Influence of Graphene Oxide on the Sensitivity Parameters of 1,3,5,7-tetranitro1,3,5,7-tetraazacyclo-octane

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Abstract: 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) is one of the most powerful energetic materials which has several applications. Decrease the sensitivity of HMX is a goal for the researchers. In this work, the influence of graphene oxide (GO) on the sensitivity parameters of HMX has been studied. Graphene oxide has been prepared in our laboratories and it was used to prepare a composite based on GO-HMX by solvent-antisolvent slurry method. The prepared samples have been studied by X-ray diffractometer (XRD). Scanning electron microscope (SEM) has been used to check the crystal morphology of each sample. Selected types of plastic bonded explosives (PBXs) based on HMX have been studied for comparison. Impact and friction sensitivities of GO-HMX and the selected PBXs were measured, and the ignition temperature was determined by deflagration test. It was concluded that the crystals of HMX have been coated by layers of GO and the shapes of the crystals have been modified. GO-HMX has lower impact sensitivity than the individual HMX and the studied PBXs while the friction sensitivity are in the same level. The GO layers caused accumulation of the heat inside the crystals during the heating process and decreased the ignition temperature of GO-HMX. GO successfully decreased the sensitivity parameters of HMX and its effect on the detonation parameters should be studied.

Keywords: Graphene oxide, HMX, sensitivity, activation energy.

1 Introduction

In the field of explosives, it is well known that modern explosives possess high performance as well as high sensitivity to different stimuli [1-3]. However, the safety of these explosives during handling and transportation is still a great challenging [4-6]. Many efforts have focused on studying the positive impact of polymers, as additives to explosive materials forming Plastic bonded explosives (PBXs), on the safety of modern explosives [7,8]. Several techniques have been used to fabricate safe PBXs with high performance and sensitivities [9,10]. PBXs showed a great interest as interesting candidates for improving the safety issues while keeping the high levels of performance of the explosive compositions. Recently, polymer content, crystals shape and size exhibited a significant influence on controlling the explosives sensitivity and performance as well as improving their safety levels [11,12]. 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) has a wide range of applications in the field of modern explosives [13]. However, many researchers have been motivated to develop an applicable method to decrease its sensitivity as a promising step to enhance its safety. Graphene oxide (GO) is a unique material that can be used for the safety performance of explosives because it has high specific surface area and contains various function group of oxygen such as epoxide, carbonyl, and
carboxyl hydroxyl [14-16]. The large theoretical specific surface area of GO together with its high oxygen content made it an interesting candidate that could help to improve properties of HMX. GO can be synthesized by the oxidation of graphite powders through the solvent-antisolvent slurry method.

In this work, a novel method for the preparation of a GO-HMX composite is presented. The effect of GO coating on the sensitivity of the new developed composition has been studied. X-ray diffractometer (XRD) and Scanning electron microscope (SEM) have been used to examine the crystal morphology of these samples. In addition, the activation energy and the ignition temperature of GO-HMX composite have been determined in comparison with the pure HMX and selected conventional PBXs samples.

2 Experimental

2.1 Materials
Sulfuric acid (H₂SO₄), Phosphoric acid (H₃PO₄) and Hydrochloric acid 5% (HCl) were purchased from Aldrich. Graphite and Potassium permanganate (KMnO₄) were acquired from WINLAB, UK. Hydrogen Peroxide (H₂O₂) was acquired from Merck (Germany). Dimethyl Formamide (DMF) was supplied by (Alfa Company, India). Pure HMX crystals were purchased from Eurenco (France). All acquired chemicals were used in the experimental work as received without any additional purification.

