Journal of Aerospace Technology and Management
ISSN: 1984-9648
editor@jatm.com.br
Instituto de Aeronáutica e Espaço
Brasil

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Journal of Aerospace Technology and Management, vol. 4, núm. 4, octubre-diciembre, 2012, pp. 443-452
Instituto de Aeronáutica e Espaço
São Paulo, Brasil

doi: 10.5028/jatm.2012.04044012

Studies on the Influence of Testing Parameters on Dynamic and Transient Properties of Composite Solid Rocket Propellants Using a Dynamic Mechanical Analyzer

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Abstract: *Dynamic mechanical analysis is a unique technique that measures the modulus and damping of materials as they are deformed under periodic stress. Propellants, which are viscoelastic in nature, are subjected to time, temperature, and frequency effects during the analysis to determine their dynamic and transient properties. The choice of parameters during the experiments like temperature, frequency, strain (%), and stress level is very crucial to the results obtained since the propellant behaves differently under different conditions. A series of experiments like strain and temperature ramp/frequency sweeps, creep, stress relaxation, etc. have been conducted using high burning rate composite propellant (burn rate ~20 mm/s at 7,000 kPa), in order to determine the precise effects of such parameters on the results obtained. The evaluated data revealed that as the temperature increases the storage modulus, loss modulus, and tan delta curves with respect to the frequency shift towards the lower side. Moreover, there is equivalency between the increase in the temperature and the decrease in the frequency, which can be used for the time-temperature superposition principles. Further, in transient tests, the relaxation modulus has been found to decrease when increasing strain levels in the given time range. Also, relaxation modulus versus time curves were found to shift towards the lower side with increasing temperature while creep compliance decreases with the increase in stress and decrease in temperature. The glass transition value of the composite propellant increases when there is an increase in the heating rate.*

Keywords: *Glass transition temperature, Storage modulus, Loss modulus, Polybutadiene, Viscoelastic properties.*

INTRODUCTION

Composite propellants are being used in several missile applications, which basically contain ammonium perchlorate – AP (from 65 to 70%), a metallic fuel like aluminium powder (15 to 20%), and a liquid binder such as hydroxyl terminated polybutadiene – HTPB (10 to 15%) along with certain process aids and diisocyanate based curatives (Boyars and Klager, 1969). Due to the presence of polymeric binder, propellants are viscoelastic in nature. Vibrational methods are used in order to determine the dynamic mechanical properties of such materials. These vibrational tests measure the deformation of the material to periodic forces. From these dynamic mechanical tests, different variables are obtained, such as: storage modulus (E'), loss modulus (E''), and loss factor (tan δ). Storage modulus is related with the energy stored during deformation, and loss one is associated with the dissipation of the energy as heat. From the ratio of the loss to storage moduli, loss factor is obtained, and it represents the damping capacity of the material. Thus, dynamic mechanical analysis is a technique that measures the modulus and damping of materials as they are deformed under periodic strain or stress (Ferry, 1980; Groves *et al.*, 1992; Foreman, 1997; Morton *et al.*, 1969). Propellants, which are viscoelastic in nature, are subjected to time, temperature, and frequency effects during the analysis to determine their dynamic mechanical property data (Tod, 1987; Hanus, 2001). The material properties that can be measured by this technique in addition to storage and loss moduli, and tan δ are: glass transition (Tg), softening temperature, degree of cure, creep, stress relaxation, and so on.

Exhaustive literature survey reveals that a number of studies have been carried out to evaluate the effects of binders,

Received: 06/07/12 Accepted: 08/08/12

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humidity, and composition on the dynamic mechanical properties of propellants, viz. Bhagawan *et al.* (1995) studied the dynamic mechanical properties of different binders and corresponding propellants in terms of storage modulus and tan δ, they were: HTPB, CTPB, PBAN, HEF-20, and ISRO polyol. Such authors found that polybutadiene binders exhibited lowest Tg value (around -60 °C), while ISRO polyol had the highest one (~ -20 °C) and the propellants had higher moduli than their corresponding binders at any temperature. Cogmez *et al.* (1999) also attempted to compare the dynamic data of two HTPB-based propellants with different solid compositions, viz., one with 87% solid loading having 16% Al as metallic fuel, and the other with 86% solid loading without metallic fuel; the former propellant was found to be less stiffer and more dissipative than the latter at higher temperatures.

Studies have also been performed on the transient properties like creep and stress relaxation by Mohandas *et al.* (2000), who studied the effect of humidity on the transient properties of propellants having the standard composition of HTPB/Al/AP. It was found that when propellant is exposed to high relative humidity (RH) levels, the creep strain increases and equilibrium stress during stress relaxation decreases by a factor of two. Further to this, Musanic (2002) studied double-based propellants and the effect of testing parameters like frequency, heating rate, length to thickness ratio, etc. on their dynamic mechanical properties (storage modulus, loss modulus, tan δ).

