

## Article

# Dynamic mechanical analysis for characterization of solid rocket propellants – transitions in double base propellant

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## Abstract

Dynamic mechanical analysis has been applied to characterize frequency dependency of transitions observed in double base solid rocket propellant. Two transitions were observed one designated  $\alpha$  at temperature interval from 213 to 273 K with peak in  $\tan \delta$  around 258 K and second above room temperature designated  $\beta$  with peak in  $\tan \delta$  around 338 K. Apparent activation energies were calculated from peak and onset values of dynamic properties measured at frequencies from 0.1 to 20 Hz. The activation energies found for the  $\alpha$  transition were higher than for the  $\beta$  transition. Absolute values of these activation energies varied significantly depending on the dynamic property used for evaluation.

**Keywords:** DMA, Dynamic mechanical analysis, Propellant, DBP, Transition

## 1. Introduction

The usual way of characterization of mechanical properties of solid propellants relies on a series of tests at various temperatures and deformation rates. These tests are usually conducted using standard universal testing machines in tensile or compression configuration. With this approach one sample is used at discrete temperature and deformation rate. A scatter in an experimental data of such tests requires testing of at least 3 samples at each combination of deformation rate and temperature. The amount of samples required to make full picture of mechanical behavior is rather high. The tests in production as well as in routine controls are often reduced to a few temperatures - one at low temperatures, one at room temperature and one at high temperature - commonly 233, 293 and 333 K. This is completely insufficient for detection of minor changes in propellants in course of production or aging studies.

One of the methods that yields useful information on microstructural behavior of materials in broad temperature region is a dynamic mechanical analysis (DMA). Its advantage is in that it uses one small sample for the entire temperature interval of interest. Some authors even reported the use of the same sample repeatedly throughout the entire aging studies<sup>1)</sup>.

The mechanical spectra reflecting the mobility of molecular chains (or its parts) in double base propellants (DPB) are known to exhibit 2 or 3 transitions depending on the composition in the temperature range from 93 to 373 K. There has been some doubt about the interpretation of these transitions<sup>2)</sup>.

The DBP are generally believed to show ductile fracture at room temperature in standard tensile or compression tests<sup>3)</sup>. It has been pointed out by Ward<sup>4)</sup> that the brittle to ductile transition was originally believed to be related to mechanical relaxations and in particular with glass transition temperature. This was shown to be true for some polymers but failed with others. It was then proposed that brittle to ductile transition is in case of materials that exhibit more than one transition related to low temperature relaxations. This again worked only for some materials and according to Ward<sup>4)</sup> it was later shown that hypothesis about relationship between transition behavior and ductile to brittle transition has no general validity. The brittle to ductile transition occurs at relatively high strains, whereas DMA measurements must be carried out in linear region.

The purpose of this article is to demonstrate typical behavior of DBP in DMA temperature scan, show frequency dependence of both transitions and compare calcu-

lated apparent activation energies obtained from various dynamic properties.

## 2. Theoretical

### 2.1 Theory of DMA operation

In dynamic mechanical testing a periodical strain is applied to a sample and a resulting stress is measured. A viscoelastic material to which a sinusoidally varying strain is applied will after initial transition period exhibit a sinusoidal stress response, which can be divided into two components of modulus ( $E^*$  - sometimes denominated  $E_d$  or  $|E^*|$ ): real part representing the storage modulus ( $E'$ ) and an imaginary part representing viscous or damping component called a loss modulus ( $E''$ )<sup>5</sup>. This separation of modulus into two components describes the two independent processes within materials – elasticity (energy storage) and viscosity (energy dissipation). The ratio of lost modulus to storage modulus is called the loss tangent (or loss factor)  $\tan \delta = E'' / E'$ . The loss factor represents a degree to which the applied dynamic stress is damped.

### 2.2 Determination of activation energy

The apparent activation energy of relaxation transition can be determined in a number of different ways using DMA<sup>6</sup>. All methods require determination of matrix of dynamic data as a function of temperature and frequency. The usual approach is to hold either frequency or temperature constant and measure dynamic properties while varying temperature resp. frequency. It is also possible to use multiple wave instead of a sine wave and than decompose the resulting signal with the aim of fast Fourier transform (FFT).

