Surface Coating of Cyclotetramethylenetetranitramine (HMX) Crystals with the Insensitive High Explosive 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB)

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Abstract: A method to crystallize the thermally stable, insensitive high explosive, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) onto the surface of another high explosive cyclotetramethylenetetranitramine (HMX) crystal is described. Amination of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) in toluene produces TATB which is precipitated by a reactive crystallization process. When the reaction is carried out in the presence of HMX, TATB crystals are found to be deposited onto the HMX crystal surface. This phenomenon was utilized to obtain in situ surface coating of HMX crystals with TATB. Both the conventional amination and the sonochemical amination methods, using dry ammonia (NH₃) gas and ammonium hydroxide (NH₄OH) respectively as the aminating agents, were studied. The coated materials were characterized by Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), Simultaneous Thermal Analysis (STA) and sensitivity tests. The results were compared with those of the virgin materials. Sonochemical amination provided a uniform coating of the HMX crystals. Coated HMX has shown substantial friction insensitivity gain as compared to uncoated HMX. However there is a drop in impact insensitivity in the coated materials.

Keywords: surface coating, cyclotetramethylenetetranitramine, 1,3,5-triamino-2,4,6-trinitrobenzene, 1,3,5-trichloro-2,4,6-trinitrobenzene, scanning electron microscope

Introduction

Cyclotetramethylenetetranitramine, commonly known as High Melting
Explosive (HMX), is one of the most powerful high explosives manufactured in bulk. It is prepared by the nitrolysis of hexamine using nitric acid and ammonium nitrate in the presence of acetic anhydride and acetic acid [1, 2]. Crude HMX resulting from this nitrolysis process is purified by evaporative crystallization using acetone [3, 4]. The crystallization process produces β-HMX crystals of a wide particle size distribution. This polymorph is useful for most military applications. About 60% of the crystallized particles are less than 250 μm (-60 BSS).

1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) is a moderately powerful, thermally stable, insensitive high explosive (IHE). It is produced by the amination of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB) in toluene with dry ammonia gas [5, 6]. TATB assumes a layered structure with a relatively large inter-planar spacing [7]. The amino groups interact with the ortho nitro groups of the same benzene ring and with a nitro group on a nearest neighbour TATB molecule. Thus infinite planar sheets of TATB with strong inter-molecular and intra-molecular hydrogen bonds are formed [8]. This layered structure imparts adhesive properties to the materials and hence TATB can be used as an energetic binder [9, 10]. The hydrogen bonds are also responsible for the insensitivity of this material to impact and friction.

The aim of this work was to crystallize TATB onto the surface of HMX crystals, enabling in situ coating of HMX crystals with TATB. The coating will impart adhesive properties to HMX. Thus HMX-based high explosive shaped charges can be made without the incorporation of conventional non-energetic binders such as wax, polyurethane, resin etc. The presence TATB on HMX crystal surfaces is also expected to impart additional insensitivity and high thermal stability to it without reducing other explosive properties.

This paper describes a novel method for crystallizing TATB onto the HMX crystal surface. The coated HMX was characterized by Scanning Electron Microscopy (SEM). The materials were also characterized for thermal properties using Differential Scanning Calorimetry (DSC) and Simultaneous Thermal Analysis (STA). The coated materials were also characterized by sensitivity tests (friction and impact). The results were compared with the corresponding parameters of the virgin materials.

Materials and Methods

HMX (purity 99%, particle size < 250 μm) and TCTNB (purity: 89%) prepared in our laboratory were used for this study. Other reagents such as toluene, NH₄OH (25% NH₃ content) etc. were of laboratory reagent grade.
Synthesis

The amination of TCTNB in toluene with ammonia produces TATB. In this study, the reaction was carried out in the presence of HMX crystals. Two different methods were adopted for the amination process namely, conventional amination and sonochemical amination. Four sets of samples were generated using different reaction conditions. Details of the synthesis conditions are given in Table 1.

