Evaluation of Nanoenergetics Based Composition B

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Abstract:

This paper discusses the preparation and evaluation of nanoenergetics-based Composition B (N-Comp B) consisting of nanocrystalline RDX and TNT. The formulation was prepared by compacting Comp B molding powder that was produced by spray drying an acetone solution of RDX and TNT. The N-Comp B molding powder was characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), differential scanning calorimetry (DSC), and high performance liquid chromatography (HPLC). Its non-shock sensitivities were evaluated in the safety tests (impact, friction, and electrostatic discharge). The nanostructure of compacted N-Comp B was characterized by focused ion beam-scanning electron microscopy (FIB-SEM) and the shock sensitivity was evaluated using small scale gap test (SSGT), which shows that the majority of the voids in the formulation are in the nanoscale range, leading to a reduction in shock sensitivity. However, when there is a large number density of voids, the reduction seems to be limited. The addition of a polymeric binder during the spray drying process mediated the compaction and is demonstrated as an effective method to reduce the size and the number density of voids, leading to a 50% sensitivity reduction compared to melt-cast Comp B. This work continues to demonstrate that the spray drying based materials processing method is a facile and versatile method for producing high performance and low sensitivity nanoenergetics-based explosives.

I. Introduction

Composition B (Comp B) is a widely used heterogeneous explosive consisting of 59.5 weight percent (wt. %) cyclotrimethylenetrinitramine (RDX), 39.5 wt.% trinitrotoluene (TNT), and 1 wt.% wax [1]. Most Comp B is produced by a melt-cast process in which a slurry of RDX crystals dispersed in molten TNT is cast and allowed to solidify into a charge [1]. During the solidification process of molten TNT, numerous voids and other defects are formed [2-4], which contribute to the relatively high sensitivity of Comp B.

To reduce the voids size and therefore the sensitivity of Comp B, nanoscale high explosives (i. e., nanoenergetics) based Comp B, N-Comp B, was prepared by spray drying an acetone solution of dissolved RDX and TNT in a recent work [2]. N-Comp B pellets were produced by compacting the N-Comp B powder. Detailed characterization shows that N-Comp B powder consists of nanoscale RDX and TNT. The nanostructure of N-Comp B was characterized by focused ion beam-scanning electron microscopy (FIB-SEM) and the shock sensitivity was evaluated using small scale gap test (SSGT). The characterization of the nanostructure shows that the majority of the voids inside the N-Comp B formulation are in the nanoscale range but have a large number density. Reduction in shock sensitivity was observed in SSGT test and is attributed to the elimination of large voids, and yet the large number density of smaller voids seems to have limited the sensitivity decrease.

In this work, we aim to further reduce the shock sensitivity of N-Comp B by introducing a polymeric binder during the spray drying preparation of N-Comp B powder. The polymer is expected to coat the nanoscale crystals of HEs in spray drying. We also hypothesized that the polymer coating can flow and significantly reduce the population of the voids in N-Comp B, leading to a reduced sensitivity. N-Comp B powder with polymer was prepared. The material was characterized in details. The compacted pellets were characterized using FIB-SEM and the shock sensitivity was evaluated using SSGT test. The results were compared to those of Comp B and N-Comp B with no polymeric binder, and were further discussed. The samples that were evaluated in this work were listed in Table 1.

Table 1. Summary of the evaluated samples.

Materials		Form	Description
Comp B		Powder/Flakes	Melt-cast Comp B
N-Comp B	N-Comp B1	Powder/pellets	As spray dried and compacted Comp B with no polymer binder
	N-Comp B2	Powder/pellets	As spray dried and compacted Comp B with a polymer binder

II. Experimental

2.1 Material characterization

The N-Comp B molding powder was characterized using scanning electron microscopy (SEM, Auriga CrossBeam Workstation, Carl Zeiss), powder X-ray diffraction (XRD, Rigaku Ultima IV XRD system with Cu Kα radiation at λ= 1.5418 Å), differential scanning calorimetry (DSC, PerkinElmer DSC 6000, at a scan rate of 5 ^{o}C/min).

The structure of N-Comp B was studied using SEM after exposing the cross-sections of the pellets by sectioning using a focused ion beam (FIB). The FIB cross-sectioning and SEM imaging (FIB-SEM) was performed at a cryogenic temperature (-135^{o}C) to reduce the radiation damage from both the electron beam and the ion beam. The surface of the specimen was coated with a ~1-2 µm thick platinum layer before FIB cross-sectioning to further protect the specimens from the ion beam damage. Structure of Comp B was also imaged after fracturing a melt-cast flake.

