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Determination of Activation Energy of Relaxation Events in Composite Solid Propellants by Dynamic Mechanical Analysis

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ABSTRACT

The shelf life of a composite solid propellant is one of the critical aspects for the usage of solid propellants. To assess the ageing behavior of the composite solid propellant, the activation energy is a key parameter. The activation energy is determined by analysis of visco-elastic response of the composite solid propellant when subjected to sinusoidal excitation. In the present study, dynamic mechanical analyzer was used to characterize six different types of propellants based on hydroxyl terminated polybutadiene, aluminium, ammonium perchlorate cured with toluene diisocyanate having burning rates varying from 5 mm/s to 25 mm/s at 7000 kPa. Each propellant sample was given a multi-frequency strain of 0.01 percent at three discrete frequencies (3.5 Hz, 11 Hz, 35 Hz) in the temperature range -80 °C to + 80 °C. It was observed that all the propellants have shown two relaxation events (α- and β- transition) in the temperature range -80 °C to +80 °C. The α-transition was observed between -66 °C and -51 °C and β-transition between 7 °C and 44 °C for the propellants studied. The activation energy for both transitions was determined by Arrhenius plot from dynamic properties measured at different frequencies and also by time temperature superposition principle using Williams-Landel-Ferry and Arrhenius temperature dependence equations. The data reveal that the activation energy corresponding to α-transition varies from 90 kJ/mol to 125 kJ/mol for R-value between 0.7 to 0.9 while for β-transition the values are from 75 kJ/mol to 92 kJ/mol. The activation energy corresponding to β-transition may be used to predict the useful life of solid propellant.

Keywords: α-transition temperature, β-transition temperature, storage modulus, activation energy, time temperature superposition, hydroxyl terminated polybutadiene, dynamic mechanical analysis

1. INTRODUCTION

Solid propellants are most commonly used in the strategic, tactical missiles and rocketry system to deliver the required thrust to the missiles or rockets due to their simple design, ease of operation, safety, reliability, long shelf life and lowest cost. Composite solid propellant is a heterogeneous mixture of solid particles of oxidizer and metallic fuel dispersed in a polymeric matrix. Hydroxyl terminated polybutadiene (HTPB) based composite solid propellants are used in many operational propulsion systems due to their better performance and established processing technology. Generally the percentage of solid particles in composite solid propellant is 80 % - 90 % and liquid binder is nearly 10 % - 20 % depending on ballistic and structural requirement[1]. The mechanical behaviour of solid propellants is mainly influenced by the polymeric nature of binder, curing agent and binder-filler interaction. The curing ratio (η_{NCO}/η_{OH}) also called R-value of the propellants plays a critical role in the cross-linking kinetics and in the mechanical properties of the solid propellant formulation[2].

Shelf life of a solid composite propellant is one of the critical aspects for the usage of solid propellants. To assess the ageing behaviour of the composite solid propellant, the activation energy is a key parameter and is calculated by various methods like dynamic NMR spectroscopy[3], Ozawa[4] and Kissinger[5] methods.

Further, HTPB-TDI based composite propellant exhibits visco-elastic response during oscillatory excitations and the material parameters are both temperature and frequency dependant[6]. One of the methods that yield useful information on both micro-structural behavior (mechanical properties) and relaxation events of composite solid propellants in broad temperature region is dynamic mechanical analyzer (DMA).

In the present study, experiments were conducted on DMA to study the viscoelastic response of the composite propellants. The aim of investigations is to determine the dependencies between the loss factor (tanδ), temperature and frequency of the composite propellant by thermo-analytical technique. Observed dependencies from the experimental results were used to generate Arrhenius plot and further to determine the activation energy. The activation energy was also determined by time temperature superposition (TTS) principle given by William, Landel and Ferry (WLF) and Arrhenius equations[7] using TTS software. The shelf life of the propellant depends on the activation energy which in turn depends on the constituents of solids and R-value (η_{NCO}/η_{OH}) in solid propellant composition. The determination of activation energy helps to predict the shelf life of the given propellant.

