Small Scale Impact Sensitivity Testing of Energetic Materials under Temperature and Relative Humidity

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Abstract

In the frame of energetic materials qualification (EMQ), sensitivity to impact is considered part of the required information about small-scale sensitivity of energetic materials. The impact test is intended to assess the ability of an energetic material to react to external stimuli resulting in the initiation of a decomposition reaction, which is used either as a measure of the stimulus required to cause reliable functioning of an energetic material, or to relatively assess the likelihood of an accidental initiation. However, many assessment methods exist and multiple factors can influence impact sensitivity measurements.

This investigation studied the effect of the temperature and the relative humidity of explosive samples on impact sensitivity test results using a BAM Impact Machine, as part of evaluating the relevance of the small-scale impact test for EMQ. This study is supported by an MSIAC literature study that was conducted to review the main impact sensitivity tests involved in the energetic materials qualification process, and how the impact sensitivity test results are affected by the test environment and the material properties. This paper presents the impact sensitivity test results on two factors of influence (temperature and relative humidity) on ammonium perchlorate (AP), TNT, RDX and Comp A-3.

At a low temperature of -40°C, the four materials tested exhibited decreased sensitivities. At high temperatures up to +60°C, AP, RDX and Comp A-3 exhibit an increased impact sensitivity that seems to be limited to a decrease in E_{50} values of less than 0.3 J/°C. On the contrary, TNT's impact sensitivity abruptly decreases between +25°C and +40°C, reaching a plateau of reduced sensitivity.

It was shown that the changes in sensitivity with temperature are reversible when the materials are agitated after conditioning, supporting with the SEM images the hypothesis that the change in sensitivity is induced by a morphological effect.

Regarding the effect of Relative Humidity (RH), AP, RDX and Comp A-3 reveal an increasing trend in impact sensitivity with an increasing RH up to 90%, while TNT becomes insensitive, exhibiting no reaction at the maximum energy level achievable by the machine. The reversibility study conducted on the effect of RH was not conclusive due to biases found in the conditioning method.

Introduction

In the frame of energetic materials qualification (EMQ), sensitivity to impact is considered part of the required information about small-scale sensitivity of energetic materials. The impact test is intended to assess the ability of an energetic material to react to external stimuli resulting in the initiation of a decomposition reaction, which

is used either as a measure of the stimulus required to cause reliable functioning of an energetic material, or to relatively assess the likelihood of an accidental initiation. However, many assessment methods exist and multiple factors can influence impact sensitivity measurements. During a recent review conducted in 2023 by MSIAC on impact sensitivity testing methods, a lack of understanding was identified on the effect of temperature and relative humidity (RH) on the small scale impact sensitivity of energetic materials [1]. This is the purpose of this study to contribute to fill in this gap for a selection of energetic materials.

The effect of temperature and RH on impact sensitivity was investigated in the framework of a joint MSIAC / Royal Military Academy (RMA) of Belgium program of work in 2023. Four energetic materials were selected for this study: RDX, Ammonium Perchlorate (AP), TNT and Comp A-3 (91% RDX and 9% Wax).

The following sections detail the materials preparation, the test methods used, and the results obtained during this study.

1. Sample Preparation and Testing Method

The four energetic materials selected for this study are RDX, AP, TNT and Comp A-3. The samples were taken from the stock available at the RMA. They are all military grade products and they were selected for their wide use in munition systems. Table 1 provides details on the supplier, the particle size and reference impact sensitivity data for these four energetic materials.

Table 1: Details on the energetic materials used in the study

Material	Type and Specification	Reference Impact Sensitivity Values
RDX	Type A Class 1 - AOP-4022 [2]	8 J [3]
AP	Type 1 - STANAG 4299 [4]	20 J [5]
TNT	General use - STANAG 4025 [6]	15 J [7]
Comp A-3	Type I Class 1 - MIL-DTL-440D [8]	Not available

For the first series of impact tests, the test samples were prepared in advance and preconditioned in the test apparatus (in a closed configuration) at three temperatures (-40°C, room temperature of about 25°C and +60°C) in a Julabo FPW-52 cryothermostat for four hours immediately before test. Different conditioning protocols have been used during the study, they are detailed later in the paper. For the tests conducted with regard to RH, the test samples were prepared in advance and preconditioned in the test apparatus (in an open configuration) at three relative humidities (room RH of about 45%, 70% and 90%) for at least 17 hours in a Memmert HCP 50 humidity-controlled chamber, at 30°C.

The preconditioned samples were then tested with the BAM Fallhammer impact apparatus available at the RMA. A Bruceton testing method was employed to determine the impact sensitivity which is given in terms of E_{50}, the drop energy in joules that leads to a 50% probability of ignition. The Bruceton methodology was conducted in accordance with the original publication by Dixon and Mood [9].

