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Thermal Damage on LX-04 Mock Material and Gas Permeability Assessment

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Abstract

RM-04-BR, a mock material for the plastic-bonded HMX-based explosive LX-04, is characterized after being thermally damaged at 140 °C and 190 °C. We measured the following material properties before and after the thermal experiments: sample volume, density, sound speed, and gas permeability in the material. Thermal treatment of the mock material leads to de-coloring and insignificant weight loss. Sample expanded, resulting in density reductions of 1.0% to 2.5% at 140 °C and 190 °C, respectively. Permeability in the mock samples was found to increase from 10^{-15} to 10^{-16} m², as the porosity increased. The permeability measurements are well represented by the Blake-Kozeny equation for laminar flow through porous media. The results are similar to the gas permeability in PBX-9501 obtained by other researchers [1,2].

1. Introduction

Accidents caused by fire, handling and transportation, and combat operations in battlefields can expose energetic materials to unexpected heat and impact that may damage the explosive charge. Thermal damage may have a profound effect on physical and chemical state of explosives, e.g., change the composition, microstructure, introduce voids and porosity, alter sample dimension. This will affect the performance and safety of explosives. Lawrence Livermore National Laboratory (LLNL) in 2003 launched a research effort to study damaged energetic materials. The main tasks of the research are to generate damaged materials by thermal means and/or mechanical means, evaluate small-scale safety, and characterize the effect of damage on material properties. One of the main goals is providing useful experimental data to help develop models for computer simulation in the ALE3D code. Prior to using explosives for thermal experiments, a mock material RM-04-BR was chosen to establish proper procedure. RM-04-BR is a mock for LX-04, a widely used plastic bonded explosive developed at LLNL. RM-04-BR consists of 85 wt.% of cyanuric acid and 15 wt.% viton A. This article describes our experimental approach and results.

2. Gas Permeation in Materials

Since gas phase reactions play an important role in the energy release during an explosion, it is important to understand gas transport in explosives. Gas permeation in explosives is highly dependent on voids and porosity but gas permeability measurements for pristine and damaged materials are not readily available. Several mock samples were sent to an external firm for permeability measurement. The results are also described in this article.

Darcy's Law and Permeability

According to Darcy's law, the flow rate of a fluid through porous media is proportional to the pressure gradient, as shown in equation 1 for one-dimensional laminar flow in the x-direction [3]:

$$V = - (K/\mu) (\partial P/\partial X) \quad (1)$$

This expression can be written in the following form for flow with a uniform pressure gradient:

$$F = A (K/\mu) (P_i - P_o)/L \quad (2)$$

Where V is the fluid liner flow rate, m/s; K is the specific permeability, m^2 ; μ is the fluid viscosity, Pa s; P is the fluid pressure, Pa; X is the distance in the direction of fluid flow, m; F is fluid volumetric flow rate at average pressure, m^3/s ; A is the cross-sectional area perpendicular to the direction of fluid flow, m^2 ; P_i , P_o are fluid pressures in the upstream and downstream, respectively, Pa; and L is thickness of the porous media for fluid transport, m.

For the flow of an ideal gas at low pressure, an approximate expression can be developed for the volumetric flow rate at standard pressure (atmospheric) and room temperature. If the gas permeability measurements are made at room temperature, the gas volumetric flow rate is reduced to F_s and can be calculated by the following equation:

$$F_s = F T_s (P_i + P_o)/(2P_s T) \quad (3)$$

Where F_s is the gas volumetric flow rate at standard pressure and room temperature, m^3/s ; P_s is the standard pressure, Pa; T is the gas temperature, K; and T_s is the room temperature (298.15 K).