Generally characterisation of mechanical properties of solid propellants depends on series of tests at various temperatures and deformation rates. These tests are usually

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conducted using standard universal testing machines in tensile and compression mode.

The scattered experimental data of such tests require testing of at least three to five samples at each combination of deformation rate and temperature. The number of samples required to make complete understanding of mechanical behaviour is rather high. The tests carried out in production as well as in routine quality controls are often limited to a few temperatures - one at high temperature, one at room temperature and one at low temperature which are inadequate for detection of micro-structural changes in solid propellants in course of production and ageing studies[8].

Dynamic mechanical analyzer is one of the most appropriate method to investigate relaxation events. Boyd in his review article[9] has demonstrated that the interpretation of viscoelastic relaxation strength in polymers depend on the tangent of the phase lag angle (tanδ) or real (in-phase) or imaginary (out-of-phase) components of modulus also termed as storage and loss modulus respectively[10]. In this approach, only one sample is used at various temperatures and deformation rates.

The glass transition temperature (T_g) of a material also referred as α-transition is normally observed as a peak of tanδ considering the variation of tanδ with temperature. At this point material absorbs energy and modulus of the material decreases as it passes through the glass transition phase. Normally at a lower temperature, sometimes other relaxation events are observed for polymeric materials[11]. The secondary transition known as β-relaxation is normally attributed to polymer backbone configuration reorganization. The activation energy is effectively the energy barrier of the material of which has to overcome in order to undergo the structural reorganization of the β-relaxation. The activation energies corresponding to these two events were determined by Arrhenius equation which can be subsequently used to predict the shelf life of the propellants[12].

$$\ln(F) = \ln(A) - \frac{E_a}{RT} \tag{1}$$

where F is frequency (Hz), A is the pre-exponential factor, E_a is the activation energy (kJ/mol), R is the gas constant (kJ/mol-K) and T is the temperature (K).

The apparent activation energy (ΔH_a) corresponding to glass transition temperature, T_g is calculated theoretically by using WLF Eqn. (7) and TTS WLF software

$$\Delta H_a = \frac{2.303 R C_1 C_2 T^2}{\left(C_2 + T - T_{ref}\right)^2} \tag{2}$$

where C_1 and C_2 are WLF constants at T_{ref}, R is the gas constant (kJ/mol-K) and T is the temperature (K).

The apparent activation energy (ΔH_β) corresponding to beta transition temperature, T_β is also computed using TTS Arrhenius software.

2. EXPERIMENTAL

Six types of composite solid propellant formulations were studied having burn rate of 5 mm/s to 25 mm/s at 7000 kPa. The compositions details of the propellant samples studied are given in Table 1.

The DMA Q800 was used to characterise frequency dependence of transitions. The variations of storage modulus, loss modulus and loss factor were recorded using rectangular specimens (length x width x thickness= 35 x 13 x 3) mm^3 in dual cantilever mode as a function of temperature varying from -80 °C to + 80 °C at frequencies 3.5 Hz, 11 Hz, and 35 Hz. A constant strain of 0.01 % was maintained during experiments and heating rate was 2 °C/min and cooling was done using liquid nitrogen with automated cooling accessories. The storage modulus (E′), the loss modulus (E″) and the loss factor (tanδ) were calculated using Eqns. (3), (4), and (5), respectively.

