SAND98-2726C

UNCLASSIFIED

Presented at: 1998 JANNAF CS/PSHS/APS Joint Meeting, December 1998, Tucson, AZ

CHARACTERIZATION OF THERMALLY DEGRADED ENERGETIC MATERIALS: MECHANICAL AND CHEMICAL BEHAVIOR

A. M. Renlund, J. C. Miller, G. W. Wellman and R. G. Schmitt
Sandia National Laboratories*
Albuquerque, NM 87185

Abstract

We report the results of recent experiments on thermally degraded HMX and HMX/binder materials. Small-scale samples were heated confined in either constant-volume or load-controlled configurations. A main emphasis of the work reported here is developing an understanding of the complex coupling of the mechanical and chemical responses during thermal degradation.

INTRODUCTION

For the past several years we have been studying the thermal degradation of confined energetic materials (EMs) in a small-scale test we call the "hot cell". [1-5] These tests allowed us to examine decomposition of EM in either constant-volume or load-controlled configurations. We have measured properties like pellet temperature and force response to indicate extent of reaction approaching cookoff. Postmortem examination of the degraded samples was an integral part of these experiments. Our goal with these tests has been to establish an understanding of the physical and chemical state of the degraded material as it approaches cookoff, including pressure, porosity, phase, etc. Early results showed complex coupling between the mechanical and chemical processes. From the phenomenology observed in these studies we hope to build realistic constitutive models for heated and reacting EM that include chemical decomposition and describe evolving porosity changes. [6]

EXPERMENTAL

Details of our experimental configuration have been described previously. [1,2] Briefly, small-scale EM samples (<500 mg) were heated inside a cylindrical steel cell between opposing pistons sealed with o-rings. The main difference between the two experiments was that in the load-controlled configuration one of the pistons was allowed to move against a fixed applied load. Figures 1 and 2 show schematics of the experimental arrangements the constant-volume hot cell; Fig. 1 is shows the whole assembly, and Fig. 2 is an enlargement that shows the modification to allow measurement of pressure separate from the total force. The load-controlled experiment, shown schematically in Fig. 3, has been modified from previous versions to measure the displacement across the cell length. Displacement of the moveable piston and/or force measured by the load cell were recorded and indicated both mechanical processes, e.g., thermal expansion, phase transitions, compaction, and chemical processes

*Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract number DE-AC04-94AL85000.

DISCLAIMER

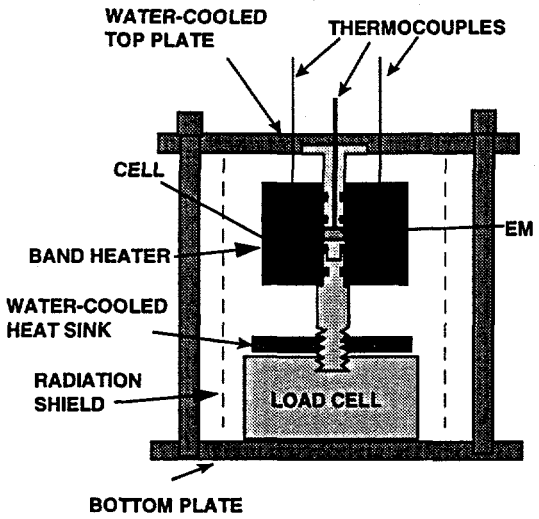

Fig. 1. Schematic of constant-volume hot cell experiment.

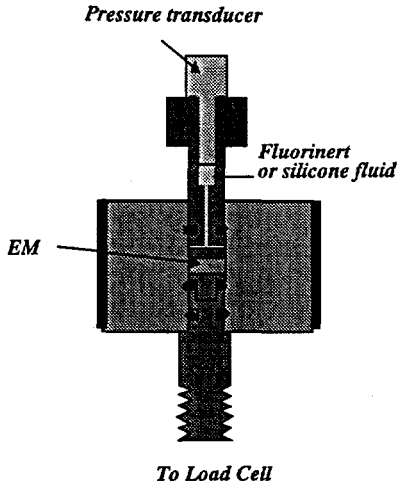

Fig. 2. Schematic showing modification to allow separate measurement of gas pressure.

such as decomposition and gas evolution. The modification to the constant-volume hot cell allowed us to monitor the gas pressure separately.

