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Production of Desensitized, Ultrafine PETN Powder

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Abstract

Pentaerythritol tetranitrate (PETN) is a widely studied high explosive (HE), most commonly used in detonator applications. In this work, we use a spray drying technique to manufacture a new "nano-powder" morphology of PETN. The spray dried PETN is several orders of magnitude smaller in particle size than traditionally prepared PETN powders. The spray dried PETN has a mostly spherical and smooth morphology, while traditional crystalline PETN typically has sharp edges and crystal facets. Small-scale sensitivity tests including drop-weight impact, friction, and electrostatic discharge (ESD) indicate the spray dried PETN is less sensitive than traditionally used forms of PETN powders. We also observed no changes in chemical properties (melt temperature and onset of decomposition) after spray drying, and the material remains in the tetragonal, crystalline phase.

Keywords: Pentaerythritol Tetranitrate, PETN, Small-Scale Sensitivity, Spray Drying High Explosives

1. Introduction

Pentaerythritol tetranitrate (PETN) is a high explosive (HE) material that is widely used in detonator applications. PETN powder comes in a variety of forms based on the manufacturing process, environmental conditions, and age[1-5] and is typically characterized for chemical purity and loose powder permeability (Fisher Sub-sieve Surface Area). The resulting performance characteristics of the detonator have been found to correlate with specific properties of the powder/pellet microstructure.[6, 7] The ability to produce a range of PETN powder sizes and microstructures would further elucidate why certain microstructural characteristics result in changes in detonation performance.

HE materials are widely used in many different applications in civil and military industries.[8] However, unintended detonations of HE during handling and storage result in accidents causing serious injury and death. Therefore, development of methods to desensitize HE for safer handling practices while not compromising performance is an area of active research. It is well known that microstructure plays a dominant role in the sensitivity of HE materials.[9-12] Existing strategies to reduce the sensitivity of HE materials include particle size reduction and controlling crystal morphology.[13, 14] A wide variety of techniques to process HE powder into size- and morphology-controlled alternatives have been developed. These techniques include mechanical size reduction such as milling, traditional crystallization, as well as spray crystallization.[13] Some efforts have utilized these techniques to design and process desensitized HE materials for safer handling.[15-17] Nanocomposites offer a more recent approach to desensitize HE materials via rapid evaporation of supercritical solutions (RESS),[18] fluid energy milling (FEM),[16] and some initial studies with spray drying.[19-21] However, the initial spray drying studies primarily focus on nano-composites of HE materials mixed with non-energetic polymers, rather than pure, single-component (neat) HE materials. Spray drying has been shown to produce ultrafine particles with a narrow size distribution, and smooth, spherical morphologies.[22] Therefore, it is important to understand the spray drying process for neat HE materials and characterize the dominant microstructural effects (particle size distribution, surface morphology, and surface area) on small-scale sensitivity for increased handling safety.

PETN is known to be a highly sensitive HE material. Because of this, typical mechanical size reduction processes, such as ball milling or jet milling, are potentially hazardous procedures

to reduce the size of PETN for desensitization. In this report, we demonstrate spray drying as a safe, non-mechanical processing method to manufacture a less sensitive "nano-powder" form of PETN. The technique of spray drying HE has been previously demonstrated, although it is still a relatively new process for energetic materials.[20,21,23,24] The process begins with a fully dissolved solution of traditional PETN in acetone; the solution is atomized into tiny droplets filled with the dissolved material, which are co-sprayed with heated nitrogen gas. As the solvent evaporates from the droplets, the particles are separated in a cyclone and collected. With this simple and safe method, we are able to achieve a never-before manufactured PETN microstructure with sub-micron-sized, spherical particles.

Here, we focus on characterizing the microstructure (namely, the particle size distribution and shape) and small-scale sensitivity response. Initial sensitivity testing of the neat, spray-dried, nano-powder PETN shows that this material is significantly less sensitive to drop-weight impact, friction, and electro-static discharge (ESD). We describe the microstructure, along with other important physical and chemical properties, and the connection to sensitivity characteristics.

