CHARACTERIZATION OF THERMALLY DEGRADED ENERGETIC MATERIALS

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Characterization of the damage state of a thermally degraded energetic material (EM) is a critical first step in understanding and predicting cookoff behavior. Unfortunately, the chemical and mechanical responses of heated EMs are closely coupled, especially if the EM is confined. We have examined several EMs in small-scale experiments (typically 200 mg) heated in both constant-volume and constant-load configurations. Fixtures were designed to minimize free volume and to contain gas pressures to several thousand psi. We measured mechanical forces or displacements that correlated to thermal expansion, phase transitions, material creep and gas pressurization as functions of temperature and soak time. In addition to these real-time measurements, samples were recovered for postmortem examination, usually with scanning electron microscopy (SEM) and chemical analysis. We present results on EMs (HMX and TATB), with binders (e.g., PBX 9501, PBX 9502, LX-14) and propellants (Al/AP/HTPB).

INTRODUCTION

Cookoff is a complex process with many material and chemical processes contributing to the potential violence of events. We have focused attention recently on characterizing energetic material (EM) in its thermally damaged state, to gain insight into what a material looks like at the point of ignition.[1-5] Time-to-event experiments do not address specifically the evolved gas pressure and properties such as cracking and porosity. Unfortunately, the chemistry and mechanics are closely coupled; the formation of gases via chemical decomposition can cause cracks and voids to form, and some of these voids may later collapse under the increased load from the gas pressure. Yet it is the specific chemical and morphological state of an EM at the time of ignition that controls the subsequent burn dynamics and potential for deflagration-to-detonation transition (DDT). We have characterized the response of various heated EMs using small-scale experiments we call "hot cells". These experiments were not intended to be cookoff tests, rather they were designed to allow acquisition of some real-time data, e.g., temperature, force and pressure, and allow us to recover samples for postmortem examination to quantify the degree of decomposition and to observe morphological changes. The aim of these experiments is both to discover the detailed changes in thermally degraded EM and to provide data for model development and validation. We expect that submodels that describe the constitutive and chemical behavior of reacting EMs will contribute to our ability to predict the violence of cookoff events.

EXPERIMENTAL

The basic apparatus is shown in two configurations in Figs. 1 and 2. These hot cell experiments allowed us to determine the chemical decomposition and mechanical response of a confined EM at elevated temperature. Briefly, a confined EM pellet was subjected to an arbitrary thermal field (up to 260°C) and the EM surface temperature and the forces generated by material expansion and gas generation were measured. The experiments were designed to minimize free volume ensuring that reactive products remained in contact with the EM. Explosive pellets (typically 6.35 mm diameter by 3.17 mm thick), were pressed to the desired densities at either Mason & Hangar Pantex Plant or at Sandia National Laboratories. The pellets were sealed inside a 50.8-mm-diameter cylindrical stainless steel cell by opposing Invar pistons; o-ring seals made of either silicone or Viton provided gas containment up to several thousand psi. The bottom piston was threaded into a load cell and the top piston usually contained a thermocouple to measure the surface temperature of the EM. In the constant-volume experiments (Fig. 1) the top piston was fixed; changes in

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DISCLAIMER

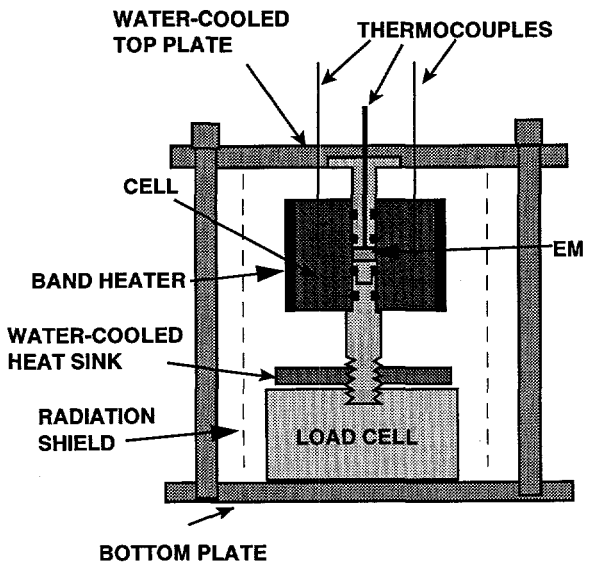

FIGURE 1. SCHEMATIC OF CONSTANT-VOLUME HOT CELL APPARATUS.

