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Research paper / Praca doświadczalna

Problems in testing impregnated projectile propellants
Problematyka badań prochów impregnowanych

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Abstract: *Impregnated projectile propellants are specific propellants (low explosives), requiring their properties to be considered during testing. Differential scanning calorimetry (DSC) and thermogravimetry (TG) are the techniques used to characterise these materials. These techniques require the selection of appropriate test conditions. The use of too high a specimen mass and rate of temperature rise, results in uncontrolled exothermic decomposition. When testing whole grains of propellants, it is necessary to use very low temperature rise rates (often below 1° C/min). Testing propellant grain fragments is not recommended due to the heterogeneity of the combustible layer. TG tests have shown that the loss of mass in propellants with high vapour pressure modifiers is greater than that resulting from water and process solvents content. This suggests the evaporation of modifiers during the test. The high vapour pressure of modifiers should be taken into account when analyses are carried out at elevated temperatures or under reduced pressure. Sometimes, during the impregnation process, there is a reduction in propellant stability. This may be due to addition of the modifier or to the reduction of stabilisers in the propellant. Impregnated propellants require tailor-made test procedures to ensure controlled decomposition and reliability of test results.*
Streszczenie: *Prochy impregnowane są specyficznymi materiałami napędowymi, wymagającymi uwzględnienia ich właściwości podczas badania. Różnicowa kalorymetria skaningowa (DSC) oraz termograwimetria (TG) są metodami wykorzystywanymi do ich charakteryzowania. Zastosowanie tych metod wymaga doboru właściwych warunków pomiarowych. Zastosowanie zbyt dużej masy próbki i szybkości wzrostu temperatury doprowadza do niekontrolowanego, egzotermicznego rozkładu. Wykonując pomiary dla całych ziaren prochu konieczne jest stosowanie bardzo małych szybkości wzrostu temperatury (często poniżej 1° C/min). Wykonywanie pomiarów dla fragmentów ziarna nie jest zalecane ze względu na niejednorodność warstwy palnej. Badania TG wykazały, że ubytki masy w prochach z dodatkiem modyfikatorów o wysokiej prężności par są większe niż wynikające z zawartości wody i rozpuszczalników procesowych. Wskazuje to na odparowanie modyfikatorów podczas pomiaru. Wysoką prężność par modyfikatorów należy uwzględniać przy analizach prowadzonych w podwyższonej temperaturze lub pod obniżonym ciśnieniem. Czasami w trakcie procesu impregnacji dochodzi do zmniejszenia stabilności prochów. Może to być związane z wprowadzanym modyfikatorem lub obniżeniem zawartości stabilizatorów w prochu.*

Prochy impregnowane wymagają indywidualnie dobranych procedur badawczych, zapewniających kontrolowany przebieg rozkładu i wiarygodność wyników.

***Keywords**: impregnated propellants, thermal analysis, thermal decomposition*
***Słowa kluczowe**: prochy impregnowane, analiza termiczna, rozkład termiczny*

1. Introduction

Nitrocellulose (NC) propellants burn in layers. Therefore the rate of gas formation should depend only on the surface area of the grain and its changes during combustion. The heterogeneity and porosity of the combustible layer causes NC propellants to exhibit deviations from the geometrical law of combustion [1]. Particularly unfavourable is the evolving surface of the propellant grain, which results in a more rapid release of gases during the initial stage of combustion [2]. This leads to a rapid build-up of pressure during firing. For this reason, the propellants may not meet the technical specifications of the ammunition and it is therefore necessary to modify their composition. The composition of a propellant can be changed not only during its production, but also afterwards, by impregnation. Impregnation is the process of introducing additional ingredients (modifiers) into the combustible layer of a propellant. This process can be carried out with a dispersing medium or without it ('dry coating', in the latter case). The first method uses an organic solvent, water or mixtures thereof, as the dispersing medium [3, 4]. The change in propellant composition is achieved by diffusion of modifiers into the combustible layer of the propellant. The dry coating method involves placing the propellant and its modifiers in a rotary mixer. When the temperature is raised, the modifiers melt and are deposited on the surface of the propellant grains [5]. During the impregnation process, thermochemical parameters (e.g.: heat of combustion, maximum pressure), ballistic parameters (e.g.: propellant energy density, dynamic vivacity) and propellant stability can be modified [6-8]. Low and high molecular weight, inert and high energy substances are used as modifiers [9-12]. Sometimes the introduction of additional compounds into the combustible layer of the propellant requires other propellant testing techniques or criteria for its evaluation [13].
This paper discusses the thermal properties of impregnated propellants and the techniques used to characterise them. Examples of correctly performed tests and recommendations for their practice are provided. It should be emphasised that the aim of this work was not to establish detailed testing procedures, but rather to highlight potential issues which researchers may encounter during experimental studies. The problem of high vapour pressure of modifiers introduced into the combustible layer of propellants and the consequences of this are discussed.

