



Dynamic mechanical analysis of double base rocket propellants

MARCIN CEGŁA¹, JACEK BORKOWSKI¹,
JANUSZ ZMYWACZYK, PIOTR KONIORCZYK

¹Military Institute of Armament Technology,
7 Wyszynskiego Str., 05-220 Zielonka, Poland, ceglam@witu.mil.pl
Military University of Technology, Faculty of Mechatronics and Aerospace,
2 Kaliskiego Str., 00-908 Warsaw, Poland, janusz.zmywaczyk@wat.edu.pl

Abstract. The article presents dynamic mechanical analysis (DMA) for solid rocket propellants testing. Principles of operation and measured values are briefly described. The authors refer to the previous research of PTFE material and literature data providing information about proper experimental conditions and influence of measurement frequency, load amplitude, and heating rate on the results of DMA tests. The experimental results of solid double-base rocket propellant testing obtained on the Netzsch DMA 242 device are presented. Mechanical properties such as the dynamic storage modulus E' , the dynamic loss modulus E'' and $\tan(\delta)$ were measured within temperature range from (-120°C) to $(+90^{\circ}\text{C})$ at the heating rate of 1 K/min. The test sample was subjected to a dual cantilever multi-frequency test. Special attention was paid to determination of the glass transition temperature of the tested propellant in reference to the NATO standardization agreement 4540 as well as influence of the measurement frequency on the glass transition.

Keywords: Dynamic mechanical analysis, solid rocket propellants, glass transition temperature.

DOI: 10.5604/12345865.1197970

1. Introduction and previous research

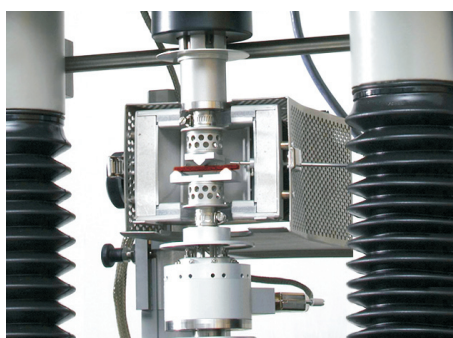
1.1. Dynamic Mechanical Analysis

Dynamic mechanical analysis is a powerful tool for conducting complex thermo-mechanical material testing. DMA allows for specification of the strength

of composite and polymeric materials under dynamic loads and their ability to irreversibly dissipate mechanical energy supplied during the periodic loads [1]. During the testing procedure, an oscillating force is applied to the investigated sample generating in-phase and out-of-phase strains. The phase shift between the applied stress and the resultant strain is determined by the phase angle δ . The dynamic storage modulus E' , the dynamic loss modulus E'' and $\tan(\delta)$ are simultaneously measured as a function of time, frequency of oscillation and temperature [1, 2]. The dynamic storage modulus E' represents the elastic properties of the material, while the dynamic loss modulus E'' represents its viscous properties [1]. In relation to the measurement cycles, these modules are proportional to the maximum energy stored and dissipated during the cycle [5]. The storage modulus is in phase with the resultant strain and the loss modulus is ninety degrees out of strain [6]. The ratio between E'' and E' given by the $\tan(\delta)$ is the damping and indicates the efficiency of the material in losing energy due to molecular rearrangements and internal friction [1]. Dynamic mechanical analysis is also suitable for determination of the glass transition temperature T_g which is 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 [8]. It is a significant advantage of the DMA method that it provides in one experiment both, temperature and frequency dependence on the measured mechanical properties. The DMA devices appear in different sizes and testing capabilities but they all share the common principle of operation [2, 3, 4]. Examples of DMA instruments are presented in Fig. 1.



TA Instruments Q800 DMA [3]



Metravib DMA +100 Thermal chamber [4]

Fig. 1. DMA devices

In previous work, the authors have tested the PTFE as a reference material in the experimental conditions similar to those that would have been used with solid rocket propellants [7]. The PTFE has stable thermal properties in the wide temperature range and can therefore be used for preliminary experiments with respect

to expensive explosive material. The sample was tested with the use of Netzsch DMA 242C apparatus and the dual-cantilever clamps. The temperature range was from -150°C to $+150^{\circ}\text{C}$, the heating/cooling rate was set to 1 K/min and the amplitude of the applied force was set to $40\ \mu\text{m}$. Figure 2 presents the dynamic force and total complex amplitude dependence on temperature.

