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Studies on the Tailoring of Particle Size and Micromeritic Properties of Reduced Shock Sensitivity RDX (RSS-RDX)

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Abstract: The microstructure of explosive particles, as well as formulations, has a significant influence on the shock sensitivity of various energetic formulations. Particle shape and specific size distributions are always important considerations in explosives processing in order to realize better process parameters. The present study aimed to explore crystallization variables required to achieve a specific particle size of Reduced Shock Sensitivity RDX (RSS-RDX). Crystallization process factors such as cooling rate, agitator speed and configuration, *etc*. have been systematically studied to understand their effect on the particle size. The study also established the crystallization process parameters required to tightly control a specific particle size distribution ranging from 50 to 500 μm by cooling crystallization. Fine particles ranging from 15 to 30 μm were prepared by an ultrasonication technique. Ultrasonic process parameters, including temperature, time and ultrasonic frequency, were studied and the process conditions were optimized. Micromeritic characterization of RSS-RDX revealed the nature of flowability, which in-turn is useful in identifying the ease of processability. Overall, our interest stemmed from an investigation which showed that careful optimization of crystallization variables can lead to a specific particle size distribution.

Keywords: crystallization, RSS-RDX, micromeritics, particle size distribution

Introduction

Reduced sensitivity RDX offers tremendous potential for reducing the vulnerability of explosive formulations. Its use in cast-cured and pressable PBX compositions has received a lot of attention and interest from the explosives community in recent years [1]. Recent literature revealed that SNPE were the first to report an Insensitive RDX (I-RDX) [2], while work conducted at DSTO [3] has shown that ADI Grade-A RDX has properties equivalent to those of I-RDX and is classified as Reduced Sensitivity RDX (RS-RDX). Dyno Nobel claimed 'reduced-sensitivity RDX', prepared by a proprietary crystallization process, passed round-robin testing [4]. It was revealed that the evaluation of RSS-RDX in the PBXN-109 formulation can reduce the sensitivity to shock, fragment impact and shaped charge jet attack [5, 6]. RSS-RDX can play a further role on the ageing characteristics in both pressable and cast cure formulations [7-10]. Recently, Chemring Nobel also introduced a reduced sensitivity RDX (RSS-RDX) made by the Bachmann process [11].

The particle microstructure [12], including density, particle size, product quality, lack of inclusions, internal and external defects, and surface texture have a large influence on shock sensitivity, processing and performance, and the desired microstructure can be obtained by different crystallization process technologies [13]. Specific particle size distributions (PSD), with preferred morphologies, are important for many reasons in explosive and propellant formulations, and a mixture of two or three (bimodal/trimodal) different sized particles are preferable for achieving specific packing densities and free-flowing properties [14]. Hence, it is essential to characterise powders for their micromeritic behaviour that includes particle size, bulk density, tapped bulk density, compressibility index/Carr's Index (CI) and Hausner Ratio (HR). The CI and HR values can give indications concerning the flowability of the powders, which it is necessary to achieve before being used in high explosive (HE) formulations.

Globally, few proprietary crystallization methods have been evolved for the preparation of RDX crystals with improved quality, however, very scant information is available on particle size distribution studies of RSS-RDX [15-17]. The present study aims to investigate the process variables, such as cooling rate, agitation speed, time and the kind of agitator, necessary for producing monodisperse RSS-RDX of a wide range of particle size distributions. Furthermore, in order to prepare particle sizes less than 50 μm, a sonocrystallization method was employed and the parameters, such as sonication time, frequency and concentration of solvent, optimized. The processability of these specific

RSS-RDX particles in formulations was studied indirectly by analyzing their micromeritic characteristics and is discussed in the present paper.