2.2 Safety tests

Basic safety sensitivity tests (impact, friction, and electrostatic discharge) were conducted according to AOP-7 and STANG 4489 ED1. As spray dried N-Comp B samples were used. Comp B sample was prepared by grinding raw material in a Wiley Mill until it passed through a 25 mesh screen and dried at ~ 50 ^{o}C to a constant weight.

The impact test (Explosives Research Laboratory (ERL) impact test) was completed using an ARDEC ERL type 12 impact tester with a 2 ½-kg drop weight. The drop height corresponding to the 50% probability of initiation measures impact sensitivity. The test method is described in STANAG 4489 Ed.1 "Explosives, Impact Sensitivity Tests."

The friction test method (BAM friction test) is described in AOP-7, 201.02.006, “BAM Friction Test.” In a typical test, a sample was placed on a porcelain plate and a porcelain pin was lowered onto the sample. Then a weight was placed on the arm to produce the desired load. Once the tester was activated, the porcelain plate was reciprocated once to and fro. The results are observed as either a reaction (i.e., flash, smoke, and/or audible report) or no reaction. Testing begins at the maximum load of the apparatus (360 N) or lower if experience warrants it. If a reaction occurs in ten trials, the load is reduced until there are no reactions observed in ten trials.

The ESD test was run per a modified variant of AOP-7, 201.03.001 with the SMS ABL ESD machine. This test determines the energy threshold required to ignite explosives by electrostatic stimuli of varying intensities. In a typical test, if there is a reaction in twenty trials, the ESD energy load is decreased until there are no reactions in twenty trials.

2.3 SSGT shock sensitivity tests

The shock sensitivity of samples was evaluated using the SSGT test according to AOP-7, 201.04.003. This is a standard test used to determine the shock wave pressure required to achieve a 50% probability of detonation. The specimens had a dimension of 5.08 mm × 38.1 mm (diameter × length) as compacted in Section 2.1. Pressed Comp B production flake was also evaluated in SSGT as a reference material.

III. Results and Discussion

3.1 Characterization of N-Comp B molding powder

SEM images of N-Comp B molding powder are shown in Figure 1. N-Comp B1 particles (Fig. 1A and 1B) and N-Comp B2 particles (Fig. 1A and 1B) have very similar morphology. Particles are larger than 10 μm and have irregular shapes. At high magnification (Fig.1B and 1D), sub-micron sized crystals can be observed from both samples. Figure 2 shows the XRD pattern of N-Comp B samples along with the pattern from melt-cast Comp B. Major peaks of RDX and TNT crystals are labeled. The XRD pattern of the molding powder is consistent with the pattern from melt-cast Comp B. However, significant peak broadening from RDX and TNT is observed in both N-Comp B1 and N-Comp B2 samples. The peak broadening in XRD analysis happens when the crystal size is small [3]. Therefore, the SEM and XRD analysis suggest that N-Comp B molding powder prepared by spray drying consists of nanoscale RDX and TNT crystals. This is consistent with previous reports of nanoenergetic materials by spray drying [4-6]. The formation of nanoscale crystals is attributed to the rapid solvent evaporation and subsequent crystal nucleation in spray drying [4-6]. Compared to other spray-dried energetic materials which are typically spherical, the irregular morphology of N-Comp B molding powder is likely due to the fusion of particles because TNT has a relatively low melting point [7].