2.2 Preparation of Graphene oxide (GO)
GO could be routinely prepared using the Hummers method [17]. However, in this work GO was prepared using the modified Hummers method after performing some modifications. Firstly, 90 ml of H₂SO₄ was added to 60 ml of H₃PO₄ in a 250 ml beaker. Then, 3.0 g of Graphite was added to the beaker with a continuous stirring in the presence of an ice bath to control the reaction temperature. Once the beaker temperature reaches 0 °C, 20 g of KMnO₄ was added. After 30 min, the beaker was removed from the ice bath and left to warm up in the room temperature. The mixture was subjected to mechanical stirring for 1 hr. Afterwards, the beaker was placed on a hotplate to keep its temperature at 60 °C for 24 hr. 500 ml of cold deionized water was then added to cool down the mixture. Then, 30 ml H₂O₂ was added which turns the brownish color of the mixture into yellow. The mixture was then sonicated for 1 hr at 40 GHz. Beaker content was washed by HCL 5% and DW until its pH reaches 6. Finally, the precipitation was dried for 12 hr using a vacuum oven adjusted at 60 °C.

2.3 Preparation of GO-HMX Composites
The second experimental step after the GO preparation was to prepare GO-HMX composite. To do so, 50 ml of DMF was added to 10 mg of the prepared GO in a 250 ml beaker. The mixture was subjected to ultrasonication for 1 hr. Then, 0.5 g of HMX was added to the mixture under continuous sonication for 2 hr at 40°C. Then, the suspension was poured in a cold-water beaker which acts as an anti-solvent. Finally, the GO-HMX composite was successfully separated after 5000 rpm centrifuge followed by washing with methanol. The composite was then dried at 50°C in vacuum oven for 12 hr.

3 Characterization

3.1 X-ray Diffraction
X-ray diffractometer (Shimadzu XRD-6000 with Cu radiation λ=1.54056 Å) was used to characterize the crystal morphology and grain size for pure GO, pure HMX in comparison to the prepared GO-HMX composite. In this work, XRD was also used to investigate the atomic arrangement together with the crystals lattice parameters. During all measurements, the operating conditions of the X-ray tube were kept constant at 30mA anode current and 40kV. However, the 2θ scan ranges from 4° to 90° continuous scanning. Scan speed was adjusted at 8 deg/min and the
preset time was 0.15 sec during the whole measurements. Figure 1 represents the XRD results for HMX-GO composite in comparison to pure HMX and pure GO.

![XRD results](image)

**Figure 1.** XRD results for HMX-GO composite in comparison to pure HMX and pure GO.

### 3.2 Crystal morphology study

Crystals morphology characterization of pure HMX, pure GO and the prepared GO-HMX crystals was done using scanning electron microscope (SEM, JOEL JSM-6010LA). Figure 2 shows the SEM micrograph of the pure HMX crystals while Figure 3 represents the SEM micrograph for the prepared GO-HMX composite.

![SEM micrograph](image)

**Figure 2.** SEM micrograph showing crystals morphology of HMX crystals.
Figure 3. SEM image showing the prepared GO-HMX crystals.

As shown in Figure 2, pure HMX microscale crystals with a particle size less than 100 µm exhibit irregular crystal shape with coarse surface. This could be the main reason beyond the high sensitivity of the pure HMX. Also, appearance of cracks and misalignment of crystals may increase the crystals sensitivity thus decreasing its safety during handling and transportations. On the contrary, Figure 3 shows the coating of HMX crystals by GO particles. Precipitation of GO particles lead to the disappearance of cracks and sharp edges of pure HMX crystals. This could decrease the sensitivity of GO-HMX composite in comparison to pure HMX crystals.

The SEM micrographs showed that the prepared GO-HMX composite exhibited the same particle size as the pure HMX. This confirms that precipitation of GO particles has successfully coated HMX crystals without affecting the used size of HMX crystals. This could be the reason beyond the disappearing of cracks and sharp edges shown in case of pure HMX crystals. Therefore, the sensitivity of the pure HMX could be decreased and thus become safer. In brief, addition of 2 wt % of GO to HMX significantly affects the morphology of HMX crystals in the prepared GO-HMX composite.

3.3 Impact sensitivity measurements

The sensitivity of the prepared GO-HMX composite towards impact was determined by a standard impact tester with exchangeable anvil (Julius Peters) [18], then compared to the impact sensitivity of the studied PBXs based on HMX. In this technique, a 2 kg drop hammer was use. Volume of the samples under investigation was kept constant at 50 mm³. The initiation probability of the tested samples was measured using the Probit analysis technique [19]. The impact energy required to successfully initiate 5 samples out of 10 was reported as sensitivity to impact of the samples as given in Table 1.

