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DEFLAGRATION BEHAVIOR OF PBX 9501 AT ELEVATED TEMPERATURE AND PRESSURE

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ABSTRACT

We report the deflagration behavior of PBX 9501 at pressures up to 300 MPa and temperatures of 150-180°C where the sample has been held at the test temperature for several hours before ignition. The purpose is to determine the effect on the deflagration behavior of material damage caused by prolonged exposure to high temperature. This conditioning is similar to that experienced by an explosive while it being heated to eventual explosion. The results are made more complicated by the presence of a significant thermal gradient along the sample during the temperature ramp and soak. Three major conclusions are: the presence of nitroplasticizer makes PBX 9501 more thermally sensitive than LX-04 with an inert Viton binder; the deflagration behavior of PBX 9501 is more extreme and more inconsistent than that of LX-04; and something in PBX 9501 causes thermal damage to "heal" as the deflagration proceeds, resulting in a decelerating deflagration front as it travels along the sample.

INTRODUCTION

When heated to a sufficiently high temperature, all explosives and propellants will ignite and react rapidly, resulting in a thermally-driven explosion. The explosion spreads from the point of initial ignition through sub-sonic propagation of the reaction by a deflagration front; the reaction front is propagating through, in many cases, material that has also been heated and therefore is altered from its initial state, or damaged. The deflagration may propagate at high pressures (100's of MPa, or several kbar). The violence of the thermal explosion depends greatly on the deflagration behavior of the heated explosive. In all materials studied to date, materials that exhibit rapid deflagration, particularly in a damaged state, give more violent thermal explosions.¹⁻³ Therefore experimental characterization of deflagration behavior at high pressure and temperatures for pristine and degraded materials provides critical information on the expected violence of thermal explosions.

Here we report deflagration rates on PBX-9501 at elevated pressures and temperatures (300 MPa & 180°C), and compare the deflagration behavior with that of the same material at ambient temperature and with that of LX-04 at high temperature as previously reported.^{4,5} We also consider the results in context of the previously-reported thermal explosion violence measurements with PBX 9501.¹⁻³ Our experiments were intended to study the effect of thermal damage and of the beta-to-delta phase transition, so were designed with a thermal soak at the final temperature.

APPARATUS AND MATERIALS

We conduct experiments using the Lawrence Livermore National Laboratory High Pressure Strand Burner (HPSB) apparatus. The HPSB contains a deflagrating sample in a small volume, high pressure chamber. The sample consists of nine cylindrical pellets, 6.35 mm diameter and 6.35 mm length, stacked on end, with burn wires placed between cylinders. Sample deflagration is limited to

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the cross-sectional surface of the cylinder by coating the cylindrical surface of the tower with Versamid 140 epoxy. Sample deflagration is initiated on one end of the tower by a B/ KNO_3 and HNS igniter train. Simultaneous temporal pressure history and burn front time of arrival measurements yield the laminar deflagration rate for a range of pressures and temperatures and provide insight into deflagration uniformity. For these experiments, the PBX 9501 samples were heated by a heating coil mounted inside the HPSB apparatus. Specific details of the experiment and the apparatus can be found in earlier reports.⁴⁻⁹

PBX 9501 contains 95% by weight HMX, 2.5% Estane binder, and 2.5% BDNPA/F nitroplasticizer. The particle size distribution is trimodal as shown in Figure 1. The material used in this study was molding powder from LLNL Lot # C-214. The powder was uniaxially pressed in a cylindrical pressing die at 85 °C to form cylindrical pellets using three pressing cycles, each of three minute duration and 200 MPa pressure (30,000 psi). Samples were pressed to a density of approximately $1.831 \text{ g/cm}^3 \pm 0.001 \text{ g/cm}^3$, which is approximately 98.7 % of the sample's theoretical maximum density of 1.855 g/cm^3 .