2. Influence of Temperature

The E_{50} results obtained for the four energetic materials conditioned at three different temperatures (-40°C, room temperature of about +25°C, and +60°C) are plotted at Figure 1. Each point corresponds to the mean value obtained from three full impact tests conducted with the Bruceton method. The error bars are calculated using the logarithmic values of the height, which were then converted into energies, as described in the Bruceton method [9]. The E_{50} values are plotted in Figure 1 and the error range is systematically indicated in the following tables of results, in squared braces below the mean values.

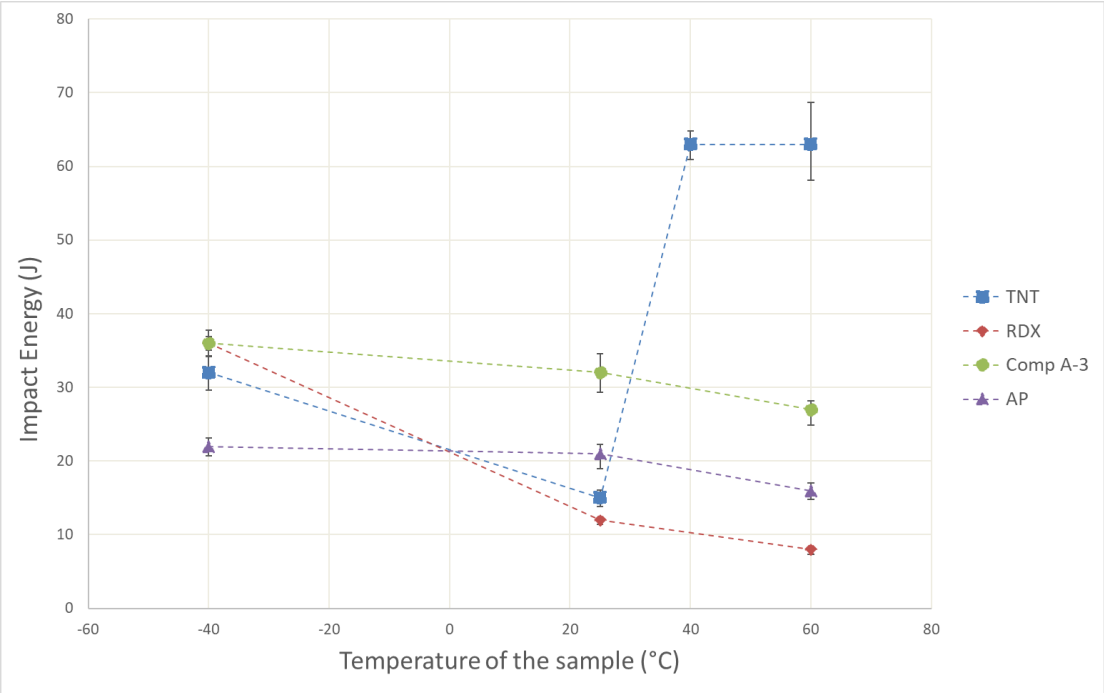

Figure 1: Impact energy as a function of the temperature for the four energetic materials considered in this study

The points at -40°C and +25°C show similar trends for all energetic materials: a decrease in E_{50}. This decrease is more pronounced for TNT and RDX. The decrease in impact sensitivity observed in this study for TNT is in accordance with previous results where a similar trend was observed from -120°C to +20°C [10]. The decrease in E_{50} indicates an increase in impact sensitivity but the results remain well above the admitted pass / fail criterion of 2 J (noting that this criterion is obtained with the 1/6 method, as defined in Test 3 (a) (ii) of the UN Manual of tests and criteria for the transport of dangerous goods [11]). It is also noted that the results obtained at room temperature for RDX, AP and TNT are close to the reference values given above at Table 1, which provides confidence in the testing apparatus and the methodology used.

The decrease in E_{50} (and subsequent increase in impact sensitivity) is further pronounced for RDX, AP and Comp A-3 at +60°C but the values at +60°C remain once again above the 2 J threshold value. As a result, the sensitivity increase observed for RDX, AP and Comp A-3 is not considered significant enough to categorize these materials as explosive materials hazardous to handle at +60°C.

For TNT, an unexpected and significant increase in E_{50} is observed at +60°C, with a value of 63 J. An additional test was conducted at +40°C which resulted in a E_{50} value of 60 J. This corresponds to a significant decrease in sensitivity that seems to suddenly occur when heating TNT, at a certain threshold temperature between +25 and +40°C, beyond which E_{50} remains at approximately the same high value. In other words, this suggests that the 50% impact energy of TNT reaches a plateau beyond a certain temperature.

