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Investigation of Crystal Morphology and Shock Sensitivity of Cyclotrimethylenetrinitramine Suspension by Rheology

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Abstract: Crystal morphology and shock sensitivity of a series of cyclotrimethylenetrinitramine (RDX) particles suspended from ethylene glycol were investigated. Flow rheology was employed to measure the rheological properties of the suspensions at constant temperature; it was observed that the stress-shear rate and viscosity behavior of the suspensions were controlled by the particle morphology. The viscosity of the RDX suspensions changed with the roundness/smoothness of RDX crystals at all applied shear rates. The suspensions containing crystals with smoother morphology showed reduced viscosity. When the viscosity data was compared to the shock sensitivity results from the RS-RDX Round Robin study, a good correlation was obtained. This study has validated the use of flow rheology to indicate the morphology and shock sensitivity of crystalline particles.

Keywords: Crystal · Morphology · Cyclotrimethylenetrinitramine · Rheology · Sensitivity

1 Introduction

The shock sensitivity of polymer bonded explosives (PBXs) is influenced by many factors including crystal size, morphology, and internal crystal defects. Spheroidization of irregular shaped cyclotrimethylenetrinitramine (RDX) crystals has been reported to reduce shock sensitivity [1]. Shi and Brenner's computational model demonstrated that the facet tips of angular crystals promote the generation of hot spots due to shock focusing and compression [2].

Optical microscopy is currently the standard method for evaluating crystal morphology [3–5]. But this method is highly subjective, time consuming, and difficult to reproduce between laboratories [6]. It is clear that a non-subjective method of assessing RDX crystal morphology is required to give reliable quantitative information that is not based on an arbitrary scoring system.

A potential technique that is thought to fulfil the criteria for an alternative method of RDX morphology characterization is flow rheology analysis of RDX suspensions. The flow behavior of particles is strongly influenced by particle shape. Irregular/angular particles show a higher resistance to flow than spherical particles as they tend to "lock up" together easier than rounder particles [7]. The effect of particle shape on rheological properties of a wide range of materials in different applications is recognized. For example the influence of particle shape on flow behavior of a powdered pharmaceutical product [8], a solid phase lubricant [9], and cement composites [10] has been reported.

Some investigations on the flow behavior relating to RDX particle shape has been conducted by viscometry of pre-cured PBX formulations [11,12]. However, the authors are unaware of any previous rheological characterization of RDX particles with different morphologies suspended in fluids. In this study we focus on investigating the influence of RDX crystal morphology on rheological properties by suspending RDX crystals in the polyethylene glycol (PEG).

2 Experimental

In this study five different RDX samples were examined. Table 1 and Table 2 list the RDX lots tested and indicates their general morphology. Polyethylene glycol (PEG) with a molecular mass of 200 g mol^{-1} (BDH, UK) was used as received for the suspending medium. PEG was chosen as the suspended medium because it is neither sensitive nor volatile and hence is expected to generate reproducible results. PEG also has the advantage of being Newtonian so any rheological properties/changes, observed between the suspensions, will not be masked by its rheological properties. All of the batches had a particle size that conformed to Class 1 specification in Mil-DTL-398. This particle size distribution has an average particle size of approximately 200–250 μm [15].

All measurements were performed with a Bohlin CVOR 150-HR rheometer (Malvern Instruments Ltd, Malvern, UK) under controlled stress mode. Parallel plate geometry with 40 mm diameter plate was used in all the experiments. A Peltier temperature control system was used to keep a con-

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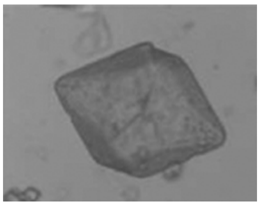
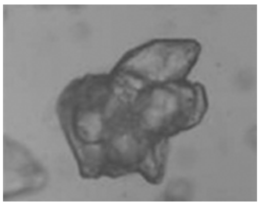
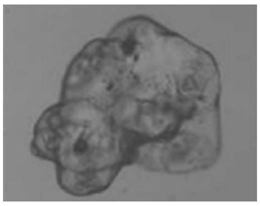
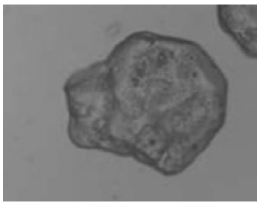
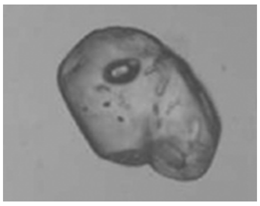
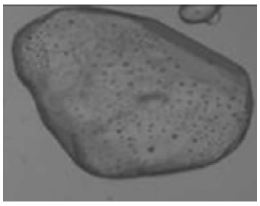
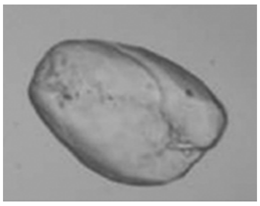
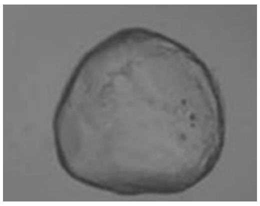
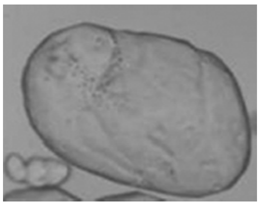
Table 1. RDX samples used in this study.