2. Experimental

2.1. Materials

Single-base modified powders stabilized with 1,3-diethyl-1,3-diphenylurea (diphenylamine) manufactured by MESKO S.A. were selected for testing. The propellants were further modified by impregnation with nitroglycerine (NG), introduced in various amounts depending on the test series.

2.2. Methods

Thermogravimetric analyses (TG) were conducted with a SDT Q600 instrument (TA Instruments). TGA measurements were performed for powder grain fragments and for whole impregnated powder grains. These measurements were performed in aluminium pans with a nitrogen flow of 100 mL·min^{-1}. The TG studies were performed at different rates of temperature increase in the range of β = 0.5-16 ºC·min^{-1} at the following range of temperatures: 30-400 ºC. The resulting thermograms were analyzed using the TA Instrument Universal Analysis 2000 software.

Stability measurements of the propellants were carried out using a TAM III flow microcalorimeter (TA Instruments). The propellant was placed in 4.3 mL glass ampoules, with the material filling the entire volume of the ampoule. The measurements were performed in accordance with NATO STANAG 4582 [17] at a temperature of 90 °C. The tested powders remains stable when stored at 25 °C for 10 years, once the value of the heat flux does not exceed 350 $\mu W \cdot g^{-1}$ for 3.43 days in this study.

3. Selected test methods for impregnated propellants

Differential scanning calorimetry and thermogravimetry are commonly used to characterise high-energy materials. These methods are also used to characterise impregnated propellants. Figures 1-4 present the results of TG and DSC tests of the same propellant under different measurement conditions (sample masses and heating rates). The presented results are intended to show the problems associated with selecting appropriate analysis conditions. Similar behaviour was observed by the authors for many different propellants. Although the figure shows results for several representative samples, this behaviour was consistently observed across many other propellants examined in this study. Figure 1 shows an example of percentage mass loss (%TG) and DSC curves plotted in a test with incorrectly chosen conditions.

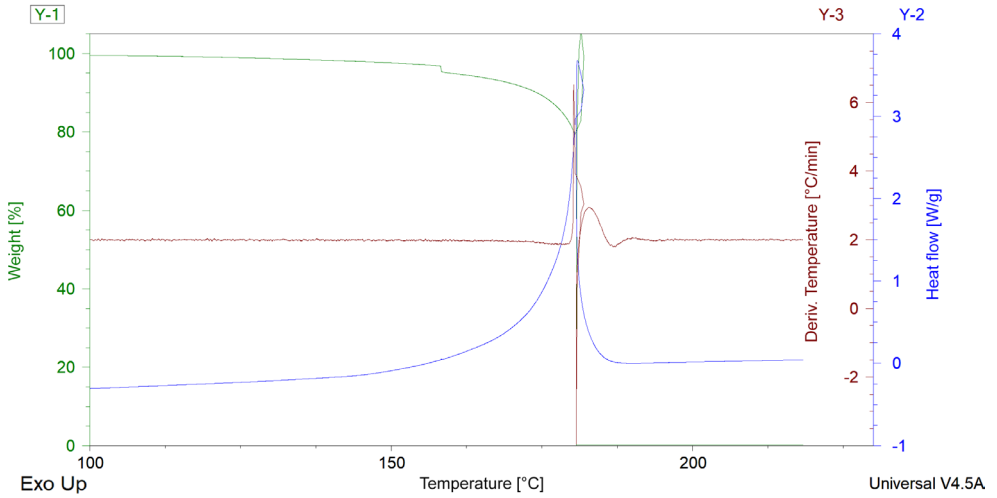

Figure 1. DSC and %TG curves of the thermal decomposition of a whole grain of impregnated propellant (3.55 mg), and the rate of change in the temperature of the specimen during the test, measured at 2 °C/min