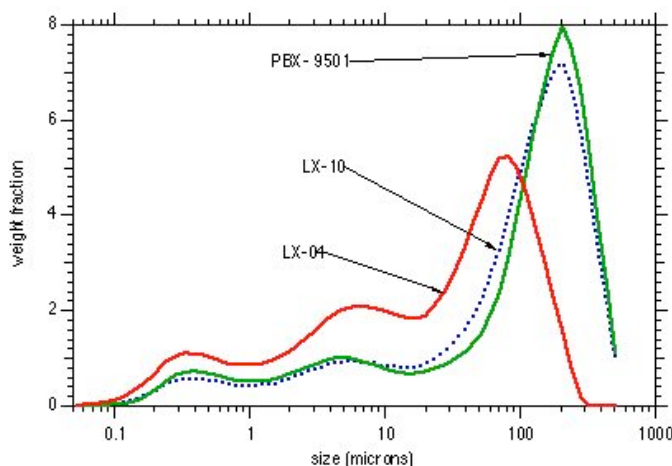


Figure 1. Particle size distribution of PBX 9501, compared with that of LX-04 and LX-10. LX-04 contains 85 wt% HMX and 15 wt% Viton A, while LX-10 contains 95 wt% HMX and 5 wt% Viton A.

RESULTS AND DISCUSSION

One goal of these experiments was to study the effect of the HMX beta-to-delta phase transition on the deflagration behavior; this transition occurs about 160°C,¹⁰⁻¹⁵ and is affected by the temporal heating profile experienced by the material. We therefore desired a uniform temperature in the sample so that the entire sample would be at the same phase. The internal heating coil used in these experiments is uniform in spatial power density, but did not provide a uniform temperature as a result of convective heat transport along the (vertical) length of the sample. Our previously-reported thermal gradient data for PBXN-109 is reproduced in Figure 2; it was measured using RTDs bonded to the outside of the burn sample at different heights replacing the burn wires. We found that the top of the sample is significantly hotter than the bottom.⁹ Close inspection of Figure 2 shows that the locations below the very top of the sample are the hottest (e.g. temperatures from top to bottom of 172.9, 175.0, 174.4, 171.4, 165.3 and 158.2°C with the bomb TC at 160.8°C). The bomb TC, the only temperature sensor during the actual deflagration measurements, was considerably cooler than the hotter regions of the sample.

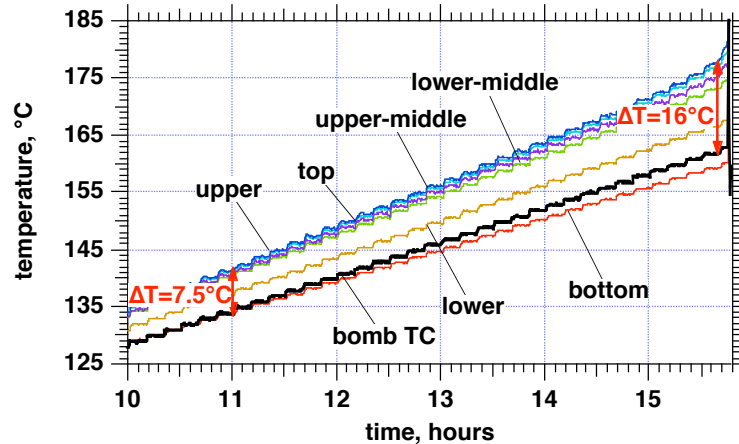


FIGURE 2. Temperature gradient along the deflagration sample as a function of temperature. The top RTD temperature sensor was located at the very top of the sample and the others were separated by approximately 9.5 mm.