However, little work has been carried out to study the effect of various testing parameters on the dynamic as well as transient properties of composite propellants, which are very significant since dynamic mechanical analyzer (DMA) analysis results may depend significantly on the conditions used during the experiment, i.e., heating rate, frequency, stress/strain level applied, temperature, and so on. Therefore, in the present study, an exhaustive data set was generated to determine the effect of various parameters like frequency, heating rate, strain (%), stress level, temperature on the dynamic and transient properties of composite propellants using different DMA test methods such as:

- DMA multi-strain- strain sweep;
- DMA multi-frequency strain – isothermal temperature/frequency sweep;
- DMA multi-frequency strain – temperature ramp/frequency sweep;
- Stress relaxation;
- Creep.

In the following section, the effect of the previously mentioned parameters will be reported.

EXPERIMENTAL

The experiments were carried out using high burning rate composite solid propellants having the following composition: HTPB, AP with tetra-modal distribution, Al and other additives with toluene diisocyanate (TDI) as the curative. The testing samples were cut from the propellant block in the form of rectangular bars containing the following dimensions: 60 x 12.5 x 3 mm. All dynamic mechanical measurements were carried out on TA Instruments Dynamic Mechanical Analyser Q800 (TA Instruments, USA). The different experiments were performed on dual cantilever clamp varying the frequency, temperature, stress, and strain levels.

Variation of dynamic mechanical properties

- DMA multistrain, strain sweep: the sample was tested at 35 ºC with amplitude increasing linearly from 0.5 to 50 μm at different frequencies. The effect of frequency on the storage modulus was determined by plotting a graph of storage modulus *versus* strain.
- DMA multifrequency strain, isothermal temperature/frequency sweep: the sample was given a series of strains at three frequencies viz., 3.5, 11, 35 Hz at 35 ºC and the effect of strain levels was evaluated on modulus by plotting a graph of storage modulus *versus* frequency.
- DMA multifrequency strain, isothermal temperature/frequency sweep: the sample was given a constant strain of 0.5% at three frequencies (3.5, 11 and 35 Hz), while varying the temperatures for subsequent tests to determine the effect of temperature on storage modulus, loss modulus, and tan δ.
- DMA multifrequency strain, temperature ramp/frequency sweep: samples were given a constant strain of 0.01%, and temperature increased from 35 to 85 ºC at the heating rates of 1, 2, and 10 ºC/minutes, at the same time the frequencies were varied to determine the frequency effect on storage modulus by plotting a curve of storage modulus *versus* temperature.

Variation of transient properties

- Stress relaxation at different strains: samples were loaded under various strain levels at 35 ºC for 30 minutes, and their relaxation moduli were determined.

- Stress relaxation at different temperatures: samples were loaded under 0.1% strain level at a series of temperatures ranging from 35 to 85 ºC for 30 minutes, and their relaxation moduli were also determined.
- Creep at different stress: samples were loaded under various stress levels at 35 ºC for a ten-minute creep time with 20 minutes of recovery, being their creep compliances compared.
- Creep at different temperatures at 1 MPa stress at a ten-minute creep time and 20-minute recovery time: samples were loaded under 1 MPa stress level at a series of temperatures ranging from 35 to 85 ºC for 30 minutes (10-minute creep time and 20-minute recovery time), and their creep compliances were determined.

RESULTS AND DISCUSSION

All the analyses were carried out on high burning rate composite solid propellant (burn rate ~20 mm/s at 7,000 kPa) using different test methods of DMA and varying parameters like temperature, frequency, heating rate, and stress/strain levels. 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% with 2 ºC/minutes heating rate at 11 Hz frequency. It is clear from Fig. 1 that the tan delta maximum is at -62.1 ºC, which is taken to be the Tg temperature. The effects of various parameters like temperature, frequency, strain, stress and heating rate on such sample being tested for various dynamic and transient properties like storage modulus, loss modulus, tan δ, relaxation modulus and creep compliance are described in details.

Influence of temperature on the dynamic and transient properties

The dynamic properties of the high burning rate composite propellant were studied using dual cantilever clamp at an oscillatory strain of 0.5% at a heating rate of 2 ºC/minutes, with temperatures ranging from 35 to 80 ºC at several frequencies. The results for the variation of storage modulus, loss modulus, tan δ with frequency for different temperatures are shown in Figs. 2 to 4, respectively. It is clear from Figs. 2 to 4 that as the temperature increases the storage modulus *versus* frequency, loss modulus *versus* frequency, and tan δ *versus* frequency curves shift towards the lower side since the temperature decreases the chains become stiffer and less mobile leading to an increase in the modulus. This also supports the fact that an increase in the temperature is equivalent to a decrease in the frequency. The transient tests of creep were also carried out for the high burning rate composite propellants using dual cantilever clamp at a fixed stress of 1 MPa at two different temperatures, viz., 65 and 75 ºC. The results obtained are presented in Fig. 5, which reveals that the creep compliance/strain increases with the increase in the temperature at a given time range. This might be due to the higher strains induced in the sample because of higher temperatures, for a fixed stress, leading to a decrease in the modulus and hence increase in the compliance that is the reciprocal of modulus.