The load-controlled hot cell has been used both to monitor the reaction progress and to provide us with an experimental means of measuring some mechanical properties of EM at elevated temperatures. In those experiments we measured displacement changes as the applied load was altered. The mechanical response tests were performed at various temperatures up to 190°C, both above and below the phase-transition temperature of HMX. The limiting high temperature range was to avoid significant reaction during the duration of these experiments. Pellets recovered from these experiments were measured and weighed after the heating cycles to assure that no significant reaction occurred. Considerable density changes were noted, however. To date, our mechanical response experiments have been performed on pressed HMX samples, without binders.

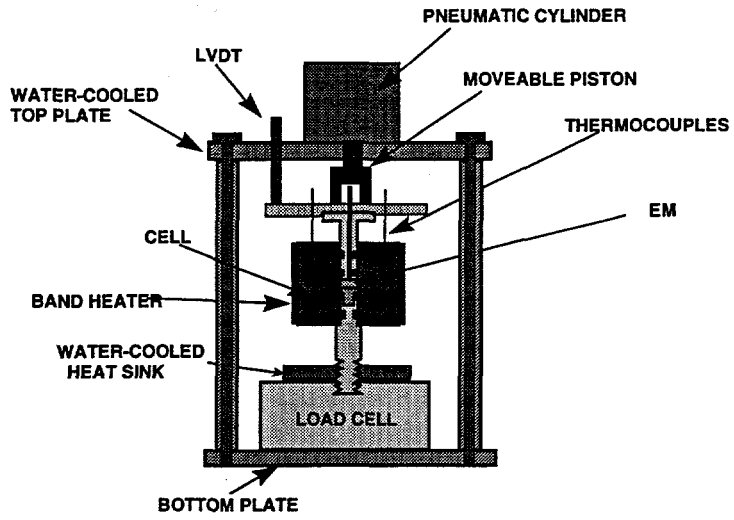

Fig. 3. Schematic of load-controlled hot cell experiment.

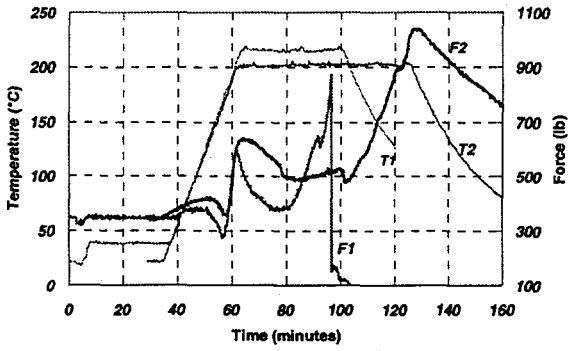

Figure 4. Temperature (T) and force (F) vs time for two separate HMX experiments.

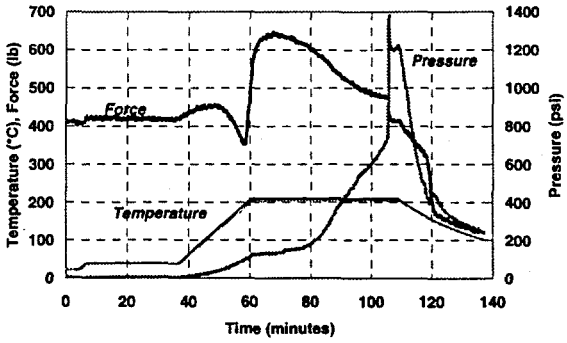

Figure 5. Temperature, force and gas pressure vs time for HMX heated in constant-volume configuration.

RESULTS

Figure 4 shows typical results obtained in the past for HMX heated in the volume-controlled configuration. The load cell measured the combined mechanical and gas pressure forces. Data obtained using the modified top piston with a pressure transducer are shown in Fig. 5. The gas pressure began increasing slowly almost immediately after the phase transition. The pressure range of the transducer did not allow us to heat the sample to the same extent of decomposition that we obtained in the experiments shown in Fig. 4. Postmortem examination of the pellet from the experiment shown in Fig. 5 indicated a 4% mass loss, due to formation of volatile gas products, and compression of the pellet because of the high load evolved.

