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# Determination of Glass Transition Temperature of Double-Base Rocket Propellants with the Use of Dynamic Mechanical Analysis

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**Abstract.** The paper presents results of Dynamic Mechanical Analysis (DMA) of double-base (DB) solid rocket propellant with special attention paid to determining the glass transition temperature. The presented experiments were carried out with the use of Netzsch DMA 242C analyzer with the dual cantilever operation mode. Advantages and drawbacks of the DMA method, measured values, as well as important characteristics of solid double-base rocket propellants were briefly described. Obtained values of the storage modulus $E'$, the loss modulus $E''$, and $\tan\delta$ were represented in dependence on temperature. The glass transition temperature of the tested propellant was determined according to NATO standard 4540 [7] at the peak of the loss modulus curve.

**Keywords:** Dynamic Mechanical Analysis, glass transition, double-base rocket propellant

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## 1. INTRODUCTION

Solid rocket propellants can be assigned to the group of viscoelastic polymeric materials with their mechanical properties being similar to that of general polymers [1, 2]. Double-base (DB) homogeneous propellants are produced from the mixture of nitrocellulose (NC: 50-60%) and nitroglycerine (NG: 30-49%) [11] with small amounts of plasticizers, stabilizers, and compounds influencing combustion [3]. The propellants are formed with the use of hydraulic press and afterwards machined to reach a desired shape [1]. The DB solid rocket propellants are homogeneous, rigid materials therefore being relatively easy to machine. Mechanical properties of DB propellants influence their proper functioning and therefore must be well studied [2]. These properties change under conditions of their storage and operation, and they are affected by chemical reactions (e.g. decomposition of NC and NG), physical process such as diffusion of additives (e.g. plasticizers), as well as mechanical loads (e.g. vibration loads, thermal stress due to cyclic heating and cooling) [2-4]. These factors have influence on the viscoelastic properties of solid propellants such us elasticity modulus, tensile strength or glass transition temperature. The change of mechanical properties can result in the formation of cracks and voids in the material leading to an increase in burning surface of the propellant causing malfunction of the rocket motor or, in the worst case explosion [2-4]. An effective and reliable tool for determining mechanical properties of solid propellants is Dynamic Mechanical Analysis (DMA). In the dynamic mechanical measurement, a sinusoidal oscillating force causes a sinusoidal stress to be applied to the sample and the result is sinusoidal strain [5]. DMA enables us to measure the mechanical properties of samples as a function of different variables such as time, temperature or frequency of the applied force. As the method uses relatively small forces, the sample responds to each sinusoidal oscillation in the same way reducing the number of samples required for the experiment. That is of special importance in case of explosive samples such as solid rocket propellants [12]. The results obtained from typical DMA measurement are the dynamic storage modulus $E'$ which represents the elastic properties of material, the dynamic loss modulus $E''$ representing viscous properties, and $\tan\delta$ representing damping of the material ($E''/E'$) [2, 3]. A typical DMA curve of $E'$, $E''$, and $\tan\delta$ dependence on temperature for the DB rocket propellant is shown in Figure 1.

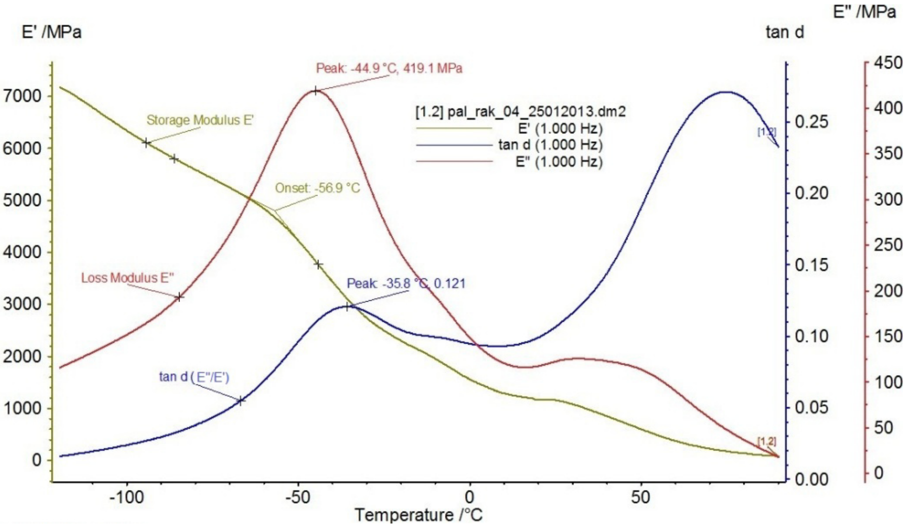


Fig. 1. DMA test result for double-base rocket propellant [3]