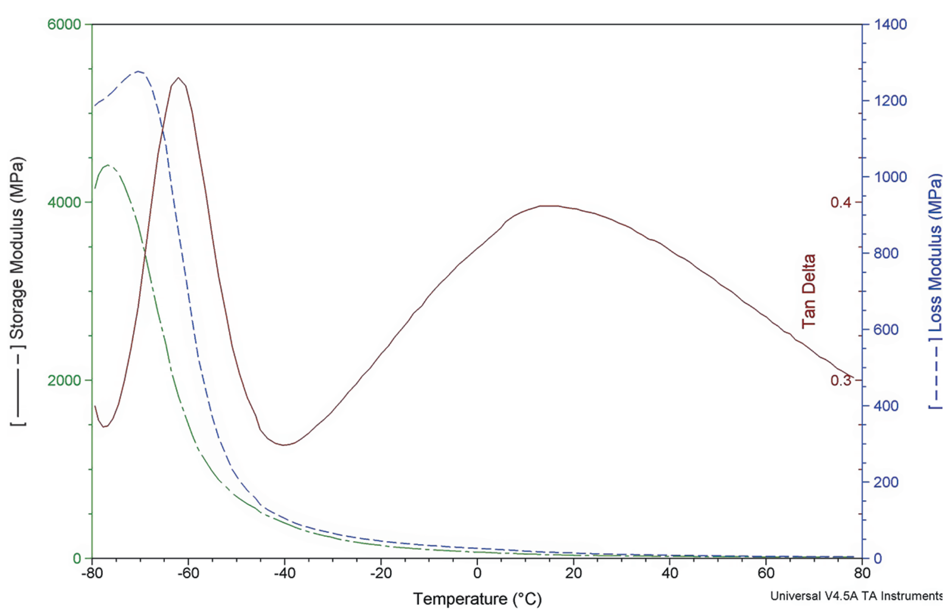

Figure 1. DMA result for a standard sample at 11 Hz with 0.01% oscillatory strain at heating rate of 2 ºC/minutes.

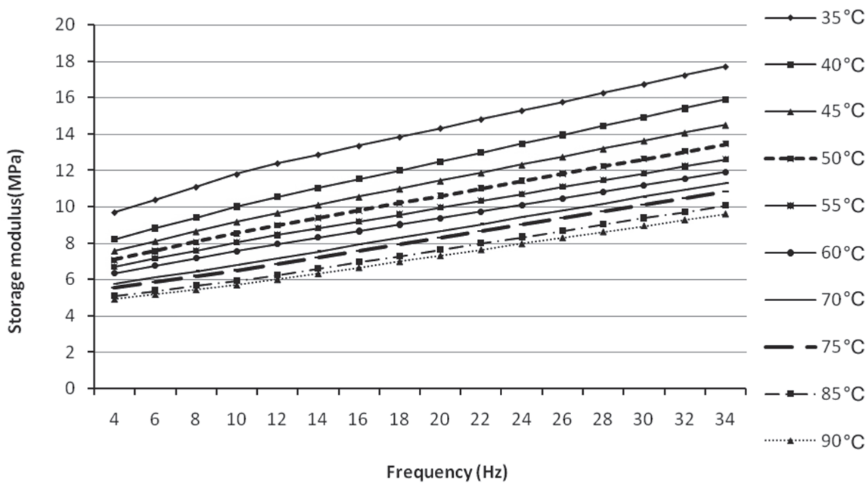

Figure 2. Storage modulus *versus* frequency for different temperatures at 0.5% strain.

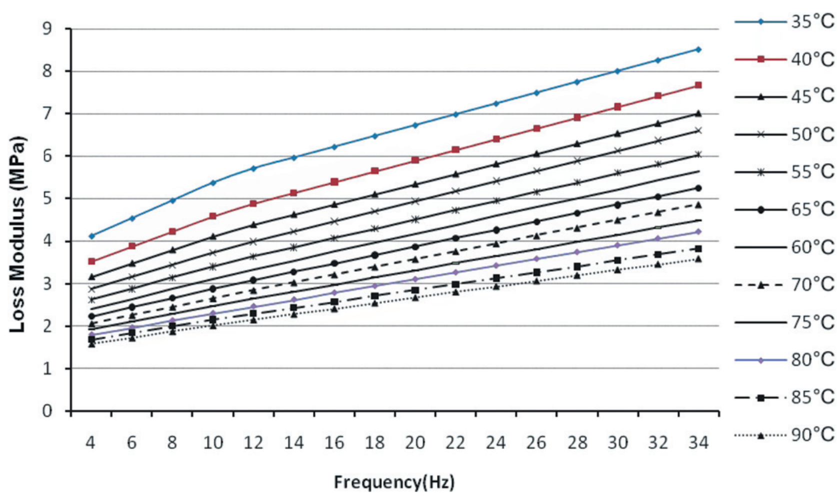

Figure 3. Loss modulus *versus* frequency for different temperatures at 0.5% strain.