Lot	Manufacturer	Grade	Lot No.	General morphology
A	Dyno Nobel	Dyno II	DDP04L001–002	Angular, very rough
B	Ordnance Systems Inc.	Holston II	–	Irregular, rough
C	Eurenco, France	I-RDX®	4904S04	Irregular, smooth
D	Royal Ordnance Defence	BAE-RO	6575	Slightly irregular
E	Dyno Nobel	Dyno RS	DDP03K001–002	Spherical, elliptical

Table 2. Typical RDX sample morphologies.

RDX sample	Examples	
A angular, very rough		
B irregular, rough		
C irregular, smooth		
D slightly irregular		
E spherical, elliptical		

stant temperature of 25 °C for all measurements. The rheometer was calibrated at 20 °C for viscosity measurement using viscosity oils, U3600 and U2400, purchased from PRA Coating Technology.

Viscometry measurements were performed to determine how/if RDX crystal morphology affects the viscosity η and shear rate γ^* of RDX suspensions with increasing shear stress σ. A total solid load of 60 wt-% RDX was prepared for each RDX sample. This amount of RDX was chosen as this was a good approximation to the proportion of RDX in the PBXN-109 formulation [16] used in the R4 shock sensitivity studies [4,17]. Anionic surfactant, (teepol, 5 wt-%) was also added to ensure good dispersion of the crystals. For each test 75 data points were collected ranging from a minimum applied shear stress of 5 Pa to a maximum of 200 Pa, with the stress levels increasing logarithmically. For each measurement an equilibration period of 15 s was taken before measurement commenced (the measurement period was set at a maximum of 30 s at each stress level). A 1 mm gap was used for samples A, C, and D. For samples B and E, a 2 mm gap was used as those samples would not flow smoothly with only a 1 mm gap to obtain reliable results. It is probably that these two batches of RDX had some larger crystals compared to the other samples tested.

3 Results and Discussion

As expected, all the suspensions showed non-Newtonian flow behavior. This departure from non-Newtonian properties is due to the presence of the RDX crystals in the suspension. Viscous forces between the crystals and the PEG alter the overall rheological properties of the suspension. The plot of the viscosity verses shear stress for PEG/5 wt-% teepol (not shown) indicated that the matrix fluid used exhibits Newtonian viscosity behavior and did not influence the results. The relationship between the viscosity and shear stress of a series of RDX/PEG suspensions is shown in Figure 1. The graph suggests that the crystal morphology influences the RDX/PEG suspension viscosity. The suspension containing very angular/irregular morphology has the highest mean viscosity at all shear stress values and the suspension made with smooth/rounded crystals has the lowest mean viscosity across the shear stress range. For all samples there is an initial rise in viscosity with increasing Shear Stress (shear thickening), which peaks at an applied shear stress between 7 and 12 Pa, then the viscosity decreases exponentially. The initial rise in viscosity is thought to be due to the suspension resisting flow deformation, as at low shear stress the crystals are closely packed together. After the peak in viscosity, the shear stress has become high enough to disrupt the particle structure in the suspen-

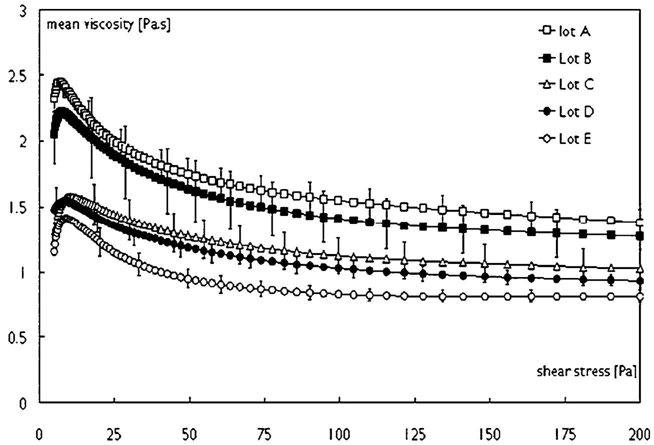


Figure 1. Plots of mean viscosity verses applied shear stress for the RDX-PEG suspensions.