During the experiments with heated samples, the only temperature sensor was the bomb TC. Therefore, the actual sample temperatures were significantly different than the reported experimental temperature. This led to two undesired perturbations in the experiment. First, the wide spread in temperature between top and bottom of the sample resulted in a non-uniform phase change, with the cooler bottom section converting from beta to delta much later in the experiment, if at all. Second, the presence of the BDNPA/F nitroplasticizer makes the PBX 9501 ignite at a lower temperature compared to other HMX formulations which contain no energetic plasticizer; in many cases the sample self-ignited at the high-temperature top region while it was still being heated as we monitored the “bomb TC”. The burn rate data were still captured, but the data analysis was made more complicated by this self-ignition. Because of these undesired perturbations, we have not previously reported these data (measurements taken in 2002); however, as time has passed and anticipated further experiments with heated PBX 9501 have not been possible, we choose to report the data here even with its deficiencies.

In order to study the damage from the beta-to-delta phase transition and from high temperature, we performed three sets of experiments, all with a prolonged period at the final temperature to allow time for thermal damage and / or phase transition to occur:

1. Heated to 155°C for 22 hours at ambient pressure.
2. Heated to 155°C for 22 hours at high pressure (120-130 MPa).
3. Heated to 160-180°C for 2-22 hours at high pressure (110-130 MPa).

We planned comparison of the first two sets to give the effect of high pressure on the thermal damage for samples below the beta-to-delta phase transition, and comparison of the last two sets to give the effect of the phase transition (planned for only the last set). However, because of the uncertainty in the actual sample temperature profile, we cannot be certain of which phase (perhaps both, at different vertical locations) the HMX is in at the time of ignition.

Typical data from an ambient temperature are shown in Figure 3. Burn wires generally report evenly and in order. Pressure generally increases in a smooth fashion, although the pressure increase occasionally accelerates through one pellet for reasons that we have been unable to elucidate (perhaps pellet uniformity, although we have seen no correlation of pellet density with occurrence of acceleration). Typical data from an elevated temperature run are shown in Figure 4. Burn wires sometimes report irregularly (out of order, very close together, or not at all) and the pressure increases in an irregular fashion.

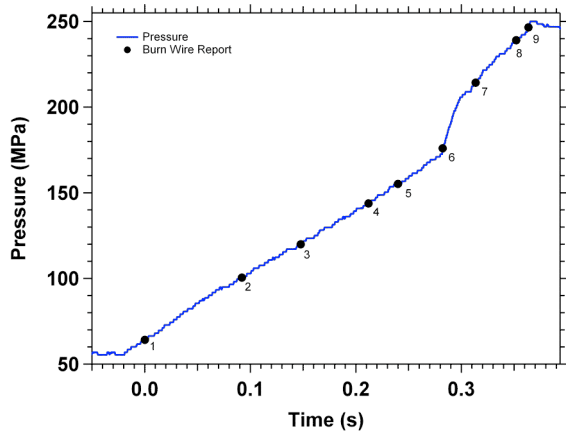


FIGURE 3. PBX-9501 temporal pressure history and burn front time-of-arrival for an ambient temperature run.

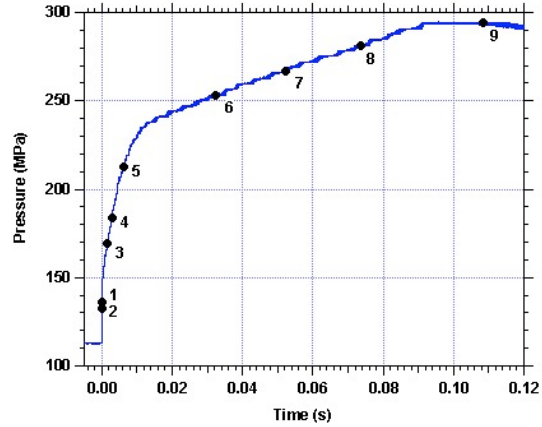


FIGURE 4. PBX-9501 temporal pressure history and burn front time-of-arrival for an elevated temperature run (BBX02084).

The experimental conditions and observations for each experiment are shown in Table 1, and in Figure 5 the deflagration rates are displayed in comparison with data for ambient-temperature PBX 9501 and with the measured deflagration rate of ambient-temperature LX-04.⁵ We use LX-04 as a reference as it burns uniformly at ambient temperature at all pressures, unlike PBX 9501.