The above results show that, except for TNT, an increase in impact sensitivity with temperature is to be expected, but seems to be limited to a decrease in E_{50} values of less than 0.3 J/°C in the examined temperature range of -40°C to +60°C.

The reversibility of the change in sensitivity observed under an increased temperature was investigated for TNT, RDX and AP. To do so, the samples were tested at ambient conditions after having been conditioned at +60°C using different preparation methods:

- **Preparation Method M1**: as for the initial tests, the samples were prepared in advance and preconditioned in the test apparatus, but they were then were allowed to cool to +25°C before being tested;

- **Preparation Method M2**: the samples were bulk conditioned at +60°C for four hours in glass vials, cooled to +25°C, prepared and placed in the test apparatus, and tested.

The results obtained with preparation methods M1 and M2 are provided in Table 2, and compared with the previous results.

Table 2: Investigation of the reversibility of impact energy results at high temperature and with preparation methods M1 and M2

Energetic material	E_{50} at + 25°C)	E_{50} at + 60°C	Method M1	Method M2
TNT	15 J [+1.0, -1.2] J	63 J [+5.7, -4.9] J	65 J [+3.1, -2.7] J	66 J [+4.8, -5.2] J
RDX	12 J [+0.1, -0.6] J	8 J [+0.1, -0.6] J	7 J [+0.6, -0.0] J	7 J [+0.2, -0.5] J
AP	21 J [+1.2, -2.0] J	16 J [+1.1, -1.2] J	16 J [+0.4, -0.6] J	17 J [+1.4, -0.6] J

The impact energies obtained on the samples tested at +25°C after heating at +60°C are considered similar for both preparation methods M1 and M2. In addition, these results are considered not significantly different to the results obtained at +60°C. This indicates that the change in sensitivity observed on the heated samples seems irreversible at first sight, which was not expected and represents a major finding of this study.

In order to further investigate the reason for this irreversibility, the morphology of the materials was analyzed by Scanning Electron Microscopy (SEM) on the pristine samples and after bulk conditioning at +60°C. The SEM pictures are given at Figure 2 through Figure 7.

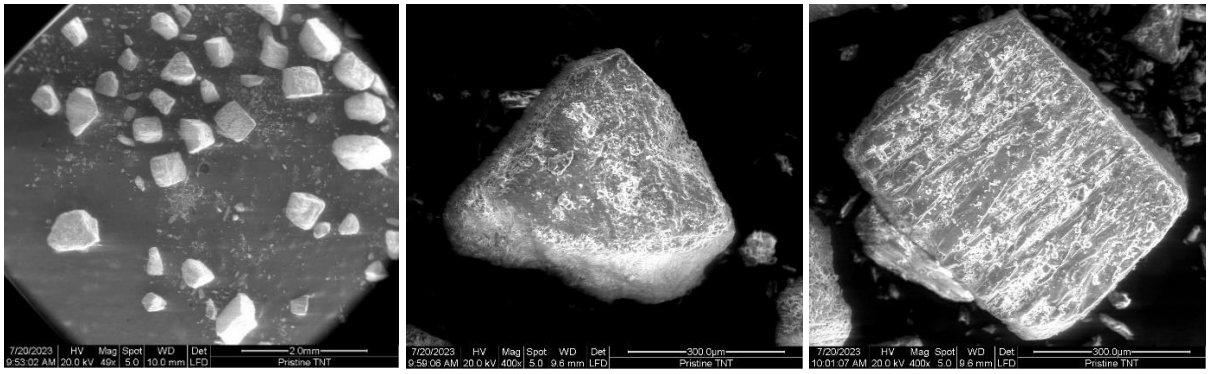

Figure 2: SEM images of pristine TNT at different scales: 2 mm, 300 µm, 300 µm.

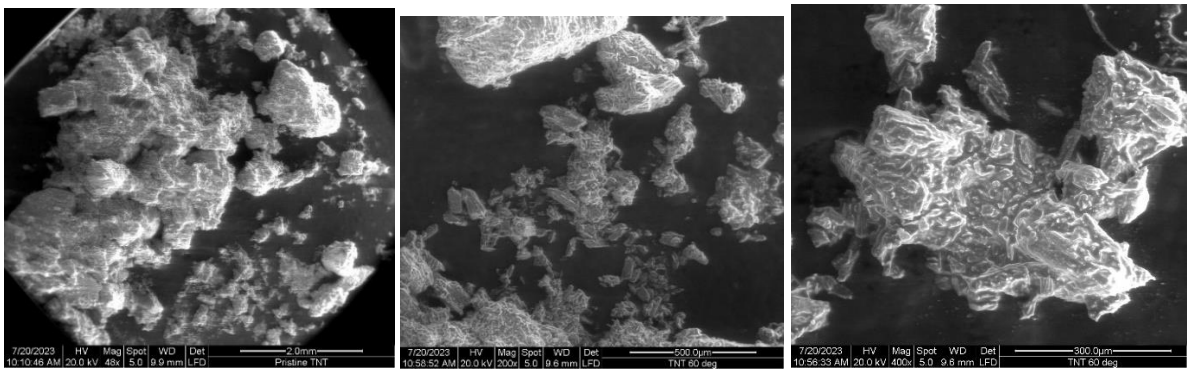

Figure 3: SEM images of bulk conditioned TNT to +60°C at different scales: 2 mm, 500 µm, 300 µm.