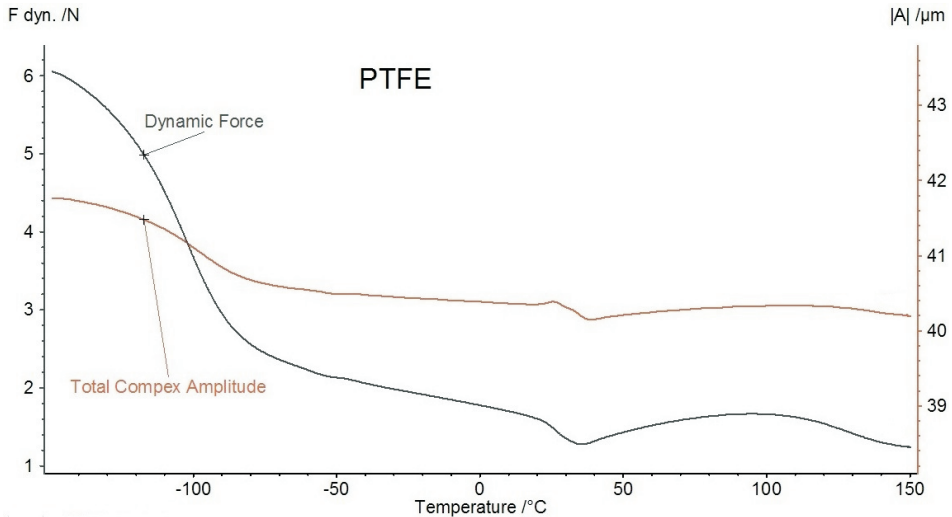


Fig. 2. DMA analysis of PTFE material [7]

It confirms the results reliable as the total complex amplitude of $40\ \mu\text{m}$ was maintained in the complete temperature range and the set dynamic force did not exceed the maximum value of 7.5 N [3].

Along with the experimental conditions, it is important to consider the influence of frequency, heating rate, and amplitude on the results of DMA experiment and glass transition temperature determination. The literature data gives information about the influence of input parameters on the results of dynamic mechanical analysis [2, 10]. Higher frequency of the applied force results in higher values of storage and loss modulus [2]. The possible cause of this phenomenon may be the fact of freezing the chain movements which leads to increase in material stiffness and at the same time the modulus values [10]. Increasing the frequency induces the elastic-like behaviour of the material while using lower frequencies gives time to soften and loose elasticity [1]. Increasing the heating rate will also increase the values of E' , E'' , and T_g . For accurate measurements it is recommended to use lower heating rates [10]. Another factor which should be taken into account is thermal expansion of polymeric samples during temperature changes. An ability of the DMA device to compensate these changes is essential for obtaining correct results [6]. The advantage of using DMA for

solid rocket propellant testing is the fact that the method does not damage the sample and therefore it can be evaluated again using different variables. On the other hand, the inability of DMA to apply high destructive forces makes it impossible to determine the failure stress of the propellant [14].

1.2. Solid rocket propellants

Solid rocket propellants can be divided into two general types considering chemical content as well as connection between ingredients. The homogeneous propellants have a uniform physical structure consisting of chemically bonded fuel and oxidizer ingredients forming a single chemical structure while heterogeneous propellants are mixture of a solid oxidizer in most cases ammonium perchlorate (AP) or ammonium nitrate (AN) and liquid combustible substances (binders) [9, 10]. Typical double base rocket propellants, consist mainly of nitrocellulose (NC) 50-60% and nitroglycerine (NG) 30-49% [9] while some authors suggest that the NG content ranges from 19 to 46% [14].

Due to their nature it is important to know thermal and mechanical properties of solid rocket propellants which may affect the proper operation of the rocket engines. The properties of propellant may change during long storage time and affect rocket motors behaviour during possible operational use [11]. The glass transition temperature is the key factor influencing the behaviour of solid propellants and DMA is the recommended method of its determination. It is underlined that T_g corresponds to the phase transition temperature of the material with effects on mechanical properties and therefore it should be tested with mechanical technique [6]. The literature data points out a few ways of determining the glass transition temperature 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 $\tan(\delta)$ [1]. According to the STANAG agreement 4540, the T_g should be obtained from the maximum peak of the loss modulus curve E'' . 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 [12]. The change of mechanical properties due to phase transition in the material can result in the formation of cracks and voids leading to an uncontrolled increase in burning surface of the propellant causing malfunction of the rocket motor or, in the worst case explosion [13].