2. Materials and Methods

2.1 Materials

The source PETN used for spray drying was taken from LANL magazine storage batches. General property comparisons were made between spray dried PETN and traditionally-prepared fine powder PETN.[25, 26] Small scale sensitivity comparisons were also made to a large particle size, blended lot of PETN (0601-02, L298) that was purchased from DuPont in 1986 and has been used as an impact standard at Los Alamos National Laboratory for several decades.[27] Henceforth, we will refer to these three PETN powders as (1) spray dried PETN, (2) fine PETN, and (3) L298 PETN.

2.2 Spray Drying of PETN

The starting material PETN was first dissolved in acetone, typically at 5% by weight. A two-fluid nozzle system in a Buchi B-290 spray dryer (Buchi, Switzerland) was used to process the solution into its final product. As the feedstock and nitrogen gas are co-sprayed through the two-fluid nozzle, the nitrogen gas atomizes the solution into tiny droplets. A heating chamber surrounding the nozzle heats the nitrogen gas as it flows through the system. Note, this is a

desirable safety aspect for HE processing: the HE solution is heated indirectly by the hot nitrogen gas. The entire system is kept under an inert nitrogen atmosphere by integrating the Buchi B-295 inert loop. After the feedstock is atomized, the simultaneous flow of solution droplets and heated nitrogen flow through the drying chamber. Most of the drying occurs here, as the majority of acetone is evaporated from the droplets, resulting in the small product particles. The dried material then flows to the cyclone separator, where the fully dried product is collected below. Any material that has not been fully dried in this process is ejected from the system to the outlet filter. The specific processing conditions include: 0.7 mm two-fluid nozzle, fixed inlet temperature of 100 °C with an outlet temperature of 50-55 °C, N_2 flow rate at 130 NL/h, and aspirator setting of 85% (no external pump was used to increase the feed rate of the solution, as the two-fluid nozzle provided a sufficient feed rate on its own of ~10 mL/min).

2.3 Particle Size Distribution Analysis

The particle size distribution (PSD) of fine PETN was measured using a commercially available Beckman Coulter PSD Analyzer (Beckman Coulter, USA). We attempted to use the same technique to analyze the spray dried PETN; however, the nano-sized PETN tends to agglomerate during the measurement and the results proved to be inaccurate. Based on previous studies using similar spray drying set-ups for HE composites, it has been demonstrated that the expected particle size is on the order of a micron.[24, 20, 28] Even with the use of surfactants, the Beckman-Coulter analysis of the spray dried powder reported mean particle sizes at least an order of magnitude larger than anticipated, which indicates cluster formation. Therefore, we used high-resolution imaging and analysis for a more accurate PSD representation of the spray dried PETN powder with a Keyence VK-1000 3D Laser Confocal Microscope (Keyence, Japan) and the associated particle size analysis software. Using this method, we compiled a sample size of ~1600 particles by combining seven separate images over a wide range of samples from the spray dried powder and measuring the area-equivalent diameter of each particle. During image analysis, singular particles were selected for the measurement to avoid inclusion of large agglomerations. While this technique may introduce sampling bias, it was determined to be the best way to obtain the particle size distribution of individual particles in the spray dried material. Based on work done by Hegel, *et al.*,[29] they demonstrated that using image analysis for adequate PSD analysis required ~700 particles, while a sample of 1000 particles or more provided a representative PSD of the particulate system. They also showed that using a large

enough sample size with image analysis provided valid and comparable results to the laser diffraction techniques commonly used.[29] Our analysis utilized a continuum statistics method to derive a probability distribution function to best describe the particle size of the spray dried PETN. A detailed description of this method can be found in the Supplemental Information.

2.4 Powder Characterization

SEM images were acquired on a JEOL 7900F field emission microscope (JEOL, Japan) taken with the lower electron detector (LED) emission capture. The samples were prepared by first dispersing a microgram quantity of material onto a standard SEM aluminum stub by wetting with hexane. When the hexane was allowed to fully evaporate, a 4 nm layer of Au:Pd (80:20) was applied with a sputter coater to reduce charging and enhance emission during imaging.

