$

where, T_0 is the reference temperature (usually glasstransition temperature, T_g) and T is the temperature at which the test is performed (K).

Exhaustive literature survey reveals that considerable use has been made of time temperature superposition principle in the field of polymeric materials/composites[6-9]. The most relevant work related to the present study is that of Tod[10], *et al.* who studied the effect of time, temperature and frequency on the dynamic mechanical property data of solid rocket propellants, viz., double base, triple base, nitramine loaded double base and generated master curves of storage modulus for the propellant and studied the effect of ageing. Hanus[11] evaluated the dynamic mechanical property data of composite solid rocket propellants and studied the variation of storage modulus, loss modulus and tan delta with temperature and frequency. Cogmez[12], *et al.* attempted to compare the dynamic data of two HTPB based propellants with different solid compositions, viz., one with 87 per cent solid loading having 16 per cent *Al* as metallic fuel and the other with 86 per cent solid loading without metallic fuel. The former propellant was found to be less stiff and more dissipative than the latter at higher temperatures. Sućeska[13], *et al.* evaluated the mechanical and viscoelastic properties changes for double base rocket propellants induced by natural ageing at ambient conditions. They found that the changes of the studied mechanical and viscoelastic properties are evident and are connected with a decrease of nitrocellulose macromolecules chains mobility due to the decrease in the plasticiser amount and chemical degradation of energetic constituents, nitrocellulose and nitroglycerine.

In the present study, we report the dynamic mechanical properties and quantify the storage life of four different composite propellants based on hydroxyl terminated polybutadiene, aluminium and ammonium perchlorate having different burning rates ranging from 5 mm/s to 25 mm/s using DMA, Q 800. The storage modulus, loss modulus, tan δ and T_g for each propellant has been evaluated. Time temperature superposition principle was applied to the dynamic properties of each of the four propellants and the respective a_T values were determined and compared. The master curves of storage modulus (log E′ versus log time plots) were also generated for each propellant.

2. EXPERIMENT

Composite solid propellants having different burning rates ranging from 5 mm/s to 25 mm/s at 7000 kPa were used in this study. The details of the composition are given in Table 1 where all the ingredients have been taken on weight percentage basis. All the tests were carried out using dual cantilever clamp in TA Instruments DMA Q800. The specimen size used was 60 mm x 12.5 mm x 3 mm. Each sample was given a multi-frequency strain of 0.01 per cent at three discrete frequencies (3.5 Hz, 11 Hz, 35 Hz) in the temperature range of - 80 °C to + 80 °C. The storage modulus, loss modulus, tan delta and T_g for each propellant was evaluated. The curves were shifted using time temperature superposition principle (TTS) software to determine the horizontal shift factors (a_T) with respect to the reference curve and master curves of storage modulus versus time were generated for each propellant.

Table 1. Compositions of the four different samples used during the test

Prope-llants	HTPB based binder and curative (per cent)	Al (per cent)	AP (per cent)	Burning rate modifiers and others (per cent)	Burning rate (mm/s)
I	10.78	18	68	3.22	5
II	10.78	17	63.7	8.52	13.7
III	11.98	17.5	64.41	6.11	19
IV	16.27	2.5	77.17	4.06	25

3. RESULTS AND DISCUSSION

During dynamic testing, an oscillatory (sinusoidal) strain (or stress) is applied to the material and the resulting stress (or strain) developed in the material is measured. For an ideal solid material (100 per cent elastic), which obeys Hooke's law, the resulting stress is proportional to the amplitude of the applied strain. The strain is in phase with the stress, *i.e.*, the phase shift (phase angle δ) between stress and strain is 0°. For newtonian fluid, the stress is proportional to the strain rate. The stress signal leads the strain signal by 90°. For a viscoelastic material, the phase angle lies somewhere between 0° and 90°.