2. Experimental procedure

Sample of double base solid rocket propellant in which main components are nitrocellulose and nitroglycerine (NC: 52.5%, NG: 28.6%) was tested with the use

of Netzsch DMA 242C analyzer with sample holder 2×16 mm in dual cantilever mode within temperature range from (-120°C) to $(+90^{\circ}\text{C})$. Cuboid samples were processed to required thickness of about 1.5 mm with the use of abrasive paper. Previous research of the authors has proven that the DMA results for thicker samples cannot be considered reliable within the glass transition region as they are too rigid to deform [7]. The investigated sample had the dimensions of $60 \times 10 \times 1.5$ mm. The effective length considered for the results is a constant distance between supports (2×16 mm). The sample was tested in a multi-frequency mode with the frequencies of 0.1, 0.5, 1, 3.33, 5, and 10 Hz. The heating rate of 1 K/min was used according to previous research and literature [2, 7, 8]. The sample was conditioned in -120°C for 20 min prior to the starting of the measurement. Dual cantilever clamps introduce shearing component to the distortion and increase the stress required for the displacement of the sample. Special attention must be paid for the clamps to be tightened evenly with similar forces to prevent twisting or distortion [1]. Dual-cantilever clamps and distribution of stress on the sample are shown in Fig. 3.

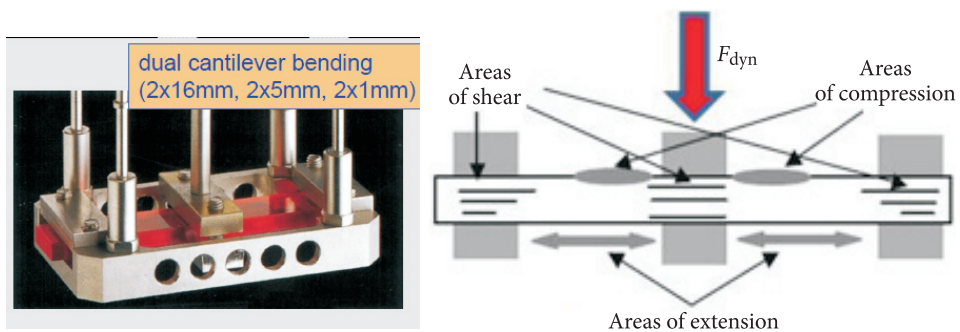


Fig. 3. Dual cantilever clamps and stress distribution [1, 2]

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 [2, 7, 8].

3. Results and discussion

The DMA data is presented as a temperature dependence of dynamic mechanical properties such as storage modulus, loss modulus, and $\tan(\delta)$. The results for the deformation frequency of 1 Hz are shown in Fig. 4. It is difficult to precisely

connect the glass transition temperature with one exact peak so, it is therefore more reliable to refer it to the glass transition region.

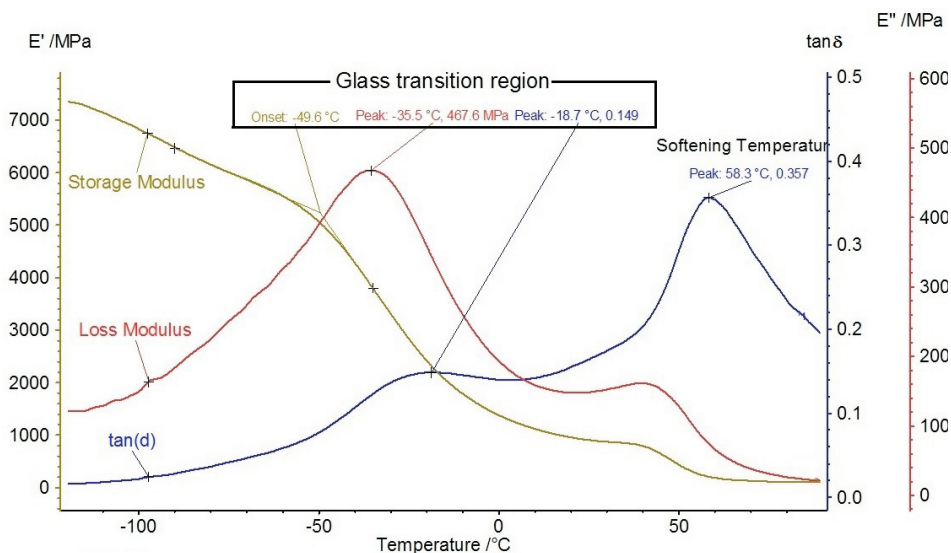


Fig. 4. Storage modulus, loss modulus, and $\tan(\delta)$ of the tested sample vs. temperature at 1 Hz