Materials and Methods

All of the reagents and chemicals used in the present study were of AR grade and used as such. Particle Size Distribution (PSD) was measured by the laser diffraction principle using a Sympatech laser diffraction particle size analyzer. The morphology of the materials was confirmed using an Optical Microscope RAX-vision Y-coo series. A helium gas pycnometer of Thermo Scientific make was used to measure the true volume of the solids by measuring changes in pressure with helium gas displacement. The bulk density and tapped bulk density were measured as per USP-II Standard Procedure under the defined tapping procedure using a Tap Density Apparatus of Veego Industries, India.

In-house prepared RDX was used for the crystallization studies. All of the studies were carried out in a Syrris automated synthesis reactor. The reactor was fitted with a 500 mL jacketed reaction vessel and a circulator system for temperature control. The three different agitators used in the study were propeller (400×40 mm), anchor (400×80 mm) and retreat impeller (400×75 mm), and were capable of agitation at a maximum of 1000 rpm. Sonocrystallization experiments were performed in a stainless steel, dual frequency (53 and 35 kHz) ultrasonic bath (make: MAC, Pvt, Ltd., India).

Results and Discussion

High Energy Materials Research Laboratory (HEMRL), India, has developed a process for making Reduced Shock Sensitivity RDX (RSS-RDX) from RDX prepared by the nitric acid process [15]. The prepared RSS-RDX has been incorporated in PBX-109 formulations containing aluminum powder and Hydroxyl Terminated Polybutadiene (HTPB) as the binder. The PBX charge filled tubes were subjected to the large scale gap test to obtain the minimum detonation pressure required for initiation of the charge. The shock sensitivity results revealed that the RSS-RDX based PBX-109 required approximately double the shock initiation pressure compared to the standard RDX based PBX, as shown in Table 1 [18]. The results from the large scale GAP test also showed that this result is comparable with those for the RS-RDX from other countries and which created interest in developing IM formulations based on RSS-RDX.

However, it was realized that the mix-fluidity of the PBX formulations was poor, arising from the poor control of particle size distribution of the RSS-RDX employed for the above studies. This restricted its further evaluation and hence this study attempted to develop the methodology required for achieving specific particle size distributions by optimizing the crystallization variables of the HEMRL developed process.

Table 1. Shock sensitivity results of PBX-109 formulations by the gap test [18]

Conventional RDX				Reduced Shock Sensitivity RDX (RSS-RDX)		
Sl. No.	Attenuator thickness (mm)	Detonation result	Detonation pressure (kbar)	Attenuator thickness (mm)	Detonation result	Detonation pressure (kbar)
1	50	no go	22.69	45	no go	26.86
2	40	go	31.78	35	no go	37.62
3	45	go	26.86	30	no go	44.52
4	50	no go	22.69	25	go	52.69
				30	no go	44.52
Average	47.5	--	24.7	27.5	--	48.4

Tailoring of particle size

The different and specific size distributions, along with the desired morphology of the particles in a particulate product, are important for many reasons in explosive formulations. Particle size has an influence on the shock sensitivity of formulations. Particle size and shape also play a vital role in achieving the desired bulk density, as well as the theoretical maximum density, and in improving the processability by decreasing the viscosity of cast formulations. Furthermore, a particular particle size, along with bimodal/trimodal size distributions, is preferred for achieving a specific density and is also important for providing free-flowing properties. Hence, it is essential to ensure production of mono-disperse particles of different specific sizes. In agitated crystallization systems, it is possible to modify the particle size distribution by optimizing parameters such as cooling rate, agitator configuration and speed *etc*. The present study identified the role of the above parameters in tailoring the particle size of mono-disperse RSS-RDX. The measured particle size in this study equates to Volume Mean Diameter D[4,3] and in all cases a true Gaussian type distribution was realized, which confirmed the mono-dispersion as shown in Figure 1. Optical microscopic images of the control and the RSS-RDX are shown in Figure 2 and confirm the regularity of the crystals resulting from this study.