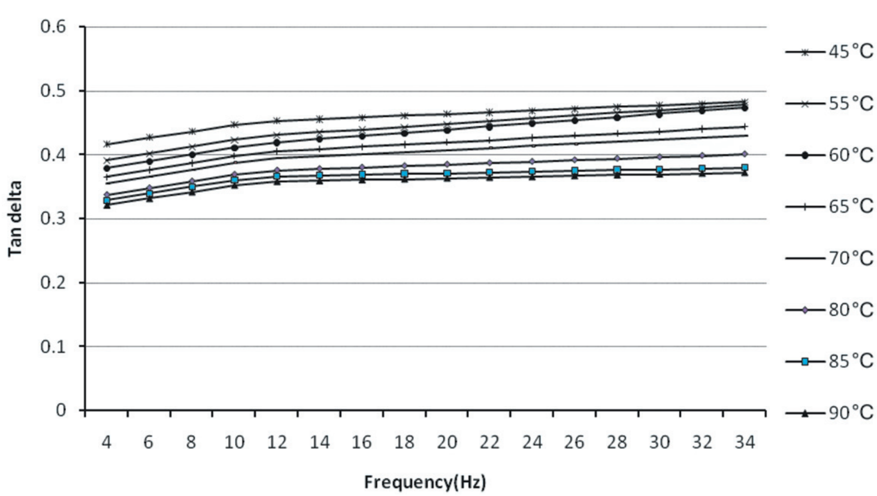

Figure 4. Tan delta *versus* frequency for different temperatures at 0.5% strain.

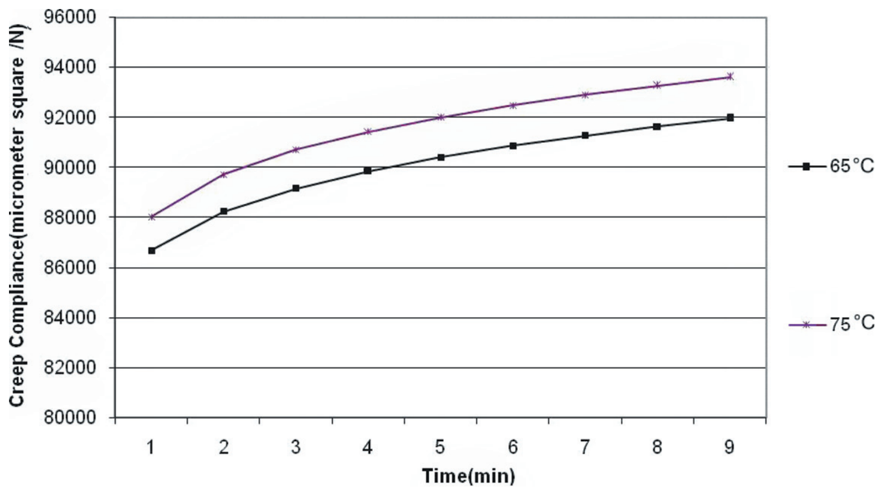

Figure 5. Creep compliance *versus* time at 1 MPa stress at different temperatures.

The transient tests of stress relaxation were also carried out using dual cantilever clamp at a fixed strain level of 0.1% strain at different temperatures, viz. 35, 40, 45 and 50 ºC. The results obtained are shown in Fig. 6, which shows that relaxation modulus *versus* time curves shift towards the lower side (the relaxation modulus decreases) as temperature increases. This might be due to the fact that at higher temperatures the polymeric (HTPB) chains become more mobile and may flow to bear the strain applied resulting in rapid decrease in stress and modulus.

Influence of frequency on the dynamic and transient properties

The frequency influence on DMA from the high burning rate composite propellant was analysed using dual cantilever clamp at different frequencies, viz, 0.1, 0.2, 1, 2, 3.5, 4.6, 11,35 Hz and so on, at a heating rate of 3 ºC/minutes with an oscillatory strain of 0.01%, and the results obtained are presented in Figs. 7 and 8, respectively. It is clear from Fig. 7 that as the frequency increases, the storage modulus *versus* temperature curves shifts upwards indicating an increase in the storage modulus with the increase in the frequency. It is also clear from Fig. 8 that as the frequency increases, the storage modulus *versus* strain curves shift towards the upper side, that is, the storage modulus values increase with the frequency. This may be due to the fact that increase in the frequency (equivalent to decrease times) freezes the chain movements resisting intermolecular slippage, and leading to a stiffer behaviour and hence increasing the modulus (Nair *et al.*, 2009; Young and Lovell, 1991).