For XRD experiments, samples were pressed, as received, onto a silicon zero background plate. The data were collected on a Bruker D8 Advance, (Bruker, USA) with Ni filtered Cu radiation (K_{ave}= 1.5418 Å) and a Lynxeye 2D silicon strip detector.

Thermal decomposition temperatures were measured by DSC using the Q2000 DSC (TA Instruments, USA) in hermetically sealed aluminum pans that contain a pinhole lid. A typical analysis utilizes approximately 1 mg of sample with 50 mL/min ultrahigh purity nitrogen purge gas at a thermal ramp rate of 10 °C/min.

Surface area measurements were taken on a Quantachrome ASiQ3 (Quantachrome Corporation, USA) in large glass bulb cells with a 6mm stem. Liquid nitrogen (77 K) was used as the coolant. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method, determined by the physical adsorption of nitrogen onto the surface of the sample at 77 K. Prior to measurement, the sample was degassed for 1 hour to remove any impurities.

2.5 Small-Scale Sensitivity Testing

Impact sensitivity was measured with a drop hammer LANL Explosives Research Laboratory (ERL) Type 12b test (no grit) on ~40 mg of powder with a 0.8 kg striker, 2.5 kg weight and sound detection equipment. The Neyer D-Optimal method was used to determine the 50% drop height using a go/no-go threshold level of 117 dB. Friction sensitivity was measured with a BAM friction instrument determining the 50% load using the Neyer D-Optimal method. Electrostatic discharge/spark (ESD) sensitivity testing was performed on an ABL ESD instrument to determine threshold initiation level (TIL). [30, 31]

3. Results and Discussion

We compare the morphology and particle size distribution of spray dried PETN to traditionally prepared PETN, and also discuss connections between the powder microstructure and the sensitivity properties.

3.1 Morphology and Particle Size Analysis

Figure 1 shows SEM images of fine and spray dried PETN powders. Figure 1a is fine PETN, and appears as rough particles with sizes ranging from one to tens of microns. The particle size distribution is relatively wide, with a mixture of large and small particles. Figure 1b is a representative SEM image of the spray dried PETN. In terms of morphology, compared to the fine PETN, the spray dried powder exhibits spherical particle shapes. The particles are smoother than the rough particles of the fine PETN, and are mostly smaller than one micron. This shows that not only is the spray dried powder much smaller in size, but the distribution of particle sizes is narrower. As seen in Figure 1b, ultrafine powders tend to agglomerate into clusters, which may change local microstructural properties.

We also imaged these powders using a Keyence 3D laser confocal microscope. Figure 2a shows a representative laser confocal microscope image of the fine PETN, which is clearly much larger in size than the spray dried powder (Figure 2b). Quantitative particle size measurements of powders are typically collected using laser light scattering techniques. At LANL, this is accomplished using laser diffraction on a Beckman-Coulter particle size analyzer that measures the size distribution of particles suspended in a liquid. The instrument uses the diffracted scattering angle of the laser light (wavelength of 750 nm), along with the assumed index of refraction from the particles to calculate the particle size distribution. This technique worked well to measure the particle size distribution of the fine PETN (shown in Fig 3a), resulting in a statistical mean and standard deviation of 85.57 μm and 46.28 μm, respectively. However, we were unable to resolve the individual PETN particles in the spray dried powder via laser light scattering. The ultrafine powder formed agglomerates and large clusters during the laser diffraction PSD analysis, even with the use of traditional surfactants, which caused inaccurate collection of data. Therefore, in order to collect statistically meaningful particle size distributions

of individual particles for the spray dried PETN powder, we used particle analysis software to analyze laser confocal microscope images. Figure 3b shows the probability distribution function (PDF) obtained for the spray dried powder based on a sample size of 1654 particles that were imaged across seven different images of the sample (statistical mean and standard deviation of the spray dried PETN PDF are 0.49 μm and 0.30 μm, respectively). Here, we can clearly see that the particle sizes of the spray dried PETN powder are at least an order of magnitude smaller than the fine PETN. Future work will explore methods such as freeze drying for separation of the clusters formed within the ultrafine spray dried powder.

