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P. C. Hsu, G. Hust, M. Dehaven, S. Chidester, L.
Glascoe, M. Hoffman, J. L. Maienschein

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MEASUREMENT OF MATERIAL PROPERTIES OF DAMAGED ENERGETIC MATERIALS

Peter C. Hsu, Gary Hust, Martin Dehaven, Steven Chidester, Libby Glascoe, Mark Hoffman, and Jon L. Maienschein

Lawrence Livermore National Laboratory
Livermore, CA 94550

We recently conducted damaged experiments on three explosives (mechanical damage on LX-04 and thermal experiments on HPP and PBXN-9) and characterized the effect of damage on some material properties. The MTS equipment was used to apply compressive cycling to LX-04 pressed parts and the results showed that older LX-04 parts became mechanically weaker than newer parts. After repeated compressive cycling for over 20,000 times, older LX-04 parts failed but newer LX-04 parts survived. Thermal insults were applied to PBXN-9 and HPP at 180 °C and 200 °C, respectively in unconfined conditions for several hours. The thermally-damaged HPP sample suffered 12.0% weight losses and a volume expansion of 20% was observed. Porosity of the damaged HPP increased to 25% after thermal exposure, which led to higher gas permeability. Burn rates of damaged PBXN-9 were 2 orders of magnitude higher than those of pristine samples but burn rates of damaged HPP were only slightly higher than those of pristine HPP. Small-scale safety tests (impact, friction, and spark) showed no significant sensitization when the damaged samples were tested at room temperature. Gas permeation measurements showed that gas permeability in damaged materials was several orders of magnitude higher than that in pristine materials. In-situ measurements of gas permeability at high temperatures were made on HPP samples and the results showed that the gas permeability increased by 3 to 4 orders of magnitude.

INTRODUCTION

Explosive charges in either confined (weaponry, munitions) or unconfined (pressed parts, shape charges, or powders stored in warehouses, magazines, bunkers, ships) environments may suffer unexpected insults, which may cause undesirable reactions. Examples of insults are fires, earthquakes, problems associated with operational handling, transportation, sudden climate change, and combat operations in battlefields. Safety/sensitivity data for the damaged materials need to be established if the materials are destined for dismantling and demilitarization. If stakeholders decide to reuse the damaged explosive charges, a comprehensive characterization of the materials would be desirable. The characterization methods may include measurements of following material properties: shock sensitivity, detonation velocity, detonation energy density, density, porosity, burn rate, gas permeability, and mechanical strength (moduli). Thermally damaged LX-04 was more shock sensitive than pristine LX-04 as reported by Urtiew et. al.¹. Hsu et. al. recently reported that damaged LX-04 and damaged

LX-17 had lower detonation velocities and lower detonation energy densities than pristine samples^{2,3}. Damaged materials expanded, became porous, and resulting in greater gas permeability and burn rate. Extensive measurements of gas permeabilities in damaged PBX 9501 were reported by Asay et. al.^{4,5}. We also found that gas permeability and burn rates in damaged material LX-10 increased several orders of magnitude^{6,7}.

LX-04 and PBXN-9 are HMX-based plastic-bonded explosives. HPP propellant is an ammonium perchlorate and aluminum based propellant. In this paper, we will describe our approach in conducting damage experiments and report our recent experimental results on LX-04, PBXN-9, and HPP.

MECHANICAL DAMAGE AND CHARACTERIZATION OF LX-04

Mechanically damaged LX-04 or aged LX-04 may exhibit different safety and sensitivity. We recently applied compressive damage on LX-04 pressed

parts and evaluated the effect of the damage on mechanical strength. Several LX-04 parts, 2" in diameter and 1" in height, 100 g each, were used for the evaluation. A MTS equipment, as shown in Figure 1, was used to apply compressive cycling on pressed HE parts to simulate conditions under material aging or mechanical insults.

The results showed that both aged LX-04 part (11-year old) and new LX-04 part (1-month old) survived a compressive cycling at 600 psi for 10,000 cycles. The older part failed at the stress of 600 psi after 20,000 cycles but the newer part survived, as showed in Figure 2. The aged part was weaker mechanically than the newer LX-04 part. Figure 3 shows the SN curve (fatigue chart) for LX-04 pressed parts. Attempts to apply stress loading at 1200 psi broke the parts but the newer part was able to sustain 10 cycles at 1000 psi. The mechanically damaged LX-04 sample was evaluated for small-scale safety. No increase in impact sensitivity, friction sensitivity, and spark sensitivity was observed.