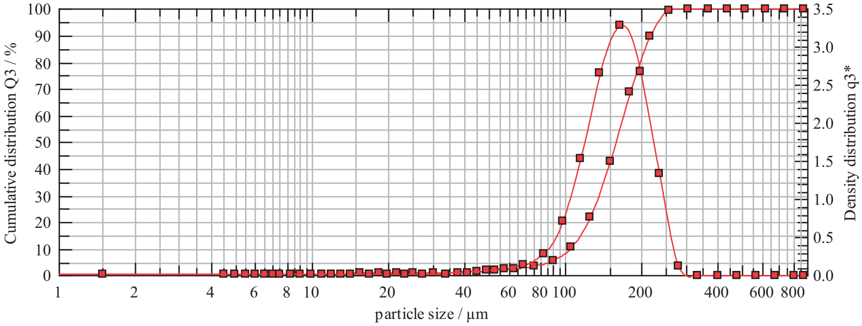

Figure 1. Mono-disperse RSS-RDX with D[4,3]: 160 µm.

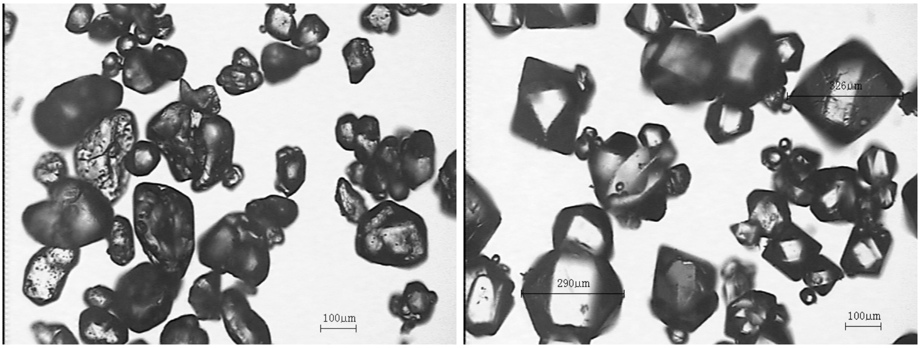

Figure 2. Microscopic images of control RDX (left) and RSS-RDX (right).

Effect of agitator configuration and RPM on size distribution

Three types of agitator configurations viz., propeller, retreat impeller, anchor, have been used in the present study. Figure 3 shows the effect of different agitator speeds (100, 300, 500 and 700 rpm) and configurations (propeller, retreat impeller and anchor) on the particle size at a uniform cooling rate of 2 °C/min. In true crystallizations, an increase in the agitator speed decreases the particle size due to the large mechanical energy transfer to the medium, which is seen in Figure 3 (irrespective of the agitator shape). However, there is a minimum energy required for mixing and hence the particle size increases from 100 to 300 rpm in the case of a propeller blade. Of the three different agitators, a propeller leads to coarser particles (280-380 µm), but beyond 500 rpm there is no significant change in the particle size when using a propeller. A retreat impeller always leads to moderately fine particles, in the range 45-175 µm. An anchor blade results in relatively medium sized particles, 150-280 µm. Relatively, the higher particle sizes generated by using a propeller, in contrast to the other configurations, may be attributed to the flow pattern and clearance from the wall. A propeller generates axial flow whereas tangential to radial flow patterns are created by anchors and impellers. Furthermore, the use of both anchor and impeller with small clearances from the bottom and the crystallizer wall, leads to better homogenization [19], resulting in smaller size distributions. Overall, by changing the agitator speed and configuration at a particular cooling rate, it is possible to tailor the particle size from 40 to 380 μm.