Combining equations (2) and (3) yields

$$F_s = AK(P_i + P_o)(P_i - P_o)T_s/(2\mu LP_s T) \quad (4)$$

The specific permeability is then calculated by equation (5):

$$K = F_s (2\mu LP_s T)/(AT_s(P_i + P_o)(P_i - P_o)) \quad (5)$$

Blake-Kozeny Equation

We treat the RM-04-BR specimens as a packed bed of particles in which the flow of air is laminar. In this case the Blake-Kozeny equation can be applied to represent the specific permeability of the mock HE [4]:

$$K = D_p^2 \epsilon^3 / [150(1-\epsilon)^2] \quad (6)$$

Where D_p is a characteristic dimension of the particles, and ϵ is the void fraction of the sample.

It is of interest to determine whether such a simple model can be applied to thermally-damaged materials. If Eq. (6) can be applied, the permeability can be determined with knowledge of the void fraction and D_p which is expected to be a characteristic dimension of the morphological features of the mock material. For the application of Eq. (6) to the permeability measurements in this work, ϵ is taken from measurements of density and D_p is a fit parameter.

3. Experimental

Several instruments and equipment were used for conducting damage material experiments and characterization of material properties. RM-04-BR, an LX-04 mock material, was selected for the verification of the experimental protocol and the performance of equipment and instruments. Also, for the preparation of thermally damaged samples under controlled conditions, a portable oven (Figure 1) was built and configured for use inside of a vessel capable of withstanding explosions involving 1.0 kg of explosive. The setup is useful for conducting thermal experiments on mock materials and explosives. Temperature control was satisfactory. We were able to control the sample temperature within ± 1 °C at 140 °C and within ± 3 °C at 190 °C, respectively. The ramp rates were 2 °C /min from room temperature to 10 °C below the desired temperature and 0.5 °C /min until the desired temperature was reached. The samples were then soaked for 22 hours at 140 °C and 3 hours at 190 °C, respectively.

Several samples were sent to Porous Materials Inc. (PMI, Ithaca, New York) for gas permeability measurement. The PMI Diffusion Permeameter examines the gas pressure changes through a known volume to determine the permeability of the sample. The amount of gas that has flown through the sample is calculated from the increase in pressure of the known volume. By analyzing the increase in pressure over time, the rate at which the gas passed through the sample can be found. The specific permeability is then calculated from equation 5.

An ultrasound probe was used to measure sound speed in some sample discs. Sample volume was measured by a micrometer and a gas pycnometer.

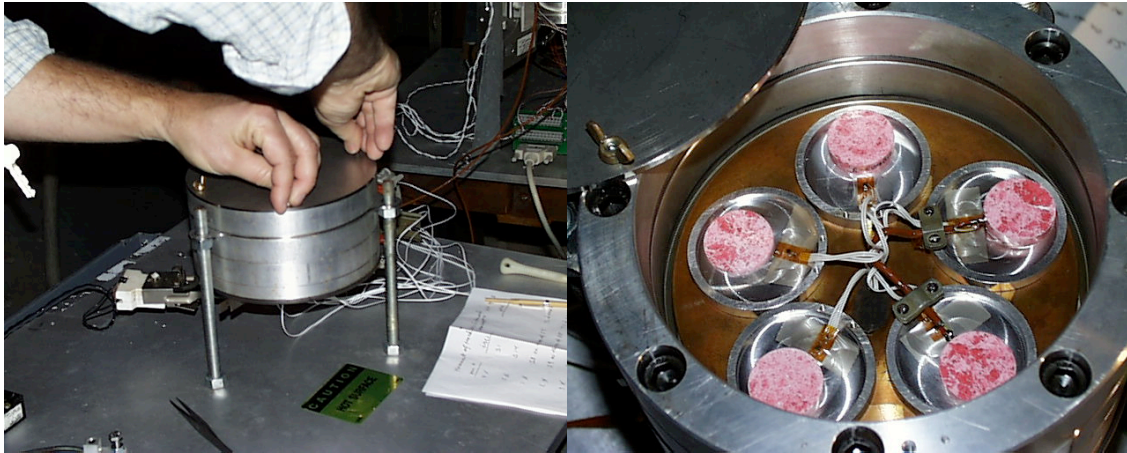


Figure 1. Portable oven used for conducting thermal damage experiment (left). Samples were placed in various pans in the oven (right).