Table 1. Transition temperatures at three frequencies of propellant

Propellant	Frequency (Hz)	α-transition temperature, T_g(°C)	β-transition temperature, T_β(°C)
Type-I	3.5	-64.38	7.82
	11	-60.97	12.1
	35	-56.88	26.42
Type-II	3.5	-62.86	11.9
	11	-59.23	20.6
	35	-54.9	33.9
Type-III	3.5	-65.2	13.2
	11	-59.6	20.4
	35	-55.97	32.2
Type-IV	3.5	-60.05	23.38
	11	-54.8	32.14
	35	-51.64	43.71
Type-V	3.5	-65.69	9.72
	11	-62.06	13.76
	35	-58.22	26.1
Type-VI	3.5	-64.68	8.98
	11	-61.45	12.96
	35	-57.62	22.30

$$E' = E^*.\cos\delta \tag{3}$$

$$E'' = E^*.\sin\delta \tag{4}$$

$$\tan\delta = \frac{E''}{E'} \tag{5}$$

where E* is the measured complex modulus of the sample and δ is the phase angle which is calculated by Eqn. (5)

$$\delta = 2\pi.f.\Delta t \tag{6}$$

where f is the frequency of the dynamic excitation and Δt is the time delay between stress and strain.

The storage modulus, loss modulus, tan delta, T_g and T_β were evaluated at three discrete frequencies for each propellants. The curves were shifted using TTS software by WLF and Arrhenius temperature dependence principle.

3. RESULTS AND DISCUSSION

The propellants studied show visco-elastic response during the dynamic testing as the phase angle lies between 0° and 90°. The analyses were carried out using dual cantilever clamp of

DMA Q800 employing the multi-frequency strain method. The variation of storage and loss modulus wrt temperature for type-I propellant at 0.01 per cent strain and at three frequencies 3.5 Hz, 11 Hz, and 35 Hz is shown in Fig. 1. As shown in the Fig.1 that the storage as well as loss modulus increases with increase of frequency in the temperature ranges from -80 °C to +80 °C.

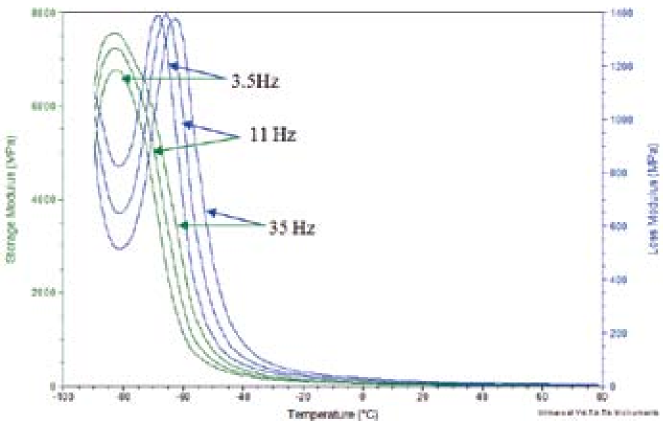

Figure 1. Storage and loss modulus *vs* temperature for type-I propellant.

The tanδ curve for type-I propellant at 0.01 per cent strain and 3.5 Hz frequency is shown in Fig. 2. As shown in the Fig. 2, there are two relaxation events in the temperature ranges from -80 °C to +80 °C. The first transition called α-transition (T_g) was observed at -64.38 °C and the second transition called β-transition (T_β) was observed at 7.8 °C for Type-I propellant at 3.5 Hz. These results at various frequencies were used in TTS software to determine the WLF constants, Arrhenius temperature dependence and subsequently in the determination of activation energy of both the transitions for each propellant (Type I to Type VI).

3.1 Relaxation Events in Different Propellant Compositions

The multi-frequency strain method was used to carry out the dynamic mechanical analysis on DMA Q800 using dual cantilever clamp with each propellant sample. The tests were conducted at 0.01 percentage of strain at three discrete frequencies (3.5 Hz, 11 Hz, 35 Hz) in the temperature range of -80 °C to +80 °C. It is observed that all the propellants have shown two relaxation events (α- and β-transition) in the