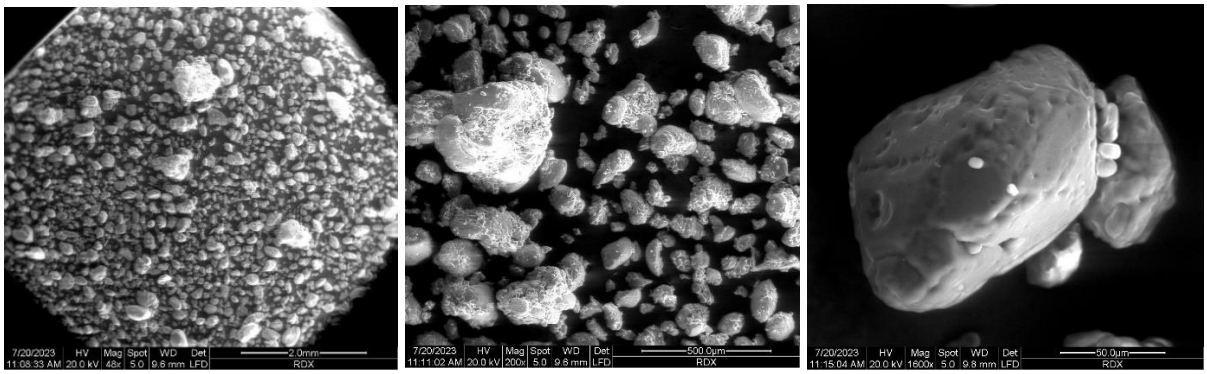

Figure 4: SEM images of pristine RDX at different scales: 2 mm, 500 µm, 50 µm.

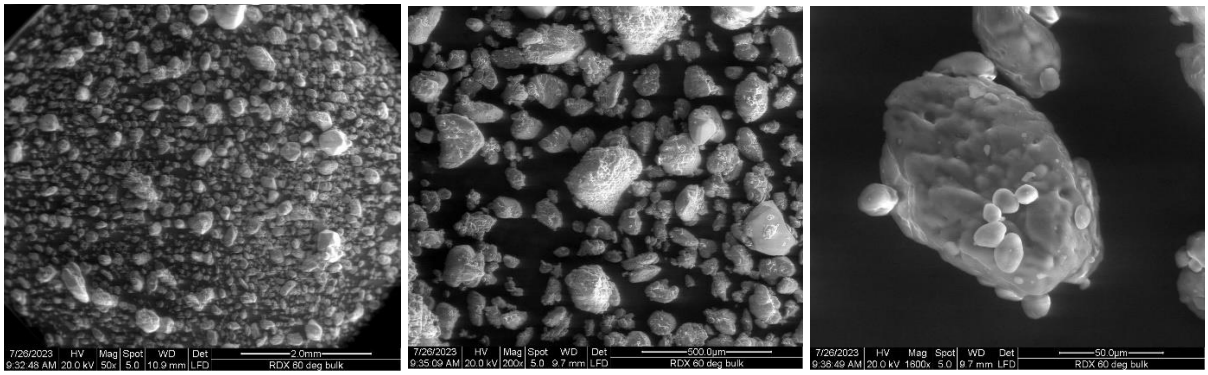

Figure 5: SEM images of bulk conditioned RDX to +60°C at different scales: 2 mm, 500 µm, 50 µm.

