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THE ROLE AND IMPORTANCE OF POROSITY IN THE DEFLAGRATION RATES OF HMX-BASED

MATERIALS

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ABSTRACT

The deflagration behavior of thermally damaged HMX-based materials will be discussed. Strands of material were burned at pressures ranging from 10 – 300 MPa using the LLNL high pressure strand burner. Strands were heated in-situ and burned while still hot; temperatures range from 90 – 200 °C and were chosen in order to allow for thermal damage of the material without significant decomposition of the HMX. The results indicate that multiple variables affect the burn rate but the most important are the polymorph of HMX and the nature and thermal stability of the non-HE portion of the material. Characterization of the strands indicate that the thermal soak produces significant porosity and permeability in the sample allowing for significantly faster burning due to the increased surface area and new pathways for flame spread into the material. Specifically, the deflagration rates of heated PBX-N-9, LX-10, and PBX-9501 will be discussed and compared.

INTRODUCTION

The deflagration rates of energetic materials are important to the performance and safety of the material, especially in cook-off scenarios. Material deflagration is one of the key stages in thermal explosions and knowledge of the burn rate as a function of pressure is particularly important in understanding and predicting the material response after it has ignited. Energetic materials containing HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) have been well characterized and, in many situations, these materials can be used as a model for other energetic materials.

The deflagration rates of HMX-based materials have been reported previously at a wide range of conditions.¹⁻⁴ High pressure studies by Maienschein et al. focused on materials that were packed to near their theoretical maximum density (TMD). In many scenarios, a material density may be significantly lower than TMD; for example heating, pressure cycling, or impacting an explosive may introduce porosity and lower the density of the material. Understanding the deflagration behavior of these low-density, high-porosity samples is important in safety planning and predictive modeling.

Maienschein et al. did a series of hot burns in which the HMX-formulation was heated prior to burn initiation. There are four known polymorphs of HMX, the most stable at room temperature is the β -polymorph. At 159 °C, the β -polymorph changes to the δ -polymorph,⁵ although this transition temperature changes with pressure.^{6,7} δ -HMX is approximately 7% larger in volume than β -HMX, however, when the material is formulated with a binder and pressed to a high density the transition from β to δ can result in volume changes of approximately 15% due to inefficient packing of the larger δ -polymorph crystals.⁸ Consequently a pressed part that has been heated beyond the polymorph transition will have considerably higher porosity than the original part. In Maienschein et al.'s study, LX-04 (85 wt% HMX, 15 wt% Viton A) was heated and pressurized to variety of different conditions. In general, experiments where the material remained in the β -polymorph showed little or no increase in burn rate. In contrast, burns where the HMX was allowed to phase convert to the δ -polymorph resulted in burns that were nearly 40

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times faster than the β -polymorph experiments. Since two variables changed simultaneously, i.e. the HMX polymorph and the sample porosity, it is impossible to say which variable accelerates the burn rate.

In this work, we measured the burn rates of HMX formulated with different binder types and prepared at different densities. The explosive PBXN-9 contains 92.8 wt% HMX, 5.3 % plasticizer, and 1.9 % polyacrylate elastomer binder (HYTEMP 4454). This explosive formulation serves as a model system for studying varying degrees of porosity as thermal exposure drives off the plasticizer leaving a lower density HMX/binder formulation. The explosive LX-10 contains 95 wt% HMX and 5 wt% Viton A and serves as a model system as it has a stiff and inert binder that changes little with temperature. Finally, PBX-9501 contains 95 wt% HMX, 2.5 wt% BDNPA/F, and 2.5 wt% Estane. Like PBXN-9, the plasticizer in PBX-9501 is more reactive than HMX and begins to decompose and flow out of the sample prior to HMX decomposition. In contrast, the plasticizer in PBX-9501 is a nitro-plasticizer and, therefore, considerably more energetic than the plasticizer used in PBXN-9. Hence the PBX-9501 provides insight into the influence of a reactive plasticizer coupled with sample porosity.