Figure 6 shows the response of a few HMX/binder materials. The data indicated that the binder both affected the overall decomposition and the mechanical response of the material. Figure 7 shows the response of a series of HMX/Viton formulations with different amounts of Viton. The data in the latter experiments were performed with the separate pressure measurement as well as the load cell measurement. The percentages of Viton in the formulations are 5, 10 and 15%

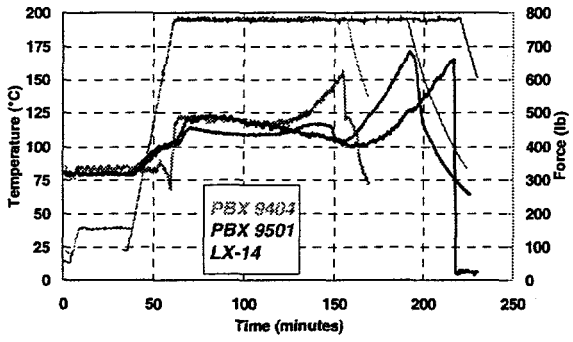

Fig. 6 Response of HMX-formulated EMs in the constant-volume hot cell configuration.

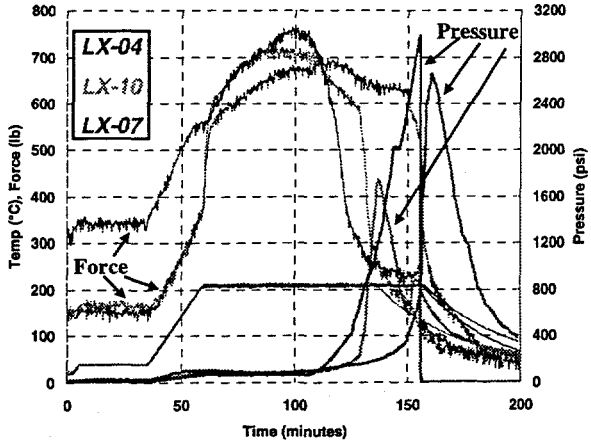

Fig. 7. Response of HMX/Viton formulation in constant-volume hot cell configuration.

for LX-10, LX-07 and LX-04, respectively. The phase transition was obscured for the higher Viton concentrations because of the response of the binder to accommodate the increased HMX volume.

Our studies of the mechanical response of heated EMs is just developing. We have adapted existing hardware to perform these tests. Results on compressed HMX pellets are shown in Figs. 8 and 9 for two experiments at slightly different temperatures and initial HMX pellet densities. Both indicated that the phase transition occurred but the kinetics of the phase transitions clearly differed. Also, we observed significant mechanical creep of hot HMX.

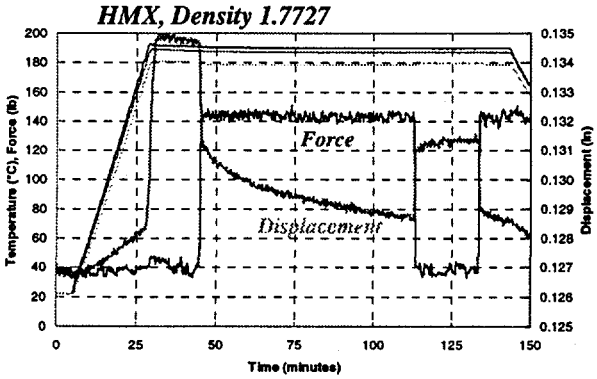

Fig. 8. Mechanical response of heated HMX.

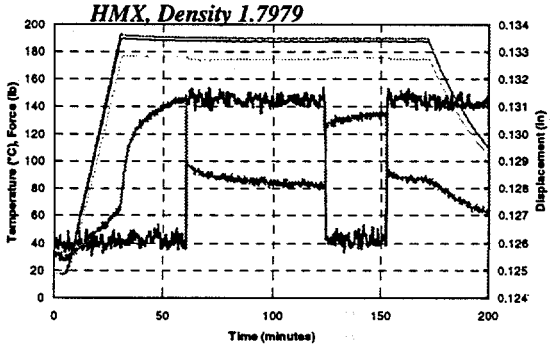

Fig. 9 Mechanical response of heated HMX.

DISCUSSION

The results presented above are a status report of work in progress. One important finding of these experiments is that thermal decomposition of confined EM is a complex and coupled response. We chose to emphasize HMX initially because it has been extensively used and studied. Also, the β-δ phase transition in HMX may affect its reactivity.[7,8]

We believe that we now understand at least some of the features observed in our initial tests and shown in Fig. 4. The relaxation observed during the heating ramp (before the phase transition) is most likely due to mechanical creep under high applied loads (above 6,000 psi). This creep appears to be a temperature and load-dependent process. The β–δ HMX phase transition, though clearly observed in the constant-volume experiments, was not quantifiable; we do not know what fraction of the HMX in the pellet converted to the δ–phase. It is unlikely that the strong confinement and small free volume in the hot cell configuration could accommodate a complete phase transtion of all the HMX material. The best available phase diagram indicates that at these temperatures and pressures both phases are thermodynamically stable. [7] We hope to address this in the future using spectroscopic and acoustic monitoring of the HMX.