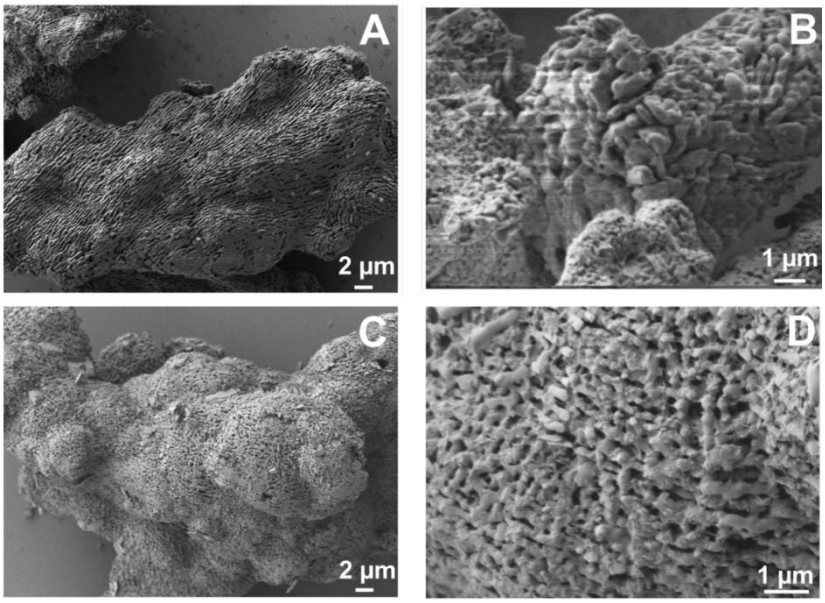

Figure 1. The SEM images of N-Comp B samples. (A) and (B): N-Comp B1 molding powder at low and high magnifications. (C) and (D): N-Comp B2 molding powder at low and high magnifications.

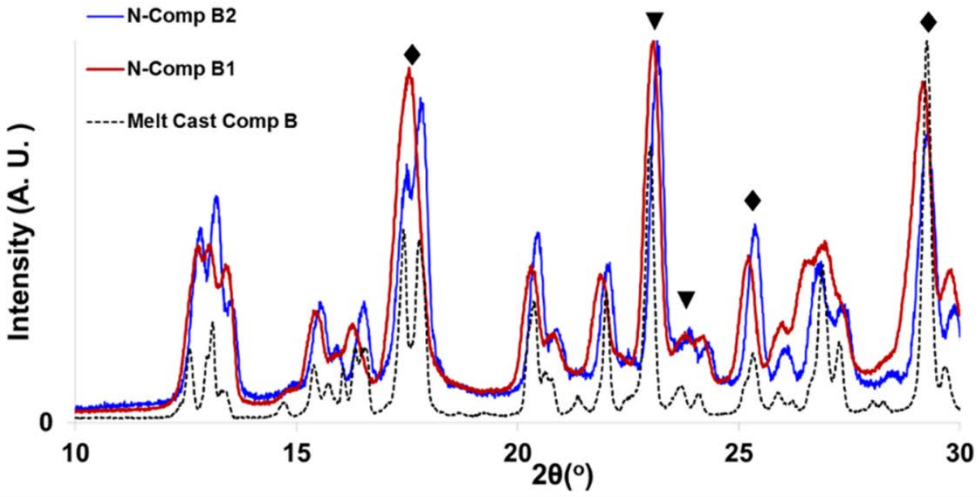

Figure 2. The X-ray diffraction (XRD) patterns, of N-Comp B molding powder and melt-cast Comp B (♦, RDX and ▼, TNT).

The DSC analysis of N-Comp B molding powder and melt-cast Comp B is shown in Figure 3. The peaks at ~ 80 ^{o}C and 230 ^{o}C corresponds to the melting temperature of TNT phase and the decomposition temperature of the material, respectively. Fig. 3 shows that there is a left-shift of the melting temperature from N-Comp B compared to melt-cast Comp B. This is probably due to the nanoscale size of TNT crystals. The decomposition temperature of N-Comp B1 is almost identical to that of melt-cast Comp B.

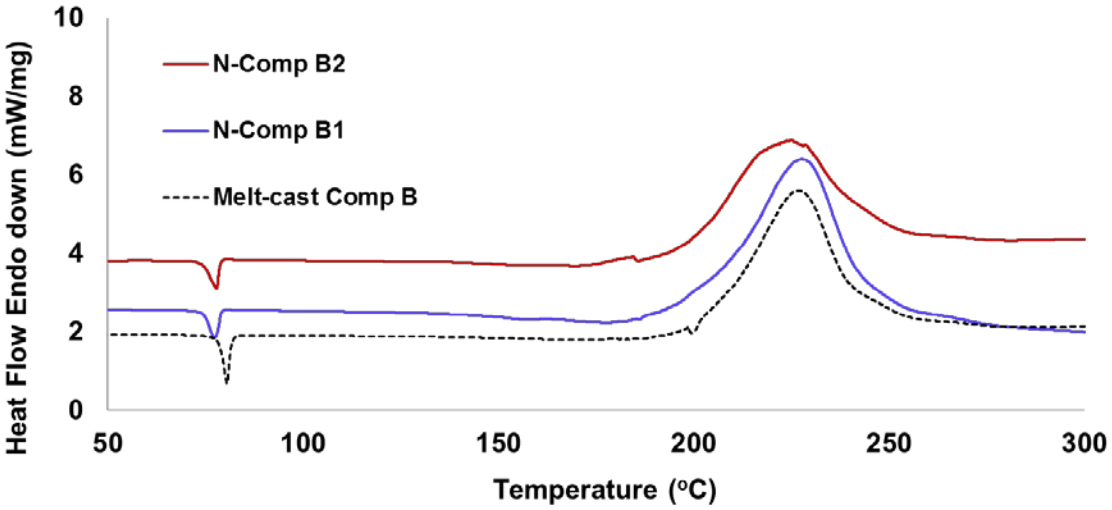

Figure 3. DSC analysis of N-Comp B1, N-Comp B2, and melt-cast Comp B obtained at a scan rate of 5 °C/min.