When performing measurements at a linear temperature increase, we must select the initial and final temperatures, the heating rate, and the sample mass. When analysing impregnated propellants, the measurements are usually carried out on the entire propellant grain, which, for many geometries, requires the use of samples with a mass of several milligrams. Using an excessively large sample mass or a high heating rate may lead to an uncontrolled decomposition process, as shown in Figure 1.

During decomposition, the rate of increase in the temperature of the specimen was more than three times higher than that planned in the temperature program. Uncontrolled decomposition will be clearly detected with instruments whose sensors have a low heat capacity. When interpreting or presenting test results, the temperature of the measurement sensor, reference sensor or furnace can be shown on the X axis. The correct approach is to correlate the resulting DSC and %TG curves to the temperature of the measurement sensor. If the software for test result interpretation uses the temperature of a reference sensor, an error occurs, the magnitude of which depends on the thermal output generated in the transformation under test. If the temperature of

the reference sensor is on the X axis and the sensor itself has a large heat capacity, the operator will not notice a problem with the associated incorrect test conditions. The primary method of limiting the course of uncontrolled decomposition is to reduce the mass of the test specimen. In Figure 2, the DSC and %TG curves are shown for a specimen of a lower mass. The test was performed at a temperature rise rate of 2 °C/min.

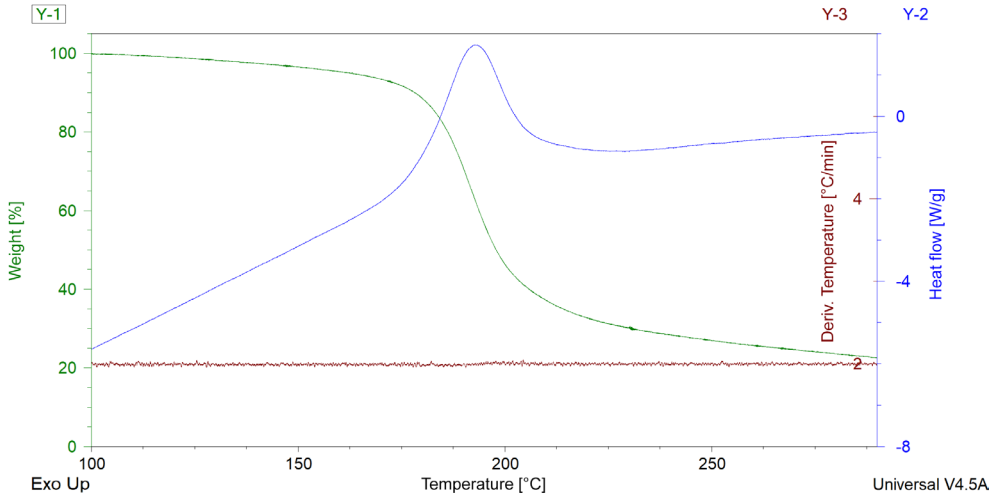

Figure 2. DSC and %TG curves of the thermal decomposition of a partial grain of impregnated propellant (0.18 mg), and the rate of change in the temperature of the specimen during the test, measured at 2 °C/min

The use of a smaller-mass specimen resulted in a controlled decomposition process. There was no rapid acceleration of the decomposition process caused by self-heating of the specimen. The planned rate of temperature rise was maintained throughout the test.

Fragmentation of the propellant grain may affect the results obtained in measurements of thermal properties. Figure 3 presents the %TG and DSC results obtained for fragments of modified propellant grain.