EXPERIMENTS AND CALCULATIONS

LLNL HIGH PRESSURE STRAND BURNER

Deflagration rates are measured using the LLNL high pressure strand burner, shown in Figure 1. This experimental technique is described in detail in the literature.^{2,9} Briefly, burns are performed under constant volume in an atmosphere of argon. The pressure is measured in-situ throughout the burn and burn progress is monitored via silver break wires that are embedded within the sample. A typical sample consists of nine individual pellets (0.25 in diameter by 0.25 in tall) and 10 burn wires, the exterior surface is encapsulated by an organic-polymeric material to prevent flame spread down the sides. The sample is prepressurized to a desired pressure using Argon, the burn is initiated via an igniter train (igniter wire, BKNO₃ and a thin HNS pellet), and the sample burns resulting in a rise in pressure on the order of 3-5 times the initial pressure. Many towers may be burnt in order to investigate a pressure range of 10-600 MPa.

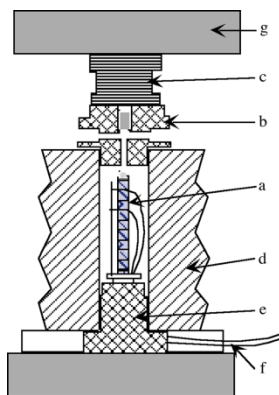


Figure 1. Strand burner schematic composed of a) nine segment burn sample with burn wires evenly spaced between segments (only two wires shown for clarity) and igniter on top, b) top plug with inlet and outlet ports and pressure transducer in center, c) load cell, d) pressure vessel, e) bottom plug with wire feed-throughs, f) signal wires to electronics, g) load frame (top and bottom).

Typical pressure and flame front time-of-arrival data are shown in Figure 2. These results represent a well behaved burn because the wires are burned in order and the pressure rise stops after the last burn wire. The burn wire data should cover the time span of the pressure signal. Any significant deviation from this indicates anomalous behavior. For example, the report of all burn wires before the pressure reaches a maximum indicates that the deflagration front passes rapidly down the sample and leaves still-reacting material behind. This behavior is indicative of flame spread through the sample or of

propagation of the flame down the side of the sample; although a coating of Halthane 88-2 should inhibit the latter.

To calculate deflagration rate as a function of pressure, the length and time-of-arrival for each pair of pellets is used, and the corresponding average pressure for this segment of the sample is calculated. The temporal pressure data can be used to calculate vivacity and surface area.¹⁰⁻¹²

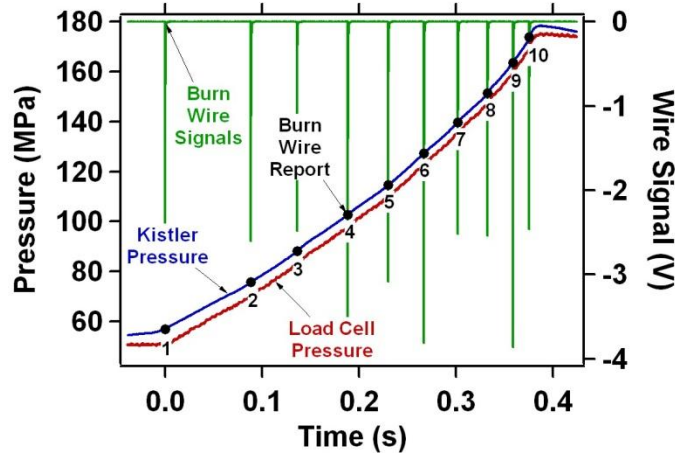


Figure 2. Typical strand burner data, showing temporal pressure behavior and flame-front time-of-arrival signals resulting from the burn wires.

CALCULATIONS

The pressure dependent deflagration rate is fit to the Vieille equation:

$$B = aP^n \quad (1)$$

where B is the burn rate (mm/s), a is the burn rate coefficient (mm/s·MPaⁿ), P is the pressure (MPa) and n is the pressure exponent (dimensionless).

MATERIALS

PBXN-9 was used as received, in powder/prill form, from BAE systems (Lot number BAE06F08-064). The formulation, based on the certificate of analysis for this specific lot number, is listed in table 1; the dioctyl adipate is a non-energetic plasticizer and Hytemp 4454 is a polyacrylate elastomer binder. LX-10 (LLNL lot number B-253) was pressed to two different densities in order to meet our experimental needs; formulation and pressing details for LX-10 are listed in Table 1. PBX-9501 (LLNL lot number C-214) pressing and formulation details are listed in Table 1.

Table 1. Formulation and pressing details for samples used in this study.

