

Thermal Properties of Energetic Materials—What Are the Sources of Discrepancies?

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Abstract: Thermal analysis is widely used to investigate the properties of a variety of energetic materials, including the mutual compatibility of components of energetic material mixtures. Although thermal analysis methods are a valuable source of information about energetic materials, their use requires careful consideration of the employed methodology, as well as an understanding of the thermally induced processes taking place within energetic materials. Several case studies involving the study of energetic materials are presented, in order to highlight some of the most relevant issues in the application of thermal analysis methods. Some recommendations about the application of thermal analysis methods and accompanying methodologies for estimating other properties of energetic materials are also included.

Keywords: energetic materials; thermal analysis; methodology; measurement



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1. Introduction

Energetic materials are widely used in a variety of civil (mining, demolitions, tunnel construction, aeronautics, and astronautics) and military applications [1,2]. The increasing demands placed on these areas of application translate into the need for energetic material (EM) formulations exhibiting ever higher performance benchmarks (the velocity of detonation, brisance, air blast pressure, etc.). Simultaneously, however, the risk associated with the manufacture, handling, storage, and use of energetic materials [3,4], as well as the potential for the intentional misuse of EMs, should be minimised [5]. The safety of EMs is directly related to their susceptibility to initiation by various means, such as mechanical (friction, impact) [6,7], electrostatic [8], and thermal stimuli.

Whereas mechanical and electrostatic sources of initiation can be limited and controlled to an extent, thermal stimuli are inherently inseparable from the processing and use of EMs. This is well-exemplified by melt cast EMs, a class of materials that need to be resistant to the high-temperature regimes employed during their processing [9]. Consequently, to assure EM safety, detailed and precise information about their susceptibility to thermal decomposition and thermal initiation is essential.

Despite the above, the information reported about the thermal properties of various substances, including EMs, is often insufficiently reliable. While the reliability of thermochemical data in a given work may raise no concerns by itself, a comparison of multiple works on the same material can reveal significant discrepancies between the reported results. Methodological issues and insufficiently precise descriptions of experimental procedures are two more identified points of concern regarding the reliability of reported thermochemical data [10,11], with the former compromising the validity of reported thermochemical data and the latter precluding verification of data through the repetition of the reported experiments. These issues are further exacerbated by the lack of experiment repetition or the lack of statistical work-up if the experiments have been repeated.

In this work, we provide a brief overview of the most commonly used methods for conducting thermochemical investigations for EMs and discuss several cases of discrepancies between thermochemical results reported for selected EMs, attempting to shed light on the failure modes underlying these discrepancies.

2. Methods of Investigation

Differential scanning calorimetry (DSC) is among the most commonly used thermoanalytical methods for studying EMs and prospective EMs. The method relies on measuring the temperature difference between an investigated sample and a reference maintained in a controlled temperature environment, using the measured temperatures for the calculation of heat flow to the sample and reference (Figure 1) [12]. Most commonly, a temperature ramp is applied, but isothermal measurements can also be conducted, particularly when investigating the thermal stability. It should be noted that due to its limited sensitivity, DSC is indicated as a screening method for initial coarse assessments [10].

