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Preparation of sub-micron nitrocellulose particles for improved combustion behavior

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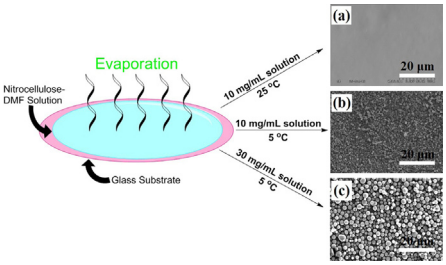
HIGHLIGHTS

- Sub-micron nitrocellulose particles are prepared using solvent evaporation.
- The size of nitrocellulose particles depends on the solution concentration.
- The burn rate of nitrocellulose sample increases with decreasing particle size.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel method to prepare sub-micron nitrocellulose particles with spherical shape is demonstrated. The morphology of the nitrocellulose can be controlled by the solvent and the growth temperature. Using dimethylformamide (DMF) at a growth temperature is 5 °C, reproducibly yielded spherical nitrocellulose particles. The final diameter of the prepared nitrocellulose particles can be further tuned by concentration. The smallest particles in this study were found to have diameters of 500 nm at a concentration of 5–10 mg/ml with 2 micron spheres formed at 30 mg/ml. Furthermore, the thermal properties and the burn rates of the prepared materials are studied by differential scanning calorimetry and digital high-speed photography, respectively. In comparison to the bulk nitrocellulose material, the sub-micron nitrocellulose particles have lower decomposition activation energy, a 350% increase in burn rate, and a more complete combustion.

1. Introduction

Engineering and fabricating high speed propulsion systems are critical technologies for military devices, aeronautical engineering, and national security. Preparing advanced energetic materials (EMs) and propellants is a challenging, and active, research topic. Developing materials with higher energy release, faster burn rates, controlled ignition, and safer EMs are of great interest [1–4].

Currently, preparing multidimensional nano- or micro-scale EMs is the most efficient method for enhancing the energy release, ignition, and combustion behaviors of EMs [5–11]. Generally, combustion reactions are mainly limited by specific surface area. With the decrease of the particle size, more molecules are displayed on the surface, which increases the free surface energy and specific surface area and consequently improves the combustion reaction. As a result, the burn rate of nano- or micro-scale materials is significantly faster than macro-scale bulk materials and offers faster energy release and more complete combustion than the bulk. For example, the burn rate of aluminum (Al) particles significantly increases from about 1 mm/s to 10 mm/s when the size decreases from 1000 nm to 100 nm [10]. In the case of organic energetics the burn rate of nano-scale 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) has been observed to double (30 mm/s) in comparison to the macro-scale RDX powder (15 mm/s) [11]. Therefore, it is of continued interest to develop simple, high efficiency and low cost methods

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for preparing nano- or micro-scale EMs and to improve combustion behaviors.

Nitrocellulose (NC), also called cellulose nitrate, is obtained by the nitration of cellulose. The highly nitrated NC, with a nitrogen content of more than 12%, is an important energetic material commonly used as a propellant or explosive [12–15]. It is a leading material for propellant formulations and has been used for well over a century [16–21]. Therefore, it is important to develop novel methods to prepare nano- or micro-scale NC materials to improve the combustion behavior. Furthermore, the low-nitrated NC is an important industrial polymer with wide-ranging applications in coatings, filtration and membranes for immunoassays, enzyme immobilization, biosensors, and the isolation of proteins, RNA, and DNA [22–24]. By preparing nano- or micro-scale NC materials significantly increases the surface area and broadens applications in separations, purification science and biomedicine [25,26].

To date, a series of techniques have been applied to fabricate nano- or micro-scale NC materials, such as sol–gel methods [22], simple mixing [23], electrospinning [19], and solvent evaporation [24]. For microscale particles, Tanyolac et al. [24] reported a modified solvent evaporation technique that has promise for large-scale processes. This method requires a large amount of surfactant, sodium dodecyl sulphate, and two other polymers (Pluronic PE6800 and polyvinyl alcohol) to aid in the formation of microparticles. However, this method is limited to rather large particles (125 μm to 250 μm), and, ultimately, was not deemed be suitable for synthesizing nanoparticles.