Material	Formulation	Pressing Conditions	Density (g/cm ³)	%TMD
PBXN-9	92.8 wt% HMX 5.3 wt% dioctyl adipate (DOA) 1.9 wt% Hytemp 4454	Uniaxially pressed at LLNL 138 MPa, 3 minute dwell	1.744	98
LX-10	95 wt% HMX 5 wt% Viton A	Uniaxially pressed at LLNL 207 MPa and 105 °C; 5 minute dwell. Shims used when pressing to 92% TMD	1.860 1.749	98 92
PBX-9501	95 wt% HMX 2.5 wt% Estane 2.5 wt% BDNPA/F	Uniaxially pressed at LLNL 207 MPa and 85 °C; three 3-minute dwells	1.832	98.8

RESULTS AND DISCUSSION

PBXN-9 MEASUREMENTS

Elevated temperature burns of PBXN-9 were performed in order to study the practical impact(s) of thermal insult on the material. In all these experiments, the PBXN-9 strand was assembled and inserted into the pressure vessel. The vessel was purged with Argon, sealed at near ambient pressure, and heated. In all the experiments, the sample was ramped to a desired temperature (184 °C, 150 °C, 110 °C or 90 °C) at ca. 1.7 °C/min and held for 2 hours. The vessel was then pressurized to ca. 13 MPa and the sample was ignited. The order of heating before pressurization is important because pressure can inhibit many of the processes of interest (e.g. β - δ polymorph transition in HMX, evaporation of DOA, etc).

Results of these elevated temperature experiments are shown in Figure 3 and summarized in Table 2. At 90 °C, the sample shows little-to-no change in the burn rate compared with the ambient temperature burns. At 110 °C there is only a slight if any acceleration of the burn rates. These low temperature burn results are not surprising. Maienschein et al. demonstrated that LX-04 could be heated up to ca. 150 °C without significant changes in the burn rate.² One might expect the temperature to accelerate the burn by lowering the amount of energy needed to decompose the sample. In fact, previous studies at milder pressures have shown that temperature can change the burn rate of HMX, however, as the pressure rises, the temperature effects decrease.¹ At the pressures relevant to this study, temperature alone is not expected to change the burn rate significantly; most likely the burn rate error bars due to random errors are larger than the changes expected due to the thermochemistry.

At 150 °C the PBXN-9 sample appears to burn approximately 21 times faster than the ambient temperature burns; and with remarkable reproducibility (two strands were burned at this temperature and are reported in Figure 3). This result is surprising in light of Maienschein et al.'s results in which LX-04 at 150 °C burns only 1-3 times faster than ambient temperature results. An explanation for these accelerated burn rates will be discussed below.

At 184 °C, PBXN-9 burns extremely fast, and the reproducibility of these burns is impressive (two strands were burned). These highest temperature burns are approximately a factor of 100 faster than the ambient temperature burns. This is faster than the acceleration factor observed previously on LX-04 heated to 180 °C and soaked for 18-22 hrs. However, due to changes in heating mechanism, these published LX-04 burns may be rather conservative; recent measurements of LX-04 at 180 °C appear to burn at rates similar to those observed for PBXN-9 at 184 °C. Presumably, the HMX is able to undergo its polymorph transition from β – δ in the 2 hour soak used for the PBXN-9 experiments.

Also included in Figure 3 are the ambient temperature experiments on LX-10. These results were first published by Maienschein et al.²; the rapid and erratic burn rates at $P > 150$ MPa is attributed to a mechanism termed “deconsolidative burning”. At these pressures, Maienschein et al.² proposed that the LX-10 begins to deconsolidate or break apart producing cracks and pores that expose new and unburnt material. The flame can rapidly penetrate into these newly exposed areas via convective burning resulting in a rapid and erratic burn. One can see how the PBXN-9 burn rates at 184 °C are similar to the maximum burn rates for LX-10 during deconsolidative burning.

Recently, we reported on the kinetics, mechanisms, and morphological changes in PBXN-9 after various thermal insults.¹³ The most important observation from these experiments was the fact that the plasticizer evaporates or decomposes at relatively low temperatures. Using the kinetic parameters from our recent study, we calculated the percent decomposition using the thermal profiles from each experiment. In the 150 and 184 °C experiments we calculated 5% weight loss, this is most likely loss of the plasticizer, which was initially present at 5.3% in the PBXN-9 formulations. It is logical that both 150 °C and 184 °C have the same amount of weight loss because the barriers to subsequent reactions, e.g. HMX and binder decomposition, are significantly higher and inaccessible at these relatively mild temperatures. At 110 °C we calculate, based on the decomposition kinetics reported,¹³ that the sample should lose 0.8% of its weight. Finally, at 90 °C, we calculate the sample to only lose 0.014%. Loss of the plasticizer in the strand will introduce porosity in the strand. In addition, above ca. 167 °C, the HMX will undergo the β - δ transition which lowers the density and introduces additional porosity into the sample.