The analyses were carried out using dual cantilever clamp of DMA employing the multi-frequency strain method. A typical DMA curve of high burning rate composite solid propellant is shown in Fig. 1, wherein the composite propellant was given an oscillation strain of 0.01 per cent

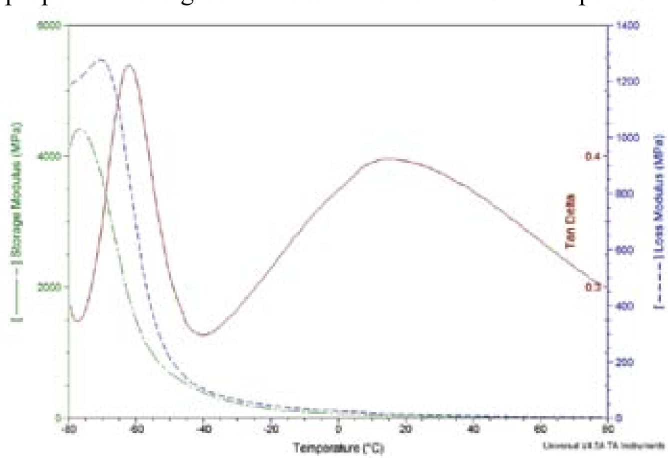

Figure 1. DMA result for a standard sample at 11 Hz with 0.01 per cent oscillatory strain at heating rate of 2 °C.

with 2 °C/min heating rate at 11 Hz frequency. It is clear from the figure that the maximum value of tan delta is at - 62.06 °C which is taken as glass transition temperature. These results at various frequencies were used in TTS software to determine the constants of WLF equation, master curves and subsequently in the prediction of storage life for each propellant.

3.1 Influence of Propellant Compositions on Glass Transition Temperature

Different tests on DMA were carried out using dual cantilever clamp with each sample being given a multi-frequency strain of 0.01 per cent at three discrete frequencies (3.5 Hz, 11 Hz, 35 Hz) in the temperature range of - 80 °C to + 80 °C. The T_g values for all propellants at the three frequencies, viz., 3.5 Hz, 11 Hz, 35 Hz are shown in Table 2. It is clear from Table 2 that T_g values lie in the range - 54 °C to - 67 °C which are dependent on the polymer content (HTPB) in the composition, the degree of cross-linking between HTPB and TDI, solid loading and the frequency of test. The increase in frequency leads to an increase in the T_g value which is supported by the fact that an increase in frequency freezes the chain movements introducing stiffness in the chains. The propellant IV has shown the highest T_g values at all frequencies. This is because the propellant IV has the highest amount of HTPB and TDI leading to greater cross-linking between the two, thus, making the propellant stiffer in comparison to other studied compositions.

Table 2. T_g value of four propellants with different burning rates at different frequencies

Propellants	Frequency (Hz)		
	3.5	11	35
I	-64.38	-60.97	-56.88
II	-66.42	-62.33	-58.47
III	-65.69	-61.85	-58.22
IV	-62.85	-58.02	-54.19

3.2 Influence of Propellant Compositions on C_1 and C_2 for WLF Equation

The temperature and frequency scans of all the four propellants were transferred to TTS software and TTS was applied to each of propellants' viscoelastic properties. The horizontal shifting of curves with respect to the reference temperature (T_g) shows conformance to the WLF equation. The values of C_1 and C_2 constants for each of the propellant are given in Table 3 with the corresponding standard error calculated from the formula given below.

Table 3. Value of constants C_1 and C_2 in the WLF equation for the four propellants

Propellants	C_1	C_2	Standard error
I	16.69	126.8	85.42
II	17.46	133.3	172.21
III	19.61	136.9	145.27
IV	24.28	168.9	132.05

$$\text{Standard Error} = \frac{\left[\frac{\sum (x_m - x_c)^2}{n-2}\right]^{1/2}}{\text{Range}} \times 1000 \qquad (3)$$

where x_m is the measured value of x for each data point, x_c is the calculated value of x for each data point, n is the number of data points, and range is the maximum value of x_m – minimum value of x_m.

Table 3 infers that the values are almost comparable for the propellants I, II, and III while propellant IV shows the highest values for both the constants. The log a_T (*i.e.*, x-shift) versus temperature curves for each propellant is shown in Fig. 2 which shows decreasing trend of x-shift with temperature for all the propellant compositions.