The method used in this paper for determination of activation energy ( $E_a$ ) of transitions consists of a measurement of dynamic properties at various frequencies and constant heating rate. In this case  $E_a$  can be determined according to Arrhenius equation<sup>4,7</sup> (Equation 1) from the plot of inverse of the temperature  $1/T$  vs.  $\ln$  (log of base  $e$ ) of frequency<sup>8</sup>. An easy to identify point on the temperature dependence of dynamic property (peak of  $E''$ , peak of  $\tan \delta$ , onset of  $E'$  or  $E^*$ ) is chosen and appropriate temperature is evaluated (a constant activation energy through the process is expected).

In Arrhenius equation  $f$  stands for frequency (Hz),  $E_a$  for

activation energy ( $\text{J mol}^{-1}$ ),  $R$  for universal gas constant ( $8,314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and  $T$  for temperature (K).

$$\ln f = A - \frac{E_a}{RT} \tag{1}$$

## 3. Experimental

### 3.1 Instrumentation

Dynamic mechanical properties were measured on a dynamic mechanical analyzer DMA 04 DX produced by RMI. The measurements were carried out over the temperature range from 173 K up to 393 K with heating rate  $0.5 \text{ K min}^{-1}$  and frequencies 0.1; 0.2; 0.5; 1; 2; 5; 10; 20 and 50 Hz. Single cantilever fixture was used.

### 3.2 Sample preparation

All samples described herein were prepared from the same propellant grain. The samples in form of rectangular bars  $40 \times 10 \times 5$  (2) mm were prepared by die cutting of slices milled from the propellant grain. The propellant contained nitrocellulose (NC), nitroglycerine (NG), nitrotoluenes, ethylcentralite and some ballistic and technological modifiers.

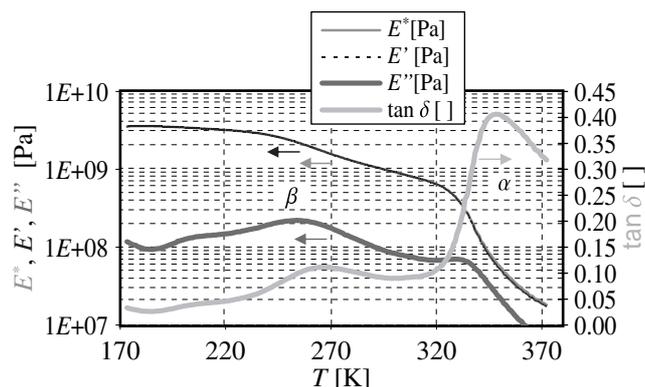


Fig. 1 Temperature scan of tested double base propellant at frequency 1 Hz, heating rate  $0.5 \text{ K min}^{-1}$ , single cantilever bending with constant amplitude of deformation  $\pm 0.03 \text{ mm}$ .

Table 1 Temperatures [K] of relaxation processes from onsets of  $E^*$ ,  $E'$  and peak values of  $\tan \delta$  and  $E''$ .

$f$ (Hz)	$E^*$ onset		$\tan \delta$ peak		$E'$ onset		$E''$ peak		$E''$ int. $\alpha$
	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$	
0.1	309.1	223.7	332.4	254.9	310.8	227.5	310.4	241.7	316.7
0.2	308.8	226.9	333.4	255.1	309.3	226.7	313.5	243.7	318.2
0.5	310.0	225.2	334.6	256.1	310.3	226.9	314.5	244.9	319.3
1	310.4	227.0	336.5	259.9	309.0	227.0	317.4	246.8	320.3
2	310.6	228.9	338.3	260.0	309.9	228.3	317.6	247.9	321.0
5	310.3	229.5	340.4	262.8	308.6	228.9	318.5	249.7	322.0
10	311.4	230.4	X345.2	265.7	311.0	229.4	320.6	251.1	323.0
20	312.0	229.0	XXX	266.7	311.6	231.0	320.7	252.7	323.5