The advantage of using DMA for solid rocket propellant testing is the fact that the method doesn't cause critical damage to the sample and therefore it can be evaluated again using different variables. In addition to this, DMA method provides in one experiment both, temperature and frequency dependence on the measured mechanical properties. However, on the other hand, the inability of DMA to apply high destructive forces makes it impossible to determine the failure stress of the propellant [12]. Dynamic Mechanical Analysis is considered a most sensitive method for determination of the glass transition temperature. The glass transition ($T_g$) is considered a major phase transition in polymers resulting in significant change in physical and mechanical properties of the material as it goes from rigid glassy to rubbery state. The glass transition temperature is affected by chemical composition and in case of solid rocket propellants by the amount of plasticizers. In the DB rocket propellants, nitrocellulose is plasticized by nitroglycerine, therefore the concentration of nitroglycerine and NC/NG ratio has a significant influence on the mechanical properties as well as on the transition temperatures [12]. It is however difficult to precisely connect the transition temperature with one exact spot as there are a few ways of determining $T_g$ from the DMA plot basing on the characteristic points. This can be done by the onset of the $E'$ curve, peak of the $E''$ or peak of the $\tan\delta$ [5]. In Figure 1, these points refer to the values of –56.9°C, –44.9°C, and –35.8°C, respectively. It is a well-known fact, that glass transition does not occur in a strictly defined point, but within a region [6] which in that case is the difference between $E'$ curve onset (–56.9°C) and the first peak of the $\tan\delta$ (−35.8°C) which amounts −21.1°C. As one can see, the peak of the loss modulus is located in the central part of that region at –45.0°C.

According to literature [6], as well as relevant NATO standard [7], $T_g$ is defined by the maximum of loss modulus curve. The glass transition temperature of solid rocket propellants, determined by DMA, is particularly important in case of their resistance to dynamic loads during ignition and rocket take-off at very low temperatures [8]. Depending on the type of material and required properties, it defines the upper or lower limit of operating.

## 2. EXPERIMENTAL PROCEDURE

The DMA experiments were carried out with the use of Netzsch DMA 242 C analyzer in dual-cantilever mode with sample holder 2 × 16 mm. The measurements were conducted within the temperature range from –120°C to +80°C, at heating rate of 2 K/min and with load frequency of 1 Hz, recommended by relevant standard [7]. According to Netzsch DMA recommendation given in manual [9], the dynamic force should not exceed 8 N and the static force should be set to zero. The amplitude of test sample deformation was established at 30 μm.

A sample of homogeneous double-base rocket propellant Bazalt 2a with density 1.59 g/cm$^3$ was carefully processed with sand paper to achieve desirable length, width, and thickness. Previous work of the authors has proven that sample thickness is a key factor in case of running a proper DMA measurement as the experiment can only by reliable when the established amplitude is reached within the complete temperature range [3]. Samples with relatively high thickness were too rigid at temperatures below 0°C, for the selected amplitude to be achieved. For that reason, sample of the Bazalt 2a propellant was processed to the thickness value of 1.6 mm. Strain in a dual cantilever clamps is explained in Figure 2.

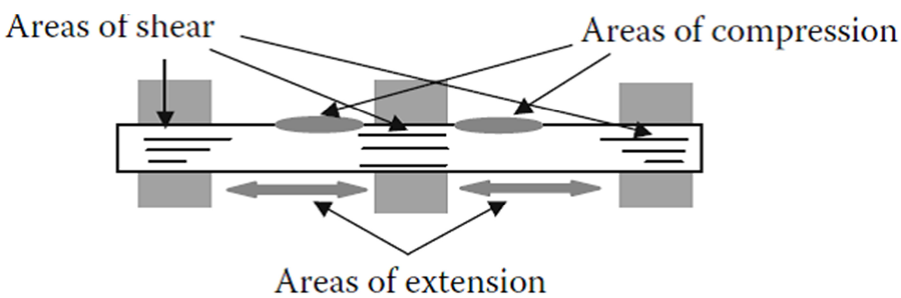


Fig. 2. Strain and shear regions in dual cantilever mode [5]

In the dual cantilever test mode, the sample is held firmly by both ends and subjected to sinusoidal force with the use of the pushrod.

