



Effects on the surface structure of organic energetic materials using spin coating



Xin Zhang, Brandon L. Weeks*

Department of Chemical Engineering, Texas Tech University, Lubbock, TX 79409, USA

ARTICLE INFO

Article history:

Received 17 May 2013

Received in revised form 5 October 2013

Accepted 21 October 2013

Available online 31 October 2013

Keywords:

Organic energetic materials

Pentaerythritol tetranitrate (PETN)

Crystal growth

Manipulation

Spin coating

ABSTRACT

Thin films of energetic materials are widely studied to understand thermodynamic properties, sensitivity, nanodetonics and coarsening. In this work we investigate the fabrication of thin film energetic materials through spin coating to yield reproducible materials to study. The crystalline structure of these energetic materials is found to have a strong dependence on experimental parameters, such as the rotational speed and solution concentration. In this study, thin films of pentaerythritol tetranitrate (PETN) produced by spin coating have been systematically investigated giving films with controlled morphology.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Organic energetic materials are a class of materials with a high amount of stored chemical energy that can be rapidly released to produce a significant amount of heat and pressure on the surroundings. These materials have been widely applied in mining, demolition, military weapons, and aeronautical applications [1–5]. Currently, efforts are expanding to design and synthesize more powerful [6], ‘green’ energetic materials [7] and improve the performance and safety of existing energetic materials [8,9]. One new avenue of research is tailoring the performance of energetic materials by modifying physical properties of these materials without changing the chemistry. It is well accepted that sensitivity, burn rate and stability strongly depend on the size, shape, and density of the energetic material [10–14]. For example, Szczygielska et al. indicated that hexanitrohexaazaisowurtzitan (CL-20) crystals with rounded facets show lower friction sensitivities than crystals of irregular shape and sharp-edged agglomerates [13]. Heijden et al. noted that a change in the shape of the cyclotrimethylene trinitramine (RDX) crystals from faceted to spherical shape led to a significantly less shock sensitive compound [14]. Most research in this area has focused on increasing the surface area or explosives without understanding the underlying mechanisms.

To date, a series of techniques have been applied to manipulate the crystalline structure of organic energetic materials, such as mixing [15–17], sol–gel methods [18–20], physical vapor deposition [21–25],

and dip-pen nanolithography [26]. Among these techniques, mechanical mixing and sol–gel methods are the most popular for fabricating organic energetic material crystals at the micro-/nano-scale, and can be used to prepare various composites that are applied for special performance. For example, when mixing pentaerythritol tetranitrate (PETN) with less than 1% weight of single-wall carbon nanotubes, the resulting composite showed improved ignition properties compared to pure PETN crystals [15]. Micro-scale energetic crystals also can be modified by incorporating small quantities of a polymer (typically 5–10% by weight) into the matrix, also known as polymer-bonded explosive (PBX) or plastic-bonded explosive [16,17]. In comparison to the monomolecular organic energetic materials, the PBX composite is normally more insensitive and thermally stable to avoid accidental detonation and can be fabricated into a particular shape. Therefore, addition of various materials may increase or decrease the sensitivity of an explosive.

Unlike production of explosives in solution or by mixing in the solid phase, it is possible to observe and control the structure of organic energetic materials on a substrate by making a thin film. These thin films can then be studied in a controlled environment to study the sensitivity and performance at the micro-/nano-region. One primary advantage of thin films is that a very small sample size is needed (nanograms) making the procedure inherently safer. Physical vapor deposition is a popular method for depositing organic energetic materials as thin films. For example, Zhang et al. [21] observed that the structure of PETN deposited on silicon substrates was dependent on the deposition vapor flux. When the deposition rate is 0.03 nm/s, PETN formed symmetric tumbleweed crystals on the substrate. However, when the deposition rate was increased to 2.5 nm/s, the film morphology showed a transition from a dendritic crystal to a regular hexagonal single crystal. The primary disadvantage of vapor deposition is that heating is often required to facilitate the

* Corresponding author.

E-mail address: brandon.weeks@ttu.edu (B.L. Weeks).

deposition rate while many energetic materials are thermally unstable and will decompose when heated.

Spin coating is a popular technique to produce thin films of various organic materials on substrates and does not require external heating. Therefore, this method allows for the fabrication of a wide range of thermally sensitive compounds including explosives. In this work we show that spin coating can be used to reproducibly fabricate thin films of energetic materials with controlled morphology through solution concentration and rotational speed of the spin coater.

2. Experimental details

2.1. Materials

PETN is one of the most common high explosives and is primarily used in detonators. It is a monomolecular crystal and a benchmark material for primary and secondary high explosives. Therefore, PETN is chosen for the optimization of crystal growth conditions in this report. PETN powder (particle size less than 100 mesh) was provided by Lawrence Livermore National Laboratory with purity > 99% without further purification. Glass substrates (VWR International) were diced into $1.25 \times 1.25 \text{ cm}^2$ pieces and treated with Piranha solution (98% H_2SO_4 and 30% H_2O_2 in volume ratios of 3:1) for 30 min at 70 °C, rinsed with de-ionized water and dried with compressed N_2 . *Caution: Piranha solution reacts violently with most organic materials and must be handled with extreme care.*

2.2. Preparation of PETN samples

Thin films were prepared by first dissolving the PETN powder in acetone. The concentration of the PETN solutions ranged from 0.005 M to 0.06 M. The solution was deposited on the glass substrates at room temperature by spin coating (Single wafer spin processor, Laurell Technologies Corp., North Wales, PA). The spin coater rotational speed was adjusted from 500 rpm to 6000 rpm and the spin time was held at 3 min. When the spin time was shorter than 3 min, significant solvent was incorporated within the films and a broad particle size distribution was observed.