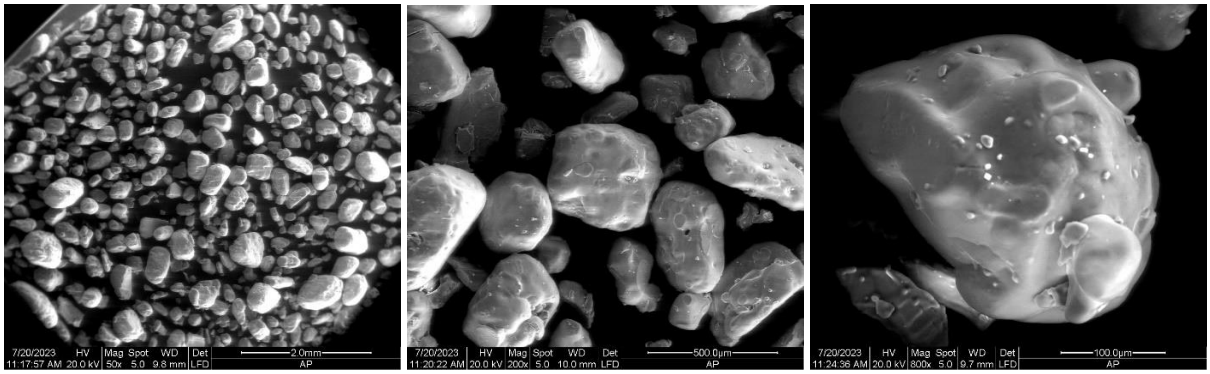

Figure 6: SEM images of pristine AP at different scales: 2 mm, 500 µm, 100 µm.

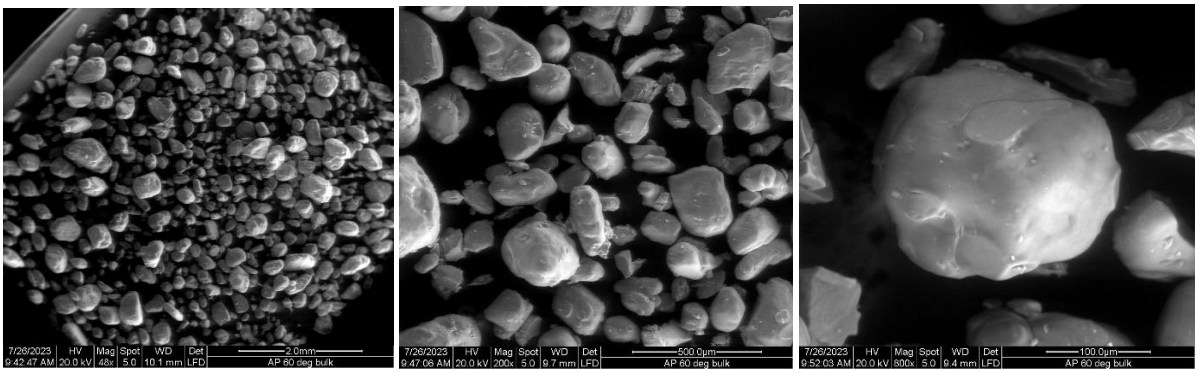

Figure 7: SEM images of bulk conditioned AP to +60°C at different scales: 2 mm, 500 µm, 100 µm.

Pristine TNT exhibits a bimodal particle size distribution composed of big grains distributed around 300 µm, with sharp edges and pointed shapes, and fine grains of a few micrometers in size, as can be seen in Figure 2. After being conditioned at +60°C, we observe grain agglomerates, as evidenced in Figure 3.

This agglomeration observed on the heated TNT samples could be associated with a sintering phenomenon, which is the process of compacting and forming a solid mass of material by bonding particles, without melting it to the point of fusion. This could be caused by the harder and sharper particles being observed at ambient temperature that concentrate the stresses at localized points, necessitating a lower amount of energy to generate a localized temperature rise of sufficient magnitude to react under impact. The softer and agglomerated particles observed at +60°C, on the other hand, would tend to undergo plastic deformation or crushing, making it challenging to achieve such localized energy concentration [12], which may explain the decreased impact sensitivity obtained above a certain temperature. This hypothesis has not been validated in the frame of the present study and would require further testing and analysis.

For RDX and AP, relatively homogeneous grain shapes and sizes can be observed, and the grain morphologies are comparable between pristine and +60°C-conditioned materials. Thus, the morphology and structure of RDX and AP at the microscale level do not allow one to conclude that there is a significant morphological effect to explain the increase in sensitivity from room temperature and +60°C, and the irreversibility observed after conditioning at +60°C.

In order to further investigate the irreversibility aspects of the results obtained at +60°C, further impact testing was conducted on TNT, RDX and AP applying a new preparation method M3 that includes an agitation of the samples:

- **Preparation Method M3**: the samples were agitated at 200 rpm while being bulk conditioned for four hours at +60°C in glass vials, cooled to +25°C, prepared and placed in the test apparatus, and tested.

The results obtained with preparation method M3 are provided in Table 3, in comparison with the previous results.