3.2 Structure of Comp B

SEM images of cross-sections that were prepared by FIB are shown in Figure 4A and 4B for N-Comp B1 and N-Comp B2, respectively. Although individual crystals cannot be differentiated from each other, all the features are on the nanoscale level. Surprisingly, at a relatively high TMD of about 94.5%, the N-Comp B1 formulation has a large number density of voids, which are estimated to be approximately 5/μm^2, although majority of the voids have dimensions in the nanoscale range. Many of the voids are also observed to be interconnected.

Interestingly, the nanostructure of N-Comp B2 seems to be very different from N-Comp B1: (1) the voids seem to have evens smaller average size; (2) the number density of voids is dramatically reduced, to an estimated lever of 1.8/μm^2; and (3) there is no interconnection between voids due to the smaller number density of voids. Therefore, the introduction of a polymeric binder during spray drying seems to be a very effective measure regarding to decrease the number density of voids and further reduce the size of voids in N-Comp B. This is attributed to the formation of a polymer coating on the surface of nanoscale crystals during spray drying, which could flow and fill the voids during compaction as evidenced from the higher achieved %TMD compared to N-Comp B1 under similar compaction conditions.

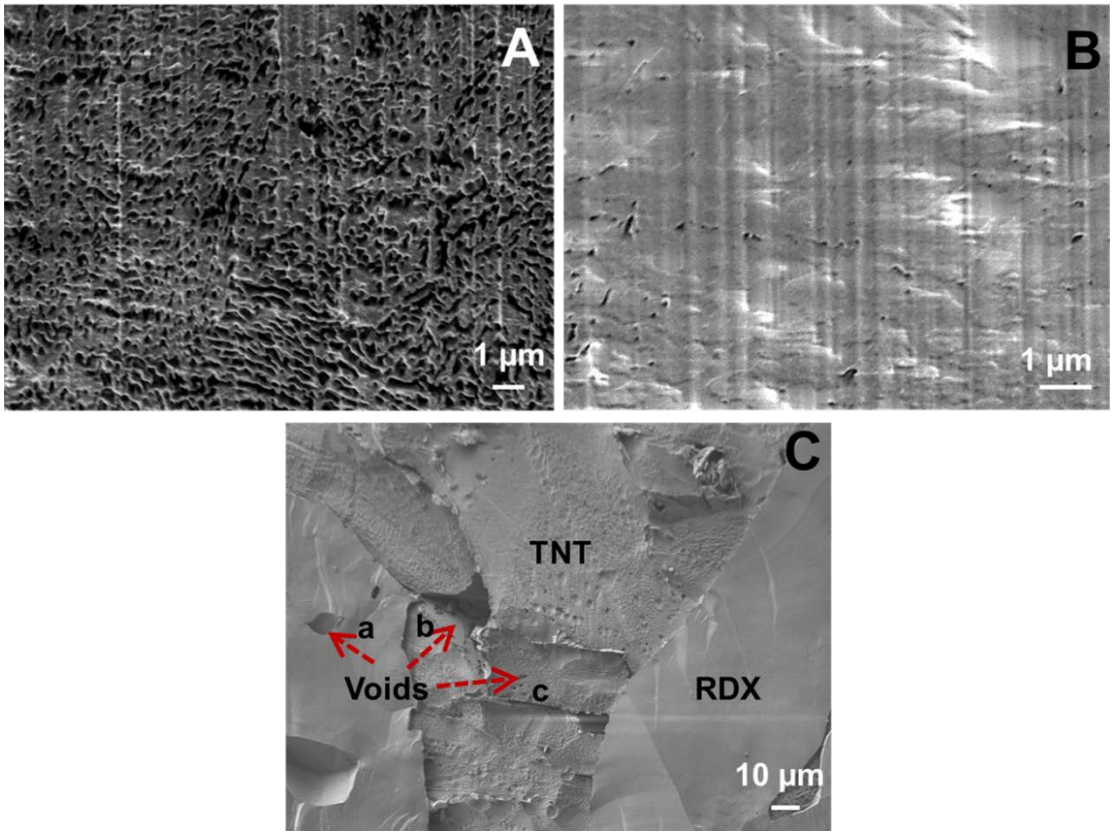

Figure 4. Structures of Comp B. (A) and (B), the SEM images of cross-sections prepared by FIB from N-Comp B1 and N-Comp B2, respectively; (C) the SEM image from a fractured surface of melt-cast Comp B.