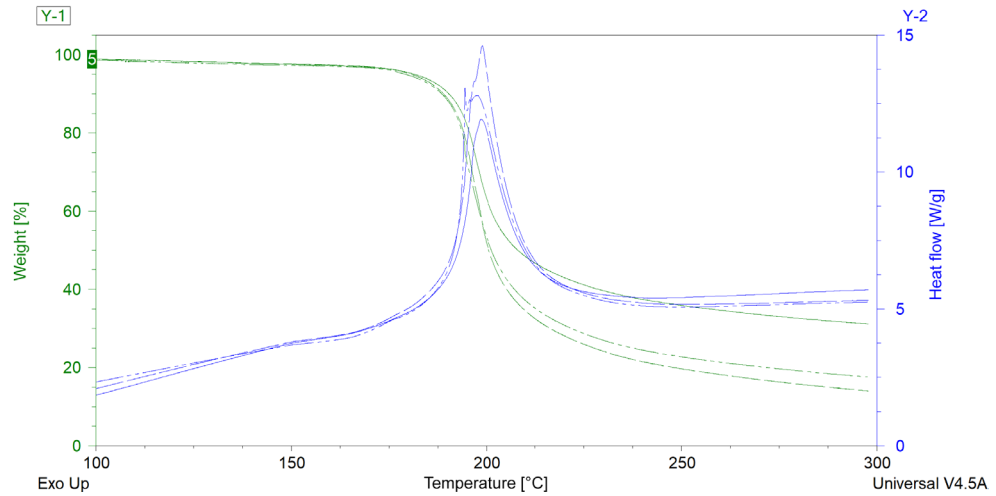

Figure 3. DSC and %TG curves of the thermal decomposition of a partial grain of impregnated propellant (0.4-0.5 mg), measured at 5 °C/min

In Figure 3, large differences between the individual measurements are visible. The difference in the mass of the residue after the measurement is particularly significant, ranging from 14% to 31%.
Unfortunately, the method of reducing specimen mass should not be used in the testing of impregnated propellants. This is due to the presence of a large heterogeneity of components in the combustible layer of the propellant grain. Added macromolecular components only settle on the surface of the grain, while low-molecular components only penetrate the combustible layer to a limited depth. For this reason, tests should be performed on whole propellant grains. Figure 4 shows an example of %TG and DSC curves for the whole propellant grain at a temperature rise rate of 1 °C/min.

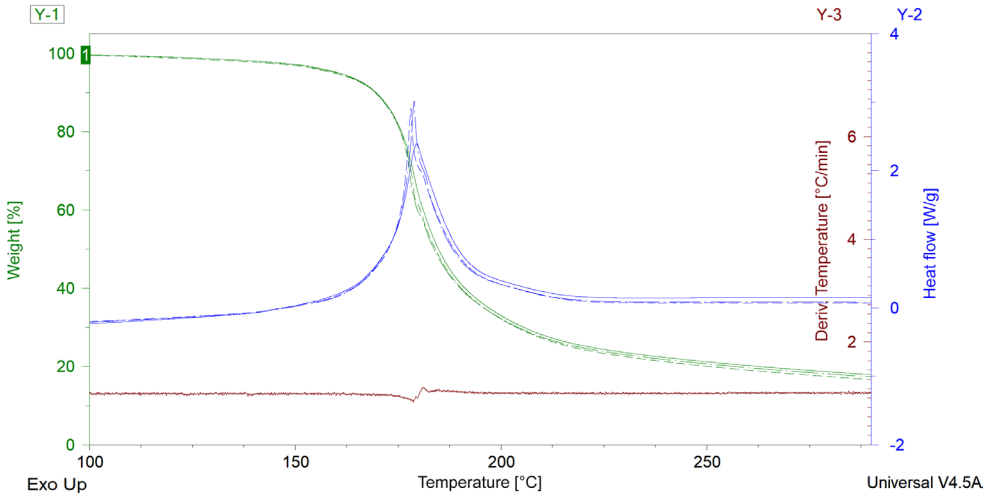

Figure 4. DSC and %TG curves of the thermal decomposition of the whole grain of impregnated propellant (3.1-3.6 mg), and the rate of change in the temperature of the specimen during the test, measured at 1 °C/min