It should be noted that storage modulus *versus* temperature curves at various frequencies can be shifted using time-temperature superposition (TTS) principle to determine the

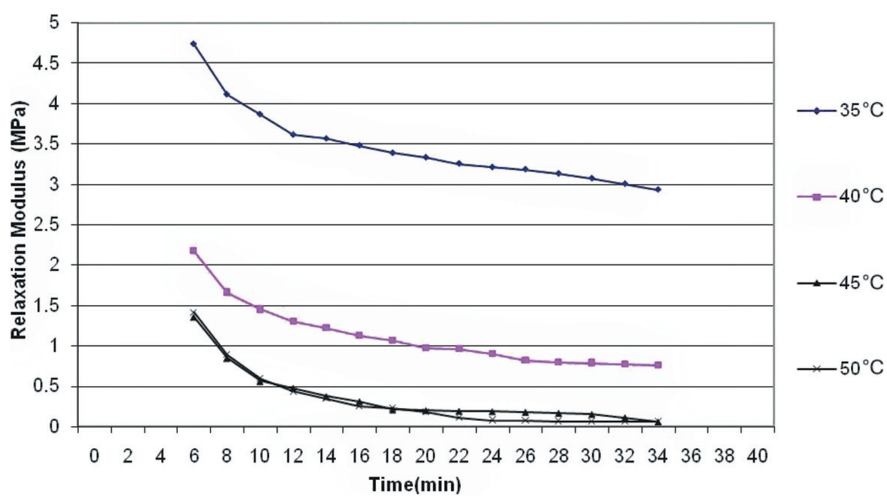

Figure 6. Relaxation modulus *versus* time at different temperatures at 0.1% strain.

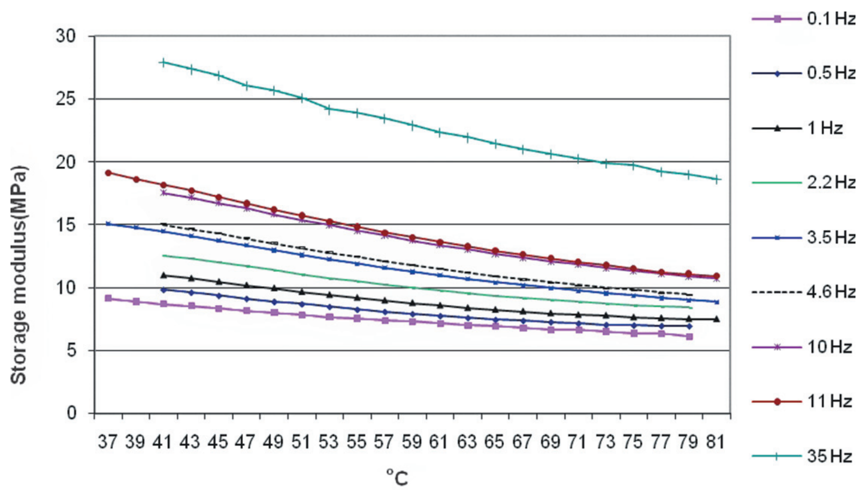

Figure 7. Storage modulus *versus* temperature at different frequencies at 0.01% strain.

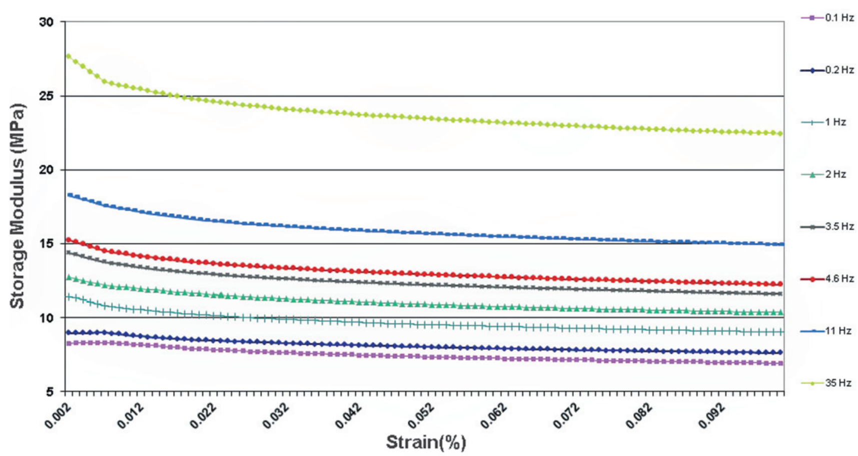

Figure 8. Storage modulus *versus* strain in different frequencies at 35 ºC.

master curve at a single reference temperature, thus increasing the frequency range in which the sample properties can be known beyond the frequency range, where the sample was tested. The TTS principle states that an increase in frequency has the same effect on the measured viscoelastic property as decreases in temperature or in time. The amount of shifting along the horizontal (x-axis) of each curve to align with the reference temperature curve in a typical TTS plot is generally described by the Williams-Landel-Ferry (WLF) equation (Eq. 1):

$$\log a_T = -C_1(T-T_0)/[C_2+(T-T_0)] \quad (1)$$

where
C_1 *and* C_2 are constants,
T_0 is the reference temperature (K),
T is the measurement temperature (K), and
a_T is the shift factor.