We recently measured and reported the gas permeability of PBXN-9 at 150 and 180 °C after 75 min thermal soak and correlated the permeability with sample porosity.¹³ At 150 °C, the sample is approximately 93.8 % of the theoretical maximum density (TMD) and at 180 °C, it was 89.4% of TMD.¹³ All of these results are summarized in Table 2; they indicate a correlation between burn rate and sample density/porosity.

The most logical explanation for these heated burns is that various mechanisms are able to introduce different degrees of porosity in the strand and porosity is the main variable responsible for accelerating the sample burn. This hypothesis was put forth previously by Maienschein et al. but their study was unable to eliminate the possibility that the polymorph of HMX played a roll. In our study, at 150 °C, the HMX remains in β -form yet the sample burns significantly faster. Apparently, 5% weight loss of the plasticizer produces enough porosity to accelerate the strand burn rate significantly. At 184 °C, the HMX undergoes the β - δ transition, which introduces more porosity in the sample and consequently, the burn rates are 5 times faster than the 150 °C experiments.

PBXN-9 at 184 °C is not nearly as erratic as the LX-10 burns at elevated pressures. At this elevated temperature, one would expect the porosity of PBXN-9 to be relatively homogeneous throughout the tower, since the two mechanisms of porosity (DOA loss and polymorph transition) are equally prevalent along the full length of the tower. Hence, the mechanism of burning PBXN-9 at 184 °C is probably quite convective. In contrast, the LX-10 deconsolidative burning most likely involves more of a dynamic cracking where the material maintains its high density in regions but experiences sever cracking along the tower. Further work is underway to understand and measure these mechanisms of deconsolidative and convective burning.

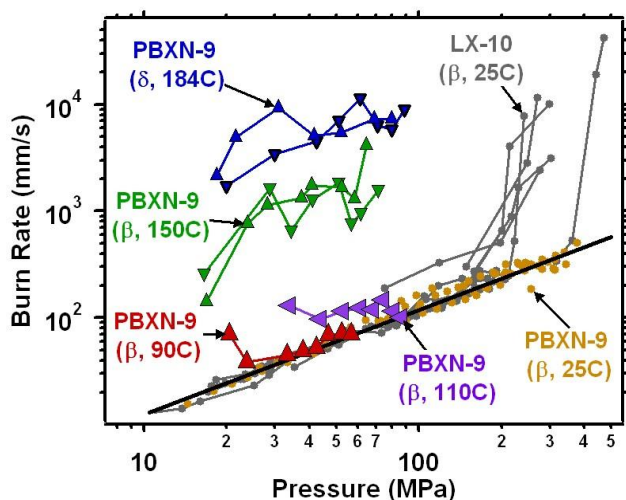


Figure 3. Pressure dependent deflagration rates for PBXN-9. Refer to Table 2 for quantitative analysis.

Table 2. Summary of strand conditions at each temperature

Material	Temp (°C)	% wt loss ^a	% TMD ^b	HMX polymorph ^c	Burn acceleration factor	a	n
PBXN-9	25	0	98	β	1	1.3	0.98
PBXN-9	90	0.014	Not measured	β	1	3	0.8
PBXN-9	110	0.8	Not measured	β	1.5	59	0.2
PBXN-9	150	5	93.8	β	21	9	1.3
PBXN-9	184	5	89.4	δ	100	340	0.7
LX-10	25	0	92	β	ca. 85	2	2.3
LX-10	180	unknown	unknown	δ	ca. 85	2	2.0

^acalculated based on chemical kinetics from ref¹³

^breported in ref¹³

°inferred based on sample temperature and the known transition temperature

LX-10 MEASUREMENTS

In order to test our hypothesis that porosity is the main driving force in accelerating the burn rates of HMX-formulations, LX-10 strands (95% HMX, 5% Viton-A) were pressed to a lower density and burned. Figure 4 shows the results of LX-10 burns in which the sample was pressed to 92% TMD (blue squares). The strands all burned rapidly and erratically. LX-10 strands were also pressed to 98% TMD, heated to 180 °C and burned hot. The density of these heated strands is unknown but expected to be large because HMX has undergone the β - δ transition. These strands also burned rapidly and erratically. In general the 92% TMD and 180 °C data both show a burn acceleration factor of ca. 85. These LX-10 burn rates vary quite a bit but in general they overlap well with the 184 °C PBXN-9 data. Collectively, the PBXN-9 and LX-10 data demonstrate that porosity plays a major role in dictating the burn rate of HMX-based explosives.