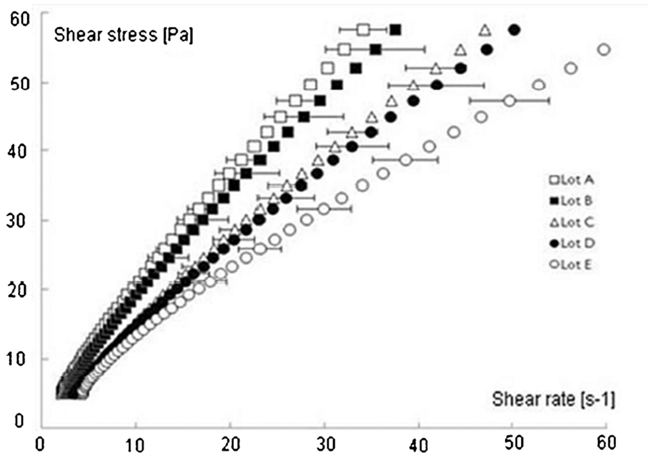


Figure 2. Plots of mean shear rate verses applied shear stress for the RDX-PEG suspensions.

sion allowing flow to occur, i.e. the yield stress has been reached. Smoothing caused by collisions and grinding between crystals may also be occurring leading to reduction in viscosity. This reduction in viscosity seems to be greatest for the suspensions containing crystals from lots A and B, the most rough and angular shaped crystals. Suspensions containing smoother crystals from lots C, D, and E show a less pronounced reduction in viscosity. Crystals that are rougher will undergo a greater change in morphology as they become smoother than crystals that initially have a smooth shape.

The influence of morphology on viscosity relies on how crystals of different morphology allow fluid flow to occur. Crystals with rough/angular morphology are expected to flow less easily as they tend to "jam up" in the suspension. This jamming character is expected since rough particles touch each other during flow, therefore restricting flow to occur as evidenced by increasing viscosity. According to lubrication theory smooth particles do not come into physical contact under finite forces and hence flow freely showing lower viscosity [13]. A similar behavior is observed in our results. As particle morphology becomes rounder/smoother there is less resistance to flow because the crystals can slip against each other resulting in a lower viscosity. This agrees with Dexter et al. [12] who reported that the morphology of RDX crystals affects the viscosity of precured PBX formulations. A formulation made with rounder crystals had a lower viscosity then an equivalent formulation made with angular crystals. This is an important consideration in PBX processing.

Figure 2 shows how the shear stress that each RDX-PEG suspension undergoes changes as a function of the shear rate. For all the suspensions, at shear rates below approx. 20 s^{-1} the relationship between shear rate and shear stress is not linear. At higher shear rates this relationship becomes more linear. At lower shear rates RDX crystals are able to agglomerate, which results in the non-linear behavior. The transition from the non-linear to linear region indicates where the yield stress is reached. The yield stress is the stress that is required for particle agglomerates to be broken up in the suspension. The linear portion of the curves represent where the suspension flows viscously. Similar observations were reported by Müller et al. [14] who saw a yield stress point in suspensions of spherical particles. The close proximity of the crystals in these agglomerates affects their movement due to hydrodynamic interaction, which has a strong influence of the rheological behavior of the suspension. It has also been noted that when non-spherical particles (such as RDX crystals) are suspended in a Newtonian matrix the particles arrange themselves into preferred directions. This produces an anisotropic structure, where flow occurs easier in the preferred crystal alignment, leading to non-Newtonian behavior [15]. At higher shear rates the crystal agglomerates are broken up and the interaction between crystals becomes weaker, so the Newtonian behavior of the PEG matrix suspending the crystals becomes more predominant.

The rough/irregular crystal suspension has the lowest shear rate at all measured shear stresses, whereas the rounder/smoother crystal suspension has the highest shear rate. The gradient of each line is the viscosity. Therefore, rough/irregular crystal suspensions have the highest viscosity indicated by the steepest gradient, whereas the rounder/smoother crystal suspension has the lowest viscosity and gradient.