The WLF equation is typically used to describe the time/temperature behaviour of polymers in the *Tg* region, and it has been reported in the literature to predict the performance of polymers (Foreman, 1997).

Influence of strain level on the dynamic and transient properties

The influence of strain level on the dynamic properties of the high burning rate composite propellant was tested using dual-cantilever clamp at 35 ºC at frequencies from 3.5 to 35 Hz at various strains, ranging from 0.001 to 3% strain, and the results obtained are shown in Fig. 9. It is clear from Fig. 9 that as the strain applied on the sample increases the storage modulus *versus* frequency curves shift downwards, that is, the storage modulus decreases on increasing the oscillatory strain. This is well-supported by the fact that the

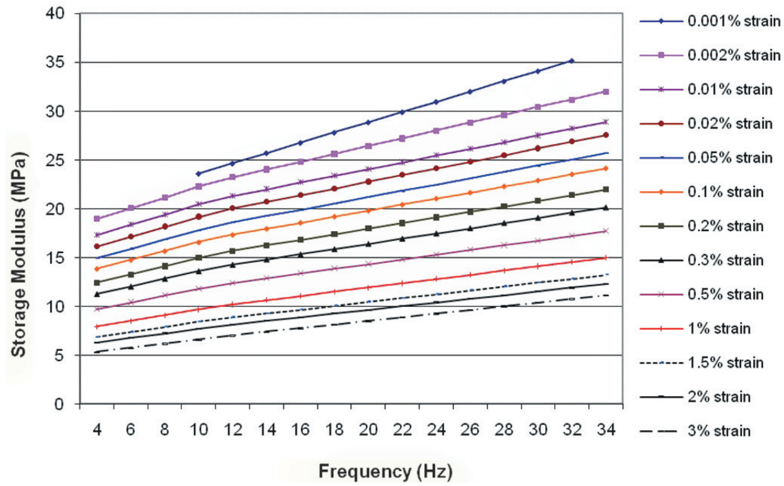

Figure 9. Storage modulus *versus* frequency for different strains at 35 ºC.

elastic component of a material is obtained by the stress ratio from each strain, therefore, if the strain increases, the storage modulus will drop. The effect of strain level was also studied on the stress relaxation behaviour of the high burning rate composite propellant using dual cantilever clamp at 35 ºC with strains varying from 0.01 to 2% for 40 minutes each. The results obtained can be seen in Fig. 10, which shows that the relaxation modulus decreases with increasing strain levels in the given time range, a quite obvious fact since the modulus is obtained by stress ratio from strain, as the strain increases the modulus decreases.

Influence of stress level on the dynamic and transient properties

The effect of stress applied on the composite propellant when it is subjected to creep was determined by testing the samples in dual cantilever clamp at 35 ºC for a ten-minute period with the stress applied varying from 0.1 to 3 MPa and measuring the corresponding creep compliances. A plot of creep compliance *versus* time for high burning rate composite propellant under creep subjected to different stress levels at 35 ºC is shown in Fig. 11, which infers that as the stress level increases the creep compliance *versus* time curve shifts downwards, that is, the creep compliance decreases with increase in stress. Since the creep compliance is the reciprocal of modulus and this is the ratio of stress by strain, therefore, as the stress level increases the modulus increases accordingly, leading to decrease in the compliance. Fig. 11 also reveals that the difference between creep compliance for stress values around 0.1 and 0.5 MPa is more than the difference between the creep compliance for stress values around 2 and 3 MPa. This may be accounted to the fact that at higher stress values the material is strained beyond