The glass transition region is limited by the onset of the storage modulus and the first peak of the $\tan(\delta)$. The second peak on the $\tan(\delta)$ marks the beginning of material softening [8]. The glass transition temperature value is obtained from the peak of the loss modulus E'' measuring at -35.5°C , according to STANAG 4540 agreement. It recommends using the frequencies of 0.1, 1, and 10 Hz but for data reduction purposes the result should be presented for the frequency of 1 Hz [6]. Temperature dependence of dynamic loss modulus for three set frequencies is presented in Fig. 5.

It must be mentioned that the glass transition temperature is affected by chemical composition and in case of solid rocket propellants by the amount of plasticizers. In the double-base 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 [14].

Additionally, the activation energy for the glass transition was calculated with the use of Netzsch DMA software. The calculation is based on the $\tan(\delta)$ peaks determined at different frequencies and the Arrhenius relationship. According to literature, the activation energy calculation is more reliable based on the $\tan(\delta)$ than on the loss modulus E'' [15].

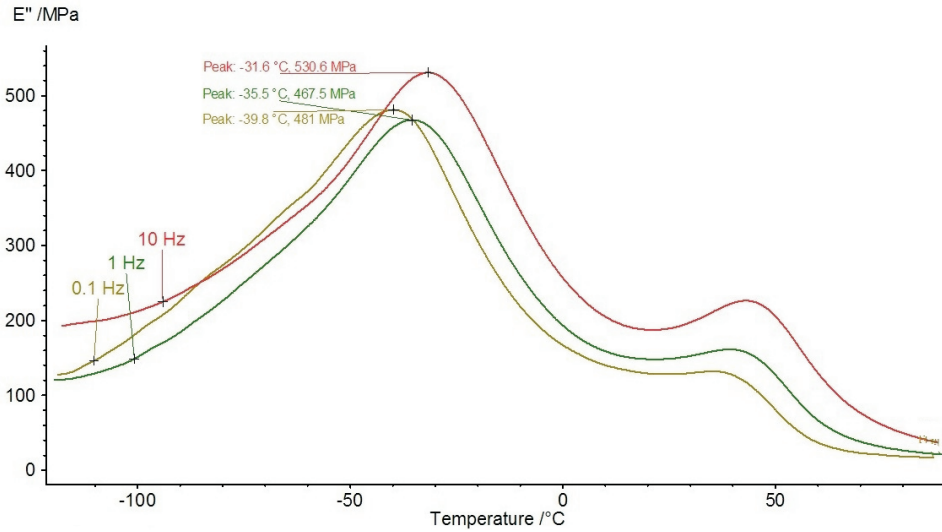


Fig. 5. Glass transition determination acc. to STANAG 4540 agreement

The temperature dependence of E' , E'' , and $\tan(\delta)$ can also be used to determine the temperature range of safe operation of the propellant ranging from the glass transition temperature and the softening temperature. Due to the increase in stiffness at the glass transition point, cracks and voids can appear what leads to uncontrolled