Table 3: Investigation of the reversibility of impact energy results at high temperature and with preparation methods M1, M2 and M3

Energetic material	E_{50} at + 25°C	E_{50} at + 60°C	Method M1	Method M2	Method M3
TNT	15 J [+1.0, -1.2] J	63 J [+5.7, -4.9] J	65 J [+3.1, -2.7] J	66 J [+4.8, -5.2] J	16 J [+1.2, -0.9] J
RDX	12 J [+0.1, -0.6] J	8 J [+0.1, -0.6] J	7 J [+0.6, -0.0] J	7 J [+0.2, -0.5] J	11 J [+0.7, -0.6] J
AP	21 J [+1.2, -2.0] J	16 J [+1.1, -1.2] J	16 J [+0.4, -0.6] J	17 J [+1.4, -0.6] J	21 J [+0.7, -0.9] J

The results obtained with Method M3 that includes an agitation of the samples are similar or equal to those obtained at +25°C. These results demonstrate the reversibility aspect of the high temperature effects for TNT, RDX and AP at impact sensitivity.

As a conclusion for the influence of temperature, it was shown that the impact sensitivity of AP and RDX increases as the temperature to which they are subjected increases from -40°C to +60°C, meaning that temperature unfavorably affects impact sensitivity for these energetic materials. The microscopic observations conducted on these materials do not explain this phenomenon and further studies need to be conducted. However, the observed increase in impact sensitivity over this temperature range is considered marginal and should not result in greater precautions to be taken when handling RDX or AP which have been subject to temperatures up to +60°C.

For TNT, after an increase in impact sensitivity between -40 and +25°C, an unexpected and significant decrease was observed to occur beyond a certain temperature between +25 and +40°C. The SEM pictures of TNT after heating at +60°C have evidenced TNT agglomerates that do not appear on pristine TNT and that are suspected to be the reason for the decreased sensitivity observed when TNT is tested after heating at +60°C, and without agitation.

It was shown that agitating the samples after heating was sufficient to come back to the same impact sensitivity as the one obtained at ambient conditions, which proves the reversibility nature of the high temperature effect on impact sensitivity for RDX, AP and TNT. SEM pictures of the samples prepared with Method M3 would be necessary to further investigate the effect agitation had on the particles' morphology and thus better understand the observed reversibility aspect.

3. Influence of Relative Humidity

The E_{50} results obtained for the four energetic materials conditioned at two different RH levels (70% RH and 90% RH) are plotted at Figure 8 in comparison to the values obtained at ambient conditions (about 45% RH, 25°C). As for the previous results, each point corresponds to the mean value obtained from three impact tests and the error bars are calculated using the previously mentioned methodology. The E_{50} mean values and corresponding error ranges are given at Table 4.