The shearing strain that occurs at the ends and centre of sample is due to the stiff cantilever clamping.

This has an effect on the properties measured which may differ from the ones obtained by 3-point bending technique. Special attention must also be paid to the end clamps to be tighten evenly to prevent twisting or distortion [5]. DMA input parameters' values such as static and dynamic force were accepted according to Netzsch recommendation with respect to dual cantilever mode. The assumed amplitude was earlier chosen using trial and error method in order to fulfil the requirement of maintaining its value on the constant level throughout the whole temperature range. The sample dimensions, experimental conditions, as well as propellants chemical composition [10] are listed in Table 1.

Table 1. Material and measurement characteristics

<table>
<tr><th colspan="5">Sample characteristics</th></tr>
<tr><td colspan="2">Thickness/width/length [mm]</td><td>Density [g/cm$^3$]</td><td colspan="2">Chemical Composition</td></tr>
<tr><td colspan="2">1.59/10.4/59.6</td><td>1.59</td><td colspan="2">NC: 56.8%, NG: 36.3 %, EC*: 2.4%, vaseline: 0.4%, graphite: 0.1%, $Pb_3O_4$: 0.5%, $NiO_2$: 0.5%, SCuPb: 3.0% [9]</td></tr>
<tr><th colspan="5">DMA Input parameters</th></tr>
<tr><td>Temp. range, [°C]</td><td>Heating rate, [K/min]</td><td>Static Force, [N]</td><td>Dynamic Force, [N]</td><td>Amplitude, [µm]</td></tr>
<tr><td>–120÷+80</td><td>2</td><td>0</td><td>7.5</td><td>30</td></tr>
</table>

*ethyl centralite

## 3. RESULTS AND DISCUSSION

Results of the DMA tests of Bazalt 2a double-base rocket propellant, as the storage modulus $E'$, the loss modulus $E''$, and $\tan\delta$ dependence on temperature are shown in Figure 3.

The storage modulus $E'$, the loss modulus $E''$, and the $\tan\delta$ were received in a single DMA measurement. As one can see, the storage modulus $E'$ exhibits a significant decrease at temperature –53.2°C (onset temperature) which is related to the softening of the material. The loss modulus $E''$ shows characteristic peak at –42.3°C with the value of 366.8 MPa.

The peak of the loss modulus is most often referred to as the glass transition temperature $T_g$, however, it is also known that transition from the glassy to viscoelastic state does not occur in a strictly defined point but within a certain region [6].