Table 1. Data on synthesis of HMX coated with TATB

<table>
<thead>
<tr>
<th>Sample</th>
<th>Amination type and conditions a</th>
<th>HMX (g)</th>
<th>TCTNB (g)</th>
<th>Toluene (ml)</th>
<th>NH₃ (g)</th>
<th>NH₄OH (ml)</th>
<th>Product (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>sonochemical</td>
<td>9.0</td>
<td>1.7</td>
<td>115</td>
<td>Nil</td>
<td>15</td>
<td>9.8</td>
<td>95.7</td>
</tr>
<tr>
<td>2</td>
<td>sonochemical</td>
<td>8.0</td>
<td>3.4</td>
<td>115</td>
<td>Nil</td>
<td>30</td>
<td>10.2</td>
<td>97.2</td>
</tr>
<tr>
<td>3</td>
<td>conventional</td>
<td>16</td>
<td>6.8</td>
<td>250</td>
<td>Nil</td>
<td>60</td>
<td>19.6</td>
<td>93.4</td>
</tr>
<tr>
<td>4 b</td>
<td>conventional</td>
<td>16</td>
<td>6.8</td>
<td>250</td>
<td>2.5</td>
<td>Nil</td>
<td>19.5</td>
<td>92.9</td>
</tr>
</tbody>
</table>

a Reaction temp. 50-60 °C, time: 3 h, hot water washing was given to samples 1-3 to remove NH₄Cl;
b hot water digestion was not carried out to remove NH₄Cl.

Conventional amination was carried out using either dry ammonia gas or NH₄OH as the aminating agent. A 2 l pressure reactor (Parr Instrument Company, USA, Model 4532M) was used. The typical procedure was as follows: 16 g HMX was added to a solution of 6.8 g TCTNB in 250 ml toluene in the Parr reactor, which was then sealed. The reaction mixture was kept under vigorous stirring (agitator: 200 rpm ) and NH₃ gas (2.5 g), metered through a mass flow meter, was fed continuously into the system for 3 h at 60 °C. After completion of the reaction (indicated by a pressure rise and a drop in temperature), the mixture was cooled and the supernatant toluene was decanted off. The remaining yellow solid mass was digested in water (500 ml) at 90 °C for 1 h. The slurry was filtered, the solid was washed with hot water and then dried in an oven at 80 °C for 1 h. Thus, HMX coated with TATB (19.5 g) was obtained.

For sonochemical amination, an Emco ultrasonic bath (Emco Instruments Ltd, Pune, India) operating at 25 kHz frequency was used and NH₄OH was used as the aminating agent. The typical procedure was as follows: 8.0 g of HMX was added to a solution of 3.4 g of TCTNB in 115 ml toluene in a 250 ml round bottom flask (glass). The flask was placed in the ultrasonic water bath. The solution was stirred with the help of a mechanical stirrer (glass) to disperse the HMX crystals in the TCTNB-toluene solution. 30 ml of NH₄OH solution was added and the amination was carried out for 3 hours at 55-60 °C with the application of ultrasound. After completion of the reaction, the slurry was filtered and the
solid was washed several times with hot water to remove the NH₄Cl impurities. The cake was dried in an oven at 80 °C for 1 h.

Characterization

**Thermal analysis**

DSC analysis was carried out on a Perkin Elmer DSC instrument (Model: DSC-7) with a sample quantity of 1-2 mg; heating rate: 10 °C/min; nitrogen as initial purge gas (flow rate: 40 ml/min). Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out on a STA (TA Instruments, New Castle, DE, USA; Model: SDT Q 600) with sample quantity ~1 mg and heating rate of 5 °C/min under an inert atmosphere of ultra pure N₂ (flow rate: 100 ml/min).

**SEM analysis**

An environmental SEM (FEI, Eindhoven, The Netherlands; Model: Quanta 200) was used for crystal imaging. Images were taken at room temperature using a tungsten filament as the electron source of 10-20 kV energy. A Large Field Detector (LFD) was used for secondary electron imaging under a pressure range of 0.1 to 1.0 torr. The morphological study was carried out using voltages below the charging limit.

**Sensitivity tests**

Friction sensitivity of the samples was determined using a Julius Peter apparatus. The impact sensitivity was tested with 20 mg of samples by the Fall Hammer method (Bruceton staircase method) using 2 kg drop weight.

Results and Discussion

TCTNB is highly soluble in toluene (solubility 125 g/100 g at 20 °C) whilst HMX is only sparingly soluble in toluene (solubility 0.0375 g/100 g at 20 °C). HMX is also unreactive to ammonia. Hence, the HMX crystals remain intact and suspended in the TCTNB-toluene solution during amination.

