Chemosphere xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Insights into the dissolution and the three-dimensional structure of insensitive munitions formulations

Susan Taylor [a,*], David B. Ringelberg [a], Katerina Dontsova [b], Charles P. Daghlian [c], Marianne E. Walsh [a], Michael R. Walsh [a]

[a] Cold Regions Research and Engineering Laboratory, 72 Lyme Road, Hanover, NH 03755-1290, USA
[b] Biosphere 2 Earthscience, University of Arizona, 845 N. Park Avenue, Tucson, AZ 85721-0158, USA
[c] E.M. Facility, Dartmouth College, 7605 Remsen, Hanover, NH 03755, USA

HIGHLIGHTS

- First micro-computed tomographs of detonated insensitive munitions (IM) particles.
- Dissolution forms hole-riddled IMX 101, IMX104 and PAX21particles.
- Particles resulting from detonations are fractured.
- Precipitation dissolving IM particles will change composition over time.
- Three-dimensional data are the key to developing physically based dissolution models.

ARTICLE INFO

Article history:
Received 29 March 2013
Received in revised form 4 June 2013
Accepted 5 June 2013
Available online xxxx

Keywords:
Insensitive munitions
DNAN
NTO
Raman spectroscopy
Dissolution
Micro-computed tomography

ABSTRACT

Two compounds, 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO) are the main ingredients in a suite of explosive formulations that are being, or soon will be, fielded at military training ranges. We aim to understand the dissolution characteristics of DNAN and NTO and three insensitive muntions (IM) formulations that contain them. This information is needed to accurately predict the environmental fate of IM constituents, some of which may be toxic to people and the environment. We used Raman spectroscopy to identify the different constituents in the IM formulations and micro computed tomography to image their three-dimensional structure. These are the first three-dimensional images of detonated explosive particles.

For multi-component explosives the solubility of the individual constituents and the fraction of each constituent wetted by water controls the dissolution. We found that the order of magnitude differences in solubility amongst the constituents of these IM formulations quickly produced hole-riddled particles when these were exposed to water. Micro-computed tomography showed that particles resulting from field detonations were fractured, producing conduits by which water could access the interior of the particle. We think that micro-computed tomography can also be used to determine the initial composition of IM particles and to track how their compositions change as the particles dissolve. This information is critical to quantifying dissolution and developing physically based dissolution models.

1. Introduction

The US military is testing explosives that detonate only when intended, i.e. when munitions are fired, and that do not detonate during transport or handling. Two compounds, 2,4-dinitroanisole (DNAN) and 3-nitro-1,2,4-triazol-5-one (NTO), are less sensitive to heat and shock than trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and are being tested as their replacements. DNAN and NTO, along with RDX, nitroguanadine (NQ) and ammonium perchlorate (AP), are the main ingredients in IMX 101, IMX 104 and PAX 21, three insensitive munitions (IM) formulations belonging to the suite of new explosive formulations whose sensitivity to shock and heat are tailored by altering the relative proportions of constituents.

Dissolution of explosive formulations depends both on the solubility of their individual components and on the fraction of each constituent exposed to water. Their dissolution kinetics in water is important to understand because, once dissolved, they can be transported off base by groundwater, an outcome that can

* Corresponding author. Tel.: +1 603 646 4239.
E-mail address: Susan.Taylor@erdc.usace.army.mil (S. Taylor).

0045-6535/$ - see front matter Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.chemosphere.2013.06.011

trigger regulatory action and close training ranges. We used Raman spectroscopy to locate the main constituents in IM particles and optical measurements to quantify changes to the structure of these explosives after timed submersions in water. Lastly we used micro computed tomography (μCT) to image the three-dimensional distribution of the various components in IMX 101, IMX 104 and PAX 21. These three formulations were chosen for study because they are being, or soon will be, used in rounds fired at training ranges.

2. Materials and methods

We tested samples obtained from a production factory and particles collected from field detonations. Factory samples of DNAN, NTO, IMX 101, IMX 104 and PAX 21 were obtained from BAE Systems. Detonation residues of IMX 101 were obtained from tests conducted on 105-mm howitzer rounds by National Technical Systems. PAX 21 and IMX 104 residues were collected after low order detonations of 60- and 81-mm mortars, respectively (Walsh et al., 2012).

Samples were optically imaged using a Keyence VHX digital microscope (Elmwood Park, NJ) fitted with a 20–200× lens. To measure the effect of water on the three dimensional structure of IM formulations, we imaged the surfaces of IMX 101, 104 and PAX 21 pieces, placed these in water for a series of timed submersions and then re-imaged the surfaces. Each particle was stuck to a glass slide using double stick tape and was totally submerged in MilliQ water for 1, 2, 4, 8, 16, and 32 h. The software used to run the microscope allowed us to measure the dimensions of the particles and we measured four different transects on each particle after each submersion.

