PETN: Variation in Physical and Chemical Characteristics Related to Aging

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Abstract

Physical and chemical analyses of five PETN (pentaerythritol tetranitrate) batches have been conducted to assist in defining powder acceptance criteria for qualification of newly manufactured powders, as well as for examination of potential changes related to aging and thus changes in performance. Results showed that 1) repeatable Fisher Sub-Sieve Sizer measurements (which relate well to historic performance data) could be obtained with consistent sample setup and measurement techniques; 2) BET nitrogen adsorption estimates of surface area correlate well with Fisher measurements and appear less variable; 3) PharmaVision particle size analyses show promise in discriminating among PETN batches; and 4) SEMs are extremely useful in semi-quantitative discrimination among batches. Physical and chemical data will be related to performance data (to be obtained) to develop quantitative physical and chemical tests useful in predicting performance over time, i.e., as powders age.

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INTRODUCTON

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FISHER MEASUREMENTS

Specific surface area measurements of PETN powder (Fig. 1) were obtained using a Fisher Model 95 Sub-Sieve Sizer (FSSA).[1] The FSSA specific surface area was affected by a number of factors, including sample preparation (pressing) method and the measurement time after pressing. For each sample the FSSA calculated surface area appeared to decline over time, reaching a stable value within 5 to 40 minutes after pressing. The apparent decrease in specific surface with time may simply be a mechanical relaxation of the sample in the sample tube, resulting in a lower pressure drop across the sample and a lower calculated specific surface.

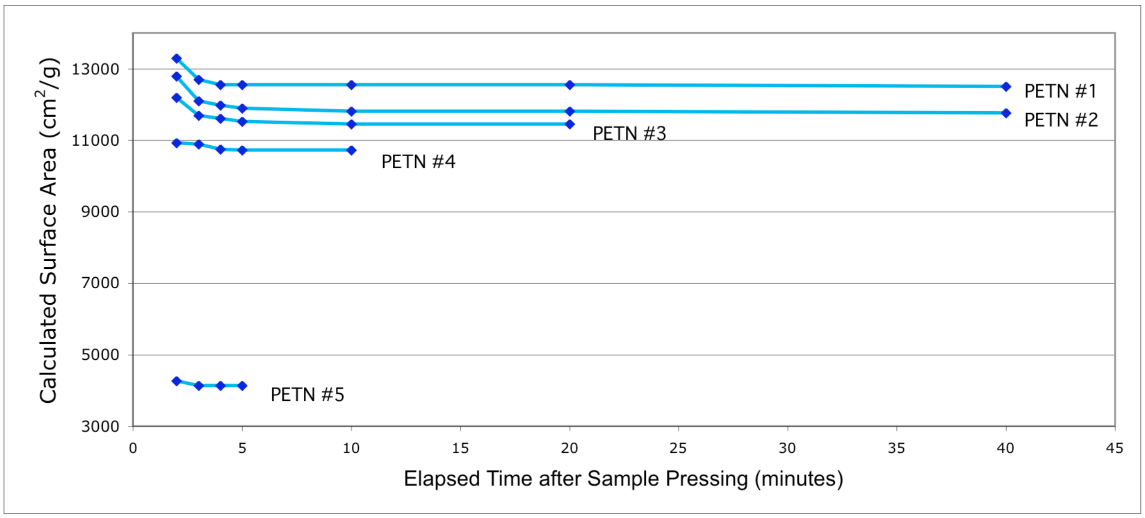

Fig. 1 FSSA calculated specific surface for five PETN batches.

[1] Data were obtained by J. Archuleta and D. Monroe, 2005.

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It should be noted that the FSSA apparatus directly responds to the pressure drop across a porous sample at a known flow rate. Based on this pressure drop, the FSSA approach calls for calculating mean particle size and surface area through a complex, non-linear set of equations developed for the cement industry by Gooden and Smith[2] and the earlier work of Carman.[3] So, FSSA does not directly measure either particle size or surface area. Regardless of these issues, FSSA measurements are repeatable with consistent sample preparation and measurement technique.