In Figure 4, only small differences between the individual measurements are visible. The mass of the residue after measurement ranges from 16% to 18%. By reducing the rate of temperature rise, the decomposition process was controlled. There was no rapid acceleration of the decomposition process caused by self-heating of the specimen. The heat output generated during the decomposition process caused only minor divergence in the temperature rise rate.
During many tests or manufacturing processes, impregnated propellants are exposed to elevated temperatures. Figure 5 shows TG testing of specimens of a base propellant and a propellant impregnated with different nitroglycerine (NG) contents.

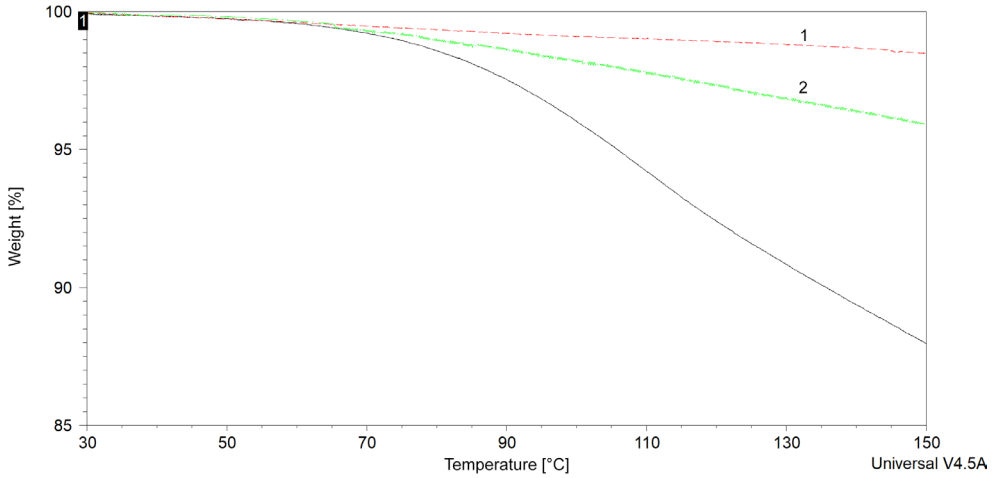

Figure 5. The %TG curves of the 5 and 15 phr NG base propellant and impregnated propellant grains: red (dashed 1) for the base propellant, green (dashed 2) for 5 phr NG and black (solid) for 15 phr curves, tested at 2 °C/min

The exothermic decomposition of the propellant began at a temperature of about 150 °C and, therefore, the loss of mass observed up to this temperature was mainly caused by the evaporation of low-molecular-weight components. Table 1 shows the loss of mass at 100 and 140 °C.

Table 1. Loss of mass values at 100 and 140 °C for the base propellant and the propellant impregnated with different NG contents, tested at 2 °C/min

Tested sample	Mass loss [%] at temperature [°C]	
	100	**140**
Base propellant	0.85	1.26
5 phr NG impregnated propellant	1.78	3.55
15 phr NG impregnated propellant	3.91	10.56

The propellant specimens of interest contained 0.8 ±0.1% water. The water content was determined using the Karl Fischer method. The volatile removable components content in the base propellant was 1.3%. The content of removable volatile components was determined in accordance with Standard BN-66/6093-09. The loss of mass shown in Table 1 for the impregnated propellant specimens was much higher than the water and process solvent content. This indicates that evaporation of modifiers might have also occurred during the test. When testing propellants impregnated with high vapour pressure components, attention should be paid to all processes operated at elevated temperatures or under reduced pressure, such as testing for the heat of combustion or volatile removable components, as well as stability and compatibility testing. In such tests, the modifiers could be brought to the point of evaporation, thereby affecting the results.
The impregnation process can reduce the stability of the resulting propellant. Figure 6 shows the results of stability tests on a base propellant and a propellant impregnated with different NG contents. The tests were completed using a TAM III flow microcalorimeter.