FIGURE 1. MTS equipment for compressive cycling experiment



FIGURE 2. The 11-year old LX-04 part broke at the stress loading of 600 psi for 20,000 cycles; top (before), bottom (after)

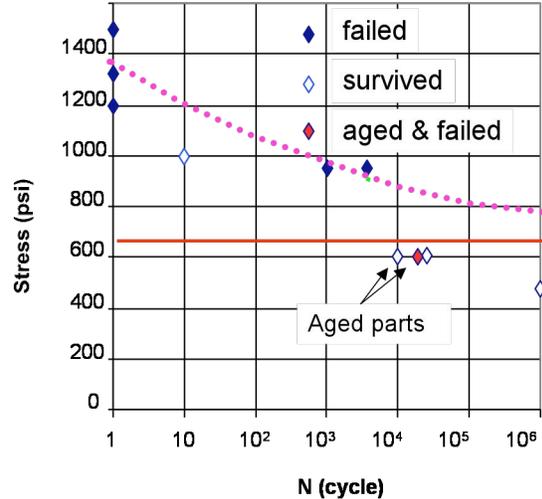


FIGURE 3. SN curve (fatigue testing) for LX-04 pressed parts; blue for newer parts and red for aged part

THERMAL DAMAGE EXPERIMENTS

Thermal damage experiments were conducted remotely in a shot tank. The process conditions were estimated from the ODTX (one dimensional time to

explosion) data. The ODTX system at the Lawrence Livermore National Laboratory can precisely measure times to explosion and minimum ignition temperatures of energetic materials⁸. These measurements provide insight into the relative ease of thermal ignition and allow for the determination of kinetic parameters (7). Table 1 lists times to explosion data for several explosives and process conditions for thermal experiments. A safety factor of 3 was used for all thermal damage experiments to avoid any unwanted explosion. Most specimens were not confined which allowed for expansion during the thermal experiment without restraint to simulate fire incidents of explosive charges stored in unconfined environments. They were subsequently characterized for small-scale safety, volume, density, and gas permeability at ambient condition. Some samples were potted to stainless steel holders in a radially-confined condition for gas permeability measurements.

TABLE 1. ODTX data vs. thermal damage process conditions

Samples	ODTX, hours	Process conditions
LX-04	@< 183 C, >20 hours	
	@ 183 C, 20 hours	
	@192 C, 6.6 hours	140 C, 22 hours, 190 C, 2 hours
LX-10	@200 C, 1.1 hours	
	@190 C, 6.1 hours	
	@181 C, > 28 hours	180 C, 4 hours
LX-17	@ 259 C, 2.9 hours	
	@250 C, 7.2 hours	
	@ 240 C, > 28 hours	190 C, 4 hours, 250 C, 2 hours
PBXN-9	@192 C, 1.6 hours	
	@181 C, 7.0 hours	180 C, 3 hours
	@171 C, 15.4 hours	
HPP	@166 C, >138 hours	
	@233 C, 2. hours	
	@227 C, 3.4 hours	
	@209 C, > 24 hours	200 C, 6 hours

CHARACTERIZATION OF THERMALLY DAMAGED HPP PROPELLANT

Measurements of Density, Volume, Porosity, and Small-scale Safety Tests

Small-scale testing (drop hammer, spark, and friction) was performed on damaged HPP samples, which were heated to 200°C for 6 hours and cooled to room temperature. The results are shown in Table 2 along with dimensional measurements. HPP samples suffered 12.0% weight losses after thermal exposure at 200 °C, this is very different from what were observed for other thermally-damaged energetic materials^{2,3,6,7}. This might be attributed to the evaporation and decomposition of the binder, the plasticizer, and other ingredients in the material at high temperature. Samples expanded significantly and cracks were formed (Figure 4), which resulted in higher porosity and gas permeability.

The HPP specimens were characterized with a pycnometer for volume, density and porosity. The density obtained from the gas pycnometer is often called true density because it is very close to the theoretical maximum density (TMD) of the material if fraction of closed pores in the sample is insignificant. This approach was described elsewhere⁶. Table 2 lists the density and porosity measured at ambient temperature. Total porosity increased by 27% due to the irreversible thermal expansion and the loss of ingredients. Most pores and voids were open pores, which would contribute to gas flow in the material and would lead to faster burn rates and higher gas permeability. Similar observations were made on other materials⁹.

Small-scale safety testing showed no apparent changes in impact, friction and spark sensitivities for the damaged HPP samples.