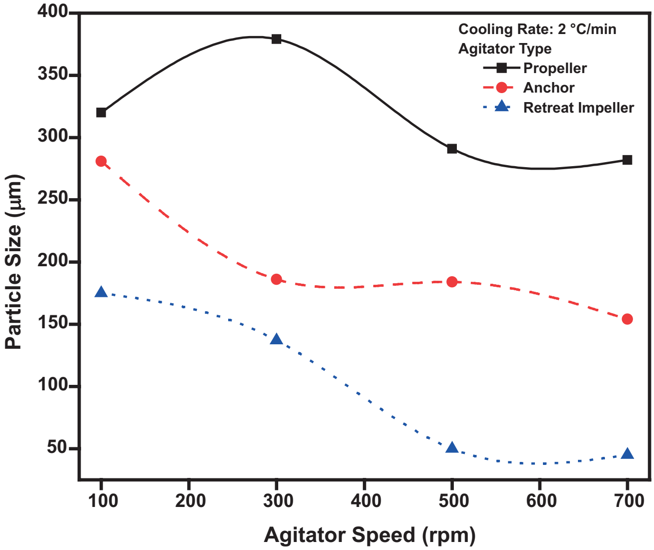

Figure 3. Effect of agitator shape and speed on PSD.

Figure 4 compares the effect of all of the configurations at two selective agitator speeds (400 and 700 rpm) at a uniform cooling rate of 10 °C/min. The propeller configuration generates coarser, monodisperse particle sizes of about 280 μm (at 400 rpm), decreasing to 245 μm at 700 rpm. The anchor blade generates particle sizes of 150 and 90 μm at 400 and 700 rpm respectively, while the retreat impeller does not alter the particle size significantly with change in speed.

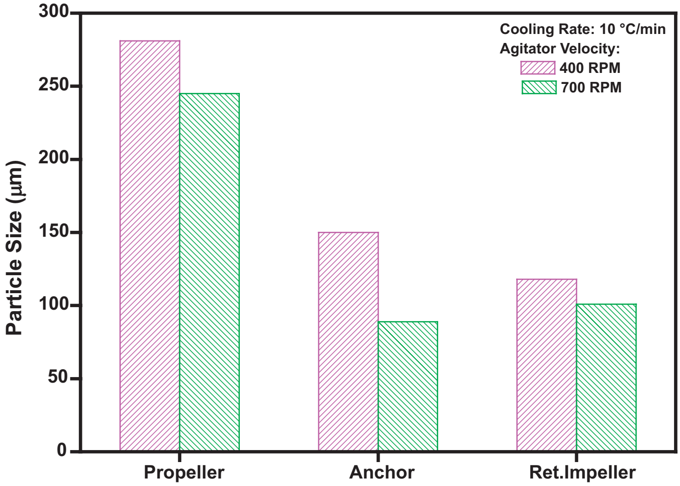

Figure 4. Effect of agitator at two speeds.

Effect of cooling rate on size distribution

In the present study, different linear cooling profiles (0.5, 2, 5 and 10 °C/min) have been employed with all three agitators at a specific agitation speed viz., 400 rpm (Figure 5). In general, a higher cooling rate causes a decrease in particle size in the crystallization. About 400 μm particles were obtained with a relatively low cooling rate (0.5 °C/min) using a propeller agitator. However, above 5 °C/min no significant effect of the cooling rate on particle size was observed. In the cases of the anchor and retreat impeller, no influence of the cooling rate on the particle size was observed and particle sizes of 150-170 μm and 110-130 μm respectively were obtained.

Figure 6 compares the effect of all the blade configurations at an agitator speed of 700 rpm at two selected cooling rates 2 and 10 °C/min. Of all the agitators, the propeller generates relatively larger particle sizes, about 280 and 245 μm at 2 °C and 10 °C/min respectively. The anchor blade results in moderate particle sizes, 154 μm (2 °C/min) and 80 μm (10 °C/min), while the retreat impeller generates relatively fine particles of about 45 μm (2 °C/min). Overall, it is seen clearly that a higher cooling rate lowers the particle size at enhanced agitator speeds.