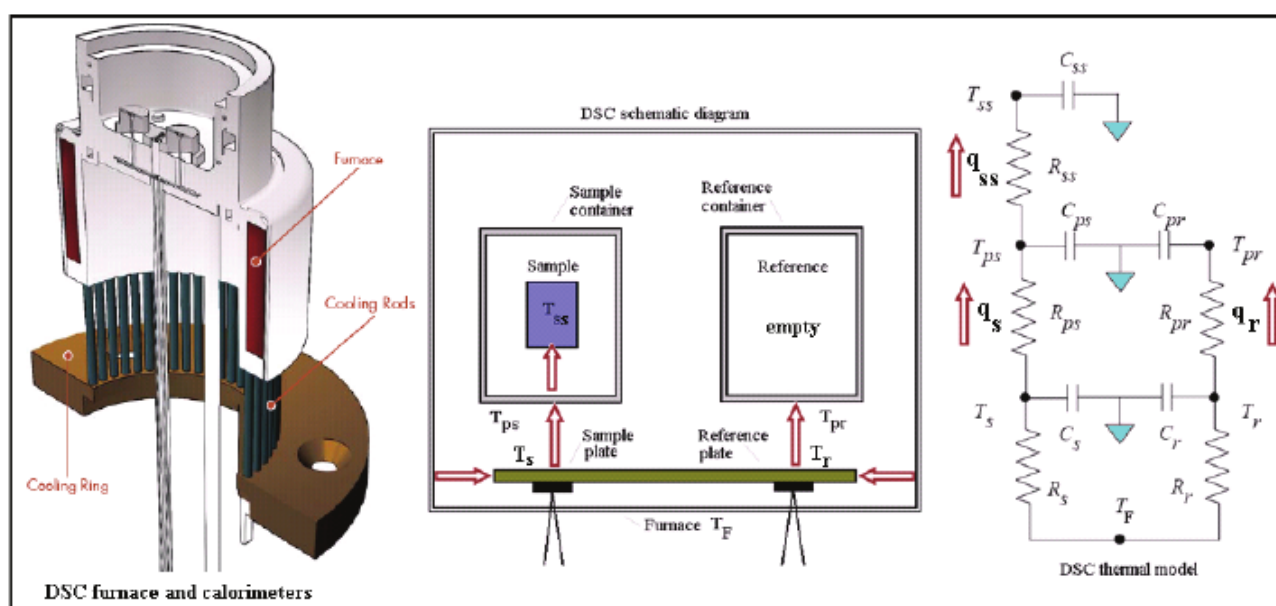


Figure 1. Schematic depiction of a commonly used differential scanning calorimeter. Reproduced from [13] under a CC-BY licence.

Thermogravimetry (TG) is a method that precisely measures the change in mass of a sample as a function of temperature (heating or cooling) or changes in mass as a function of time under isothermal conditions. The sample is typically placed under a vacuum, generally below 0.01 Pa. There are also other solutions, in which the pressure in the measuring chamber is up to 10 MPa. The use of modern constructions (the Cahn balance) makes it possible to measure mass changes in the order of micrograms for a sample of 10 g (Figure 2). The temperature range is generally between 25 and 1000 °C [14].

Differential thermal analysis (DTA) is a method based on recording the temperature difference between the test and reference substances as a function of time or temperature. Both samples are heated or cooled in a controlled manner under identical ambient conditions.

Since the reference substance should not undergo any transformations that are accompanied by thermal effects, the measured temperature difference depends on the rate of heat absorption or release by the test substance sample. The measurement of the temperature difference is typically achieved using a thermocouple differential system, the classic diagram of which is shown in Figure 3. Placing temperature sensors directly in the sample is the reason for the high sensitivity of the measuring system, but at the same time it allows chemical interactions between the sample and the thermocouples. In modern DTA systems, vessels with the test substance are placed on the differential thermocouple welds, which

allows some of the disadvantages of the classical system to be eliminated. The DTA method enables thermal effects, which accompany the processes occurring during the heating of the test substance, to be studied. These processes can be endothermic or exothermic chemical reactions (decomposition, oxidation, or reduction) and phase transformations (recrystallisation or melting) [15].