The observed relaxation after the phase transition has two probable explanations; mechanical creep or a reverse phase transition to the β-phase. Whichever process, its rate was obviously temperature-dependent. The decomposition can generate gas pressure in excess of 10,000 psi, sufficient to cause the o-rings to fail. This gas pressurization both affected and was affected by the mechanical response of HMX. Referring to Fig. 5, it appeared that, after the final temperature was achieved, the gas pressure increased while the force measurement (combined gas pressure and mechanical response) fell. This coupled behavior was

demonstrated by the step-wise change in both measurements at 105 minutes. These observations lead us to believe that the relaxation after the phase transition was most likely due to creep, with increasing decomposition causing first void formation and then additional compaction of the solid due to the higher pressures contributed by evolving gas products. Examination of the recovered pellet using scanning electron microscopy showed formation of voids during the experiment. Unfortunately, postmortem examinations are not entirely satisfactory because it is never possible to determine how the cooling and disassembly could affect the morphology. We are trying to develop an acoustic probe that could provide real-time morphology information on thermally degraded EMs.

Binder affected the decomposition of EMs both by influencing the chemistry and the mechanical response of the material. The largest relaxations measured after the β–δ phase transition were for Estane or Viton-containing materials. They frequently relaxed to states below the force initially applied to the β–phase material at room temperature. We believe that the relaxation may result from the material, at elevated temperature, becoming more compressible. Postmortem examination showed significant binder migration, especially for LX-11 (80% HMX, 20% Viton). Such changes could lead to a material with a more rapid burn rate, even in the absence of significant decomposition. The resulting porosity would be inherently connected, facilitating the transition to deconsolidated burning. Such materials may give more violent cookoff events.

The mechanical response experiments are still in progress. We are attempting to eliminate contributions to the displacement measurement from merely hardware effects. Nevertheless, we have observed sufficient detail to begin to conceptualize the components of a realistic constitutive model for heated HMX. [6,9] We plan future studies on HMX formulated with various binders and on pure binder materials.

REFERENCES

1. Renlund, A. M., Miller, J. C., Trott, W. M., Erickson, K. L., Hobbs, M. L, Schmitt, R. G., Wellman, G., and Baer, M. L., "Characterization of Thermally Degraded Energetic Materials," Proceedings of 11th International Detonation Symposium, Snowmass, CO (1998).

2. Renlund, A. M., Miller, J. C., Trott, W. M., Erickson, K. L. and Hobbs, M. L., "Characterization of Energetic Materials at Temperatures Approaching Cookoff," JANNAF Propulsion Systems Hazards Subcommittee Meeting, West Palm Beach, FL (1997).

3. Hobbs, M. L., Schmitt, R. G., Renlund, A. M., "Analysis of Thermally-Degrading, Confined HMX," 1996 JANNAF Propulsion Systems Hazards Subcommittee Meeting, Monterey, CA (1996).

4. Renlund, A. M., Miller, J. C. and Erickson, K. L, "Characterization of Energetic Material Response to Thermal Environments," 1996 JANNAF Propulsion Systems Hazards Subcommittee Meeting, Monterey, CA (1996).

5. Renlund, A. M., Miller, J. C., Hobbs, M. L., Baer, T. A., and Baer, M. R., "Experimental and Analytical Characterization of Thermally Degraded Energetic Materials", 1995 JANNAF Propulsion Systems Hazards Subcommittee Meeting, Huntsville, AL (1995).

6. Hobbs, M. L., Baer, M. R., and Gross, R. J., "A Constitutive Mechanical Model for Energetic Materials," Twentieth International Pyrotechnics Seminar, IIT Research Institute, Colorado Springs, Colorado, 423 (1994).

7. Karpowicz, R. J., and Brill, T. B., AIAA Journal, 20, 1586 (1982).

8. Brill, T. B. and Karpowicz, R. J., Journal of Physical Chemistry 86, 4260, (1982).

9. Schmitt, R. G., Wellman, G. W., Renlund, A. M., and Miller, J. C., "A Constitutive Model for Confined HMX During Cookoff", 1998 JANNAF Porpulsion Systems Hazards Subcommittee Meeting, Tucson, AZ (1998).