2.3. Morphology characterization

The crystal structure was monitored by optical microscopy (American Scope, USA). The topography of the PETN samples was characterized with an XE-100 atomic force microscope (Park Systems Inc., Santa Clara, CA) operating in contact mode using a silicon cantilever (Nanoscience Instruments, Inc. Phoenix, AZ), with a nominal spring constant of 0.01–0.1 N/m and tip diameter of ~10 nm. All AFM imaging was performed at a scan rate of 0.5 Hz.

3. Results and discussions

Spin coating with high concentration (0.06 M or greater) produced continuous thin films of PETN. However, when the solution concentration dropped below 0.06 M, non-continuous islands were formed on the substrate. In general, the particle size distribution of the PETN islands is strongly dependent on the spin coater rotational speed and solution concentration. In addition, solvent type, substrate surface energy, and the spin coating time (less than 3 min) also affect the island size. In this report, we only investigated the effect of the rotational speeds and solution concentrations. Although continuous films were often sought when using spin coating, this work would focus on non-continuous films since these were more applicable to the explosive community in simulating powder samples. Other factors were fixed, including the solvent, substrate, and the amount of solution used during deposition was 20 μL .

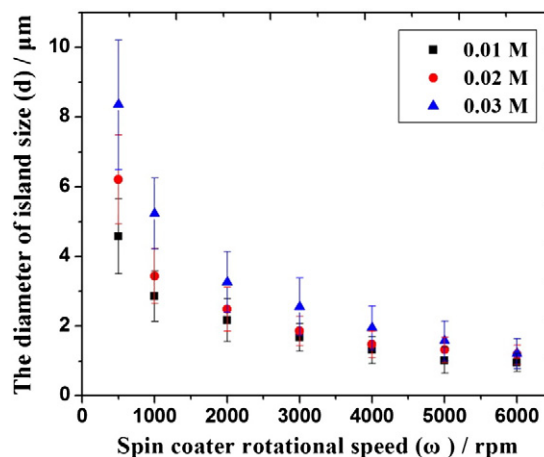


Fig. 1. PETN particle size vs spin coater rotational speed. The size of PETN island particles is obtained using AFM software. (Bars represent the range of values determined from more than 20 AFM images for each condition.)

First, to investigate the effect of the spin coater rotational speed on the island size, three concentrations, 0.01 M, 0.02 M and 0.03 M, were used at various rotational speeds from 500 rpm to 6000 rpm. The island size of each sample was then measured using AFM as shown in Fig. 1. Fig. 1 indicates that the size of island particles becomes larger with decreasing rotational speed. The higher rotational speeds (greater than 3000 rpm) provide a rather homogeneous distribution of PETN islands on the substrate of less than 3 μm . At rotational speeds below 2000 rpm a more heterogeneous distribution of PETN islands is observed within a range of 2–8 μm .

Fig. 2 shows the relationship of particle size collected at three fixed rotational speeds, 2000 rpm, 3000 rpm and 4000 rpm, using solution concentrations ranging from 0.005 M to 0.06 M. Fig. 2 shows that the size of the island particles becomes larger with increasing concentration. The lower concentrations provide a smaller and more homogeneous distribution of PETN particles on the substrate.

Spin coating is one of the most popular methods to produce uniform thin films of organic materials, especially polymers. The system analysis and modeling of the spin coating process were performed over 60 years ago [27–31]. Using cylindrical polar co-ordinates (r, θ, z) with the origin

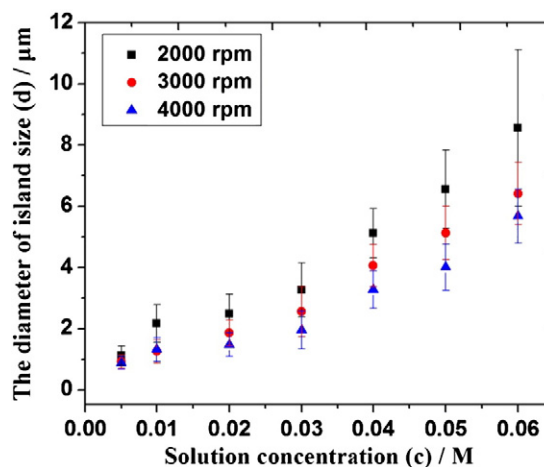


Fig. 2. PETN particle size vs PETN solution concentrations. The size of PETN island particles is obtained using AFM software. (Bars represent ranges of values determined from more than 20 AFM images for each condition.)

Download English Version:

<https://daneshyari.com/en/article/8035349>

Download Persian Version:

<https://daneshyari.com/article/8035349>

[Daneshyari.com](https://daneshyari.com)