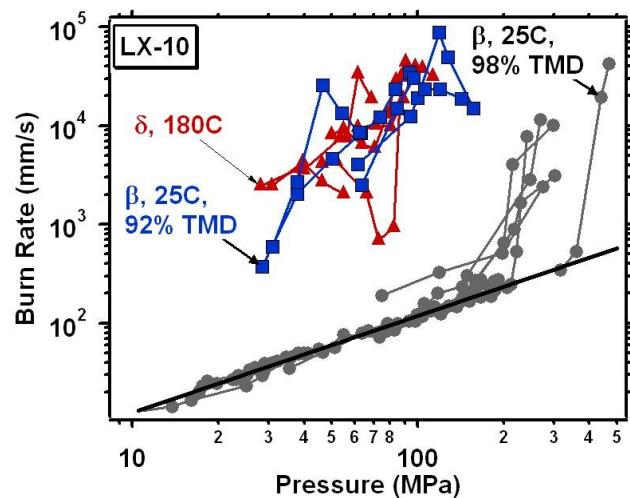


Figure 4. Pressure dependent deflagration rates for LX-10 under different conditions. Refer to Table 2 for quantitative results.

PBX-9501 MEASUREMENTS

The temperature dependent burn rates of PBX-9501 show the most unexpected results of all the HMX-based formulations studied. Figure 5 shows the results of PBX-9501 at 150 °C and 173 °C. Two strands were burned at 173 °C; both demonstrate extremely rapid deflagration rates, nearly an order of magnitude faster than PBXN-9 at 184 °C. This acceleration is most likely due to the porosity introduced via the β - δ transition and the chemical kinetics of the binder and/or plasticizer. Two strands were burned at 150 °C and both strands showed initial deflagration similar to an ambient temperature burn, but then suddenly the burn accelerated. The BDNPA/F plasticizer in PBX-9501 has a boiling point of 150 °C and there is likely to be some porosity introduced from the loss of plasticizer.¹⁴

Figures 6 and 7 show the pressure curve and break wires as a function of time for one of the 150 °C strands and one of the 173 °C strands; a second experiment at each temperature looked very similar to the results shown in Figures 6 and 7. It is interesting to compare the two pressure curves at these two temperatures. At 173 °C the pressure rises smoothly but steadily over the course of the burn. In contrast, at 150 °C the pressure rise is slow and steady and then suddenly spikes. The pressure spike could indicate that at 150 °C, PBX-9501 transitions from mostly laminar to deconsolidative burning. The pressure curve for a high pressure, ambient temperature burn is shown in Figure 8. At elevated pressures, PBX-9501 burns rapidly and erratically and the mechanism is proposed to be deconsolidative burning.² One can see the similarities between the pressure curves at 150 °C and the high pressure data. Although the timescales are quite different, because of the difference in pressure, both experiments show

an initially slow burn followed by a sudden pressure spike. We have not eliminated the possibility that these elevated temperature burns appear rapid and erratic due to an experimental artifact of the nitroplasticizer damaging the halthane encapsulation that is coated over the external surface of the tower to prevent flame flashing down the side. Further work is necessary to fully understand the mechanisms and kinetics of PBX-9501 deflagration at elevated temperature.

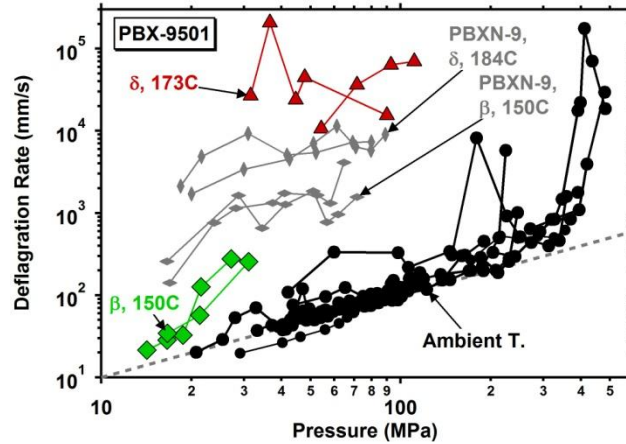


Figure 5. Pressure and temperature dependent deflagration rates for PBX-9501.