Figure 3 shows the plots of the maximum viscosity and maximum shear rates for each suspension against the mean morphology scores by optical microscopy for the RDX lot, previously published [18]. For each set of crystals a total morphology score was given by assigning each crystal into one of eight morphology bins either: sharp edges/corners; elongated/rounded; irregular rough; irregular smooth; much geometry; some geometry; elliptical and circular/spherical. Each bin had a score assigned to it (5–100)

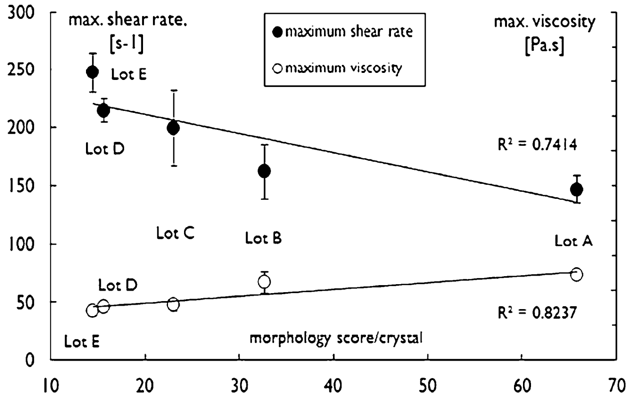


Figure 3. Maximum shear rate and maximum viscosity against the mean morphology score of the RDX lots obtained from Ref. [18].

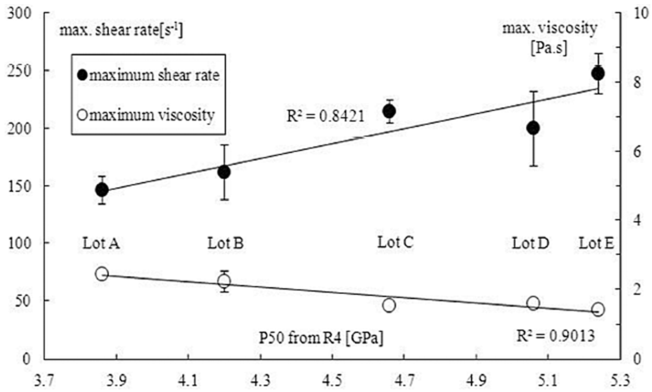


Figure 4. Maximum shear rate and maximum viscosity against previously published shock sensitivity (P_{50}) data [4].

with angular crystals given higher scores than smoother crystals. There is a strong negative correlation between maximum shear rate and the morphology scores; with increasing morphology score the maximum shear rate decreases. Conversely, the maximum viscosity increases as the morphology score increases. Both trends shows a linear relationship, initially the maximum shear rate decreases and maximum viscosity increase rapidly as morphology score increases (moving from round/smooth to intermediate morphology).

When crystal morphology becomes more angular the viscosity decreases slower. This implies that the rheological properties of the RDX-PEG suspensions are sensitive to changes in morphology of smooth crystals. A change from medium to very angular/rough morphology has only a small effect. The strong correlation between the morphology scores and the parameters measured suggests that rheological characterization of RDX suspensions could provide a non-subjective alternative to matching fluid microscopy for RDX crystal morphology assessment as used in the R^4 program.

Figure 4 shows a strong correlation between the maximum viscosities and maximum shear rates for each RDX-PEG suspension and the previously published shock sensitivity data of the RDX/PBX formulations [4,17] in a large scale gap test (LSGT). There seems to be a clear relationship between the shock pressure required for a 50% probability of initiation of each RDX sample, P_{50} (when formulated as a PBX) and the maximum viscosity when suspended in PEG. With decreasing suspension viscosity, the PBX shock sensitivity decreases (as indicated by a higher initiation pressure, P_{50}). Conversely, shock sensitivity decreases as the maximum shear rate increases.

The correlation between shock sensitivity, maximum shear rate, and maximum viscosity could be due to how well the RDX formulations can dissipate the applied shock energy. Compositions that were made with very angular crystals showed the lowest maximum shear rate and highest maximum viscosity when in suspension and were also the most shock sensitive in the large scale gap test. It is possible that the angular crystals reduce the ability of the formulation to flow and dissipate regions of concentrated shock energy (hot spots). As the crystals become smoother the formulation is able to flow better (higher shear rate) allowing hot spots to be dissipated, therefore reducing shock sensitivity. In addition to morphology, the shock sensitivity of polymer bonded explosives (PBXs) is also influenced by many factors such as crystal size, surface roughness, internal crystal defects and impurities. The good correlation between the morphology scores, the maximum viscosity and maximum shear rates indicates that measuring the rheological properties of RDX in suspension could be a method to determine crystal morphology.

4 Conclusions

RDX crystal morphology strongly affects the rheological properties of RDX-PEG suspensions. Therefore rheological analysis of RDX suspensions could possibly be employed as one of the potential tools to assess crystal morphology. It would also provide an indication of shock sensitivity. A suspension with a higher viscosity would indicate that the RDX crystals are angular rather than smooth/rounded. The good correlation between the rheological parameters and the morphology scores obtained from the microscopic analysis suggests that this method provides results that are non-subjective, fast and more reliable than the techniques so far used.

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