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# An Optical Microscopy and Small-Angle Scattering Study of Porosity in Thermally Treated PBX 9501

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**Abstract.** Heat transfer and combustion properties of a high explosive (HE) are influenced by the HE microstructure. The development of voids and cracks in an HE system under the conditions of thermal loading can have a strong impact on the safety and reliability of a weapon system. The optical microscopy and small-angle x-ray scattering (SAXS) techniques are useful tools for microstructural characterization. A combination of the tools allows lengthscales from hundreds of microns to tenths of nanometers to be probed, allowing a thorough description of a system's microstructure to be made. We present an optical microscopy and SAXS study of the effects of thermal loading on the microstructure of PBX 9501. Pressed pellets of PBX 9501, an HMX-based system, were heated in an oven at 180 °C for periods of 0, 15 and 30 minutes. Optical micrographs reveal the development of large pores in the microstructure with increasing thermal treatment as well as increased cracking and morphological changes of crystal grains, associated with the beta to delta phase transition in HMX. SAXS measurements were performed in order to quantify the observed porosity.

## INTRODUCTION

Microstructural aspects of energetic materials are known to influence shock initiation. Similar influence is found in non-shock initiation events such as the mechanical or thermal insult that might occur in accident scenarios (1). In order to ensure the safety of a weapon system, it is essential to understand the influence different microstructural parameters have on the non-shock initiation of a weapon. Consequently, characterization of microstructural changes, resulting from insult, is necessary in order to understand and simulate the conditions that lead to initiation.

Here, we present an optical microscopy and SAXS study of the effects of thermal loading on the microstructure of the HE system, PBX 9501. The effects of thermal insult vary, depending upon the

magnitude and duration of the insult and include ignition and self-sustained combustion and material sensitization (1,2). Microscopical techniques can be readily used to make qualitative, post-test assessments of microstructural damage. SAXS techniques can provide quantitative measurements of changes in microstructural parameters, such as intergranular porosity.

## MICROSCOPY AND SAXS TECHNIQUES

Optical microscopy images for the current study were obtained in reflected parallel polarized light (RPPL). This arrangement allows the return light from crystal interfaces below the plane of polish to be minimized and thus provides good grain-to-grain contrast in plastic-bonded systems. In preparation for examination, a sample is vacuum-mounted in low-

viscosity epoxy for viewing in cross-section and is polished using a series of fine abrasives (3).

In a SAXS experiment, a fraction of the x-rays incident on the sample will scatter from fluctuations in the scattering length density,  $\rho(\mathbf{r})$ .  $\rho(\mathbf{r})$  reflects the microscale structure of the sample in both density and chemical composition. The intensity of the scattered radiation,  $I(Q)$ , is measured as a function of the scattering vector,  $\mathbf{Q}$ , of magnitude  $Q = (4\pi/\lambda)\sin\theta$ , where  $\lambda$  is the wavelength of the incident radiation and  $\theta$  is half of the scattering angle.  $I(Q)$ , for a monodisperse system of non-interacting particles, dispersed in a uniform media, can be expressed as (4):

$$I(Q) = \Delta\rho^2 V\phi \langle P(Q) \rangle, \quad (1)$$

where  $P(Q)$  is the normalized, single particle form factor and is related to Fourier transform of  $\rho(\mathbf{r})$ ,  $V$  is the particle volume, and  $\phi$  is the volume fraction of scatterers.  $\Delta\rho$  is the scattering length density contrast between the average scattering length density of the particle,  $\bar{\rho}$ , and that of the surrounding media,  $\rho_s$ ,

$\Delta\rho = \bar{\rho} - \rho_s$ . The SAXS instrument used for the current studies can provide detailed structural information for particles (or pores) in the range of  $0.002 - 0.5 \mu\text{m}$  (5). Previous microstructural studies have shown that HE systems possess structures that are larger than  $1 \mu\text{m}$  (3). In order to increase the range of sizes accessible by our instrument, we have employed a technique known as multiple small-angle x-ray scattering or MSAXS. With this technique, there is potential to extend the range of lengthscales by an order of magnitude (6). Eq. 1 is applicable when each scattered x-ray undergoes one scattering event. In order to achieve such conditions experimentally, very thin samples, having a small  $\phi$  must be studied. By increasing the thickness of a sample, the probability that x-rays will undergo multiple scattering events increases. The scattered intensity can then be described as (6):

$$I_{\text{MSAXS}}(Q) = \frac{1}{2\pi} \int_0^{r_{\text{max}}} J_0(Qr) h(r) dr. \quad (2)$$

While not explicitly shown here, Eq. 2 is dependent

upon the sample thickness,  $t$ ,  $\lambda$ ,  $\phi$ , and  $\Delta\rho$ . The details of this technique will be discussed elsewhere (7), but the important point is that the measured intensity for structures undergoing multiple scattering will appear at larger values of  $Q$  than the corresponding single scattering intensity. So, scattering signals from structures, which would normally be out of the range of a given instrument, will now be accessible.