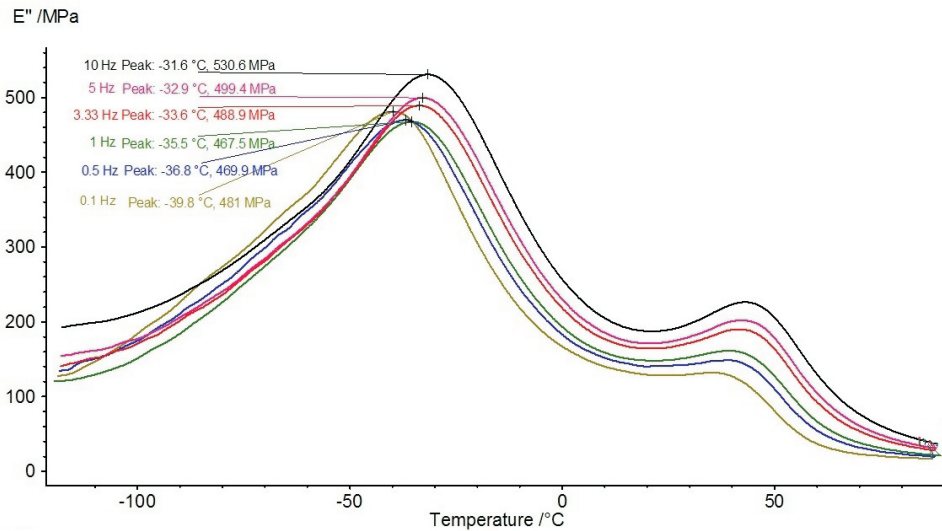


Fig. 6. The loss modulus dependence on temperature for all tested frequencies

increase in burning surface of the propellant. This can result in rocket motor overload during ignition and in the worst case in explosion. When exceeding the upper temperature limit, the propellant insert will not maintain its shape during prolonged storage as well as under dynamic loads during rocket take-off [8].

The loss modulus dependence on temperature in a multi-frequency test mode confirms the previously discussed increase in the glass transition temperature with the growth of applied frequency. The mentioned dependence is shown in Fig. 6 and the activation energy for the glass transition is shown in Fig. 7.

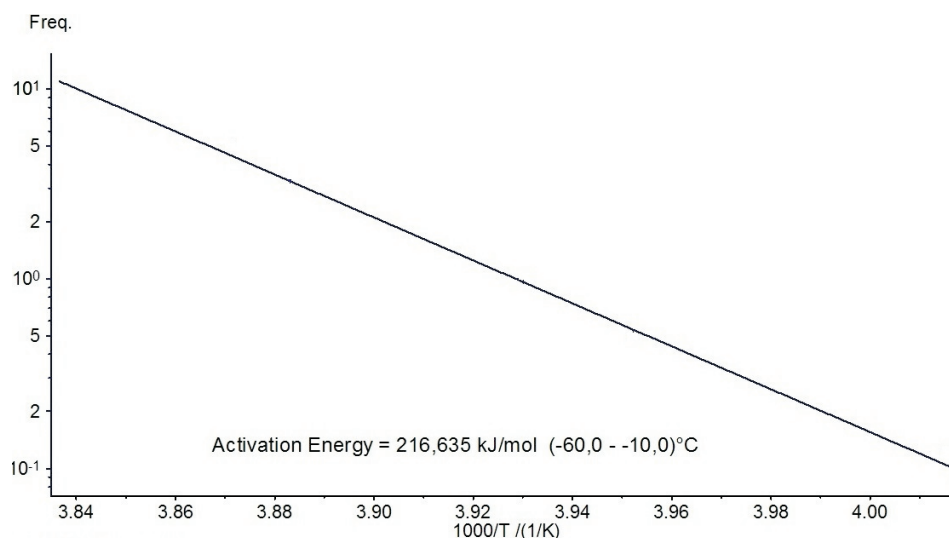


Fig. 7. Activation energy for glass transition based on the $\tan(\delta)$ peak and the Arrhenius relationship

4. Conclusions

1. A sample of solid double-base rocket propellant was tested with the use of Dynamic Mechanical Analyser in the multi-frequency mode. The results can be considered reliable as the established deformation amplitude of 30 μm was achieved in the complete temperature range.
2. Influence of frequency on the value of the glass transition temperature was shown. The increase of T_g was observed with the growth of frequency.
3. The glass transition temperature $T_g = -35.5^\circ\text{C}$ of the tested propellant was determined according to STANAG 4540 agreement as a temperature corresponding to the peak of the loss modulus curve E'' or the frequency of 1 Hz. The value was measured with the following input parameters: frequency of 1 Hz, heating rate of 1 K/min, total amplitude of 30 μm with the dual-cantilever mode.

The obtained glass transition temperature can define the lower limit of operation for the tested rocket propellant.

4. Activation energy for the glass transition based on the $\tan(\delta)$ peaks, determined at different frequencies, was calculated with the Arrhenius relationship. Its value is 216.235 kJ/mol.
5. Dynamic Mechanical Analysis has proved to be an effective and safe method for testing solid double-base rocket propellants and a reliable for determination of the glass transition temperature. A great amount of information was collected from a single measurement. Relatively small stress applied along with small sample size make the method safe for operators and the device in case of sample ignition.

This work was supported financially by the European Regional Development Fund under the Operational Programme Innovative Economy 2007-2013, POIG.02.02.00-14-022/09.

Received September 14, 2015. Revised February 1, 2016.