X - misleading, XXX – impossible to determine

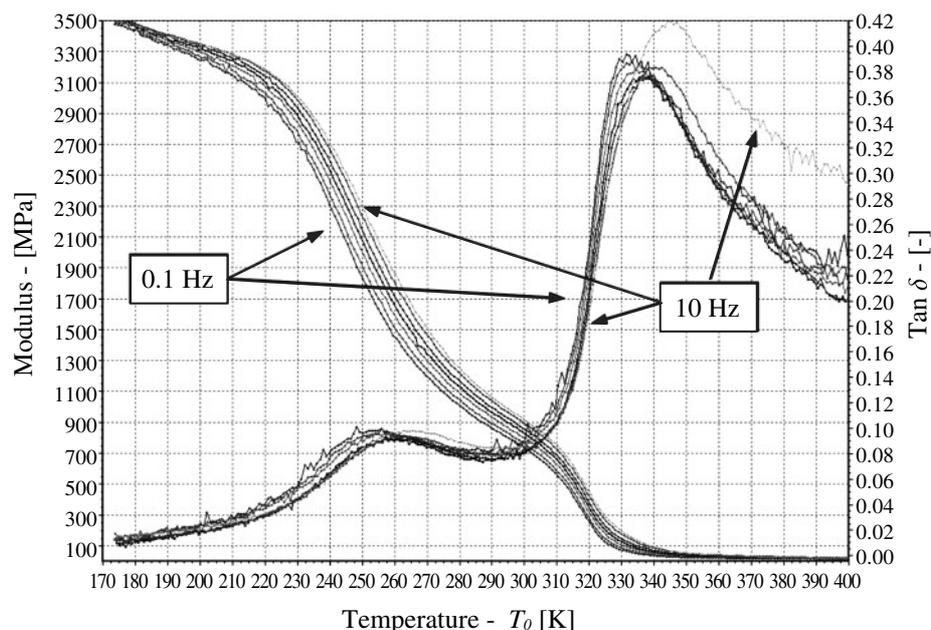


Fig. 2 Dynamic modulus and  $\tan \delta$  measured during temperature scan of tested double base propellant at frequencies 0.1, 0.2, 0.5, 1, 2, 5 and 10 Hz (20 Hz is not displayed), heating rate  $0.5 \text{ K min}^{-1}$ , single cantilever bending with constant amplitude of deformation  $\pm 0.03 \text{ mm}$ .

#### 4. Results and discussion

Two relaxations were observed in dynamic mechanical spectra of tested propellant which is in agreement with findings of most authors<sup>2), 9-11)</sup>. The relaxation at higher temperatures (above 323 K) was designated  $\alpha$ , the relaxation below room temperature was designated  $\beta$  in accordance with<sup>2)</sup> and are shown in Fig. 1. The  $\beta$  transition is often denominated as a glass transition and the  $T_\beta$  as a glass transition temperature, but we have some doubts about this and will therefore denominate it simply  $\beta$  without ambition to explain its origin here.

The temperature regions of both  $\alpha$  and  $\beta$  transitions were found to be heating rate as well as frequency dependent. This is in agreement with data presented by<sup>9)</sup> although they conclude otherwise. The effect of heating rate was measured but will not be discussed in this contribution.

The frequency dependency was determined from temperature scan at heating rate  $0.5 \text{ K min}^{-1}$ . It was found that both  $\alpha$  and  $\beta$  relaxations are frequency dependent as can be seen from Fig. 2.

The temperatures of the transitions determined from  $E^*$ ,  $E'$ ,  $E''$  or  $\tan \delta$  at measured frequencies are summarized in

Table 1. The values of  $E^*$  and  $E'$  onsets are difficult to determine (user dependent) and therefore show higher scatter. Since the  $\alpha$  peak of  $E''$  was not sharp to give a clear maximum we decided to test intersection point of tangents (Fig. 3) as another criterion. Values determined in this way are denominated “ $E''$  int.” in Table 1 and 2.

Results of measurements at 50 Hz were found to be totally out of the expected range probably due to a resonance and were therefore omitted from the calculations. The peak temperatures of  $\tan \delta$  at 10 Hz was influenced by unknown factor and shifted to higher temperatures. A sharp drop to negative values instead of peak was observed at 20 Hz and higher temperatures. The  $\tan \delta$   $\alpha$ -peaks were therefore also excluded from the calculations. The increase in magnitude was also observed much higher than for the other frequencies. The values of transition temperatures increase with increasing frequency independently of the parameter evaluated.

Measurements at linear heating rate are sometimes damned because of the temperature change during cycle. We have reported in our previous paper that isothermal measurements are superior if very small temperature steps

Table 2 Slopes, activation energies and determination coefficients calculated from onsets of  $E^*$  and  $E'$  and peaks of  $\tan \delta$  and  $E''$ .