3.2 Material Characterization

To characterize the spray dried PETN and further compare to fine and L298 PETN, we used powder X-ray diffraction (XRD), differential scanning calorimetry (DSC), and BET surface area. The powder XRD patterns for the fine and spray dried PETN are compared in Figure 4. All of the peaks in the two patterns are in the same positions, and the results indicate that both powders are in the tetragonal phase. It appears that no additional polymorphs form after spray drying; this is important for HE materials since the presence of some polymorphs may cause undesirable changes in material properties.[32, 33]

DSC experiments were used to confirm that processing PETN powder with spray drying did not alter important chemical properties. We examined two relevant features for HE materials, namely the melt temperature and the onset of decomposition temperature. It was found that for the fine (starting material for spray drying) and spray dried PETN, both the melting temperature (~140 ºC) and onset of decomposition (165-166 ºC) remained the same between the two samples. The DSC curves for both samples are shown in the Supplemental Information.

BET surface area measurements were also used to compare the surface area of spray dried PETN to the standard L298 PETN. L298 PETN was determined to have a surface area of 0.082 m^2/g (average particle size = 331.7 μm),[27] while the spray dried PETN has a surface area of 1.507 m^2/g (average particle size = 0.49 μm). Due to the extremely small particle sizes processed with the spray drying technique, the surface area of the material is also dramatically increased.

3.3 Small-Scale Sensitivity

After confirming that the material phase and chemical properties remained unchanged after spray drying, we compared the small-scale sensitivity response of the L298, fine, and spray dried PETN powders. All of the powders were tested using standard small-scale sensitivity analysis techniques including drop weight impact, friction, and ESD testing.[34] Table 1 shows the statistical results of the sensitivity tests. Each test used ten to fifteen samples to achieve adequate statistical data for comparison. All three small-scale sensitivity tests listed in Table 1 play an important role in understanding the sensitivity of an HE material in regards to handling and accidental hazards. The first test is drop weight impact testing. In this experiment, a 2.5 kg weight is dropped onto a striker with ~40 mg of powder. Two microphones measure the decibel (dB) output of the impact. If both microphones record over 117 dB, a reaction is recorded ("go"). Any measurement under 117 dB is considered a "no go". Based on multiple drops, the required height for at least 50% "go" reactions is recorded as the impact 50% height value. If a greater height is required, more energy is needed to initiate a reaction, and the powder is therefore less sensitive than a powder with a smaller drop height value. With these measurements, we observe that the spray dried PETN required almost double the height (21.8 mm) than the other PETN powders (L298 = 11.8 mm and fine = 11.1 mm), showing that the spray dried PETN is less sensitive to impact.

In a friction test, a small amount of powder is placed on a rigid plate. A pin is placed on top of the plate and quickly drug across the powder on the plate. Different weights can be hung from the end of the apparatus to apply more force to the pin. The operator determines if the friction causes reaction via observation of sound, smoke, and light. The force from the weight is recorded as the necessary force to induce a reaction of the sample. Again, we observed that the spray dried PETN powder (average of 201.5 N) required the most force to cause a reaction in response to friction, as compared to the L298 (average of 60.1 N) and the fine (average of 134.7 N) PETN powders. This indicates that the spray dried PETN is less sensitive to friction compared to the traditional PETN powders.

The final sensitivity test is electrostatic discharge (ESD) testing. For this test, a sample is loaded into a small hole in a plastic sample holder. The sample is covered with tape, and a spark

is induced on the sample at varying levels. If the tape is broken, reaction of the sample occurred, whereas if the tape is still intact, then the sample did not respond sufficiently. This is important for HE materials, as small electrostatic charges can cause serious accidents. With this experiment, we observed that all of the PETN samples had similar ESD thresholds.