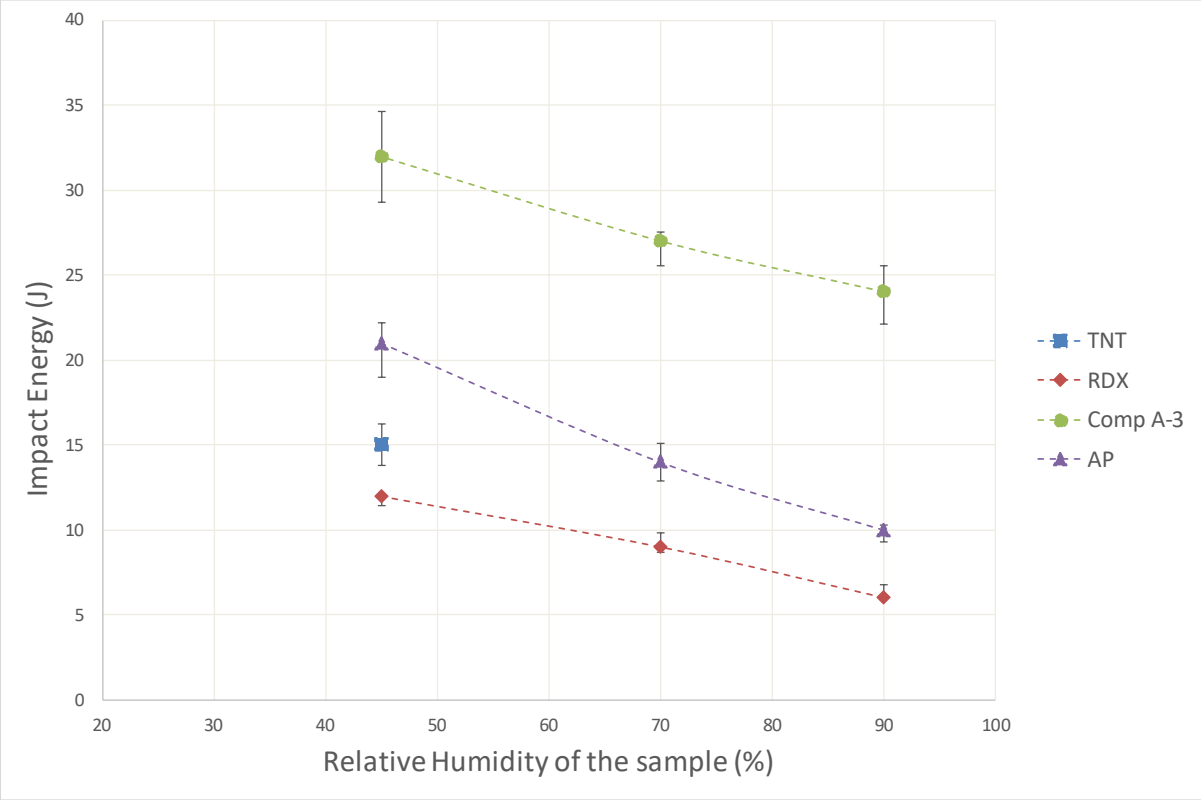

Figure 8: Impact energy as a function of the relative humidity for the four energetic materials considered in this study

Table 4: E_{50} values obtained on the tested energetic materials under different % RH

Energetic material	E_{50} at room RH (approx. 45%)	E_{50} at 70% RH	E_{50} at 90% RH
TNT	15 J [+1.1, -1.2] J	> 100 J	> 100 J
RDX	12 J [+0.1, -0.6] J	9 J [+0.8, -0.3] J	6 J [+0.8, -0.0] J
AP	21 J [+1.2, -2.0] J	14 J [+1.1, -1.1] J	10 J [+0.3, -0.7] J
Comp A-3	32 J [+2.6, -2.7] J	27 J [+0.6, -1.5] J	24 J [+1.6, -1.9] J

The results obtained on RDX, AP and Comp A-3 reveal a decrease in E_{50}, indicating an increase in impact sensitivity, with increasing RH. It can be highlighted that the value of 6 J obtained for RDX at 90% RH approaches the 2 J threshold for a material

to be considered hazardous to handle [11]. The increase in sensitivity for AP and Comp A-3 with increasing RH are less concerning in terms of safety and handling aspects, with higher E_{50} values of 10 J and 24 J at 90% RH for AP and Comp A-3, respectively.

The results obtained for RDX, AP and Comp A-3 under RH were not expected. Indeed, they deviate from the expected trend of a decreased sensitivity with a higher relative humidity, as observed by Coffey and DeVost [12]. This unexpected outcome could be attributed to various factors that may influence the behaviour of the tested materials at high RH. The presence of impurities, temperature fluctuations, moisture distribution, or the samples preparation method could impact the observed sensitivities. This would require further investigation.

As for the study in temperature, TNT stands out from the three other tested materials by showing a significantly decreased impact sensitivity at increased RH levels. Indeed, no reaction was observed up to 100 J, which is the maximum energy value achievable by the BAM machine at RMA. This explains why there are no points plotted at 70% and 90% RH in the graph at Figure 8.

Bulk conditioning of TNT samples in glass vials was conducted at 90% RH. The samples were then dried at +60°C, and analysed by SEM. The images are shown at Figure 9.

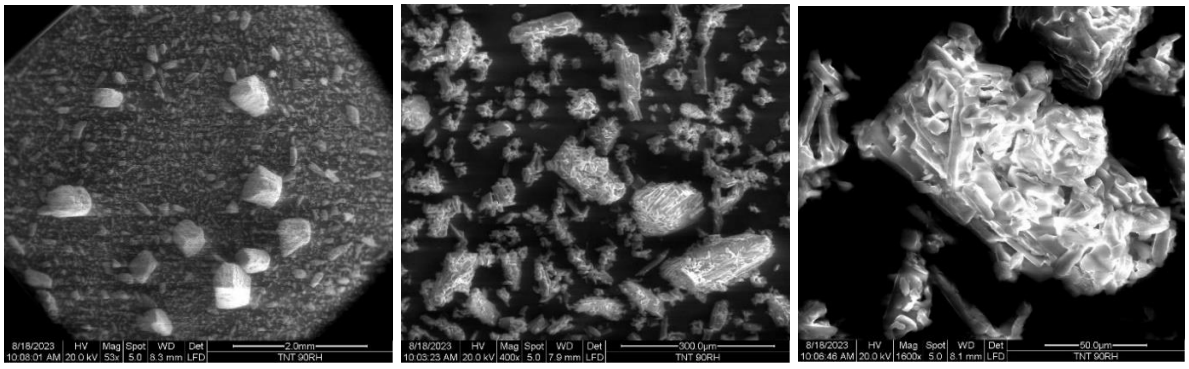

Figure 9: SEM images of bulk conditioned TNT to 90% RH at different scales: 2 mm, 300 µm, 50 µm.