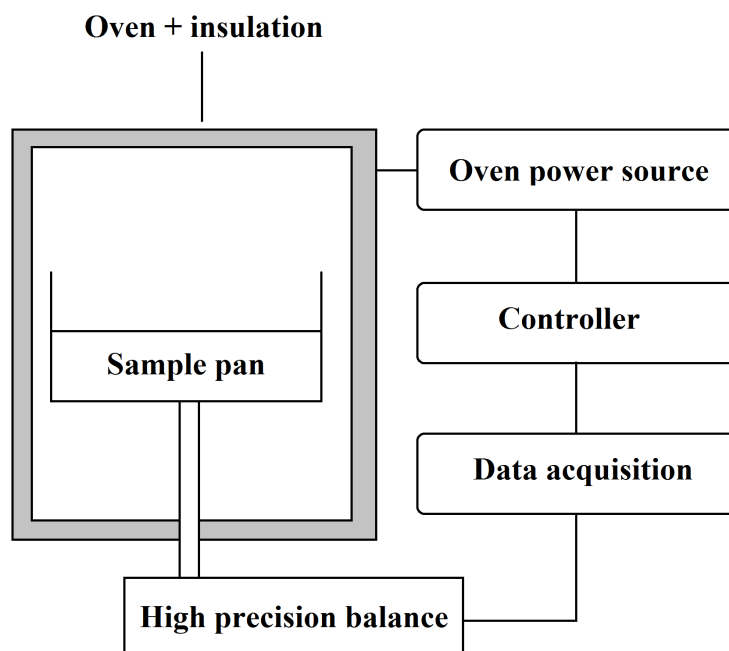


Figure 2. Schematic depiction of a thermogravimetric analyser module. Based on [14,16] and a variety of schemes provided by equipment manufacturers.

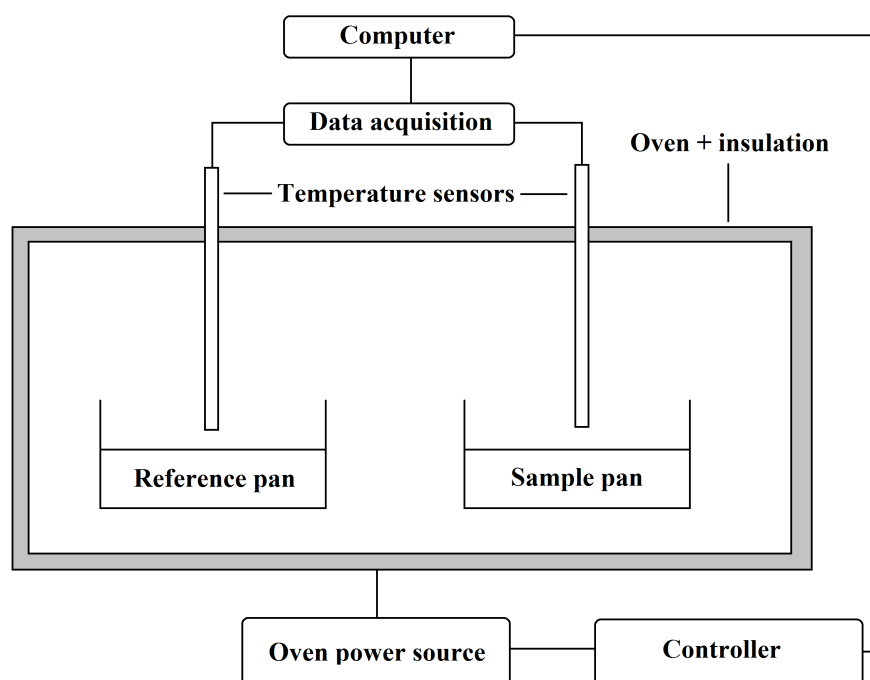


Figure 3. Simplified schematic depiction of a differential thermal analyser, based on [15,16] and a variety of schemes provided by DTA equipment manufacturers. Modern DTA instruments largely utilise reference and sample vessels placed in contact with thermocouples rather than allowing sample–thermocouple contact.