Herein, we report, for the first time, a simple method to prepare uniform sub-micron NC particles by using solvent evaporation at a controlled temperature. The morphology of the NC strongly depends on the growth temperature and solvent, where the particle size can be tuned by concentration. The new protocol is more cost-effective and simpler than previous methods of preparing nano- or micro-scale NC particles. Furthermore, the thermal properties, and the burn rates, of the prepared materials are studied by differential scanning calorimetry and digital high-speed imaging, respectively. In comparison to the micro-scale NC particles, the nano-scale NC particles have lower decomposition activation energy, faster burn rate, and more complete combustion.

2. Experimental

2.1. Materials

Nitrocellulose (NC; 4–8% in ethanol/diethyl ether, 11.8–12.2 wt.% nitrogen) was purchased from Sigma–Aldrich Inc. This solution was dried as a solid film before use by evaporating the organic solvent and subsequent drying at 70 °C in a vacuum oven until a constant weight is achieved. All organic solvents, including tetrahydrofuran (THF), methanol (MeOH), ethanol (EtOH) and dimethylformamide (DMF), were purchased from Sigma–Aldrich Inc. and were used as received. Glass microscope slides (VWR International) were cut down to 1.25 cm × 1.25 cm pieces and used for imaging studies. Glass petri dishes (VWR International) of 7.5 cm × 7.5 cm were used for burn rate studies and further cut into 0.6 cm × 5 cm producing multiple samples. All glass substrates were cleaned 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. The substrates were stored in desiccators prior to use.

2.2. Fabricating procedures of NC materials

The solid NC was completely dissolved in all the organic solvents used, including THF, MeOH, EtOH and DMF, to make 5 mg/mL, 10 mg/mL and 30 mg/mL NC solution. The various NC materials were prepared by dropping various concentration NC solutions onto the glass substrates followed by evaporation at different temperatures. Samples were then dried at 70 °C in a vacuum oven until a constant weight is achieved.

2.3. Characterization methods

2.3.1. Scanning electron microscopy (SEM) analysis

The morphologies of the prepared materials were examined by a Hitachi S4300 scanning electron microscopy. All samples were sputter coated a thin layer of gold (about 5 nm) to ensure good conductivity. Low accelerating voltages (3 kV or 5 kV) were used to minimize sample charging and damage.

2.3.2. Atomic force microscope (AFM) analysis

AFM images were collected using 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.

2.3.3. Differential scanning calorimetry (DSC)

A DSC was used to conduct thermal analysis of the different NC materials. DSC (Model Q20) was supplied by the TA instruments. All samples were characterized in the temperature range of 40–300 °C in a crimped aluminum pan at the heating rate of 2, 5, 7.5 and 10 °C/min. The sample size in the pan was around 1 mg. Nitrogen was used as the inert gas in the DSC furnace.

2.3.4. Burn rate measurement

The burn rates of the different NC materials were measured in ambient atmosphere using a digital high-speed camera (Phantom v710). All samples were 0.6 cm × 5 cm and ignited by a CO_2 laser (Firestar f-series, 400 W Max, 10200–10800 nm) at room temperature. The thickness of all NC films was around 100 μm (±15%) and all NC films were situated 20 cm from the laser head.

3. Results and discussion

3.1. Fabrication and characterization of NC materials

Initially, we examined the effect of different solvents and temperatures for the preparation of NC materials. As shown in Table 1 (Entries 1–12), four solvents, including THF, MeOH, EtOH and DMF, and three temperatures, 5 °C, 25 °C and 45 °C, were used to optimize the process. The solution concentration for all samples was 10 mg/mL. Fig. 1 shows the typical morphology of the different NC samples as observed by SEM. All samples prepared at 25 °C and 45 °C, regardless of solvent, were bulk materials and did not show any microstructure. For example, Fig. 1(a) shows a smooth surface structure of NC sample, which was made at 25 °C using DMF as solvent. However, by decreasing the growth temperature to 5 °C, the morphology of the NC materials changed significantly. Changing the solvent to THF at 5 °C, the NC sample became rougher and formed pores, as shown in Fig. 1(b). With DMF as a solvent, the NC sample formed the sub-micron spheres, as shown in Fig. 1(c) and (d). Using MeOH or EtOH as a solvent produced continuous films similar to those in Fig. 1(a).

Since DMF was observed to produce spherical particles, we next examined the effect of a variety of concentrations (Table 1, Entries