REFERENCES

- [1] MENARD K., *Dynamic Mechanical Analysis — A Practical Introduction*, Second Edition, CRC Press, Taylor & Francis Group, 2012.
- [2] Netzsch DMA 242 C Manual.
- [3] DMA Q Series, Getting Started Guide, TA Instruments, 2004.
- [4] www.metrovib.acoemgroup.com
- [5] PN-EN-ISO 6721-1, *Determination of dynamic mechanical properties — part 1 general principles*, 2011.
- [6] NATO Standardization agreement 4540, *Explosives, procedures for dynamic mechanical analysis (DMA) and determination of glass transition temperature*, Edition 1, 2002.
- [7] CEGŁA M., ZMYWACZYK J., KONIORCZYK P., *Badania dwu-bazowego paliwa raketowego za pomocą dynamicznej analizy mechanicznej*, PTU, 3, 2014.
- [8] CEGŁA M., ZMYWACZYK J., KONIORCZYK P., MISZCZAK M., BORKOWSKI J., FLORCZAK B., *Determination of Glass Transition Temperature of Double-Base Rocket Propellants with the Use of Dynamic Mechanical Analysis*, PM, 6, 1(19), 2015, 11-18.
- [9] FOLLY P., MADER P., *Propellant Chemistry*, *Chimia*, 58, 6, 2004, 374-382.
- [10] WANI V., MEHIVAL V.W., JAIN S., SINGH P.P., BHATTACHARYA B., *Studies of the influence of testing parameters on dynamic and transient properties of composite solid rocket propellants using a dynamic mechanical analyzer*, *J. Aerosp. Technol. Manag.*, Sao Jose dos Campos, 4, 4, 2012, 443-452.
- [11] SUCESKA M., MUSANIC M., FIAMENGO I., *Study of mechanical properties of naturally aged double base rocket propellants*, *CEJEM*, 7(1), 2010, 47-60.
- [12] MISZCZAK M., BORKOWSKI J., TERENOWSKI H., *An analysis of test methods on physicochemical properties of solid rocket propellants on the basis of the Polish standards*, PTU, 110, 2009, 133-141.
- [13] HERDER G., WETERINGS F.P., DE KLERK W.P.C., *Mechanical Analysis on Rocket Propellants*, *JTAC*, 72, 2003, 921-929.

- [14] TUCKER J., *A Whole Life Assessment of Extruded Double Base Rocket Propellants*, PhD Thesis, Department of Engineering and Applied Science, 2012.
- [15] LI G., LEE-SULLIVAN P., THRING R.W., *Determination of activation energy for glass transition of an epoxy adhesive using dynamic mechanical analysis*, Journal of Thermal Analysis and Calorimetry, 60, 2000, 377-390.

M. CEGŁA, J. BORKOWSKI, J. ZMYWACZYK, P. KONIORCZYK

Badanie stałych dwubazowych paliw raketowych za pomocą dynamicznej analizy mechanicznej

Streszczenie. W artykule przedstawiono badanie dwubazowego paliwa raketowego za pomocą dynamicznej analizy mechanicznej (DMA). Autorzy przytaczają wcześniejsze badania materiału PTFE oraz dane literaturowe w celu wyjaśnienia zasad działania urządzeń DMA, przedstawienia właściwych warunków prowadzenia badań. Wyjaśniony zostaje wpływ parametrów badawczych, takich jak szybkość ogrzewania/chłodzenia czy częstotliwość przyłożonej siły, na wyniki. Przedstawiono wyniki badań stałego dwubazowego paliwa raketowego przeprowadzonych za pomocą urządzenia Netzsch DMA 242C. Dynamiczne właściwości mechaniczne takie jak moduł zachowawczy E' , moduł stratności E'' , oraz tangens kąta przesunięcia fazowego zostały zmierzone w zakresie temperatur od -120°C do $+90^{\circ}\text{C}$, przy prędkości ogrzewania wynoszącej 1 K/min , dla sześciu wartości częstotliwości przyłożonej siły. Zastosowano uchwyty typu podwójny wspornik (ang. *dual-cantilever*). Szczególną uwagę poświęcono wyznaczeniu temperatury zeszklenia badanego paliwa w oparciu o porozumienie normalizacyjne STANAG 4540 oraz wpływu częstotliwości przyłożonej siły na wartość temperatury zeszklenia.

Słowa kluczowe: Dynamiczna Analiza Mechaniczna, stałe paliwa raketowe, temperatura zeszklenia

DOI: 10.5604/12345865.1197970