For the above methods, when employing a temperature ramp, the heating rate should be adjusted so that the magnitude of thermal gradient within the samples is minimised. To this effect, Equation (1) below can be employed [17]. This has been exemplified by an arbitrary 0.6 K gradient being achieved for a 20 mg sample disc ($r = 2.5$ mm, $L = 1$ mm, $\rho = 1$ g/cm³, $k = 10^{-7}$ m²/s) at a heating rate of 10 K/min and proportionately smaller samples being required to maintain this temperature gradient at higher heating rates [12].

$$\Delta T = \frac{3qL^2}{8k} \quad (1)$$

where:

- ΔT —temperature gradient (K)
- q —heating rate (K/min)
- L —sample disc thickness (m)
- k —sample thermal diffusivity (m²/s)

It should also be noted that the abovementioned thermal analysis methods can be used for the initial assessment of the ability of a material to undergo explosive decomposition and to even estimate its shock sensitivity [18]. This is currently a standard safety procedure in pharmaceutical development, but despite its high relevance to the study of new EMs, the methodology remains virtually absent from works dedicated to EMs despite the literature offering no evidence of any inaccuracies of this methodology [19,20].

3. Case Study: Poly(3-nitratomethyl-3-methyloxetane) (PNIMMO)

Poly(3-nitratomethyl-3-methyloxetane) (PNIMMO) is a polyoxetane (Figure 4) that is utilised as an energetic binder in a variety of applications, such as composite propellants, low vulnerability ammunition, and plastic bonded explosives [21,22].

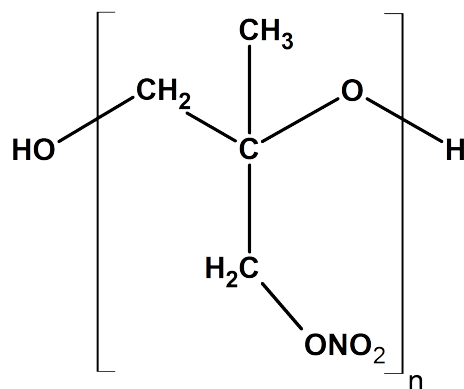


Figure 4. Chemical structure of PNIMMO.

Differential scanning calorimetry (DSC) investigations of the decomposition temperature of PNIMMO reveal a single sharp decomposition peak, with no evidence (e.g., pre-peaks) of any processes occurring at lower temperatures. Depending on source, the peak maximum is located at 202.7 °C (PNIMMO-A) [23], 207.1 °C (PNIMMO-B) [24], approx. 218 °C (PNIMMO-C) [25], and 218.9 °C (PNIMMO-D) [26]. Even though the measurements were reported to have been conducted in nitrogen, at a heating rate of 10 K/min, the divergence between these results is noticeable (>15 K) and sufficient to influence the outcomes of standardised assessments (e.g., the STANAG 4147 evaluation of the compatibility of mixtures of energetic materials [27]), leading to tangible and potentially severe consequences.

It should be noted, however, that the information about the investigated PNIMMO sample is limited in the reports, in one case consisting solely of a batch number and approximate date of manufacture, with a lack of relevant information about the method of synthesis, the initiating agent, or the parameters of the produced polymer (e.g., the molecular weight) greatly obfuscating any follow-up analysis.

Despite the above, among the DSC-tested PNIMMO samples, two (**PNIMMO-B** and **PNIMMO-D**) have been synthesised via a virtually identical procedure, using the same initiating system (boron trifluoride diethyl ether adduct and 1,4-butanediol). The samples were found to have number average molecular weights of 5867 (**PNIMMO-B**) and 2610 g/mol (**PNIMMO-D**), but DSC investigations indicate that **PNIMMO-D** has a peak maximum temperatures higher by approx. 12 K than **PNIMMO-B** while having approximately half the average molecular weight. The two PNIMMO samples are both linear polymers (due to the use of the difunctional 1,4-butanediol) and are expected to differ only in terms of their molecular weight. Therefore, the direct analysis of the DSC results would lead to the absurd conclusion that increasing PNIMMO molecular weight reduces the thermal stability of the polymers. As this is obviously not the case, the validity of the methodology used to assess the decomposition temperature via DSC needs to be questioned.