Raman spectra were collected using a ThermoScientific DXR Raman microscope (Waltham MA). A 532 nm laser set at 10 mW power was used to collect surface spectra through a 10× objective with a 50 μm pinhole yielding a spot size of approximately 2.1 μm. An average of 10 one-second sample exposures were collected from the wavelength range between 57 and 3388 cm^{-1} at a resolution of 5.8–8.8 nm.

A SkyScan 1172 X-ray microtomograph was used to image the IM formulations. Except for mounting the sample no preparation was needed. We used a 40 kV voltage, a 250 μA source current and a 1.3 Megapixel X-ray camera to take shadow transmission images (radiographs) of each IM particle from different angles as the particle rotated on a stage. From these radiographs, cross sectional images perpendicular to the *z*-axis of the particle were reconstructed using a modified Feldkamp cone-beam algorithm, creating a complete three-dimensional (3-D) representation of the internal microstructure of, and components in, the particle. The cross sections are ~6 μm apart and we can quantify the areas of the matrix and of the crystal components in each section using Image J (Rasband 1997–2012).

3. Theory/calculation

Melt casting, a process where crystalline constituents are added to a molten matrix and then cooled is used to produce conventional high explosives, such as TNT and Composition B (Comp B-60% RDX, 39% TNT, 1% wax), and the IM formulations studied here. In the case of Comp B, 100 μm crystals of RDX are added to molten TNT. For IMX 101, 360 μm NTO and 300 μm NQ crystals are added to molten DNAN; for IMX 104, ~300 μm NTO crystals and 4 μm RDX crystals are added to DNAN; and for PAX 21, 200–400 μm AP crystals and mainly 8 μm RDX crystals are mixed into DNAN (Pelletier et al., 2010; Rutkowski et al., 2010).

These IM formulations, however, differ from Comp B in that most of their crystal constituents are much more soluble than their DNAN matrices whereas the RDX is less soluble than the TNT matrix in Comp B. This suggests that as NTO, NQ and AP dissolve they will leave holes in the DNAN matrix, thereby increasing DNAN's surface area and its dissolution rate. Furthermore, because the solubility of NTO, NQ, AP and DNAN differ by orders of magnitude, we expect them to dissolve at different rates that will be based on their solubility and the fraction of their surface exposed to water. The 3D relationship of the constituents and their relative crystal sizes in IM formulations is, therefore, key to understanding and modeling the rate at which IM particles dissolve.

The dissolution kinetics of IM compounds in water is of interest because DNAN (Davies and Provatas, 2006), RDX (ATSDR, 1995; Mukhi and Patiñoz, 2008) and AP (Motzer, 2001) may be toxic to people and the environment. AP, for example, impairs thyroid function and fetal development in fish (Crane et al., 2005). Unfortunately, AP is also very soluble in water and is persistent and mobile in groundwater (Motzer, 2001). Both DNAN and NTO are more soluble than TNT and RDX (Table 1) increasing the likelihood that they too, could reach groundwater. Contaminated groundwater migrating off a military base can trigger regulatory actions that close the ranges to live-fire training.

4. Results

Fig. 1 shows optical images of DNAN, NTO and the IM formulations we studied along with pie charts showing the compositions of the formulations. DNAN is a cream-colored particle composed of many small crystals. It abrades easily as evidenced by the powdered DNAN on its surface. NTO is a translucent crystal that occurs as ~500 μm, equi-dimensional grains most of which look twinned and are highly reflective in visible light. IMX 101 and 104 are white crystalline substances with visible NTO crystals embedded in the DNAN matrix. PAX 21 has a yellow DNAN matrix, caused by the

Table 1
Properties of DNAN, NTO and other compounds found in IM formulations.

	Solubility at 25 °C $mg\ L^{-1}$	Density $g\ cm^{-3}$	Mol. wt. $g\ mol^{-1}$	X-ray atten[a] $cm^2\ g^{-1}$	Mol. formula	Reference
DNAN	276	1.34	198	0.235	$C_7H_6N_2O_5$	Boddu et al. (2008)
NTO	16642	1.05	128	0.236	$C_2H_2N_4O_3$	Spear et al. (1989)
TNT	100	1.65	227	0.236	$C_7H_5N_3O_6$	Brannon and Pennington (2002)
RDX	60	1.82	222	0.241	$C_3H_6N_6O_6$	Brannon and Pennington (2002)
HMX	5	1.81	296	0.241	$C_4H_8N_8O_8$	Glover and Hoffsommer (1973)
NQ	3800	1.55	104	0.240	$CH_4N_4O_2$	Haag et al. (1990)
AP	217000	1.95	117	0.517	NH_4ClO_4	Motzer (2001)

[a] X-ray attenuation is a function of the photon cross-section and absorption coefficient of the material. We calculated the attenuation of the different compounds using Xcom a photon cross section program and database from the National Institute of Standards and Technology (NIST).