In comparison, Figures 4C shows an SEM image from fractured melt-cast Comp B. The RDX crystals, with a smooth surface and crystalline facets, are embedded in the continuous TNT matrix, as labeled in the figure. The TNT crystals are in the commonly observed needle-like/columnar shape [8-10]. Both RDX and TNT crystals are large, on the order of hundreds of microns. Both intra- and inter-crystal voids can be observed. The voids are relatively large (tens of microns), especially the inter-crystalline voids which are generally located adjacent to the tip of TNT crystals.

3.3 Safety tests

The results of safety tests, including impact, friction and ESD, of N-Comp B molding powder and Comp B are summarized in Table 2. The results from the impact test show that N-Comp B molding powder has much lower impact sensitivity than Comp B and the addition of polymer further reduces the sensitivity of N-Comp B. Nanoscale RDX and TNT in N-Comp B powder may contribute less to the friction and hot spots formation in impact test, leading to reduced impact sensitivity.

Results from friction test indicate that N-Comp B and Comp B are not friction sensitive. Particularly, N-Comp B2 has no reaction under the instrument maximum load in the friction test. The N-Comp B has moderate ESD sensitivity. The results from the safety tests suggest that N-Comp B, especially N-Comp B2, has reduced non-shock sensitivities and is safer to handle compared to Comp B.

Table 2. The results of safety tests (impact, friction, and ESD).

Materials		Impact (cm)	Friction (N, go/no-go)	ESD (J, go/no-go)
Comp B		33.9	318/282	---
N-Comp B	N-Comp B1	51.6	252/240	0.051/0.040
	N-Comp B2	69.5	360	0.040/0.031

3.4 SSGT sensitivity test

The shock sensitivities from SSGT test are reported in Table. 3. Melt-cast Comp B is used as the reference material and its SSGT shock sensitivity as described in shock wave pressure is treated as the reference point (100%). A value larger than 100 (%) means that the material is less sensitive than the melt-cast Comp B. At a relatively lower %TMD, N-Comp B1 illustrates a value of 116 (%), a 16% shock sensitivity reduction over melt-cast Comp B. The shock sensitivity of N-Comp B2 is impressive with a normalized value of 150 (%), or a 50% sensitivity decrease compared to melt-cast Comp B.

The reduced shock sensitivity from N-Comp B is attributed to the nanoscale size of voids, as they require stronger shock wave pressure to reach the critical temperature so that they can survive the conduction and continue to burn [11-13]. The sensitivity test and the nanostructure characterization also suggest that the number density of voids has a significant effect on the shock sensitivity. With a large number density of voids of ~ 5/μm^2, N-Comp B1 has only a slight sensitivity reduction compared to melt-cast Comp B. The large number density of voids and the interconnection between voids are believed to cause hot-spot merging, leading to the formation of critical hot-spots despite of the small void size [13]. Dramatic sensitivity decrease from N-Comp B2 is attributed to the small void number density of ~ 1.8/μm^2.

Table 3. Results from SSGT sensitivity test.

Materials		% TMD	SSGT Sensitivity (%)
Comp B		95.2	100
N-Comp B	N-Comp B1	94.8	116
	N-Comp B2	98.4	150

IV. Conclusion

Nanoenergetics-based Comp B (N-Comp B) consisting of nanoscale RDX and TNT crystals was prepared by spray drying and mechanical compaction. Structural characterization shows that the majority of the voids inside the formulation are in the nanoscale range, leading to a reduction in shock sensitivity. However, when there is a large number density of voids, the

reduction seems to be limited. The addition of a polymeric binder during the spray drying process mediated the compaction process and was demonstrated as an effective method to reduce the size and the number density of voids, leading to a 50% sensitivity reduction compared to melt-cast Comp B. This work continues to demonstrate that the spray drying based materials processing method is a facile and versatile method for producing high performance and low sensitivity nanoenergetics-based explosives.

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