Not only is the peak maximum temperature established by DSC questionable (Table 1) but a comparison of DSC and thermogravimetric data reveals that decomposition of PNIMMO, evidenced by a gradual loss of sample mass, takes place at temperatures much lower than those indicated by DSC. This is observed for both **PNIMMO-D** (a loss of approx. 10% of sample mass before 200 °C is achieved, starting at approx. 120 °C) and for **PNIMMO-B** (a similar loss of mass, starting at approx. 80 °C). An in-depth study of **PNIMMO-C** corroborates the above, while providing evidence that the decomposition of this polymer takes place at temperatures as low as 77 °C [25]. The mechanism of thermal decomposition was investigated at 129 °C for a low-molecular weight ($M_N = 1600\text{--}2000$ g/mol) PNIMMO sample, indicating that both depolymerisation and O-NO₂ bond scission take place [28]. Both these processes are highly significant from the perspective of the performance of PNIMMO as depolymerisation will translate into the loss of the mechanical strength of this binder, whereas nitrate bond scission will affect its combustion properties. Moreover, since corrosive and highly reactive NO₂ is emitted during this degradation, its evolution may result in misfires or the accidental initiation of any PNIMMO-containing devices exposed to elevated temperatures, constituting a significant threat that would be entirely unexpected if working solely on the basis of the reported DSC results for PNIMMO.

Table 1. Summary of DSC and supporting data for PNIMMO reported in literature.

PNIMMO	Molecular Weight (Mn) [g/mol]	Carrier Gas/Heating Rate [K/min]	Decomposition Temperature [°C]	T ₁₀ [°C] ¹	T _g [°C]	Ref.
PNIMMO-A	-	N ₂ /10	202.7	-	-36	[23]
PNIMMO-B	5867	N ₂ /10	207.1	80	-30.2	[24]
PNIMMO-C	-	N ₂ /10	218	77	-	[25]
PNIMMO-D	2610	N ₂ /10	218.9	120–200	-35.6	[26]
PNIMMO	1600–2000	N ₂ /10	-	-	-	[28]
PNIMMO	2500	N ₂ /2 and 10	200 and 213	-	-	[29]
PNIMMO	3400–3500	N ₂ /10	218.2	-	-	[30]

¹ Temperature, at which 10% of initial mass loss is observed.

4. Case Study: Assessment of the Thermal Compatibility of EM Formulation Components

Although multiple sources of thermal compatibility tests for binary or multicomponent EM formulations are available, the vast majority of reports dedicated to such studies employ one or more of the several procedures described in STANAG 4147 [27] for this purpose. Of those methods, the DSC method appears to be most commonly employed, likely due to its simplicity and feasibility of working with small (in the order of 1–2 mg) EM samples. The procedure involves acquiring, in at least duplicate, the DSC thermograms of each component of the EM formulation by itself as well as in binary mixtures with other components of the investigated EM formulation. These thermograms should be acquired at a heating rate of 2 K/min, with the procedure giving no indication on the type of pans (sealed, open, pinhole,

and high-pressure), hinting at the use of aluminium pans but allowing pans made from other materials. The assessment relies on several criteria: (1) the difference in signal temperatures observed for the investigated formulation and for its components; (2) the appearance or disappearance of additional signals; (3) the changes in signal shapes.

In the literature, the implementation of this methodology is very diverse as both higher and lower heating rates than the indicated one are employed. This can strongly influence the result of the assessment, due to the aforementioned issues of thermal gradients and thermal lag. Both of these deviations from the standard or the use of different types of pans can drastically influence the obtained thermogram and, therefore, the result of the compatibility assessment [29].

Similarly, the evaluation of the changes in peak position has various interpretations. In some works, this change in position is interpreted as the difference between the signals of the EM formulation components [29], whereas other works assume the interpretation that only the shift of the signals should be taken into account [30]. This is largely an issue of the source procedure, which does not clearly indicate which of the two interpretations, if any, is the intended one. Such ambiguities and resulting differences in interpretation can make the difference between, e.g., the mixtures of PNIMMO with CL-20 being assessed as compatible or incompatible.