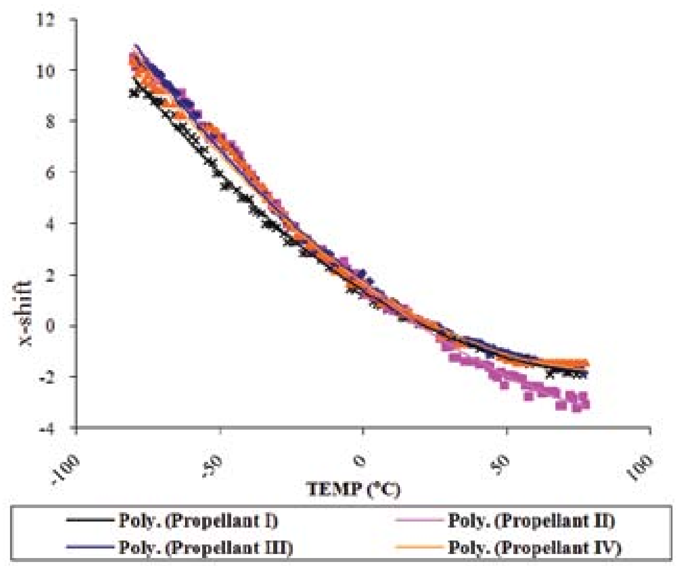

Figure 2. Comparison of log a_T versus temperature curves of propellants with different burning rates.

3.3 Influence of Propellant Compositions on Master Curves of Propellants

The master curves of storage modulus, i.e., log E′ versus log ω for each propellant are shown in Fig. 3 which shows that the master curves are similar for all the four propellants. However, at lower frequencies the master curves shift towards

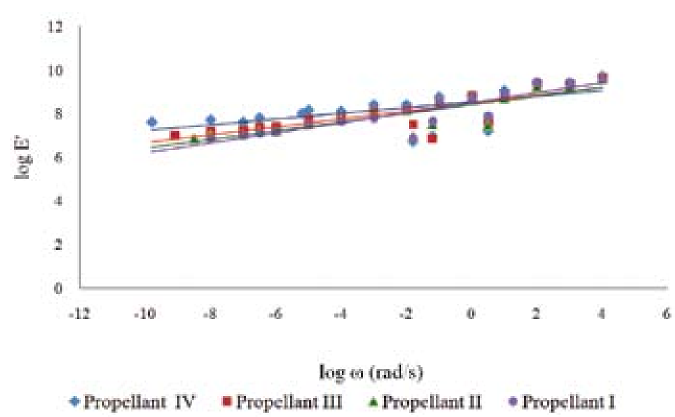

Figure 3. Comparison of master curves (log E′ versus log ω) for propellants with different burning rates.

the upper side as the burning rate of the propellant increases which depends on the percentage of fine and coarse ammonium perchlorate (AP), binder and curative. Further, the extra points on the graph not in line with the master curve indicate that horizontal shifting is not enough for applying WLF to propellant materials, therefore, they behave like thermo-rheologically complex materials.

3.4 Influence of Propellant Compositions on Storage Life of Propellant

The comparison of the E′ vs *t* (in years) curves for all the propellants are shown in Fig. 4. It is clear from the figure that the drop in storage modulus with time follows power law relationship. Moreover, the modulus of propellant IV is the highest. This is due to the higher degree of cross-linking between HTPB and TDI because of their greater content in the composition leading to a stiffer product. The drop in the storage modulus is also observed in case of propellant IV. The empirical equations relating the storage modulus (MPa) with the time (in years) for the four studied propellants can be presented as:

Propellant I : $E' = 8.612\, t^{-0.22}$

Propellant II : $E' = 11.17\, t^{-0.17}$

Propellant III : $E' = 21.30\, t^{-0.19}$

Propellant IV : $E' = 51.17\, t^{-0.09}$

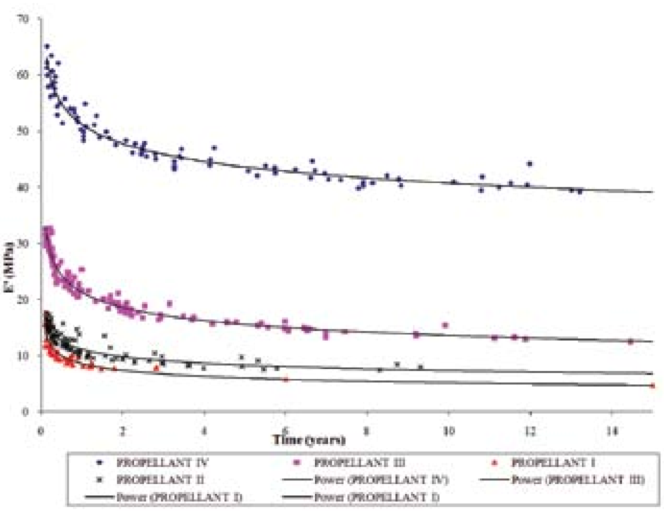

Figure 4. Comparison of E′ versus time curves of propellants with different burning rates upto 10 years.