	$E^*$ onset		$\tan \delta$ peak		$E'$ onset		$E''$ peak		$E''$ int. $\alpha$
	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$	$\alpha$	$\beta$	
slope [K]	-158544	-36832	-53351	-26890	x	-57542	-50331	-30189	-80868
$E_a$ [kJ mol <sup>-1</sup> ]	1318	306	444	224	x	478	418	251	672
$R^2$	0.8807	0.7688	0.9353	0.962	x	0.7726	0.9397	0.9961	0.9962

X - impossible to determine (too much scatter)

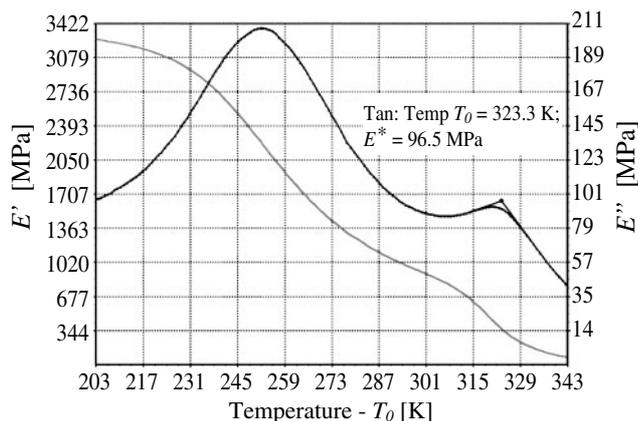


Fig. 3 Determination of  $E''$  int. values for temperature scan presented on temperature scan at 20 Hz, single cantilever bending with constant amplitude of deformation  $\pm 0.03$  mm.

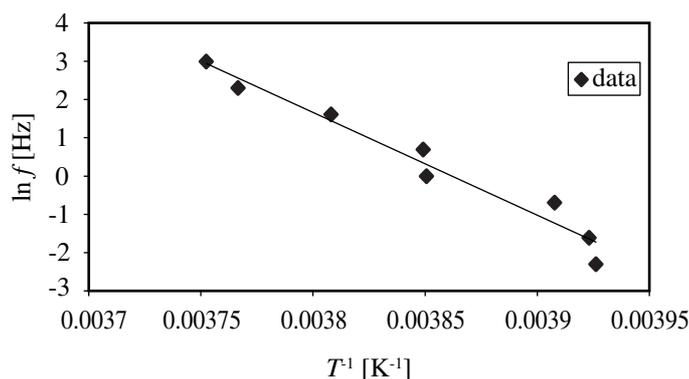


Fig. 4 Plot of  $\ln f$  vs.  $1/T_\alpha$  based on temperatures from the peak of  $\tan \delta$ . The line represents linear least square fit.

are used<sup>6)</sup>. It is evident from values in Table 1 that standard 10 K step would be absolutely insufficient in this case.

The values presented in Table 1 were used to calculate apparent activation energies of  $\alpha$  and  $\beta$  transitions. The activation energy related to particular transition was obtained by multiplying the slopes of the  $1/T$  vs.  $\ln f$  plot with universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ). Since transition temperatures depend on selected criterion the slopes differ for  $\tan \delta$  peak,  $E''$  peak,  $E^*$  onset and  $E'$  onset. The resulting plot of  $\ln f$  as a dependency of  $1/T$  for  $\alpha$  transition determined from  $\tan \delta$  peaks is presented in Fig. 3 for demonstration. In this case the slope was determined to be  $-26890 \text{ K}$ .

The results calculated from other dynamic parameters are summarized in Table 2. Very high scatter in the results of values calculated from onsets was observed (values of onsets of  $E'$  for  $\alpha$  transition were not even possible to evaluate). The calculated activation energies for  $\alpha$  transition are in all cases higher than those calculated for  $\beta$  relaxation.

## 5. Conclusion

The results obtained from the measurement of typical double base propellant clearly indicate, that there are two transitions in the mechanical spectra of this propellant - one in the region below room temperature and one above room temperature. They are both frequency dependent with the activation energies being higher for high temperature  $\alpha$  transition.

The absolute values of activation energies calculated from onsets of  $E^*$  and  $E'$  are believed to be less reliable than the ones from peak values due to difficulties with precise onset determination and therefore higher scatter in temperatures. Difficulty with determination of temperature corresponding to the  $E''$  maximum for the  $\alpha$  relaxation resulted in application of method of intersecting tangents. The dependency of  $\ln f$  on inverse of temperatures found by this method gives excellent coefficient of determination but the activation energy is higher compared to the one from  $E''$  peak.

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