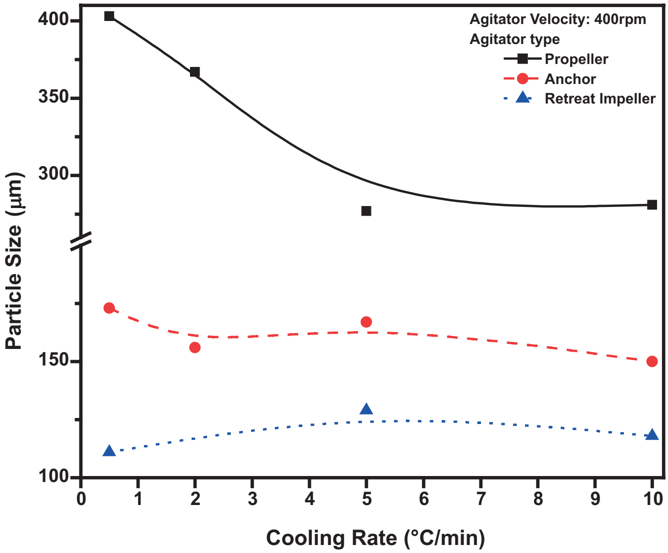

Figure 5. Effect of cooling rate on PSD.

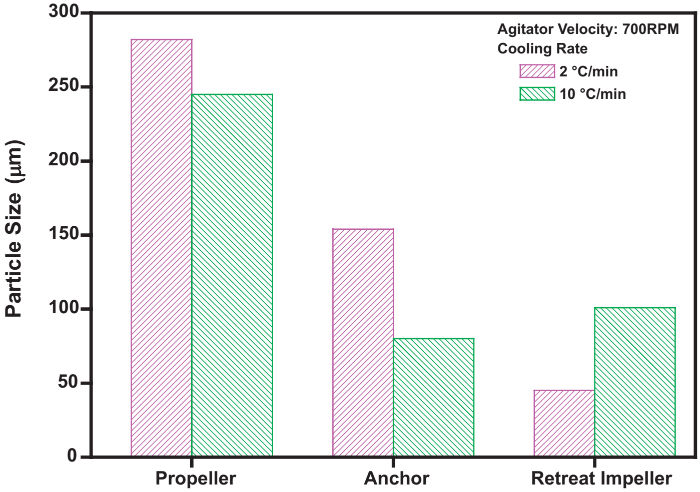

Figure 6. Effect of agitator and cooling rate on PSD.

Ultrasonication study on size distribution

In the explosives industry, the use of fine particles is essential and especially so for sheet explosives formulations, when particles in the range of 15 to 30 µm are used. The tailoring of the particle size of RSS-RDX by employing cooling crystallization techniques most commonly results in particles in the range of

50-500 μm. In order to prepare finer particles, a sonocrystallization technique using an ultrasound frequency generator has been adopted in the present study. The effect of various sono-crystallization parameters, such as temperature, time, ultrasound frequency and the concentration of RDX on the resultant particle size, is discussed.

Table 2. Effect of Sonocrystallization process parameters on particle size distribution

Temperature (°C) @ (53 kHz)		Time (min) @ 53 kHz		Ultrasonic frequency (kHz)		Concentration (%) @ 53 kHz	
Temp (°C)	PS (μm)	Time (min)	PS (μm)	Frequency (KHz)	PS (μm)	% of RDX	PS (μm)
15	26	3	17	35	30	15	23
25	28	5	28	53	28	20	26
40	29	10	26	-	-	27	28

Table 2 explains the effects of sonocrystallization parameters on particle size reduction/alteration. Particle sizes of about 25 to 30 μm are obtained by varying the temperature of crystallization at 53 kHz frequency for a period of 5 min, which indicated that there is no profound effect of temperature on particle size. However, the residence time has an influence on particle size, which may be attributed to size reduction followed by the agglomeration of fine particles. Hence, it is preferable to have a lower residence time of about 3 min to achieve fine particles of about 15 μm. The experiments were also carried out by varying the ultrasound frequency, as this is directly correlated to the energy imparted to the particles, however no significant change was observed in particle size for a given RDX concentration. The concentration of RDX in the solvent was also varied from 15 to 27% (w/v). The results indicated that it is appropriate to use dilute solutions for generating fine particles. Overall, it is possible to obtain relatively fine particles (15-30 μm) by the sonocrystallization technique using ultrasonic transducers, in contrast to a conventional cooling crystallization.