TABLE 2. Dimensional measurement and small-scale test results on heated and then cooled HPP samples

Test	Pristine	Damaged
Weight, g	4.575	4.018 (-12.2%)
Bulk volume (cm ³)	2.579	3.111 (+20.6)
Bulk density (g/cc)	1.774 (98.28% TMD)	1.292 (71.44% TMD)
True density (cm ³)	1.803 (99.73% TMD)	1.781 (98.52% TMD)
Total porosity, %	1.72	28.56
Fraction of open pores, %	1.45	27.08
Fraction of closed pores, %	0.27	1.48
Drop Hammer (cm)	30	53

Friction	1/10 @ 7.8 kg	1/10 @ 7.2 kg
Spark	0/10 @ 1.0 J	0/10 @ 1.0 J



FIGURE 4. Microscopic picture of a cylindrical pressed part (1" diameter); large cracks formed after the thermal exposure

Gas Permeability in Explosives

Most of the energy release of explosive decomposition occurs in the gas phase and thus it is essential to know how the hot gases permeate through the network of explosive particles. Since pressed parts are packed particles, the gas flow in explosives is highly dependent of density, particle size, and porosity, the Blake-Kozeny equation¹⁰ can be used to relate permeability, porosity and particle size, as shown below,

$$K = D_p^2 \epsilon^3 / [150(1-\epsilon)^2] \quad (1)$$

where K is permeability, D_p is a characteristic dimension of the particles or effective particle diameter, and ϵ is the void fraction of open voids in the sample, which allow gas to flow through freely. The fraction of open pores (voids) can be measured with the gas pycnometer if the bulk volume and the maximum theoretical density are known. By using Eq. (1), it is possible to estimate permeability for a given porosity; porosity for a given permeability; and particle size for a given porosity and permeability. The Blake-Kozeny equation has been used to correlate the gas flow in the mock LX-04 explosive fairly well⁷ as shown in Figure 5.

The application of the Blake-Kozeny equation to fit the gas permeation in various explosives was further validated with recent experimental data on several HMX-based explosives, as shown in Figure

6. It seems that reasonable agreement was observed between the model and the experimental data.

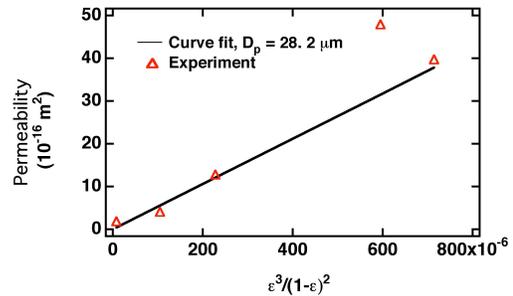


Figure 5. Permeability versus $\epsilon^3/(1-\epsilon)^2$ for mock LX-04

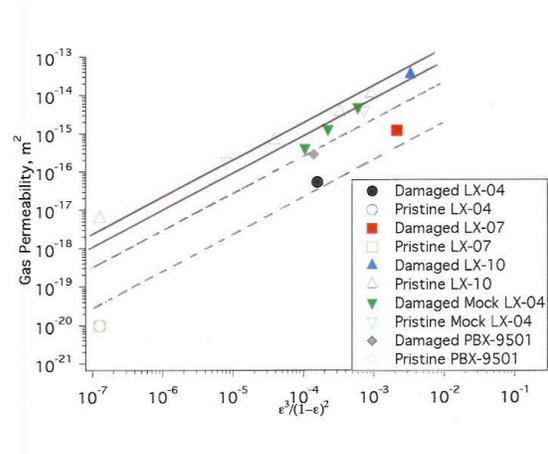


Figure 6. Permeability versus $\epsilon^3/(1-\epsilon)^2$ for several HMX-based formulations; top first line was for pristine LX-10; second line was for damaged mock LX-04; the dash lines show trends only

Gas Permeability Measurements on Pristine and Damaged HPP Samples

Gas permeability measurements were made on several pristine HPP samples and pre-damaged HPP samples (200 C for 6 hours) and the results are shown in Table 3. The unconfined parts, after the thermal exposure and cooled, were glued to sample holders for gas permeability measurement. Table 3 indicates that the pristine HPP samples were not gas permeable ($< 10^{-20} \text{ m}^2$), similar to what were observed for other high density pristine samples and other energetic materials^{6,9}. Table 3 also

shows the confinement during thermal insults affects gas permeability. The gas permeability in the confined sample was lower than that of the unconfined sample. The confinement may have somewhat restricted the sample from thermal expansion during thermal exposure. More study is needed before a more concrete conclusion can be made.

Table 3. Gas permeability in pristine and pre-damaged HPP samples measured at room temperature

Sample description	Gas permeability, m^2	Note
Pristine	$< 10^{-20}$	Below the detection limit
Pre-damaged HPP (unconfined)	7.8×10^{-16}	Unconfined during thermal insult
Pre-damaged HPP (radially confined)*	3.3×10^{-17}	Radially confined to a sample holder during thermal insult

*The pre-damaged sample was glued to a sample holder before the thermal experiment.