## EXPERIMENTAL AND RESULTS

For the microscopy studies, samples of PBX 9501 were pressed ( $\rho = 1.81 \text{ g/cm}^3$ ), at ambient temperature, into cylinders of  $1.27 \text{ cm}$  diameter and  $1.27 \text{ cm}$  thickness. The samples were thermally treated by placing them (unconfined) in an oven at a temperature of  $180 \text{ }^\circ\text{C}$ , corresponding to the delta phase of HMX, for 0, 15, and 30 minutes. Digital images were collected in reflective light, using a Spot camera (Diagnostic Instruments) and a DMRXA microscope (Leica). The spatial resolution of the microscope optics was matched with the camera pixel characteristics to nearly meet the Nyquist limit.

SAXS experiments were performed at the University of New Mexico/Sandia National Laboratory Small-Angle X-ray Scattering Laboratory, employing the Bonse-Hart (5). Measurements were performed on cylindrical samples,  $0.9 \text{ cm}$  in diameter, ranging in thickness from  $0.05 - 0.3 \text{ cm}$ . The samples were pressed at ambient temperature to a density of  $1.79 \text{ g/cm}^3$ . At this time only SAXS data for pristine (no thermal treatment) PBX 9501 are available.

### Optical Microscopy Results

Thermal treatment of the PBX 9501 samples resulted in a 14% increase in volume for the 15-minute specimen while the volume of the 30-minute specimen increased by 16%. The theoretical volume increase for a single crystal of HMX having undergone the beta-delta phase transition is only 7%, suggesting that additional microstructural changes have occurred.

Optical microscopy studies of the pristine and thermally insulted PBX 9501 samples were preformed in order to understand these changes. Figure 1 is an RPPL image of the pristine specimen polished on the face. Individual, large grains are easily distinguished from the surrounding matrix of

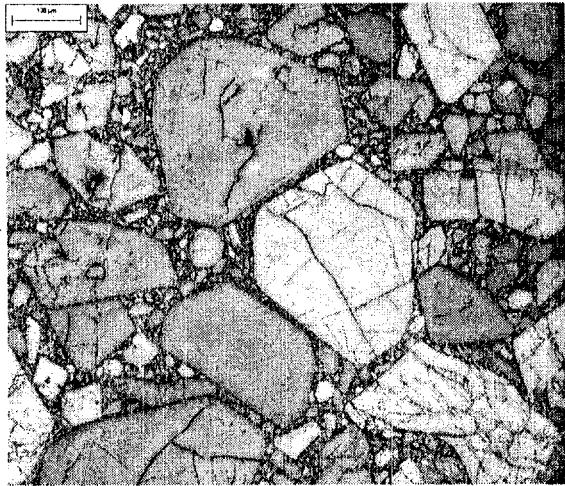


Figure 1. RPPL image of pristine PBX 9501.

fine particles mixed with binder. Most of the large grains exhibit fracture.

The heated specimens were cut along the cylindrical axis for observation of the cross-section. Figure 2 (15-minute treatment) and Figure 3 (30-

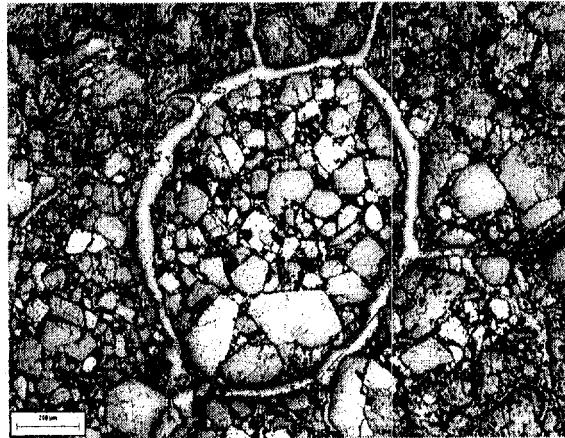


Figure 2. RPPL image of oven-heated PBX 9501-15-minute treatment.

minute treatment) were taken at half the resolution of

Figure 1 in order to show a larger field of view. After 15 minutes of heating (Figure 2), numerous pockets of apparently undisturbed microstructure and partially transformed crystals were found. The surrounding regions contain fully transformed material. In addition, we see the development of large channels in the microstructure.

Figure 3 displays the resulting microstructure after the 30-minute treatment. Significant cracking is seen, distributed uniformly throughout the sample. In contrast to the sharp crystalline facets seen in Figure 1, we see smooth, rounded edges. In some regions, individual grains are difficult to identify. In comparison to the pristine microstructure, there appears to be a loss of the fine HMX particles. The regions in Figure 1, identified as a matrix of fine particles mixed with binder are no longer present.