The presence of three nitro groups makes TCTNB very susceptible to nucleophilic attack by NH₃ at the ortho positions. Thus all of the chlorine atoms are replaced by amino groups through an aromatic nucleophilic substitution reaction and TATB is produced along with NH₄Cl as a by-product. The physicochemical nature of this reaction is complex. NH₃ gas diffuses into toluene and then reacts with TCTNB. Both TATB and NH₄Cl are sparingly soluble in toluene. As a result, supersaturation is reached very quickly and nucleation of
TATB crystals starts. These tiny nuclei grow further through surface integration and finally settle onto the HMX crystal surfaces. Thus, this process facilitates the in situ formation of a TATB layer on the HMX crystal.

An SEM study was carried out for all of the samples. The photographs of virgin HMX and TATB crystals are shown in Figures 1 and 2 respectively. The virgin HMX crystals are of prism shape with smooth surfaces whereas virgin TATB crystals are rod shape with a porous surface. The HMX crystals coated with TATB are shown in Figures 3-8. The photographs reveal that TATB crystals are deposited on the HMX crystal surface. It appears as though each HMX crystal has been jacketed with a layer of TATB particles. This view also resembles a natural snowfall on rocks.

Figure 1. SEM of virgin HMX crystals.
Figure 2. SEM of virgin TATB crystals.
Figure 3. SEM of sample 3.
Figure 4. SEM (close view) of sample 4 A (crude). (Obtruded NH₄Cl globules are seen on deposited TATB particles.)
The nature of the TATB deposition on the HMX crystal surface varies from one sample to another depending upon the process conditions. Conventional amination with NH₄OH (sample 3) imparts poor coating. Most of the TATB particles were found to be precipitated separately (Figure 3). Conventional amination with ammonia gas shows better deposition of TATB. The SEM photograph of the crude product (sample 4A) isolated before digestion in hot water is shown in Figure 4. The rounded globules (marked by a circle) extruding from the surface are NH₄Cl. The dry amination of TCTNB with NH₃ gas produces TATB and NH₄Cl. They are co-precipitated and deposited on the surface of the HMX. The growth of inorganic NH₄Cl crystals is faster than the growth of...
TATB, resulting in NH₄Cl globules obtruding out of the deposited TATB layer (Figure 4). These globules disappear in water-digested material as NH₄Cl is highly soluble in water, leaving pores on the surface (Figure 5). The view of the coated crystal under higher magnification (Figure 5) indicates that the average size of TATB crystals are < 20 μm.

Sonochemical amination was carried out with NH₄OH solution. Two samples were prepared by varying the quantity of TCTNB and NH₄OH (ref. Table 1). The precursor (TCTNB) limits the quantity of TATB produced in the process and thus the % TATB in HMX is controlled. The SEM photograph reveals that the coating is better and more uniform in the sonochemical process compared to the conventional process. Some uncovered surface was observed with sample 2 (Figure 6). The quantity of TATB formed in the process (< 10% of HMX) may not be sufficient to cover all of the available surface of HMX. Sample 3 synthesized with an increased quantity of TCTNB (produced ~20% of TATB w.r.t HMX) shows better coating with almost 90% HMX crystal surface covered (Figure 7). The view of these crystals under higher magnification (Figure 8) indicates that the average size of the TATB crystal is < 10 μm.

The results of the above experiments indicate that there is a strong association between the crystals of HMX and TATB. The deposition is probably induced by minimization of the Gibbs free energy (ΔG) of the nascent TATB crystals which may be considered as the driving force [11]. The driving force for such phenomena may also be due to the formation of hydrogen bonds between the nitro groups of HMX and the amino groups of TATB as shown in Figure 9. TATB deposition is better in the sonochemical process compared to the conventional process. The ultrasonic wave also creates micro-cracks on the HMX crystal surfaces which help to bind the TATB crystals.

Thermal analysis data reveals some interesting decomposition phenomena. The DSC of virgin HMX shows melting at 270 °C followed by the decomposition peak temperature of 280 °C. The decomposition temperature remains unchanged in all of the TATB coated HMX samples (Table 2). A typical DSC curve is shown in Figure 10. The unaltered decomposition peak temperature data indicates that the thermal behavior of HMX remains intact in the coated materials. However, the expected additional gain in thermal stability for HMX owing to its surface coating with a thermally stable explosive, TATB, is not observed. A reduction in the heat release value (ΔH) is observed in the coated materials. This is indicative of the influence of TATB (which is less energetic than HMX) in the decomposition process.
Figure 9. Hydrogen bonds between nitro groups of HMX and amino groups of TATB at the crystal interface.