Table 1. Experimental conditions and observations for deflagration measurements with PBX 9501. In all cases the sample was held at the maximum temperature before ignition, either for 22 hours or until self-ignition. The approximate deflagration time was determined as the duration of increasing pressure during the experiment. The final column indicates the deflagration rate normalized to ambient temperature deflagration at similar pressures, using the deflagration duration as a measure of rate.

Run #	Maximum bomb temp, °C	Soak pressure, MPa	Deflag. pressure, MPa	Self-ignition / ignition time	Approx deflagr. duration, seconds	Acceleratory / deceleratory deflagration	Approx. rate normalized to LX-04
BBX02074	155	0.1	130	No	0.004	Decel	70
BBX02081	155	0.1	130	No	0.004	Decel	70
BBX02082	155	0.1	130	No	0.004	Decel	70
BBX02084	155	120	120	Yes, 4 hrs	0.11	Decel	3
BBX02080	155	130	130	No	0.003	Decel	90
BBX02083	155	110	110	No	0.008	Accel	40
BBX02079	160	110	110	Yes, 21 hrs	0.006	Decel	60
BBX02078	165	110	110	Yes, 12 hrs	0.007	Decel	50
BBX02077	170	110	110	Yes, 6 hrs	No data	-	-
BBX02076	175	130	130	Yes, 3 hrs	0.008	Accel	40
BBX02075	180	110	110	Yes, 2 hrs	0.10	Decel	3

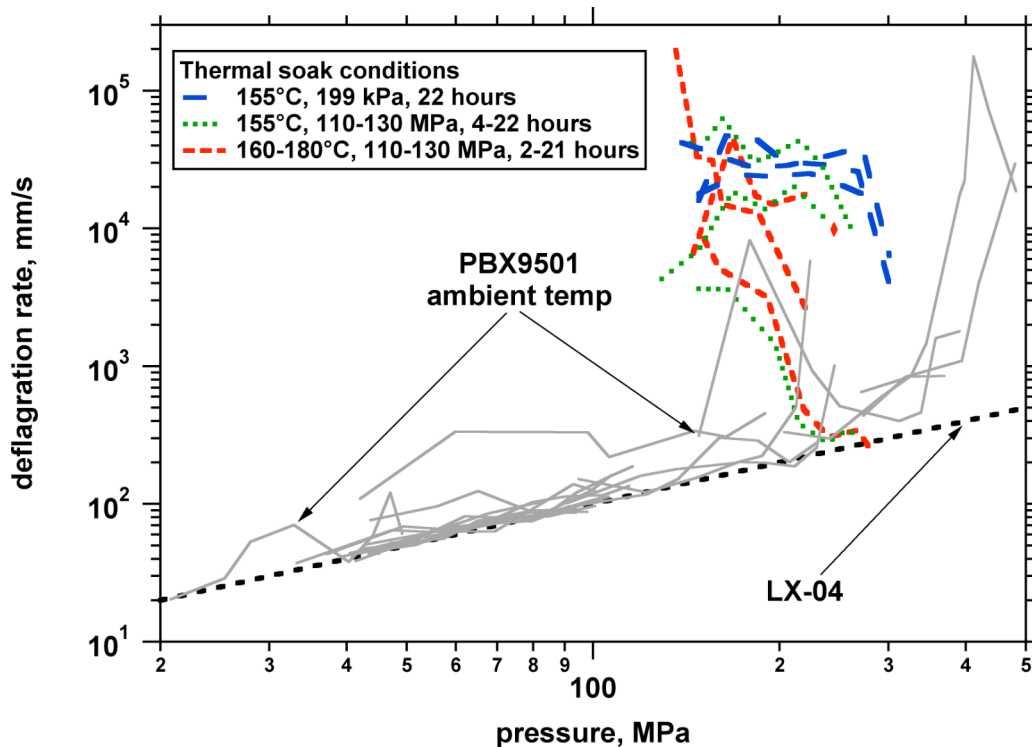


FIGURE 5. PBX 9501 deflagration data at high temperature under different thermal soak conditions. Thin gray lines show PBX 9501 data at ambient temperature, and the black dashed line represents the published fit to the LX-04.⁵