SEM

SEMS at high magnification show distinct differences in crystal morphology, even among the four higher specific surface batches (Fig. 2).[4] Batches also vary in terms of aspect ratio and edge roundness. The lowest specific surface powder (PETN #5) has a distinctly different crystal form and size (Fig.3).

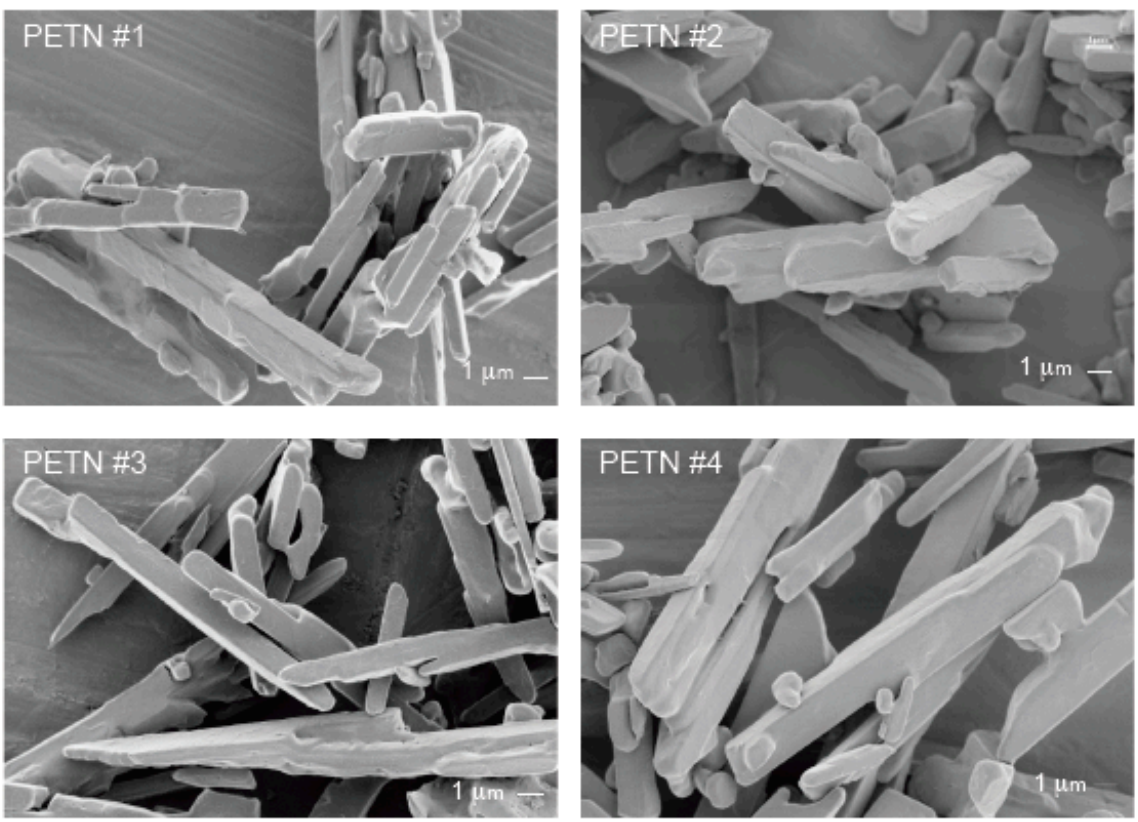

Fig. 2. SEMs for four PETN batches @ 1kV, 5000x magnification.

[2] Gooden, Ernest L. and Smith, Charles M., Ind. Eng. Chem., Anal. Ed,12, 479-482 (1940).
[3] Carman, P.C., J. Soc. Chem. Ind. 57, 225-234.
[4] SEMS by E. Roemer, 2005.