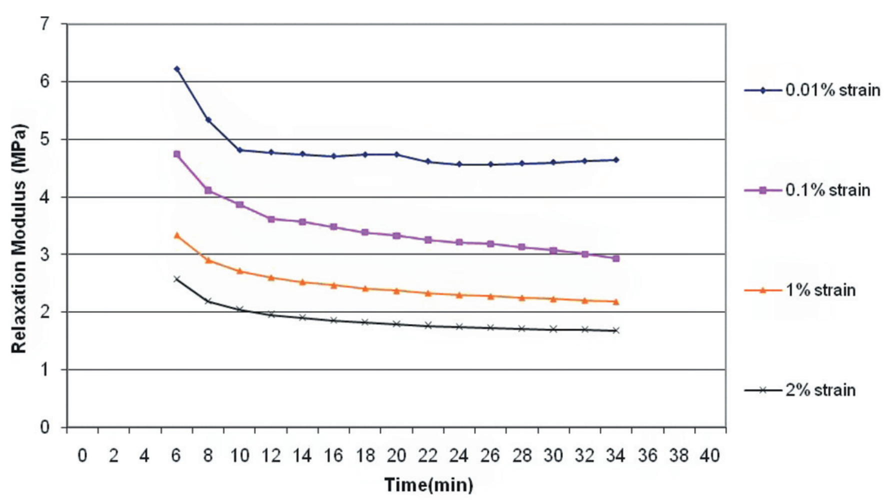

Figure 10. Relaxation modulus *versus* time for different strains at 35 ºC.

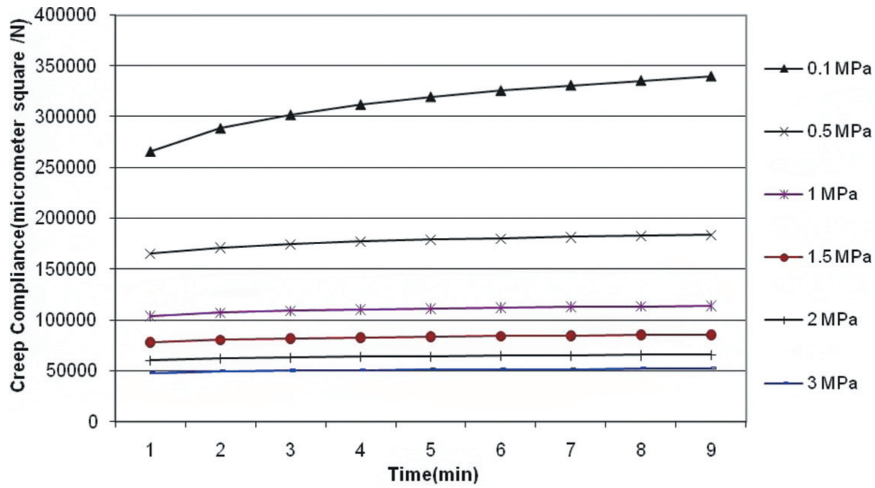

Figure 11. Creep compliance *versus* time in different stress levels at 35 ºC.

its viscoelastic limit, and a permanent set appears in the material so there is only marginal enhancement in modulus for higher stress values.

Influence of heating rate on the dynamic and transient properties

In order to determine the influence of heating rate, the tests were carried out using different heating rates, i.e., 1, 2, 5 and 10 (ºC/minutes) at three frequencies (3.5, 11, 35 Hz) from -80 to 80 ºC at a sinusoidal strain of 0.01%. The results obtained for the heating rates 1, 2 and 10 ºC/minutes are shown in Figs. 12 to 14. It is clear from such figures that as the heating rate increases, the curves shift towards the higher temperature side. The values for E', E", and tan delta obtained are higher at higher heating rates. Also, the value of Tg increases as the heating rate increases, as shown in Fig. 14. Tg at 1 ºC/minute heating rate is around -65 ºC, while at 2 ºC/minute heating rate is around -60 ºC. However, the tan δ peak (for the value of *Tg*) starts diminishing at a 5 ºC/minute heating rate. It is clear from Fig. 14 that at a 10 ºC/minute heating rate the sample does not show any peak in tan δ *versus* the temperature curve. This may be because the heat transfer from the furnace to the sample is not instantaneous, but depends on the conduction, convection, and radiation that can occur within the DMA instrument. Thus, a thermal lag is present between the sample and the furnace, and as higher the rate of heating, the greater this lag is likely to be present. Therefore, at a 10 ºC/minute heating rate, the sample is not able to acquire the required temperature in such a short term, thereby no peak is observed. Hence, lower heating rates (up to 3 ºC/minutes) are preferred to get accurate results.

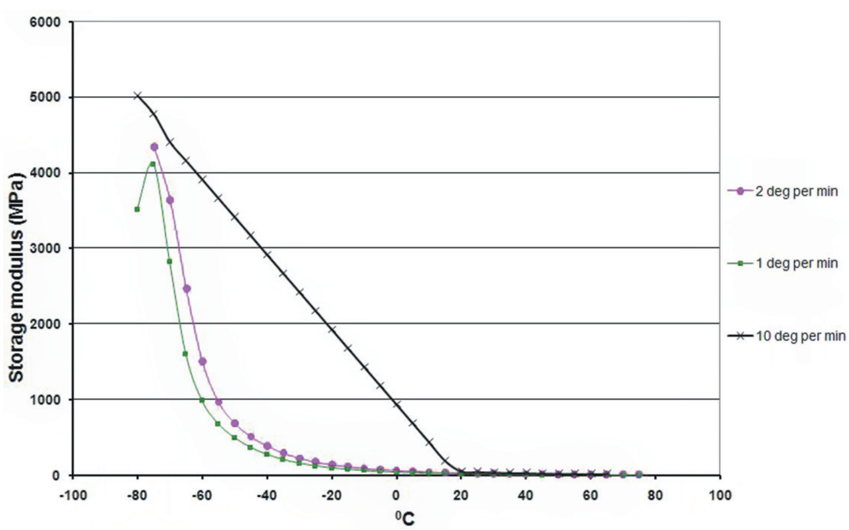

Figure 12. Influence of heating rate on storage modulus at 11 Hz frequency.