When comparing the above images with the SEM images of pristine TNT (Figure 2), it is clear that subjecting TNT grains to a high humidity level of 90%, and subsequently drying them at +60°C, affects the shape and size of the grains. Agglomerated grains can be observed, together with a higher proportion of fine particles. However, in light of the previous results on the effect of a temperature increase up to +60°C on the morphology of TNT, it is not possible to discriminate if the morphology of TNT as shown at Figure 9 is predominantly affected by the RH conditioning or by the subsequent drying at +60°C or by a combination of both.

As for the study in temperature, the reversibility of the results obtained on TNT, RDX and AP under higher RH levels was investigated. To do so, the samples were first conditioned at 90% RH / 30°C, directly in the test apparatus, in open configuration. They were subsequently dried at +60°C to ambient conditions (45% RH / 25°C) before being tested at impact.

Some evidence of incompatibility was observed on the AP samples conditioned directly in the test apparatus, leading to AP discolouration as shown in Figure 10.

Figure 10: AP samples before (left) and after (right) conditioning at 90% RH in the test apparatus.

To avoid any incompatibility issues with the test apparatus influencing the results, it was decided to condition the samples in glass vials (bulk conditioned). The results for the two conditioning methods are presented at Table 5 in comparison with the previous results.

Table 5: Investigation of the reversibility of impact energy results at 90% RH using different conditioning methods

Energetic material	E_{50} at room RH (approx. 45%)	E_{50} at 90% RH	E_{50} at room RH after conditioning at 90% RH in the test apparatus	E_{50} at room RH after bulk conditioning at 90% RH
TNT	15 J [+1.1, -1.2] J	> 100 J	79 J [+6.0, -5.1] J	14 J [+0.5, -1.2] J
RDX	12 J [+0.1, -0.6] J	6 J [+0.8, -0.0] J	6 J [+0.6, -0.3] J	9 J [+0.3, -0.9] J
AP	21 J [+1.2, -2.0] J	10 J [+0.3, -0.7] J	10 J [+0.5, -1.0] J	18 J [+1.6, -0.9] J

The E_{50} results obtained after conditioning in the test apparatus indicate an incomplete reversibility for TNT, and an irreversibility for RDX and AP. When conditioning in the glass vials, the E_{50} values for RDX and AP fall between the values at room RH, and those obtained after conditioning in the test apparatus, indicating a partial reversibility. For TNT, a complete reversibility is observed after bulk conditioning.

As was discussed previously for TNT, it is not possible to clearly separate the contribution of the conditioning at high RH and the subsequent drying at +60°C on the observed changes in sensitivity. Investigations are ongoing at the RMA to investigate how an increase in RH alone affects the morphology of the samples and the impact sensitivity.

The incompatibility evidenced on AP samples during RH-conditioning makes it even more complicated to conclude on the effect of RH conditioning for this energetic material. This incompatibility was not seen during the tests under temperature, which means it is likely a tertiary incompatibility due to the presence of AP, steel and humidity.

The conditioning method therefore has an influence on the reversibility of RH effects. The extent to which the method affects the reversibility is however dependent on the tested material, with TNT appearing to be more sensitive than AP and RDX to the conditioning method employed.

As previous studies on PETN [12] had demonstrated a reversible nature of the relative humidity effects on impact sensitivity, this phenomenon of partial or total irreversibility was unexpected and would deserve further investigation.

4. Conclusion

The results of the influence on temperature on impact sensitivity show that, except for TNT, an increase in impact sensitivity with temperature is to be expected, but seems to be limited to a decrease in E_{50} values of less than 0.3 J/°C in the examined temperature range. At high temperatures, the influence of the conditioning method on the reversibility aspects has shown to have a strong influence. The possible contribution of a change in morphology under high temperature deserves further investigation.

The results of the influence of RH on impact sensitivity revealed a change in impact sensitivity with RH for all materials: as RH increased from 45% to 90%, an increase in sensitivity is to be expected for RDX, Comp A-3 and AP, while TNT exhibits a significantly lower sensitivity under increased RH. The study of the reversibility of the RH effects does not allow to draw a firm conclusion as the results were biased by the conditioning method.

The full set of results obtained in this study demonstrate the notable influence that temperature and RH conditioning have on the impact sensitivity for the four materials tested: AP, RDX, TNT and Comp A-3. The conditioning method proved to have a significant influence on the reversible nature of the effects identified under temperature and RH.

These results thus demonstrate that the temperature and RH at which small scale impact testing is performed, together with the conditioning method used, should be considered when interpreting and comparing impact test results.

In order to generalize these findings, further investigation is required, involving a broader range of materials, a consolidation of the trends observed in the temperature and RH ranges explored in this study, and a more detailed analysis of the morphological changes of the tested materials under temperature and RH.

5. References

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