4. Results and Discussions

Discoloring

Several sample discs, 1" in diameter, were thermally damaged at high temperature. Sample discoloring occurred, as shown in Figure 2. The discoloring was very significant after heat exposure at 190 °C for only 3 hours, as opposed to 140 °C for 22 hours. This is probably due to the partial decomposition of cyanuric acid and red dye, a signature of mock explosives.

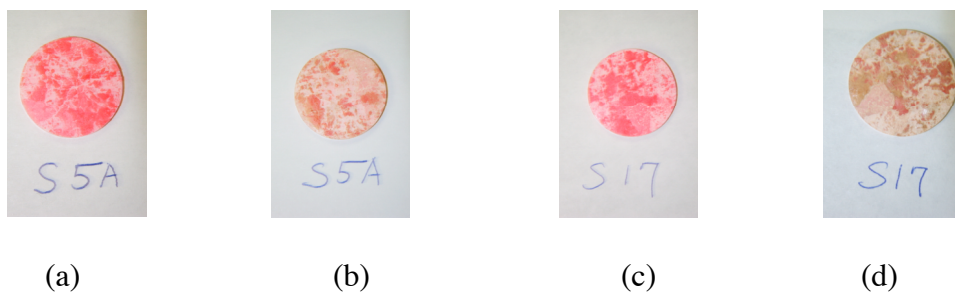


Figure 2. Discoloring of mock discs after heat treatment at 140 °C for 22 hours (b) and 190 °C for 3 hours (d). (a) and (c) show pristine samples.

Changes in Weights and Dimensions

Dimensions and weights of sample discs were carefully measured before and after thermal experiments, as shown in Table 1. The weight loss after thermal treatment was insignificant (less than < 0.5%). The sample expanded slightly (< 1.0%) in diameter and thickness. The density decreased by 1.0% and 2.5% at 140 °C and 190 °C, respectively. This result suggests that the samples have become more porous after heating.

Table 1. Changes in weights and dimensions after thermal treatment

Sample #	Weight*, , 10 ⁻³ kg	Diameter*, 10 ⁻² m	Thickness *, 10 ⁻² m	Density *, 10 ³ kg/m ³	TMD,** %	Note
S1-before	1.5909	2.5395	0.1946	1.6149	91.08	
S1-after	1.5880	2.5474	0.1951	1.5978	90.12	140 °C
% change	-0.182	+0.310	+0.257	-1.05		
S5-before	1.7491	2.5354	0.2004	1.7296	97.55	
S5-after	1.7465	2.5469	0.2007	1.7089	96.39	140 °C
% change	-0.149	+0.454	+0.150	-1.22		
S7-before	3.5422	2.5367	0.4128	1.6987	95.81	
S7-after	3.5392	2.5458	0.4166	1.6698	94.18	140 °C
% change	-0.085	+0.359	+0.920	-1.71		
S15-before	1.5938	2.5347	0.1897	1.6659	93.96	
S15-after	1.5894	2.5481	0.1910	1.6327	92.08	190 °C
% change	-0.276	+0.529	+0.685	-2.00		
S18b- before	4.8902	2.5400	0.6035	1.6000	90.24	
S-18b-after	4.8765	2.5565	0.6076	1.5643	88.23	190 °C
% change	-0.317	+0.650	+0.6794	-2.23		

(* Measurement errors for weight, diameter, thickness, density are 0.3%, 0.05%, 0.05%, and 0.05%, respectively.)

(** Theoretical maximum density (TMD) for the mock material is 1.73x10³ kg/m³.)

Sound Speed Measurement

An ultrasound probe (Figure 3) was used to measure sound speed in the mock samples and results are listed in Table 2. It seems that sound speed for S13 did not change after thermal exposure at 140 °C. Table 2 also shows that sound speeds for S18b (88.2% TMD) were 1692/952 m/s (longitudal/shear), which were considerably lower than those for S13 (94.0% TMD). It appears that the decrease in material density decreases the sound speed.