We also measured the gas permeability in-situ for HPP. Pristine part was potted to the holder, measured, followed by heating to a pre-determined temperature at a certain ramp rate, soaked, and measured. Figure 7 shows the results of the in-situ measurements. Before heating the sample, the permeability was below the machine detection limit ($10^{-20} m^2$). We then ramped it to 150 C at 1.2 C/min and soaked for 75 minutes, the permeability increased to $3.7 \times 10^{-16} m^2$, which was an indication of greater porosity as a result of thermal damage at this temperature. Further ramping to 180 C and soaking increased the permeability to $8.6 \times 10^{-16} m^2$. A calculation was made to estimate the weight losses during thermal exposure in the gas permeation system; the weight losses are shown in light blue.

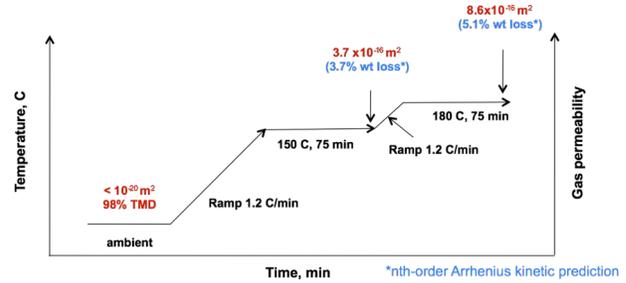


Figure 7. Permeability vs. temperature for HPP

Burn Rate Measurement for Thermally Damaged PBXN-9 and HPP

Burn rates were measured in the LLNL high-pressure strand burner. It was designed to handle burn rate measurements for pressures up to 1,000 MPa and temperatures up to 300 °C. The system was used for thermal damage on LX-10 in-situ followed by burn rate measurement at 150 °C, 180 °, and 190 °C, respectively and the results were reported elsewhere⁶. We recently made burn rate measurements on damaged PBXN-9 and damaged HPP. Burn rates were measured right after thermal damage experiments and results are shown in Figure 8 and Figure 9, respectively. Burn rates of damaged PBXN-9 were 2 to 3 orders of magnitude faster than those of pristine sample due to the effect of higher degree of damage and phase transition from beta to delta. Figure 9 shows that the burn rates of damaged HPP at 180 °C were only slightly faster than those of pristine HPP. There was no phase transition at this temperature.

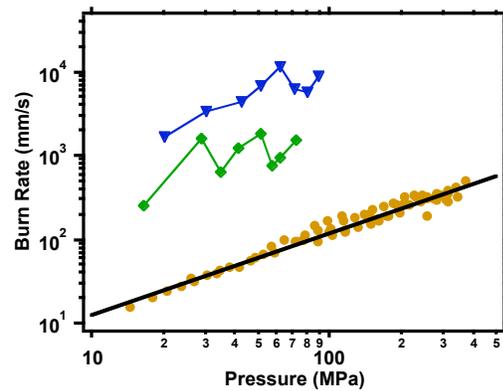


FIGURE 8. PBXN-9 burn rates; brown-pristine & burned at ambient temperature; green-damaged and burned at 150 C; blue- damaged and burned at 180 C

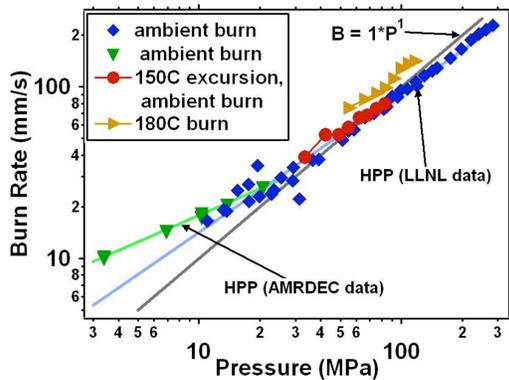


FIGURE 9. HPP burn rates at several temperatures; no significant increase was observed for damaged HPP

CONCLUSIONS

We recently conducted damage experiments on LX-04, PBXN-9 and HPP and characterized the effect of damage on mechanical strength, density, porosity, permeability and burn rate. Thermal treatment on HPP at 200 C resulted in a significant weight loss (12%). Volume expansion at high temperatures was significant and led to reduction in material density. Gas permeation measurement showed that gas permeability in some damaged samples was several orders of magnitude higher than that in pristine materials. The application of the Blake-Kozeny equation to fit the gas permeation data in various explosives was further validated with recent experimental data on several HMX-based explosives. It is possible to estimate the material open porosity with known permeability and particle diameter. It also appeared that aging played a role in mechanical strength of pressed explosives. After compressive cycling for over 20,000 times, older LX-04 parts failed but newer LX-04 parts survived. We also measured burn rates of thermally damaged PBXN-9 and HPP in a strand burner and found that burn rates of PBXN-9 were 2 to 3 orders of magnitude faster than those of pristine PBXN-9. Burn rates of damaged HPP were only slightly faster than those of pristine samples. In summary, we have found that damage changed some material properties significantly.

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