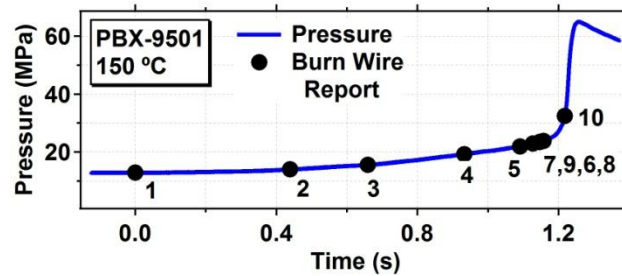


Figure 6. Pressure curve and burn wire break wires as a function of time for one of the strands of PBX-9501 at 150 °C.

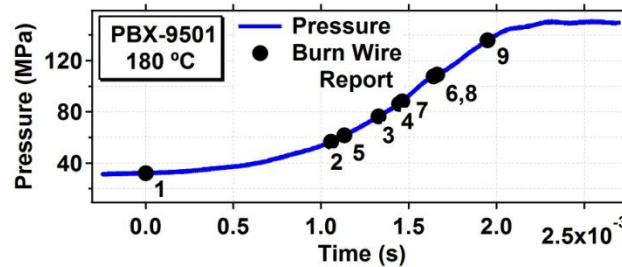


Figure 7. Pressure curve and burn wire break wires as a function of time for one of the strands of PBX-9501 at 180 °C.

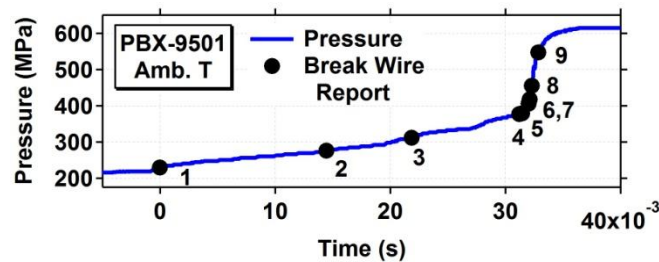


Figure 8. Pressure curve and burn wire break wires as a function of time for one of the highest pressure strands of PBX-9501 at 25 °C.

SUMMARY AND CONCLUSIONS

In summary, the main variable affecting the burn rates of HMX-based explosives is the degree of porosity in the sample. By heating PBXN-9 to different temperatures, different levels of porosity were achieved. At temperatures less than 167 °C the HMX remains in the β -polymorph and the porosity is mostly attributed to loss of the dioctyl adipate (DOA) plasticizer. Deflagration rates of PBXN-9 at 110 °C and 150 °C both show burn rates that are significantly faster than ambient temperature. Similar experiments using LX-04 at 150 °C indicate that the material burns at a rate identical to the ambient temperature burns. In experiments at 184 °C the HMX burn significantly faster than those at 150 °C due to the combined effects of DOA loss and the porosity introduced via the β - δ polymorph transforms.

In order to further support our hypothesis, samples of LX-10 were pressed to 92% of their theoretical maximum density (TMD), rather than the typical 98% TMD, and burned. The 92% TMD samples burned significantly faster than the 98%TMD samples. LX-10 samples that were pressed to 98% TMD and heated to 180 °C also burned significantly faster, at rates that overlapped with the 92% TMD samples. These results demonstrate the importance of porosity rather than the polymorph in determining the deflagration rate of HMX-based materials.

PBX-9501 samples burned a little differently than expected. When heated to 173 °C, the samples burned nearly 10 times faster than the PBXN-9 or LX-10 samples at similar temperatures. The weight percent of HMX in each of these formulations is similar and the particle size distribution in LX-10 and PBX-9501 are similar; hence the difference in burn rate must be due to the nature of the plasticizer and binder. The BDNPA/F used in PBX-9501 is an energetic plasticizer and although we expect some loss of material at these temperatures (boiling point is 150 °C)¹⁴ there must be some residual plasticizer or energetic byproducts of the plasticizer that are able to assist in the chemistry and deflagration of the HMX crystals. Further work is underway to understand the mechanisms underlying these heated PBX-9501 strand burner experiments.

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