Table 2. Sound speed in mock material

Sample #	Weight, 10^{-3} kg	Diameter, 10^{-2} m	Thickness, 10^{-2} m	Density, 10^3 kg/m ³	TMD, %	Longitudinal and shear sound speeds, m/s	Note
S13- before	5.3185	2.5392	0.6243	1.6822	94.90	2179/1155	
S13-after	5.314	2.5517	0.6274	1.6571	93.50	2203/1168	140 °C
% change	-0.085	+0.492	+0.497	-1.492	-1.48		
S18b- before	4.8902	2.5400	0.6035	1.600	90.24	Was not measured	
S18b- after	4.8765	2.5565	0.6076	1.5643	88.2	1692/952	190 °C
% change	-0.317	+0.650	+0.6794	-2.23			

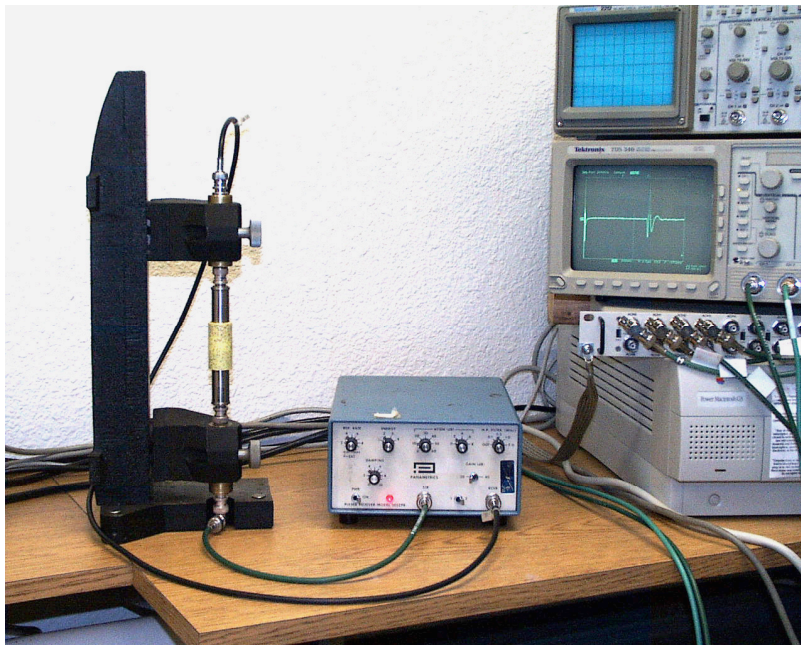


Figure 3. Ultrasound probe for material property characterization using standard ultrasonic wave propagation techniques requires measurement of both the shear and longitudinal sound speeds through the material.

Permeability Measurement

In 2003, several LX-04 mock sample discs with different densities were prepared and

sent to Porous Materials Inc. (PMI, Ithaca, New York) to evaluate whether the Diffusion Permeameter (Figure 4) made by the company is suitable for gas permeability measurement. The test results are shown in Table 3. Figure 5 shows the permeability in S8 at room temperature with an average value of $1.87 \times 10^{-16} \text{ m}^2$, which was consistent with a study by Asay etc. of Los Alamos National Laboratory [1,2].

Table 3: Permeability of air in mock samples

Sample #	Thermally Damaged?	Diameter, 10^{-2} m	Thickness, 10^{-2} m	TMD, %	Permeability *, m^2
S2	No	2.5390	0.1941	91.57	39.70×10^{-16}
S3	Yes, at 140 C	2.5494	0.2014	95.43	4.06×10^{-16}
S7	Yes, at 140 C	2.5458	0.4166	94.13	12.82×10^{-16}
S8	No	2.5375	0.4034	98.03	1.87×10^{-16}
S15	Yes, at 190 C	2.5481	0.1910	92.04	47.9×10^{-16}

(* average value, measurement errors were $\pm 15\%$.)