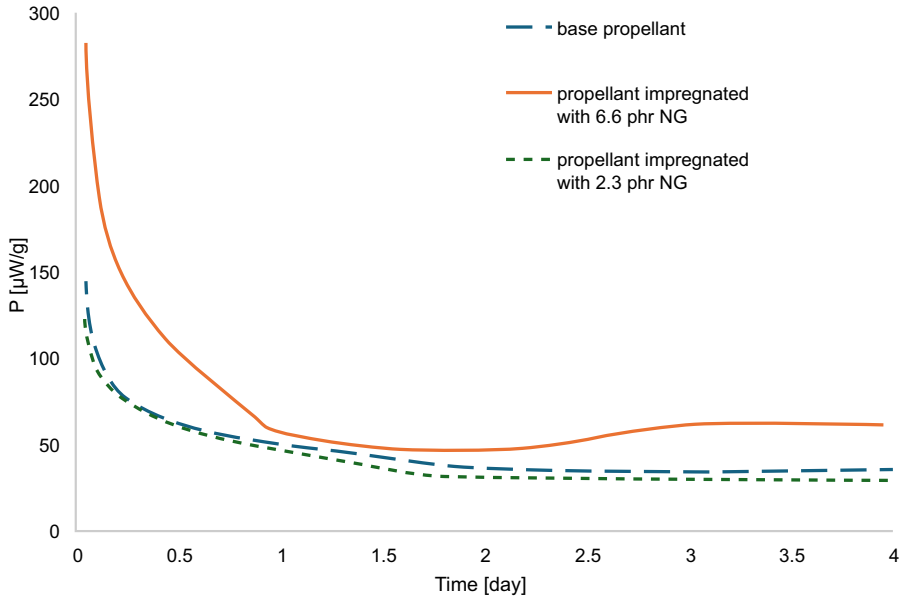

Figure 6. Heat flux vs. time for a base propellant and an NC-impregnated propellant (conditioning temperature 90 °C)

The graph shows the heat flux function for the base propellant and the two impregnated propellants. The impregnated propellants varied in the quantity of NG added. The 6.6 phr NG propellant stood out with a higher heat flux (orange plot line) than the base propellant (blue plot line). The 2.3 phr NG propellant had a similar heat output to that of the base propellant. Although the impregnation process can decrease propellant stability, the tested powders remain compliant with STANAG 4582 requirements, as their heat flux values did not exceed 350 µW g^{-1} over 3.43 days at 25 °C, indicating stability for up to 10 years of storage. This may be related to the modifier being added or to the reduction of stabilisers in the propellant. Key, in terms of safety, is the testing of the compatibility of the modifiers with the base propellant and the stability of the impregnated propellant. A number of compatibility test methods are available in the literature [14]. It is important to remember that vacuum stability testing (VST), thermogravimetry and DSC using non-hermetic vessels should not be used to determine the compatibility of modifiers which display high vapour pressure.

4. Conclusions

- Impregnated projectile propellants are specific propellants (low explosives), requiring their properties to be considered during testing. Attention should be paid to the risk of uncontrolled exothermic decomposition of the specimen during the test. This process makes it difficult to analyse the thermal decomposition and stability of impregnated propellants. When determining the kinetics of the decomposition process, the mass and the rate of temperature rise should be selected so as to ensure that the decomposition process remains controlled. This requires very low rates of temperature rise. When carrying out stability tests, specimens of relatively large mass (a few grams) are usually used. This promotes better reproducibility of tests but also increases the risk of instrument failure in the event of uncontrolled specimen decomposition. To reduce the likelihood of such an event, preliminary stability tests should be carried out on specimens in systems which facilitate rapid thermal decomposition.

- Tests on impregnated propellants are often performed at elevated temperatures (for volatile removable and non-removable components, as well as stability) or under reduced pressure (when determining the calorific value). When testing propellants impregnated with high vapour pressure modifiers, it should be noted that the modifier may evaporate during the test and change the composition of the propellant of interest.

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