The percentage drop in the storage modulus of all the propellants after 3 years, 6 years, and 10 years is shown in Table 4.

Table 4. Percentage drop in storage modulus with time (years) for propellants with different burning rates

At the end of time	Drop in E′ (per cent)		
	3 years	6 years	10 years
Propellant I	38.77	54.77	59.59
Propellant II	37.12	53.8	54.78
Propellant III	40.03	54.34	56.4
Propellant IV	36.97	46.78	48.76

Initially, in three years time, the storage modulus (E′) for propellant I reduces from 12.84 MPa to 7.86 MPa, *i.e.*, a reduction of 38.77 per cent in storage modulus. E′ of propellant II decreases from 16.70 MPa to 10.50 MPa in 3 years, *i.e.*, a reduction of 37.12 per cent. E′ for propellant III reduces from 31.52 MPa to 18.90 MPa in 3 years amounting to 40.03 per cent reduction in E′. E′ for the propellant IV reduces from 79.82 to 45.03 MPa in 3 years, i.e., a reduction of 36.97 per cent. Therefore, the percentage decrease, with respect to the initial value, in E′ with time is almost the same for all the four propellants. This is because the basic components are similar in all the four studied propellants (HTPB, TDI). However, the absolute values differ according to the composition, the high burning rate propellant being stiffer than the low burning rate propellants, thus, giving higher values of storage modulus. The drop in values of E′ after six years follows pattern of 3 years study and varies in the range 46-55 per cent as shown in Table 4. In continuation with this work further, the storage modulus of the propellant has been studied upto 10 years.

After 10 years, the drop in the storage modulus of propellant I is 59.59 per cent, *i.e.*, from 12.84 MPa to 5.19 MPa. E′ for propellant II decreases from 16.70 MPa to 7.55 MPa amounting to percentage drop of 54.78 per cent. E′ of Propellant III shows a reduction of 56.47 per cent, *i.e.*, from 31.52 MPa to 13.72 MPa. The drop in storage modulus is minimum for propellant IV (48.76 per cent, *i.e.*, from 79.82 MPa to 40.90 MPa) which is due to the stiffer chains present in propellant IV than in other propellants. Furthermore, the rate of drop of the storage modulus (E′) of propellant with time decreases as the time increases. This is evident from Table 4, which compares the percentage drop in the storage modulus after 3 years, 6 years, and 10 years. The major drop in storage modulus occurs within first six years of storage life, however, after this it remains almost constant, thus, exhibiting acceptable values of E′ even after 10 years depending upon the application of propellant.

4. CONCLUSION

The prediction of storage life of propellants having different burn rates have been carried out successfully using DMA technique. The drop in storage modulas after 3 years, 6 years, and 10 years was evaluated for the said propellants. The drop in storage modulus below the acceptable limit (minimum 10 years) may be used to predict the service life of propellants. As long as the storage modulus of propellant is within the specification of the grain design, the propellant is usable. This prediction of the storage modulus after a particular duration of time is possible with DMA and TTS in a short period of time which otherwise would require long periods of testing similar to the actual storage time.

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Contributors

Mr V.S. Wani obtained his MSc (Chemistry) from Pune University in 1981. Presently working as a Technical Officer 'C' at High Energy Materials Research Laboratory (HEMRL), Pune. His area of research include: Mechanical properties testing of propellants and high explosives.

Dr Mehilal received his PhD from Allahabad University in 1985. Presently working as a Joint Director at HEMRL, Pune. He made significant contributions in the field of plastic-bonded explosives. Presently he is working in the field of solid rocket propellants. He has published more than 100 research papers in national/international journals and filed 8 patents.

Mr Sunil Jain obtained his BE (Chemical Engg.) from National Institute of Technology, Surat in 2002 and ME (Aerospace Engg.) from Indian Institute of Sciences, Bangalore in 2010. Presently working as a Scientist 'D' at HEMRL, Pune. He has published more than 10 research papers in national/international journals. His area of research include: Solid rocket propellant processing.

Mr P.P. Singh received his BTech (Chemical Engg.) from HBTI (Harcourt Butler Technology Institute), Kanpur, in 1992. Presently working as a Joint Director at HEMRL, Pune. His area of research include: Solid rocket propellant processing.

Mr B. Bhattacharya obtained his MTech (Chemical Engg.) from Banaras Hindu University, Varanasi. Presently, working as an Outstanding Scientist and Director of HEMRL, Pune. His area of research include: Processing of composite propellants.