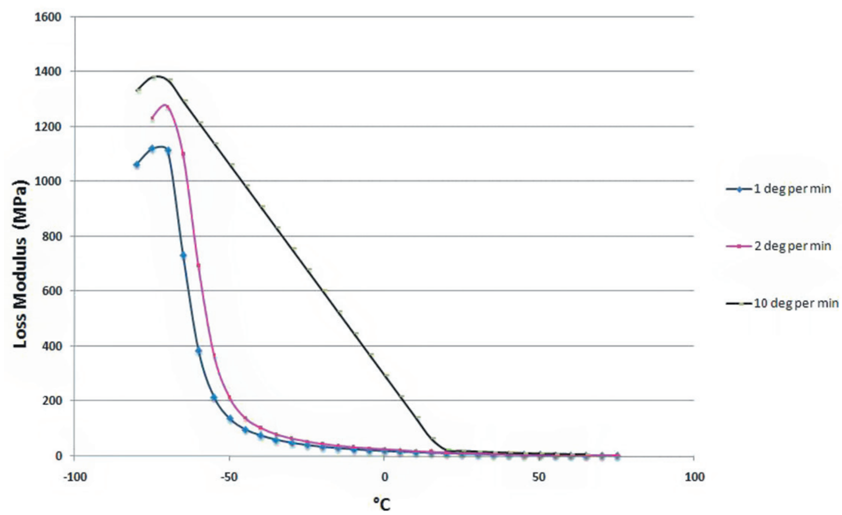

Figure 13. Influence of heating rate on loss modulus at 11 Hz frequency.

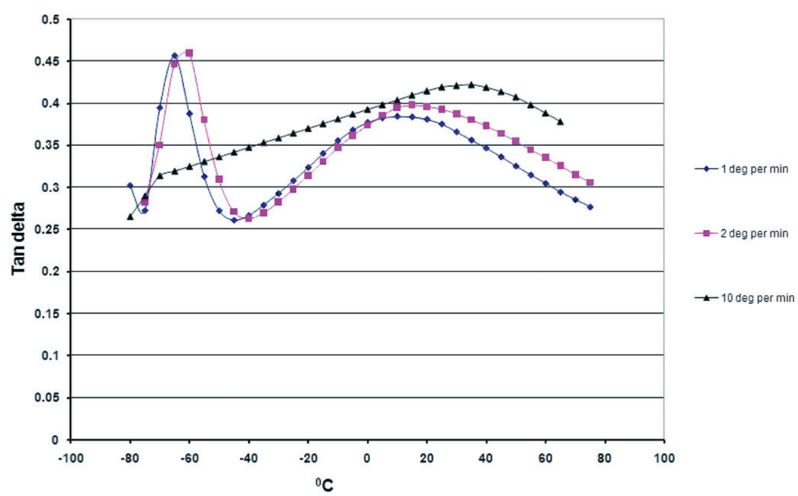

Figure 14. Influence of heating rate on tan delta and glass transition at 11 Hz frequency.

CONCLUSIONS

The influence of various parameters like temperature, frequency, strain/stress levels, heating rate on the dynamic, and transient properties of high burning rate composite propellant was studied successfully. The results revealed that experimental parameters have significant influence on DMA results. Data also showed that increase in the frequency has the same effect on the measured viscoelastic property as decrease in temperature or decrease in the time. An increase in the stress or a decrease in the temperature leads to decrease in the creep compliance, while an increase in the strain or increase in the temperature directs to decrease in the relaxation modulus. Also, an increase in the heating rate or in the frequency shifts DMA curves to higher temperatures. Very high heating rates (~10 ºC/minutes) get inaccurate results.

Therefore, to obtain accurate results, lower heating rates, which cannot be higher than 3 ºC/minutes, are preferred. Moreover, dynamic and transient properties determined at different parameters may be used to: characterize the propellant material, get the shift factors (a_T) from multifrequency strain curves at different temperatures using WLF model, develop the master curve for the propellant at the required reference temperature and be used to predict the performance of the propellant over a lifetime of its application.

ACKNOWLEDGEMENTS

Authors thank Swati Sachadeva for her whole hearted support during this study in the field of testing propellants parameters.

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