force measured by the load cell indicated mechanical responses and chemical decomposition of the EM. Invar bolts were used to assemble the fixture to an adequate preload to assure proper mechanical response. Cooling and radiation shielding were provided to protect the load cell and to minimize thermally-induced stress relief in the bolts. In the constant-load configuration (Fig. 2) the top piston was allowed to move against a fixed applied load controlled by a pneumatic cylinder. A linear velocity displacement transducer (LVDT) measured the piston movement induced by physical changes (e.g., phase transition) and gas pressurization. In both cases, the cells were heated with band heaters and cell temperatures were measured with thermocouples. The experiment was conducted inside a vacuum chamber with the valve to the pump nearly closed so that we could detect any significant leak from the cell without interference from slow outgassing from the heated assembly itself. After heating,

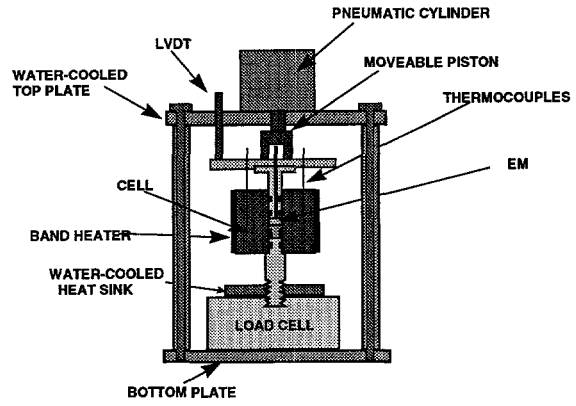

FIGURE 2. SCHEMATIC OF CONSTANT-LOAD HOT CELL APPARATUS

samples were extracted for postmortem examination for both chemical decomposition and morphology changes. In an alternate assembly for both configurations, the top piston was modified to allow a separate gas pressure measurement. In that case, a pressure transducer was sealed in the top piston and a channel, cut through to the sides below the o-ring, was filled with a non-reactive fluid. The pressure transducer thus measured only gas pressure while the load cell measured the combined gas pressure and mechanical response.

RESULTS

CONSTANT-VOLUME EXPERIMENTS

Figure 3 shows the experimental results for HMX pellets (ρ = 1.80 g cm^{-3}) heated in the constant-volume configuration at two different temperatures. The data were

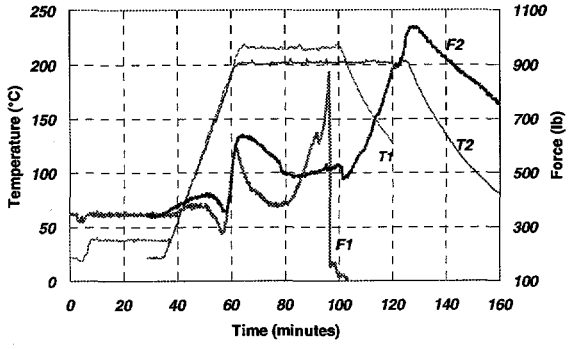

FIGURE 3. TEMPERATURE (T) AND FORCE (F) VS TIME FOR TWO SEPARATE HMX EXPERIMENTS.

highly reproducible for similar conditions and reflected primarily the EM behavior rather than thermal-mechanical response of the hardware. For clarity, only two temperature profiles (one for each experiment, T1 and T2) are displayed in Fig. 3. Temperatures were measured, however at four locations in the cell and also at the surface of the pellet. Because of active cooling along the axis of the apparatus, the final pellet temperature was generally 8 – 10 °C below that measured midway to the center of the cell. Unless otherwise stated, the temperatures displayed in the various figures are pellet temperatures. Force readings are displayed in units of pounds-force; these can be converted to psi by multiplying by approximately 20 (to reflect the 0.25" pellet diameter).