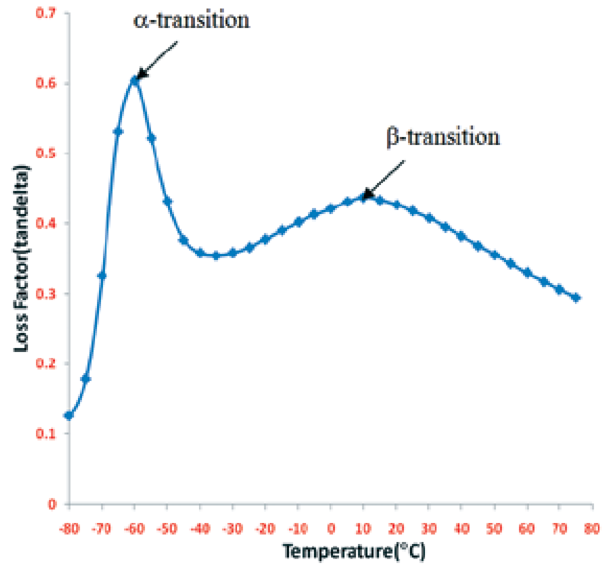

Figure 2. Variation of tan delta with temperature at 3.5Hz of Type-I Propellant.

temperature range -80 °C to +80 °C. The glass transition and beta transition temperature values at three frequencies are shown in Table 2. As shown in the Table 2 that the T_g values lie in temperature range -66 °C to -51 °C and T_β values lie in the temperature range 7 °C to 44 °C which are dependent on the R-value in the propellant composition, solid loading and frequency of test. It is also clear from the table that beta transition occurs at a higher temperature than the glass transition temperature at each frequency.

3.2 Effect of R-value (η_{NCO}/η_{OH}) on Activation Energy of Relaxation Events

The R-value (η_{NCO}/η_{OH}) of the propellants plays a critical role in the cross-linking kinetics and mechanical properties of the propellants. Generally, in composite propellant formulation, the R-value is usually maintained between 0.7 and 0.9 to achieve higher strain capability whereas in some cases it is maintained at 1.1 for better structural integrity[13]. The R-values of different test propellants under study are given in Table 1.

The mechanical spectra reflecting the mobility of molecular chains in HTPB-TDI based solid propellants exhibit two transitions in tanδ *vs* temperature plot in the temperature range from -80 °C to +80 °C at frequency 3.5 Hz, 11 Hz, and

Table 2. Composition details of different propellant samples used during the study

Propellants	Binder (HTPB+other ingredients) (wt. %)	TDI as curing agent (wt. %)	Solid ingredients (wt. %)	R-value (NCO:OH)	Burning rate @ 7000 kPa (mm/s)
Type-I	13.3	0.70	86	0.785	5
Type-II	13.29	0.71	86	0.80	5.2
Type-III	14.3	0.70	85	0.785	9.6
Type-IV	15.3	0.70	84	0.785	13.8
Type-V	17.2	0.80	82	0.828	19
Type-VI	19.75	1.25	79	1.10	25

35 Hz. The α-transition temperature (T_g) was observed in the interval from -66 °C to -51 °C for the propellants studied. The secondary transition, β-transition temperature which represents the backbone configuration reorganization of cross-linking between HTPB and toluene diisocyanate (TDI) as curing agent was observed at temperature greater than 0 °C (7 °C to 44 °C) for propellants studied.

The activation energies were calculated from tanδ peaks and onset values of dynamic properties measured at frequencies 3.5 Hz, 11 Hz, and 35Hz using Arrhenius plots as shown in Figs. 3 and 4 for each propellant. The activation energy corresponding to α- and β-transition is given in Table 4. It is found that the activation energy for α-transition (90 kJ/mol to 125 kJ/mol) is higher than that of β-transition (75 kJ/mol to 90 kJ/mol) in the solid composite propellants having R-value between 0.7 and 0.9. This is because the modulus of the material decreases as it passes through the alpha transition phase. But in case for Type-VI propellant which is having R-value greater than 1 shows very high activation energy. This is because of the greater cross-linking between binder (HTPB) and curing agent (TDI) resulting higher tensile strength in comparison to other studied propellant formulation[14].