With this small-scale sensitivity analysis, we have demonstrated the ability to consistently manufacture an ultrafine, desensitized PETN powder.[27] We have primarily linked this desensitization behavior to the particle size reduction and spherical morphology, as both ultrafine particle sizes and rounded particle morphologies have previously been shown to reduce sensitivity of HE materials.[35, 36, 23, 37, 20] Future work will more closely investigate the relationship between the microstructure and sensitivity with various sizes and morphologies of PETN powders manufactured by a variety of processes, as well as the connection to detonation performance.

4. Conclusions

We have demonstrated the use of spray drying as a novel HE manufacturing technique to produce a new microstructure of PETN. Compared to commonly used PETN powders, our new spray dried PETN is shown to be several orders of magnitudes smaller in particle size, accompanied by a large increase in surface area, with a spherical, smooth particle shape. DSC showed that spray drying does not induce any changes to the chemical properties, such as the melting temperature and onset of decomposition temperature. With XRD, we verified that the thermally stable tetragonal phase of PETN remains after spray drying. Small-scale sensitivity tests of spray dried PETN showed that the new powder is less sensitive than traditional PETN to impact, friction, and ESD testing. Future work will focus on deepening the understanding of this new microstructure and connecting its properties to sensitivity and detonation performance.

Author Contributions

Jeremy T. Tisdale: Conceptualization; Writing – Original Draft, Review, Editing; Material Preparation and Characterization; Investigation; Formal Analysis. **Larry G. Hill:** Writing – Review and Editing; Data Analysis and Methodology. **Amanda L. Duque:**

Conceptualization; Writing – Review and Editing; Data Analysis and Validation. All authors have read and agree to the published version of the manuscript.

Declaration of Competing Interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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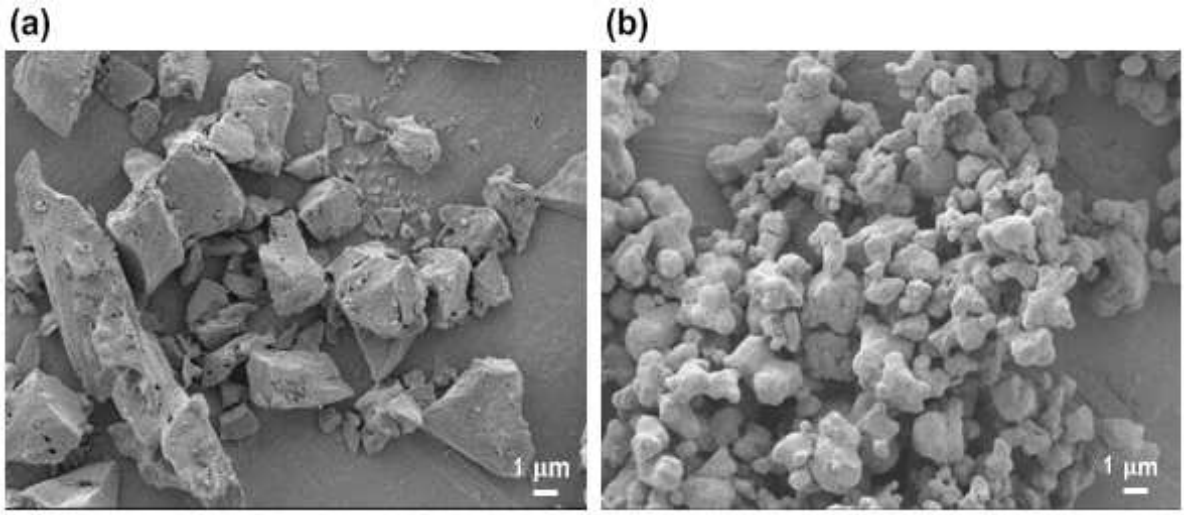


Figure 1. SEM images of (a) fine PETN and (b) spray dried PETN.