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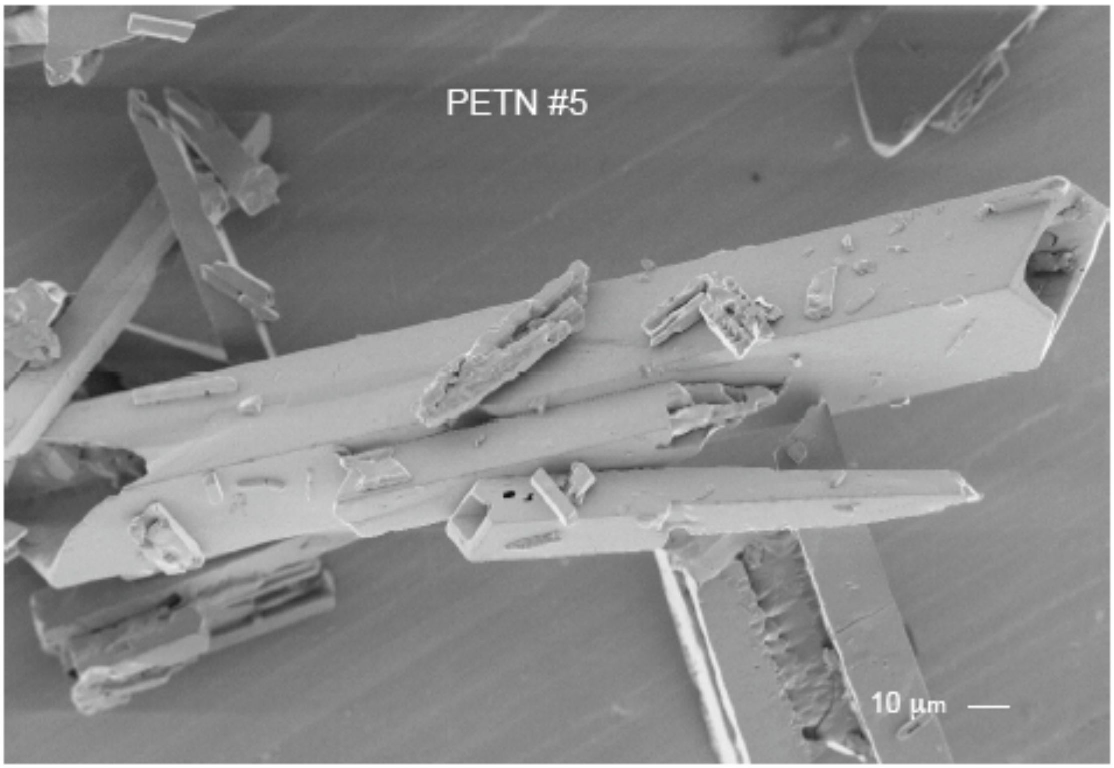

Fig. 3. SEM for PETN #5 @ 1kV, 5000x magnification

BET SPECIFIC SURFACE

The BET nitrogen adsorption method provides a direct measure of specific surface and correlates well with Fisher measurements (Fig. 4).[5] Interestingly, there is a linear relationship between FSSA calculated specific surface for the higher surface powders, i.e., above 10,000 cm^2/g. Except for PETN #5, the BET specific surface is higher in all cases than the FSSA calculated specific surface and the differences increase as the FSSA specific surface increases. So, for instance, an 11,000 cm^2/g powder as measured by the FSSA is 13,000 cm^2/g by the BET. A PETN at 13,000 cm^2/g will measure approximately 19,000 cm^2/g by the BET. PETN #5 BET and FSSA measurements are effectively equivalent, but this specific surface is in a range (3,000-4,000 cm^2/g) consistent with original development of the FSSA technique. So, for PETN samples above 10,000 cm^2/g, a fairly small range in FSSA specific surface correspond to a much larger range in BET specific surface. In all cases, the BET specific surface exceeds the FSSA value.