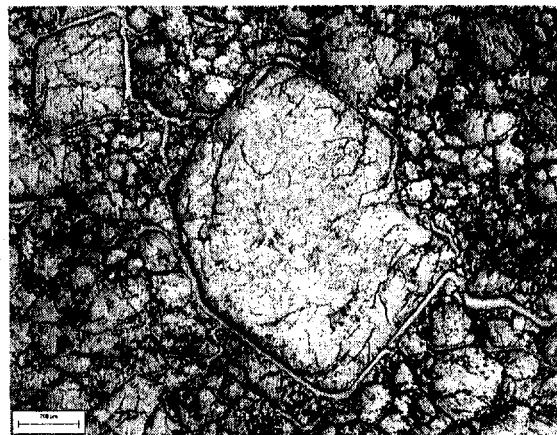


Figure 3. RPPL image of oven-heated PBX 9501-30-minute treatment.

These observations suggest that after fifteen minutes of heat treatment, a partial transition from the beta to delta phase of HMX occurred. After thirty minutes, the transition appears to be complete, as no grains identifiable as beta HMX were observed. Second harmonic generation measurements of the 30-minute sample confirm this notion (2). Additionally, we observed significant thermally induced cracking and pore development in the microstructure, which can account for the measured volume increase.

#### SAXS Results

Figure 4 shows a log-log plot of the measured SAXS lineshapes for the pristine PBX 9501 samples. Samples of different thickness were studied in order to vary the probability of multiple scattering, as discussed previously. As can be seen in the figure, the shapes of the measured curves change with

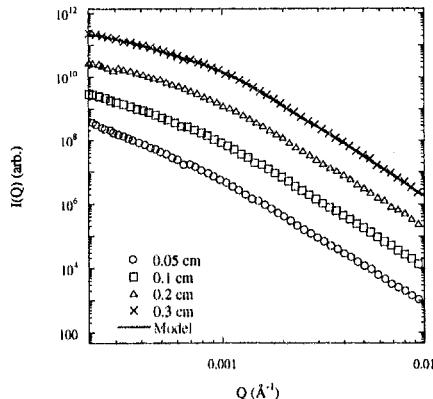


Figure 4. SAXS lineshapes for PBX 9501.

increasing thickness, a hallmark of multiple scattering.

Analysis of the scattering from the PBX 9501 system is complicated because of the three different phases present: HMX, binder, and voids. Since HMX accounts for  $\sim 90\%$  of the volume, it is considered as the continuous phase. The measured scattering thus arises from the HMX-binder, HMX-void and binder-void interfaces. With the current data, we cannot distinguish among the three contributions to the scattering signal. However it is possible to obtain a distribution that represents the average size distribution of the binder and void (pore) regions.

The data shown in Figure 4 were analyzed according to Eq. 2, taking into account polydispersity. For the model calculation, we have assumed that the pores can be represented as Gaussian distributions of spherical pores. The mean size, amplitude, and width of the distributions were allowed to vary freely during the fitting process. The solid line in Figure 4 is a representative fit of the data. Figure 5 shows the volume-weighted and number-weighted distributions of sizes obtained from the analysis. The trimodal distributions represent the probability of finding a binder or void region of a given size in the range 0 – 1.5  $\mu\text{m}$ . Averaging over

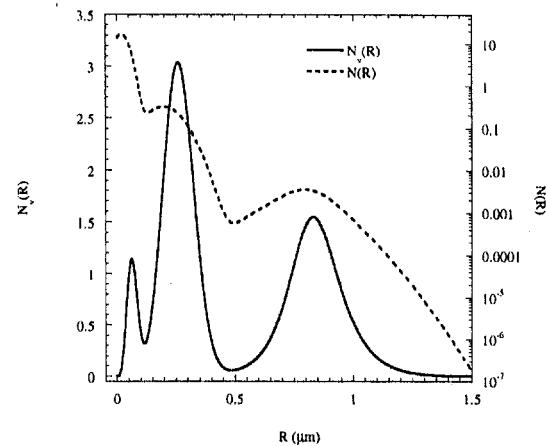


Figure 5. Pore size distributions in PBX 9501.

these distributions, we find a mean volume-weighted pore size of 0.51 ( $\sigma = 0.32 \mu\text{m}$ ) and a mean number-weighted pore size of 0.04  $\mu\text{m}$  ( $\sigma = 0.05 \mu\text{m}$ ). Considering the composition of PBX 9501 and the surface area of HMX, the average thickness of the binder region between crystals is estimated to be 0.36  $\mu\text{m}$  (8). Now, from Figure 5, we see that the number-weighted distribution shows a peak at  $R = 0.196 \mu\text{m}$ . If we assume that this lengthscale is due to the binder region, then it would correspond to a binder thickness of  $\sim 0.39 \mu\text{m}$ , in good agreement with the compositional calculation.

## SUMMARY

We have performed optical microscopy and SAXS studies of the microstructure of pristine and thermally damaged PBX 9501. Optical microscopy measurements show increased alteration of the PBX 9501 microstructure with increasing thermal insult. Evidence of the beta to delta phase transition was seen as well as the appearance of large channels and cracks. SAXS measurements performed on pristine PBX 9501 revealed a trimodal distribution of pores. In order to quantify the changes in porosity seen by optical microscopy, future scattering experiments will be made on thermally insulted PBX 9501. Small-angle neutron scattering measurements, employing contrast variation, will be performed in order to separate the scattering signals arising from the different interfaces found in PBX 9501.

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