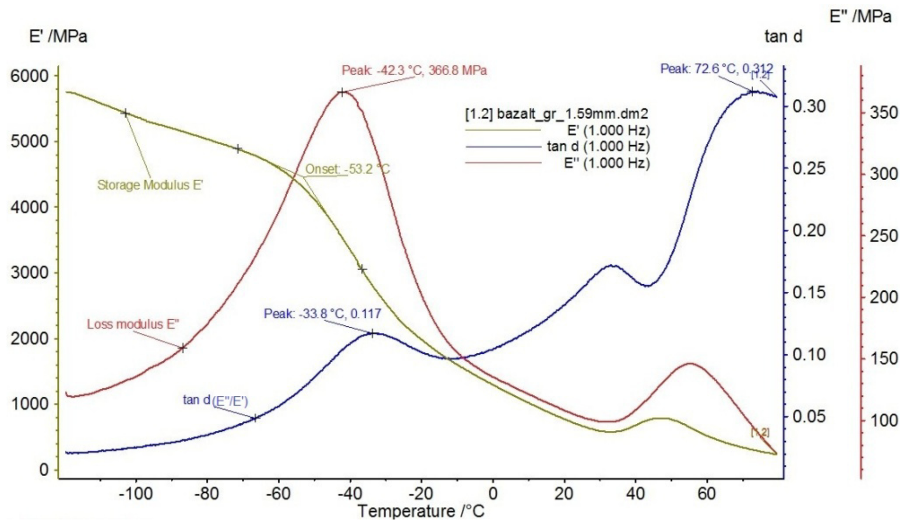


Fig. 3. Results of DMA tests of Bazalt 2a double-base propellant

The tan$\delta$ curve has two well recognizable maximums at –33.8°C ($\beta$-transition) which corresponds to the glass transition region, and at 72.6°C ($\alpha$-transition) which is connected with the further softening of the material. The $\alpha$ and $\beta$ thermal transitions are consistent with the literature data [12] ($\alpha$-transition from 110°C to 55°C, $\beta$-transition from 15°C to –33°C). According to the literature [5], there are at least few methods of glass transition determination from the results obtained by Dynamic Mechanical Analysis. In order to give complete information on the value of $T_g$, frequency of measurement, heating rate of the experiment, and amplitude established by the user must also be mentioned. Another fact which must be considered in case of DMA results evaluation is their dependence on frequency, heating rate or amplitude applied [9]. Further, DMA test should be conducted to investigate those phenomena. Additionally, the dependence of the complex total amplitude $A$ and the dynamic force $F$_dyn on temperature is shown in Figure 4.

As one can notice in Figure 4, the amplitude of 30 μm was achieved throughout the experiment and for that reason the DMA results can be considered as reliable ones. The dynamic force required for the sample to be bended to the established amplitude decreases as the temperature increases and the sample becomes soft. The programmed dynamic force of 7.5 N was not exceeded during the test. The force sufficient to achieve the amplitude of 30 μm in a temperature range from –120°C to +40°C was in a range from 2.8 N to 4.2 N. It is therefore possible to program a higher amplitude value for the Bazalt 2a propellant which will result in more accurate measurement of its dynamic properties.

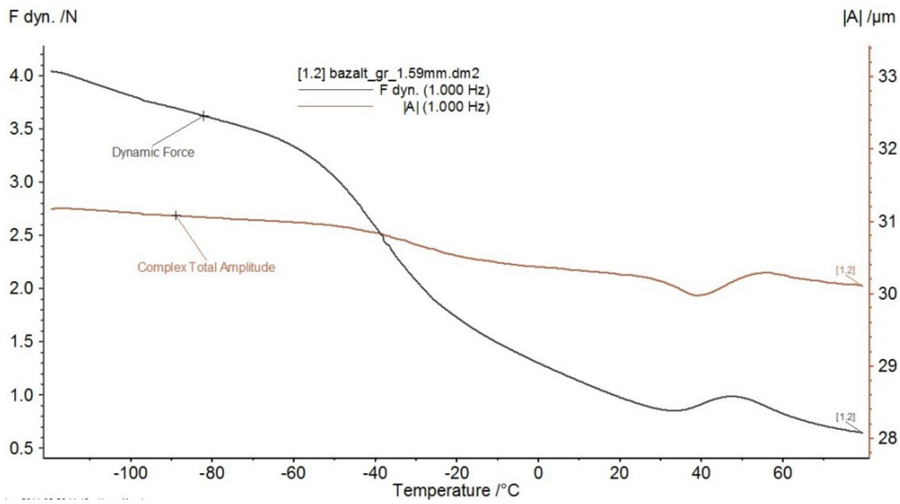


Fig. 4. Total amplitude and dynamic force dependence on temperature

## 4. CONCLUSIONS

1. A sample of solid double-base rocket propellant Bazalt 2a has been tested with the use of Dynamic Mechanical Analysis. The results can be considered reliable as the established amplitude of 30 µm was achieved in the complete temperature range.
2. The glass transition temperature has been determined according to relevant NATO standard (STANAG 4540) as the point of the loss modulus *E*" peak at –41.2°C. The value was measured with the following input parameters: load frequency of 1 Hz, heating rate of 2 K/min, total deformation amplitude of 30 µm with the dual-cantilever mode. The glass transition temperature obtained can define the lower limit of operation for the Bazalt 2a rocket propellant.
3. The experiments should be repeated for different amplitudes (20, 40 µm) in order to increase accuracy of measurements.
4. Dynamic Mechanical Analysis has proved an effective and safe method for testing solid double-base rocket propellants. A great amount of information was collected from a single measurement. The method is non-destructive and therefore allows the sample to be tested again with different input parameters. Relatively small applied stress along with small sample size make the method safe for operators and the device in case of sample ignition.

5. In order to confirm the DMA results of double-base rocket propellants, additional parameters including specific heat, thermal expansion, and thermal diffusion should be carried out. Investigation of these thermophysical parameters will be accomplished with the use of Differential Scanning Calorimetry, Dilatometry, and also KD2 Pro apparatus.

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