[5] BET data were obtained by by J. Archuleta, 2005 using a Quantchrome Autosorb Automated Gas Sorption system. FSSA data were obtained by J. Archuleta and D. Monroe, 2005.

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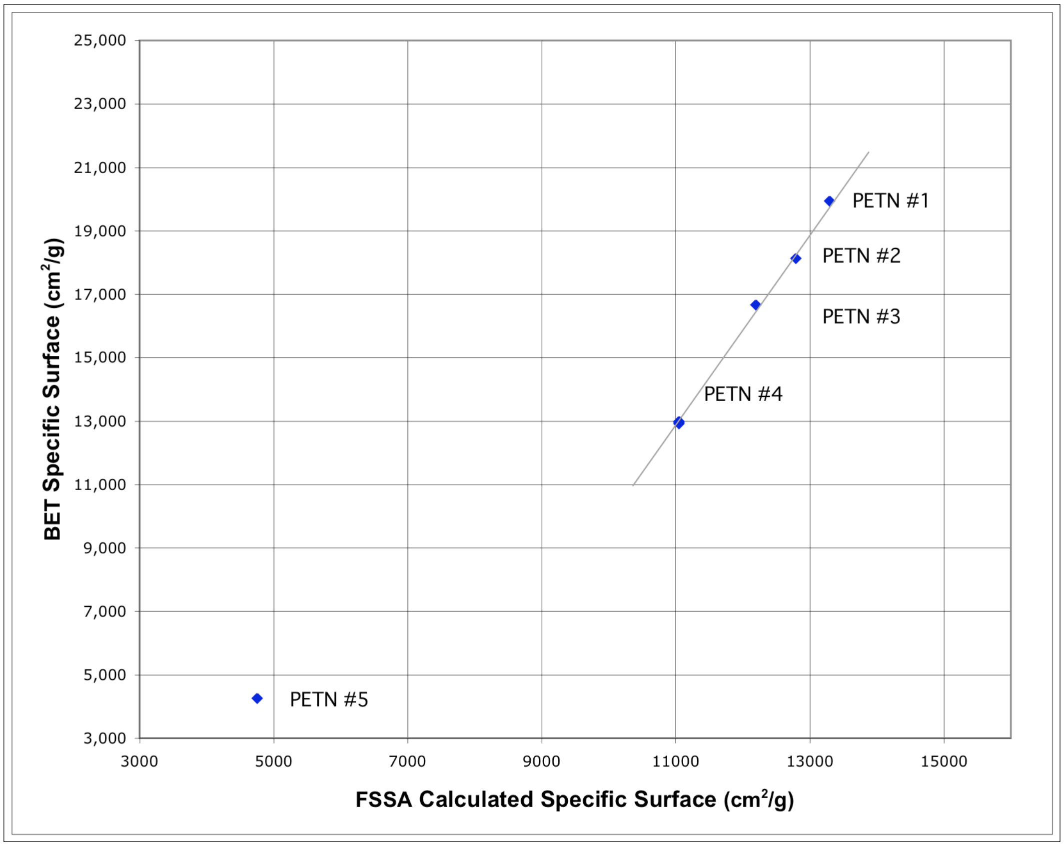

Fig. 4. BET vs. FSSA specific surface for five PETNs.

PHARMAVISION PARTICLE SIZE DISTRIBUTIONS

Particle size and morphology were analyzed using a Malvern PharmaVision 830 Particle Analyzer. The PharmaVision 830 collects photographic images across a dispersed powder sample through a microscopic lens. The images are then analyzed using intensity thresholding to identify individual opaque particles against the light background. Particle size is determined by calculating the number of pixels contained within a given particle and multiplying by the spatial calibration (in microns/pixel). The spatial calibration is determined immediately before and verified immediately after the analysis by imaging a grating of known spacing.