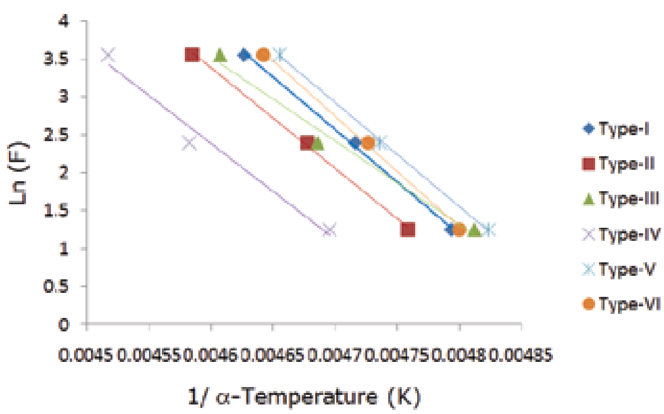

Figure 3. Arrhenius plot of α-transition for each propellant.

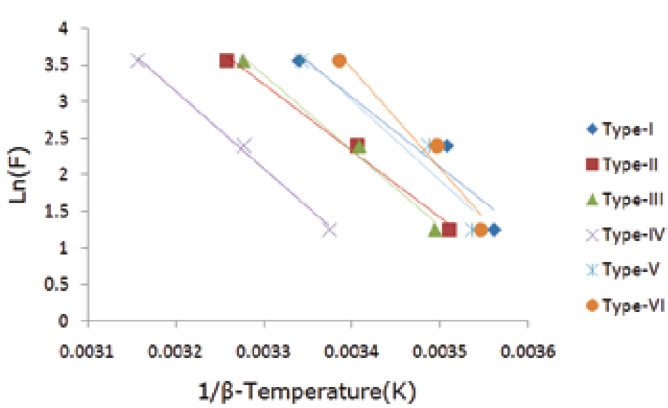

Figure 4. Arrhenius plot of β-transition for each propellant.

3.3 Activation Energy of Relaxation Events by Time Temperature Superposition

The DMA test data of each propellant was analyzed with time temperature superposition software. The amount of shift in the main transition region on changing the frequency depends on T_g and the constants of WLF equation whereas for beta transition, the shift follows Arrhenius temperature dependence, with an activation energy ΔH_a .

The activation energy of α-transition was calculated using WLF constants and that of β-transition using TTS Arrhenius software. The horizontal curve shift with respect to α-transition temperature was carried out using TTS WLF software to get the WLF constants C1 and C2 for each propellant. The horizontal curve shift for Type-II propellant is shown in Fig. 5. The constants of WLF equation are given in Table 3. The activation energy corresponding to α-transition was calculated using Eqn. (2).

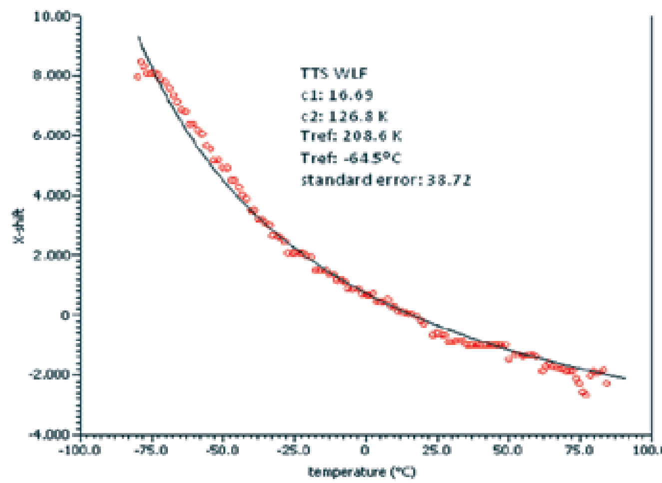

Figure 5. Time-temperature superposition WLF for type-I propellant.