It should be noted that in most works, regardless of interpretation, the signal shifts are used as the sole criterion for the evaluation of compatibility. Changes in the shape of the DSC signals, indicated as another compatibility criterion in STANAG 4147 [27], are virtually entirely ignored. Similarly, most works appear to neglect the STANAG requirement for repeating the experiments as no information is given about the number of experiments constituting the basis for the compatibility assessment nor is any statistical work-up for such repeated experiments reported.

5. Case Study: Use of Regression Methods

The activation energy for the reactions underlying the decomposition of energetic materials is frequently determined based on experiments conducted at multiple heating rates, e.g., utilising the Kissinger method (Equation (2)) [31,32].

$$\ln(\phi/T_p^2) = \ln(AR/T) - (E_A/RT_p) \quad (2)$$

where:

- ϕ —heating rate (K/min)
- T_p —peak maximum (K)
- A —pre-exponential constant
- E_A —activation energy (J/mol·K)

Since the slope of the line given by the above equation allows the activation energy to be calculated, regression analysis is commonly used for this purpose. However, each data point determining the regression line equation requires translation into a series of experiments run at a single heating rate. Consequently, obtaining even five data points for using this method requires a large number of repetitions to be conducted for the thermal decomposition experiments. Assuming the minimal statistically significant number of repetitions ($n = 5$), an input of five data points to the Kissinger method requires 25 experiments at the very least. This translates into a significant investment of both the investigated materials and time, particularly if lower heating rates and broader heating ranges are employed.

The abovementioned consumption of materials and time can be significant enough to be an issue. This has already resulted in numerous works, which have limited the number of times the experiment is repeated or have reduced the number of heating rates at which the experiments are conducted. Such an approach is commonly “justified” by reporting high Pearson correlation coefficients (R) or regression coefficients (R^2). It should be noted here that if working with small sample sizes ($n < 30$), a relevant correction should be employed (e.g., the use of the Student’s t distribution) as reporting the relevant coefficient without

further analysis compromises the reliability of the reported data. This is well illustrated by an extreme case of conducting linear regression for $n = 2$ as regression analysis will return $R = \pm 1$ and consequently $R^2 = 1$ for any two datapoints constituting the sample.

Such a critical analysis of the R/R^2 coefficients is present only rarely, with full analyses (the adoption of a confidence level and the determination of the relevant confidence intervals) being even less common [33,34]. The lack of this approach in the vast majority of works dedicated to the thermal analysis of energetic materials persists despite the existence of numerous books and scientific works on the relevant methodology and many of its applications (i.e., the statistical analysis of extremely small samples) being widely available [35,36].

6. Conclusions

On the basis of the presented examples, it can be concluded that the methods of thermal analysis are the basic tool for studying the thermal properties of energetic materials (EMs) in terms of both fundamental research—the mechanisms of the combustion process—and utilitarian applications, very often used by researchers. However, it is worth bearing in mind that the interpretation of the results of the thermal analysis of EMs requires an understanding of the sometimes complex physicochemical essence of the phenomena taking place, and the obtained results will to a large extent be a derivative of the method of performing the measurement. The method of measuring and preparing the sample for testing will also have an impact on the obtained results. To exemplify, increasing the heating rate causes an increase in the height of the DTA peaks and becomes the cause of their broadening.

The disadvantage of the DTA and TGA (DTG) methods is the use of relatively small masses (weights) for thermal analyses, which adversely affects the repeatability of measurement results, especially when testing heterogeneous materials. On the other hand, too large a sample mass causes the occurrence of temperature gradients inside the sample and hinders the rapid heat exchange between the sample and the environment. For powder samples, the degree of their compaction and grain size significantly modify the parameters determining thermal conductivity. This requires the careful preparation of samples for thermal analyses and multiple repetition of the measurements, in order to ensure the repeatability of the results of these analyses.

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