Micromeritic characterization of RSS-RDX

Micromeritic properties of an energetic material play a vital role in producing explosive formulations with optimal performance, for the realization of high Theoretical Maximum Densities (TMDs) and mix-fluidity during their processing. The present study also reports the various micromeritic properties which are in-turn useful for identifying the ease of processability of RSS-RDX.

Table 3. Flowability characteristics of specific particle sizes of RSS-RDX

Sample Name	Particle Size (µm)	True Density (g/cc)	BD (g/cc)	TD (g/cc)	CI	HR
RSSRDX-08	400	1.7956	1.075	1.159	7.347	1.080
RSSRDX-04	300	1.7986	0.976	1.122	13.040	1.150
RSSRDX-02	250	1.7986	0.934	1.059	11.790	1.134
RSSRDX-17	100	1.7992	0.609	0.779	21.810	1.279
RSSRDX-11	50	1.8001	0.570	0.741	23.070	1.300
URSSRDX-07	25	1.8025	0.482	0.699	31.110	1.451
URSSRDX-03	15	1.8027	0.538	0.762	29.400	1.417
RDX-Coarse	150	1.7961	0.807	1.047	17.785	1.216
RDX-Fine	100	1.7995	0.739	0.924	19.475	1.233

The bulk and tapped bulk density, the compressibility index and the Hausner ratio of RSS-RDX of different particle sizes (400, 300, 250, 100, 50, 25 and 15 µm), and of control RDX (coarse and fine RDX) is given in Table 3. As the particle size decreases from 400 to 25 µm, the tapped bulk density decreases from 1.16 to 0.70 g/cc and this can be attributed to the efficient packing realized in coarser particles. Particle size also plays an important role in deciding the compressibility of powders. The compressibility index (Carr's Index) and the Hausner ratio (HR) are simple measures of the flow behavior of a material. In the present study, RSS-RDX particles having D[4,3] of 400-250 µm are associated with excellent flow characteristics (CI: < 15%) due to the fact that the larger particles tend to be more free-flowing in nature due to less cohesiveness and poorer inter-particle interactions [20].

The control RDX, having 125-250 µm (coarse) and less than 125 µm (fine) particle sizes have tapped bulk densities of 1.047 g/cc (coarse) and 0.924 g/cc (fine) respectively, with moderate flowability compared to RSS-RDX. This indicates greater cohesiveness in the case of the control RDX.

The true density of all of the RSS-RDX samples was 1.80 g/cc, which indicates that the crystals are hard, without any voids or inclusions. Though the true density of RSS-RDX samples is slightly higher than the conventional RDX of similar PSD, there is no profound trend of particle size with true density. However, in general, as the particle size decreases, the true density increases.

Conclusion

Particle shape and specific size distributions are always important considerations in explosive processing in order to realize better process parameters. Crystallization process variables have been systematically optimized and their effect on particle size studied. The present study also explored the process parameters required to achieve monodisperse particle sizes of reduced shock sensitivity RDX (RSS-RDX), and to achieve the tight control of specific particle sizes D[4,3], ranging from 50 to 500 µm, by crystallization. A sonocrystallization study was also attempted, optimizing process conditions to prepare fine particles with mean diameters ranging from 15 to 30 µm . All of the prepared monodisperse RSS-RDX particles were characterized for their micromeritic properties and this inferred that RSS-RDX particles sized 400-250 µm are associated with excellent flow characteristics.

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