Table 3. WLF constants for studied propellants at Tg

Propellant	*Tg*(°C)	C1	C2(K)
Type-I	-64.5	16.69	126.8
Type-II	-59.9	17.59	122.3
Type-III	-59.6	16.76	147.1
Type-IV	-54.8	16.05	148.5
Type-V	-62.0	19.61	136.9
Type-VI	-64.9	32.69	144.6

The horizontal curve shift with respect to β-transition temperature was carried out using TTS Arrhenius software for each of the propellant. The activation energy corresponding to β-transition temperature for Type-II propellant by TTS Arrhenius are given in Fig. 6. The activation energies calculated from Arrhenius plot and TTS software is given in Table 4.

As shown in the Table 4, activation energy corresponding to α-transition is higher than that of β-transition for all the propellants. The activation energies corresponding to alpha and beta transition of propellants under study having R-value between 0.7 and 0.9 are found to be in the range 90kJ/mol to 125 kJ/mol and 75 kJ/mol to 92 kJ/mol, respectively, and they are in good agreement by both methods.

Table 4. Activation energy of relaxation events for studied propellants

Propellant	α-transition (kJ/mol)	α-transition @T_g by TTS WLF (kJ/mol)	β-transition (kJ/mol)	β-transition @T_b by TTS Arrhenius (kJ/mol)
Type-I	114.89	109.56	79.54	77.48
Type-II	110.06	125.05	75.35	79.72
Type-III	91.82	99.34	86.75	86.74
Type-IV	104.76	98.53	88.07	77.95
Type-V	114.02	122.10	91.71	97.68
Type-VI	121.48	187.45	114.17	173.6

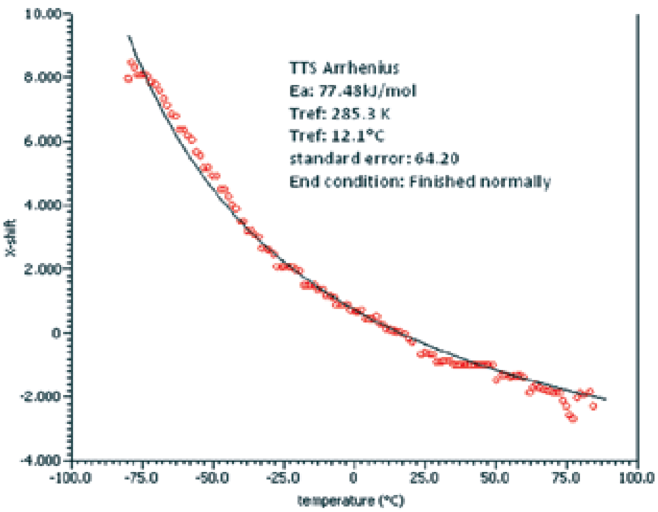

Figure 6. Time-Temperature Superposition (TTS) Arrhenius for type-I Propellant.

4. CONCLUSIONS

A successful attempt has been made to determine the activation energy of composite propellants having different burning rate varying from 5 mm/s to 25 mm/s using DMA. The data reveal that HTPB-TDI based composite propellants show two relaxation events in the temperature range from -80 °C to +80 °C and the number of experiments can be reduced significantly to one for the prediction of activation energy by Arrhenius plot which is very useful for the life estimation of composite solid propellants. The activation energy corresponding to both transition temperatures was also computed by using time temperature superposition principle. The activation energy corresponding to α-transition is higher than that of β-transition for all composite propellants studied. The activation energies corresponding to α- and β-transition of propellants under study having R-value between 0.7 and 0.9 are found to be in the range 90 kJ/mol to 125 kJ/mol and 75 kJ/mol to 92 kJ/mol, respectively and they are found in good agreement by both methods. The propellant having R-value greater than 1 shows higher activation energy. Activation energy corresponding to α-transition is 187.45 kJ/mol and that of β-transition is 173.6 kJ/mol. The activation energy corresponding to β-transition can be directly used for life estimation of composite solid propellants.

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