For the current analysis, small (approximately 10 mg) samples of each of the PETN batches were dispersed in heptane. Several drops of the PETN/heptane solution were applied to a glass microscope slide. The heptane was then allowed to completely evapo-

rate. The slide was analyzed at high magnification (approximately 100X) to determine particle size distributions.
A total of 100,000 particles were analyzed from each batch. A comparison of the volume-weighted length distributions have been plotted in Figures 5 and 6. Particles with apparent widths greater than the maximum width observed for that batch using the SEM were rejected as agglomerates and not included in calculating size distributions shown here. The results of size filtering can be large as shown in Fig. 6.

PharmaVision measurements show promise in differentiating powders on the basis of particle size distributions. However, particle widths vary between batches, so length data alone does not completely represent the particle differences apparent in SEMs.

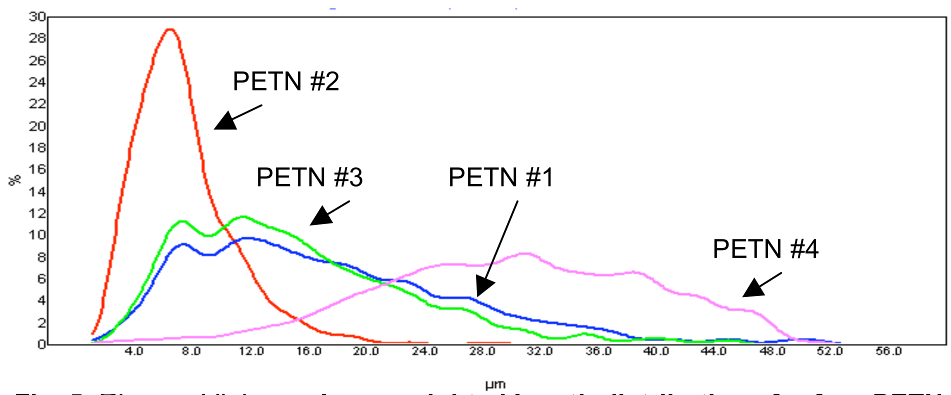

Fig. 5. PharmaVision **volume-weighted length distributions for four PETNs.**

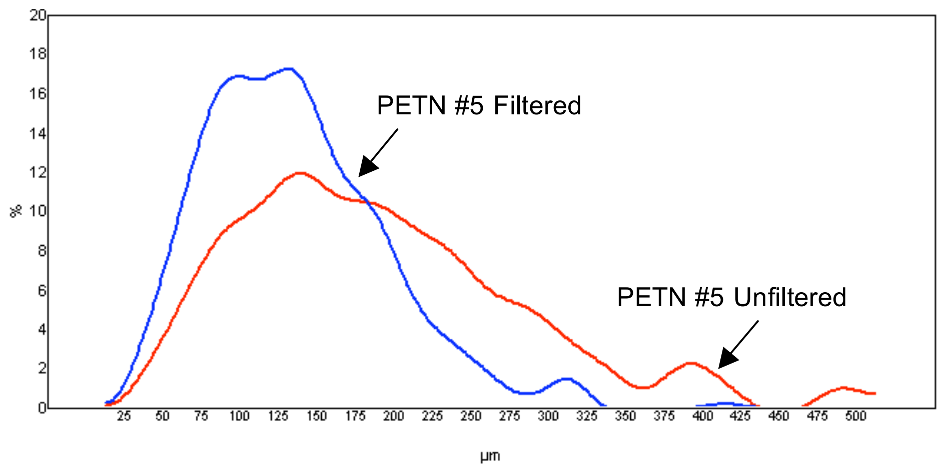

Fig. 6. PharmaVision **volume-weighted length distributions for PETN #5.**

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CONCLUSIONS

Analyses showed that PETN batches vary in their physical characteristics. These results will be related to performance data to examine the degree to which these characteristics differentiate batches (or not) on the basis of performance and aging.