Again referring to Fig. 3, several details of the HMX response were observed. The initial increase in measured force during the heating ramp was due to thermal expansion. This was followed by a force decrease (relaxation). Near 170°C (at 60 minutes) there was an abrupt increase in the force due to the β–δ phase transition.[6] After reaching the final temperature, there was again a second relaxation followed by a more gradual force

increase. This second increase was due to gas evolution from decomposition. We did not detect any leaks from the cell during the first two relaxations. The rapid force drop (just before 100 min in F1) was due to a cell vent because of o-ring failure. The cell in the second experiment (F2) remained sealed, and the late-time decrease in force was due to cooling (after 125 minutes).

By modifying the top piston to allow separate measurement of the gas pressure we obtained the results shown in Fig. 4. The gas pressure increased slowly almost

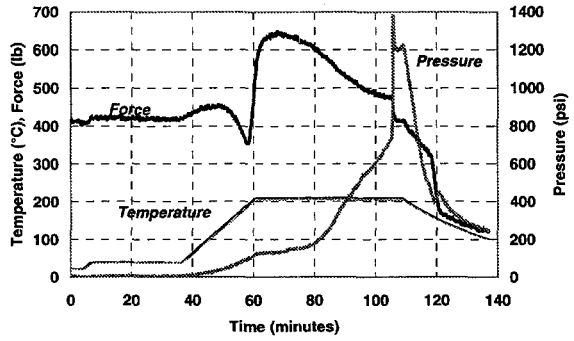

FIGURE 4. TEMPERATURE, FORCE AND GAS PRESSURE VS TIME FOR HMX HEATED IN CONSTANT-VOLUME CONFIGURATION.

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. 3. The pellet recovered from the experiment shown in Fig. 4 was sectioned and examined by scanning electron microscopy (SEM). Results are shown in Fig. 5a and 5b for an unheated and the heated pellet,

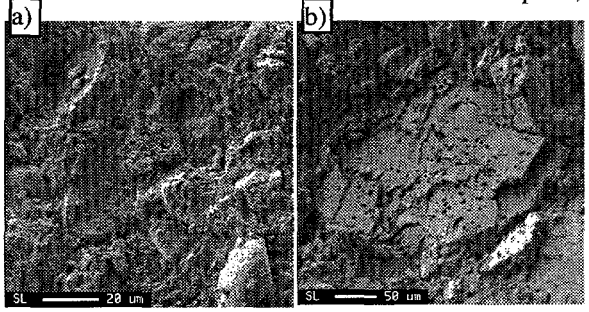

FIGURE 5. SEM RESULTS ON SECTIONED HMX PELLETS, BOTH UNHEATED (a) AND HEATED AND DECOMPOSED TO 4% MASS LOSS (b).

respectively. The porosity formed during decomposition is evident in Fig. 5b. Prior to heating the pellet was .1815 g and .1255" thick. After heating, the pellet weighed .1746 g and was .1225" thick, indicating a 4% mass loss, due to formation of volatile gas products, and compression of the pellet because of the applied load.

We studied the effect of particle size on the response of HMX using pellets pressed from powder that had been sieved from the same lot. The most significant difference was the extent of relaxation measured just prior to the phase transition. Pellets pressed from the fine HMX showed the largest decrease. We also varied the preload applied to the HMX. Generally, the higher preloads resulted in less force increase due to the phase transition.

We investigated the effects of binders by using several plastic-bonded EMs containing HMX, including PBX 9404, PBX 9501, LX-04, LX-07, LX-10, LX-11 and LX-14. Experimental results are shown in Fig. 6 for two of

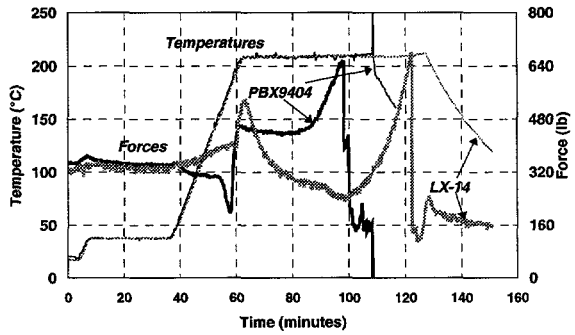

FIGURE 6. FORCE AND TEMPERATURE VS TIME FOR PBX 9501 AND LX-14 HEATED IN CONSTANT-VOLUME CONFIGURATION. PBX 9404 COOKED OFF NEAR 110 MINUTES.

these materials heated in the constant volume configuration. The β–δ phase-transition behavior of the HMX was sometimes obscured by the thermal expansion of the polymer binders. That was particularly true of the high-binder material LX-11 (80/20 HMX/Viton).