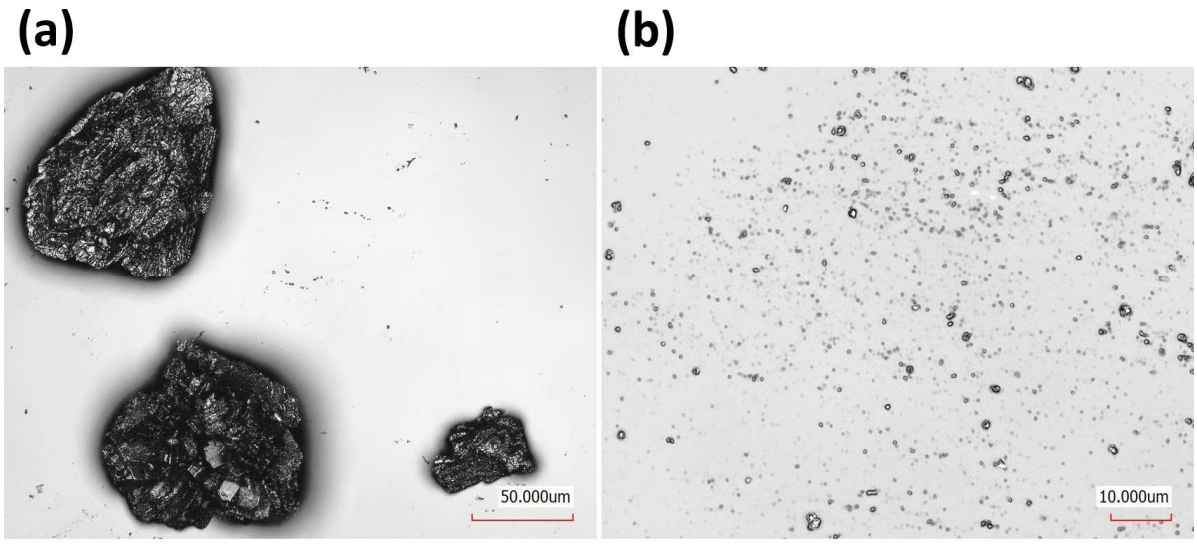


Figure 2. 3D laser confocal microscope images of (a) fine PETN and (b) spray dried PETN powders.

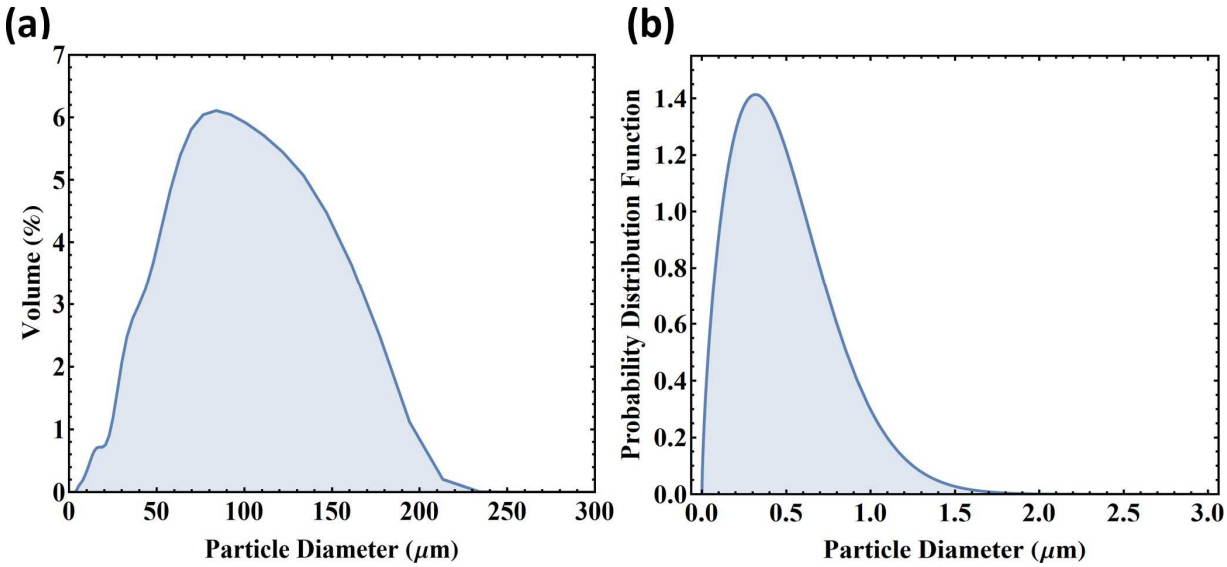


Figure 3. Particle size distributions of (a) fine PETN powder using the Beckman Coulter PSD Analyzer and (b) spray dried PETN obtained from imaging on a Keyence 3D laser confocal microscope and associated particle analysis software (sample size of 1654 particles). Details on how the probability distribution function was obtained from the data may be found in Supplementary Information.