As expected, sample S8, with a %TMD of 98.03%, has the lowest gas permeability, $1.87 \times 10^{-12} \text{ cm}^2$. Samples S2 and S15, with %TMD of 91.57% and 92.04%, respectively, have permeabilities higher than S8. Figure 6 shows the gas permeability in the mock material vs. TMD. Despite the fact that S15 is slightly denser than S2 (92.04% vs. 91.57%), the air permeability in S18 is greater than that in S2, probably because S15 has been thermally damaged previously.

The Blake-Kozeny model (see Eq. (6)) is fit to the permeability measurements listed in Table 3. The void fraction is calculated as $\varepsilon = (1 - \text{TMD})$, and the parameter D_p is adjusted to provide the best representation of the measurements. The measured and model values for the permeability are plotted versus $\varepsilon^3 / (1 - \varepsilon)^2$ in Figure 7. With this choice of the independent variable, the measurements will describe a single straight line if the model is valid. It is seen that all but one of the measurements falls on the curve-fit line, and the model provides a good representation of the data. This is a somewhat remarkable result since samples of different sizes were heated under different conditions.

The value $D_p = 28.2 \text{ }\mu\text{m}$ for a characteristic dimension of the particles is of a plausible scale. The particle size for cyanuric acid varies, but it generally falls in between several μm and $100 \text{ }\mu\text{m}$. During the wet grinding operation involved the preparation of these samples, the particle size can be reduced to several μm .



Figure 4. Diffusion permeameter for gas permeability measurement

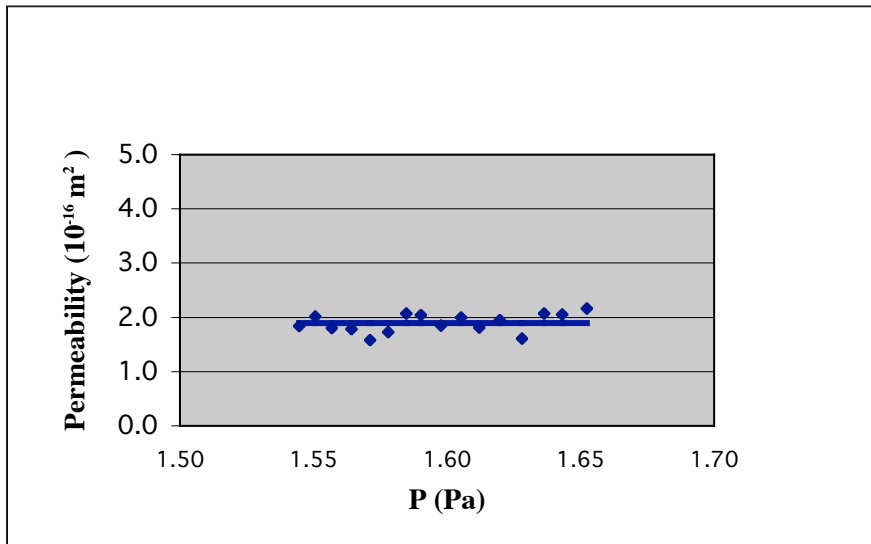


Figure 5. Permeability in mock disc S8; average value is $1.87 \times 10^{-16} \text{ m}^2$; pressure (P) in 10^4 Pa .