From the data in Table 1 and Figure 5 we draw several observations:

1. With PBX 9501, one sample out of the six heated to 155°C self ignited before the end of the 22-hour thermal soak, and all samples (5 total) heated above 155°C self ignited. In contrast, none of the LX-04 samples tested under the same conditions (same internal heater and temperature sensor configuration) up to 180°C showed self ignition.⁴ The self-ignition was driven by the highest temperature region of each sample, which was perhaps 15°C higher than the bomb temperature shown in Table 1. Inasmuch as the temperature profiles would be expected to have been similar for the PBX 9501 and LX-04 samples, the self-ignition in PBX 9501 reflects an increased thermal sensitivity of this material. This increased sensitivity is driven by the presence of the energetic nitroplasticizer BNDPA/F as well as a greater thermal sensitivity of Estane in PBX 5910 compared with the Viton A binder in LX-04.
2. Both PBX 9501 and LX-04 show initial high deflagration rates following thermal damage. However, their behaviors are rather different. As shown in Table 1, PBX 9501 shows somewhat inconsistent increases in deflagration rates, with increases of 40-to-90 fold at 155-180°C. The highest increase was at the lowest temperature, and furthermore two samples showed an increase of only 3-fold. In contrast, LX-04 was more consistent, with an increase in burn rate of 3-fold with thermal damage at 155°C, 10-fold with thermal damage at 180°C under high pressure to retard the phase change, and 40-fold with thermal damage at 180°C under low pressure where the phase change was allowed.⁴ The behavior of PBX 9501 was at the same time less consistent and more extreme. The differences between PBX 9501 and LX-04 are the binder composition and particle size distribution. In previous work we have shown that the presence of larger particles alone does not significantly change deflagration behavior,⁷ so we attribute the different

behaviors to the different binder and its lower overall fraction of the material. In particular, as noted above the nitroplasticizer in the binder is rather thermally sensitive, and the degradation and decomposition of the binder may be causing the inconsistent deflagration behavior.

3. As noted in Table 1 and Figure 5, the deflagration of almost all the PBX 9501 samples slowed as the deflagration propagated along the sample and the pressure increased. In some cases the deflagration rate approached the ambient temperature rate. One conjecture is that the temperature gradient in the sample resulted in the lower portion being less-severely degraded and not converted to the delta phase for high-temperature runs. However, the temperature gradient was similar for hot LX-04 samples and this behavior was not observed with that material. The presence of the nitroplasticizer may cause this deceleration, perhaps by catalyzing reversion of delta-phase HMX to beta phase, or perhaps by flowing into voids opened up by thermal damage and preventing the flame front from passing rapidly through. Also, thermal damage to the Estane binder may lead to partial decomposition and production of mobile species that fill the voids. These hypotheses are highly conjectural, but something is causing the PBX 9501 to "heal" as the deflagration progresses along the length of the sample.

CONCLUSION

While our results are complex and open to interpretation, we can make several observations from our data:

- PBX9501 deflagration at high temperature and pressure is relatively extreme and inconsistent when compared with LX-04; this is consistent with its behavior at ambient temperature.
- The presence of nitroplasticizer makes PBX 9501 more thermally sensitive and prone to self ignition than LX-04 with an inert binder.
- Something in the PBX 9501 causes it to "heal" and decelerate in deflagration rate as the pressure increases. The presence of the thermal gradient complicates this conclusion, as the deflagration is progressing to successively cooler material. While the initial deflagration rate is very high, the final rate is considerably lower in these samples.

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