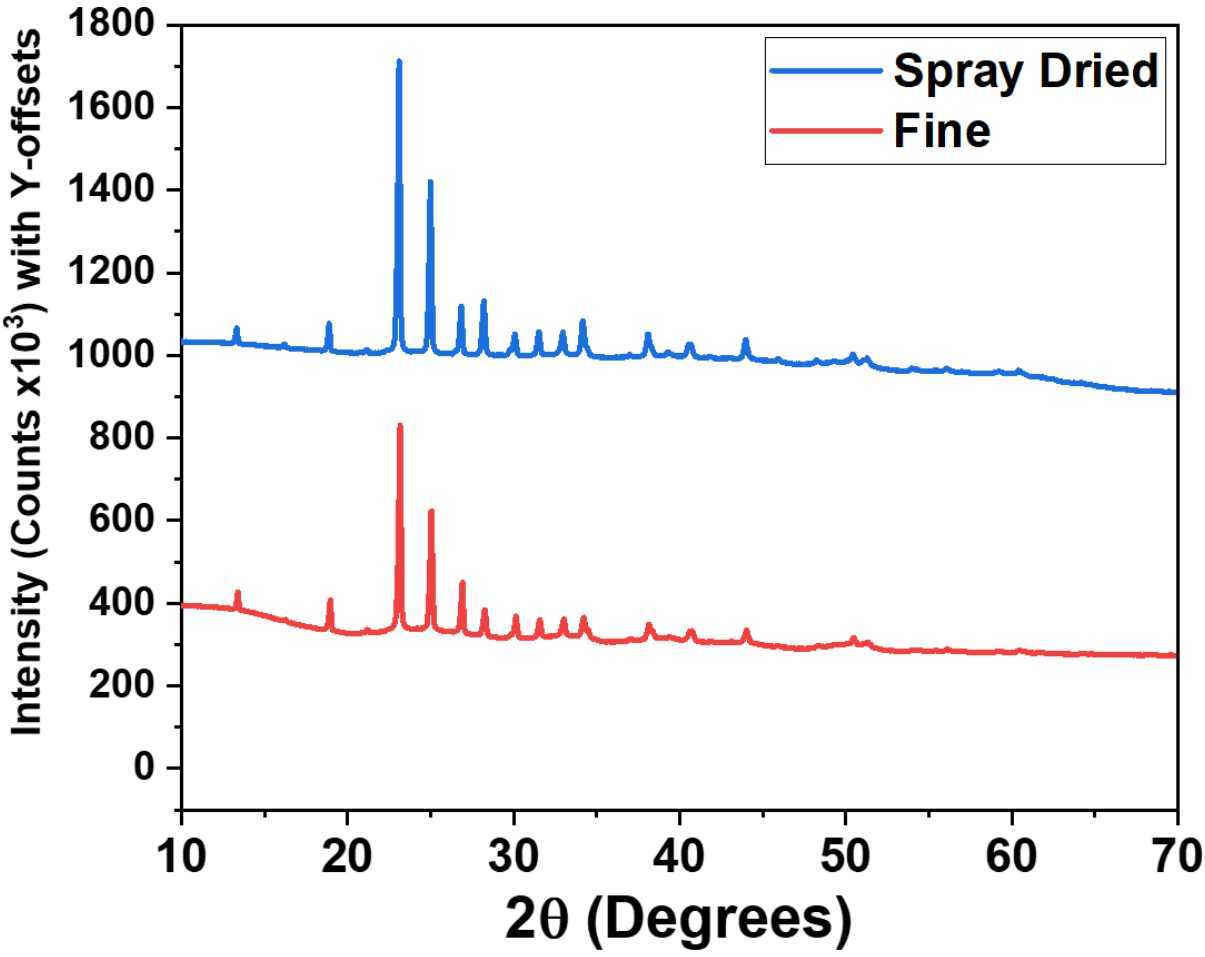
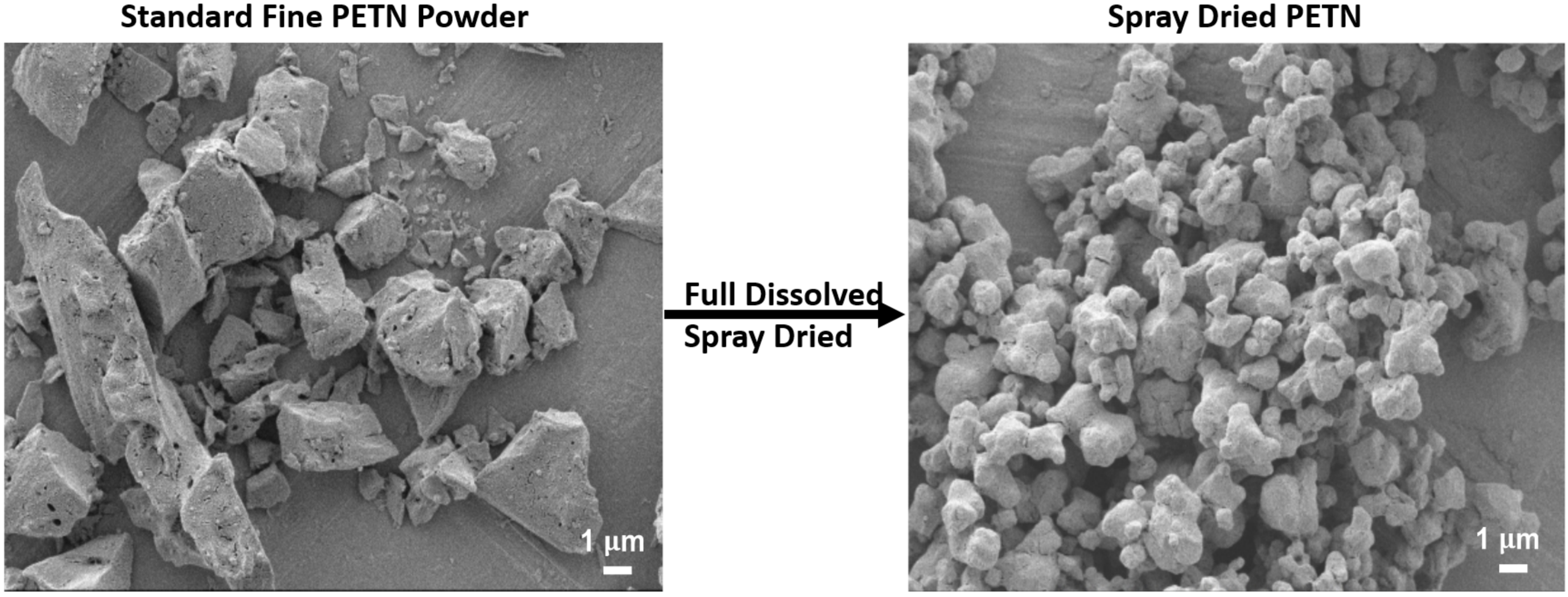


Figure 4. Powder XRD patterns for the fine and spray dried PETN powders.

Table 1. Small-Scale sensitivity testing of PETN powders.

Sample	Impact Testing		Friction Testing		ESD Testing
	50% Height (cm)	σ (cm)	50% Load (N)	o (N)	*TIL/**Screen (J)
L298 PETN	11.8	1.7	60.1	3.6	*0.125
Fine PETN	11.1	1.3	134.7	17.4	*0.0625
Spray Dried PETN	21.8	3.6	201.5	58.8	*0.125


Standard Fine PETN Powder
1 µm
Full Dissolved
Spray Dried
Spray Dried PETN
1 µm