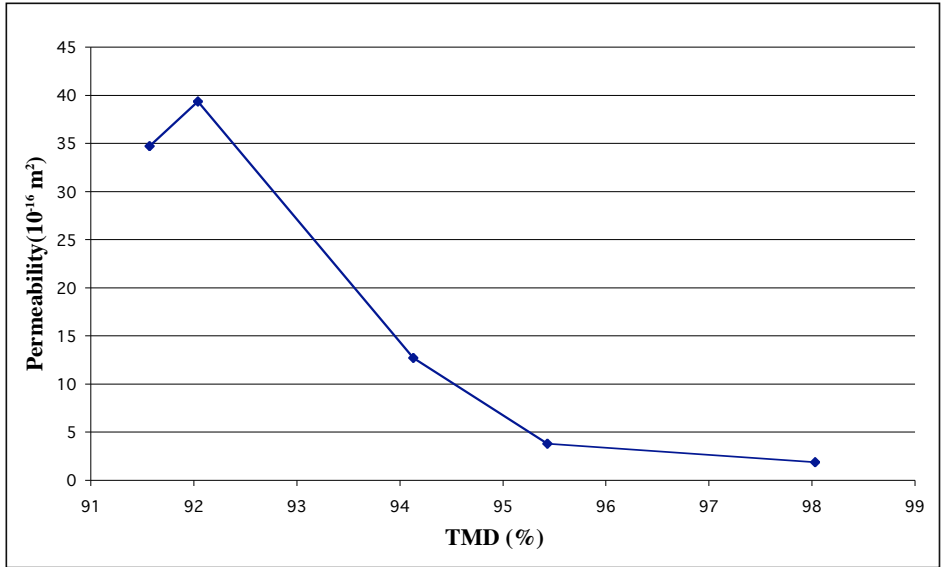


Figure 6. Gas permeability in mock samples of different densities.

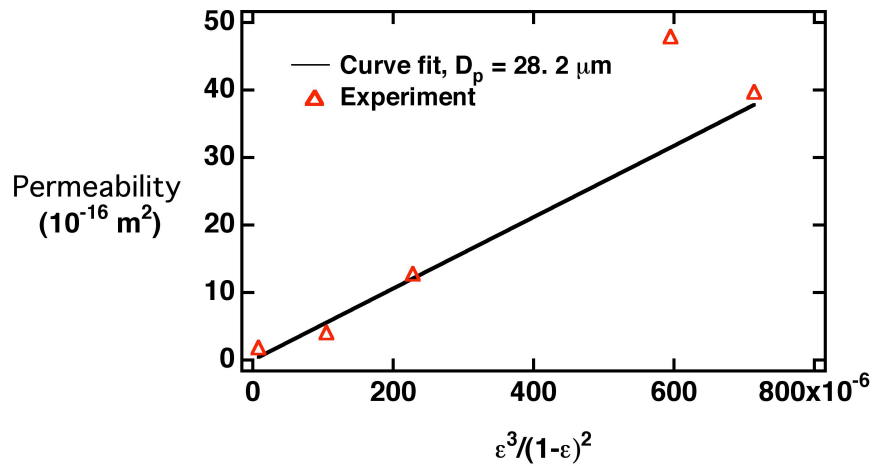


Figure 7 Permeability of mock HE versus $\epsilon^3/(1-\epsilon)^2$

5. Conclusions

Thermal damage experiments were conducted on a mock material, RM-04-BR at 140 °C and 190 °C. Sample discoloring was observed with insignificant weight loss. Sample discs expanded slightly, resulting in density reductions by 1.0% to 2.5%. Air permeability in the mock samples was measured with a commercially available permeation instrument and the results indicate that measurement of gas permeability in mock materials and explosives is possible.

The Blake-Kozeny equation provided a good representation of the permeability measurements as a function of void fraction. Since this model involves a single adjustable parameter, it is a promising candidate for thermal damage simulations involving thermal decomposition with product gas flow through the resulting porous structure.

Symbols and Abbreviations

A = cross-sectional area perpendicular to the direction of fluid flow, m².
D_p = characteristic dimension of the particles, μm.
F = fluid volumetric flow rate at average pressure, m³/s.
F_s = gas volumetric flow rate at standard pressure and room temperature, m³/s.
K = specific permeability, m².
L = thickness of the porous media for fluid transport, m.
P = fluid pressure, Pa.
P_i, P_o = fluid pressures in the upstream and downstream, respectively, Pa.
P_s = standard pressure, 1.013x10⁵ Pa.
T = gas temperature, K.
T_s = room temperature, 298.15 K.
V = fluid liner flow rate, m/s.
X = distance in the direction of fluid flow, m.
μ = fluid viscosity, Pa s.
ε = void fraction of the sample.

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