Figure 10. Typical DSC curve of HMX coated with TATB (sample 2).
A typical STA (DTA+TGA) profile of coated material is shown in Figure 11. The DTA experiment shows a decomposition pattern similar to the DSC. The TGA data reveals that there is a two-stage decomposition for the coated material (Table 2). A rapid weight loss (> 80%) is observed at 265 °C followed by a slow loss in weight (< 20%). It is observed that the percentage of weight loss at the second stage is equivalent to the TATB present in the coated material. Thus, it may be stated that the first stage decomposition is due to HMX and the second stage is for TATB. However, unlike the first stage decomposition, the slow second stage decomposition is not associated with any heat evolution or absorption (no corresponding peak in DSC or DTA). Pure TATB shows exothermic decomposition at ~380 °C. However in coated samples, TATB decomposition occurs at a lower temperature (350 °C). This may be due to the effect of HMX decomposition prior to TATB. The TGA of the crude product (sample 4A) shows one extra minor endothermic peak at 183 °C (with 10% loss in weight) for ammonium chloride decomposition (Table 2).
Table 2. Thermal analysis data

<table>
<thead>
<tr>
<th>Sample</th>
<th>STA</th>
<th>DSC</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Initial temp. of exotherm (°C)</td>
<td>Peak temp. (°C)</td>
</tr>
<tr>
<td>Virgin HMX</td>
<td>269.4</td>
<td>285.2 (exo)</td>
</tr>
<tr>
<td>1</td>
<td>269.4</td>
<td>280.2 (exo)</td>
</tr>
<tr>
<td>2</td>
<td>269.4</td>
<td>281.8 (exo)</td>
</tr>
<tr>
<td>3</td>
<td>268.6</td>
<td>280.7 (exo)</td>
</tr>
<tr>
<td>4A</td>
<td>268.9</td>
<td>183.7 (endo) 281.1 (exo)</td>
</tr>
<tr>
<td>4B</td>
<td>268.5</td>
<td>280.9 (exo)</td>
</tr>
<tr>
<td>Virgin TATB</td>
<td>345.0</td>
<td>375.0 (exo)</td>
</tr>
</tbody>
</table>

*Crude sample before water digestion, contains NH₄Cl impurity.

Sensitivity analysis for the coated material shows a peculiar trend in sensitivity when compared with virgin HMX (Table 3). As expected, the coating has improved the insensitivity to friction of HMX from 12 kg to 36 kg. Pure TATB is very insensitive to friction (36 kg) due to its graphite-like layered structure. The coated materials show similar friction insensitivity due to the presence of TATB on the HMX surface. However, the coated material is found to be more sensitive to impact than the virgin HMX. The height of 50% explosion (H₅₀) was reduced from 94 cm to 38 cm. This significant drop in height may be attributed to a greater number of hot spots in coated materials (hot spots are generally considered as a source of impact sensitivity). These hot spots are generated from the porous and rough surface of the coated materials. The coated materials obtained from the sonochemical process (samples 1 & 2) were more impact sensitive than those from the conventional process (samples 3 & 4B). As discussed earlier, the micro-cracks developed on the HMX surface by the sonication wave during sonochemical amination are probably responsible for the deterioration of the impact insensitivity. Poorly coated material (sample 3) shows the highest impact insensitivity (Table 3).
Conclusion

Amination of TCTNB in an HMX-toluene slurry enables in situ coating of HMX crystals with TATB. Sonochemical amination with NH₄OH gives uniform coating of HMX crystals as compared to the conventional method. DSC and DTA profiles of coated materials were found to be similar to virgin HMX. However, the TGA curve shows two-stage decompositions. There was a gain in friction insensitivity in the coated material due to the presence of TATB on the HMX crystal surface. However, the impact insensitivity (H₅₀) was reduced. The deposition of TATB on HMX crystals during amination may be due to the formation of hydrogen bonds between the nitro groups of HMX and the amino groups of TATB. This needs to be corroborated with further experimental evidence.

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References