3.4 Friction sensitivity measurements

BAM friction test apparatus [18] has been used to measure the sensitivity of the prepared GO-HMX composite to friction stimuli in comparison to that of pure HMX crystals. Friction measurement was done by applying the standard test conditions. Firstly, a fixed weight of tested explosive sample of 0.01g was placed on the surface of a porcelain plate. Then, the normal force induced between the porcelain pistil and the plate was regulated using different loads. Sound and smoke together with the observation of a characteristic smell coming from the decomposition products were used as an evidence of initiation of sample. Initiation probability of the tested samples was measured using the Probit analysis [19]. The normal friction force required for initiating samples was recorded once 5 samples out of 10 were successfully initiated. Table 1 summarizes the results of the sensitivity of samples to normal friction force.
3.5 Ignition temperature measurements
The ignition temperature was determined by using Chilworth deflagration test. 0.1 g of each sample was added in three test tubes and placed vertically into the heating block. The increase in the heating rate was 5 °C min⁻¹. The ignition temperature was reported at moment of ignition of the samples. The mean value of three measurements was reported in Table 1.

Table 1. Ignition temperatures and sensitivity results of the studied samples.

| No. | Explosive type            | Impact sensitivity (J) | Friction sensitivity (N) | Ignition temperature (°C) |
|-----|---------------------------|------------------------|--------------------------|---------------------------|
| 1   | HMX [8]                   | 6.4                    | 95                       | 276                       |
| 2   | GO-HMX                    | 12.3                   | 226                      | 269                       |
| 3   | HMX-Viton [8]             | 10.3                   | 304                      | 279                       |
| 4   | HMX-Fluorel [8]           | 10                     | 312                      | 278                       |
| 5   | HMX-PMMA [8]              | 12.7                   | 211                      | 267                       |

Figure 4. Impact and friction sensitivity results of GO-HMX.

Figure 4 represents the results of both the impact and friction sensitivity results of GO-HMX composite in comparison to impact and friction sensitivity results obtained for HMX-PMMA, HMX-Viton and HMX-Fluorel. These results showed that prepared GO-HMX composite exhibited lower impact sensitivity than values obtained in case of pure HMX, HMX-Viton and HMX-Fluorel studied samples. This confirms that GO has a significant impact on reducing the value of HMX sensitivity to impact. This could be attributed to the coating of GO particles to the HMX crystals which lowers potential energy on the HMX crystals. Decreasing the potential energy of HMX crystals directly affects their impact energy and as result increases their safety levels. On the other hand, the results of friction sensitivity of GO-HMX was found to be higher than that of both HMX-Viton and HMX-Fluorel. Interestingly, GO-HMX composite showed lower impact and friction sensitivities than HMX-PMMA. This could be attributed to the influence of fluorinated binders which lowers the sliding friction on the HMX crystals themselves.
These results clarify that coating of HMX crystals by GO particles greatly affects the sensitivity of PBXs based on GO-HMX composites.

Figure 5 presents the ignition temperatures of the studied samples. Addition of GO decreased the ignition temperature of the pure HMX from 276 to 269 °C. This result might be due to the ability of GO to conduct the heat to the explosive crystals and caused accumulation of the heat inside the crystals, so quick ignition happened. Also the ignition temperatures of HMX bonded by viton A and fluorel binders are higher than that of the pure HMX, in this case the binders act as inhibitors and caused increase in the ignition temperature.

![Figure 5. The ignition temperatures of the studied samples.](image-url)

4 Conclusion

In this work, GO-HMX composites with regular shaped crystals were prepared. GO-HMX samples exhibited smooth surface with the absence of cracks in comparison to the morphology of pure HMX crystals. The developed GO-HMX morphology enhanced the impact and friction sensitivities due to the successful coating of the HMX crystals. Effective coating of HMX crystals with 2 wt% of GO significantly improved the kinetic characteristics of GO-HMX composite samples which could be a direct influence of the interaction between GO particles and HMX crystals. These results make GO a promising candidate to be used as an energetic material in PBX formulations, instead of the conventional binder systems, to decrease the sensitivity of explosives.

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