PBX 9404 was the most reactive EM in the series studied. It cooked off violently after the pressure had initially vented due to o-ring failure. Violence is defined as producing significant damage to the hardware, making the cells and pistons unusable, often welding them together. The thermal excursion near 110 minutes in the temperature trace in Fig. 6 shows the time at which the cookoff occurred. PBX 9404 was the only HMX-based material that cooked off (albeit unintentionally) in the constant-volume configuration.

SEM results are shown in Figs. 7a and 7b for PBX 9501 samples. Fig. 7a is from a sectioned PBX 9501 sample that had been heated to 190°C and then immediately cooled. It did undergo the β–δ phase transition, but showed no mass loss and was chemically identical to pristine PBX 9501. Fig. 7b is from a pellet that was held at 200 °C for 1 hour. It experienced only 1% mass loss, and the recovered pellet was again chemically indistinguishable from PBX 9501. (Analysis was performed using differential scanning calorimetry, DSC, and high performance liquid chromatography, HPLC). The most significant difference between the two samples is demonstrated in the SEMs; binder migration left an open network of high-porosity areas shown in Fig. 7b.

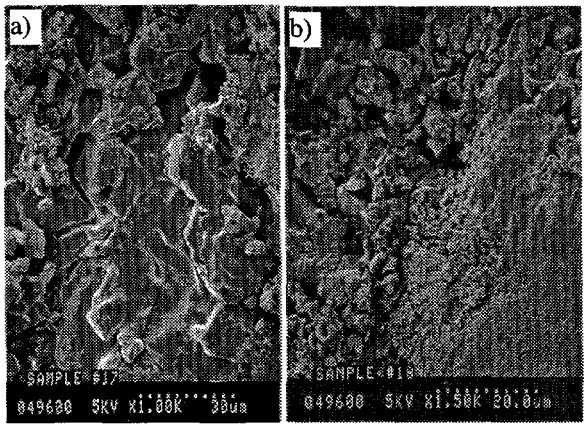

FIGURE 7. SEM RESULTS ON PBX 9501, (a) HEATED TO 190°C AND COOLED, AND (b) HEATED TO 200°C AND DECOMPOSED FOR 1 HOUR

In addition to the HMX-based materials described above we also investigated TATB materials, including the plastic-bonded PBX 9502 and LX-17. Results are shown in Fig. 8 for PBX 9502 at two different

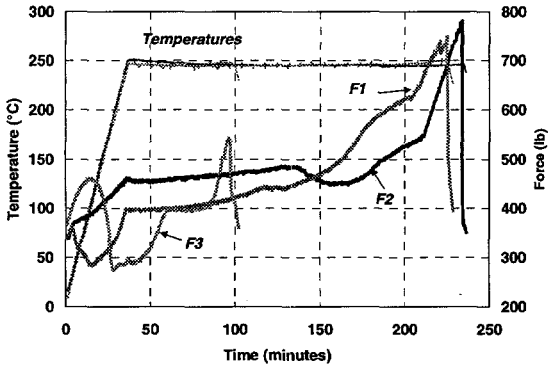

FIGURE 8. FORCE (F) AND TEMPERATURE VS TIME FOR PBX 9502 (F1 FOR ρ = 1.80 g cm^{-3}, F2 FOR ρ=1.89 g cm^{-3}) AND TATB (F3, ρ=1.80 g cm^{-3})

initial densities and for ultrafine TATB. Clearly, the responses of these materials vary significantly from the HMX-based materials described previously. In general, all materials gave excellent agreement within a series. Neither the TATB nor the 1.80 g cm^{-3} PBX 9502 were hot-pressed. The early relaxation behavior during the heating ramp reflected the additional compression of the pellet under heat and load. The 1.89 g cm^{-3} PBX 9502, however, had been hot-pressed to achieve the needed density. It showed primarily thermal expansion during the heating ramp. After reaching temperature, the TATB reacted more quickly than the PBX materials. All three experiments were stopped when the gas pressure vented due to o-ring failure.

Figure 9 shows results from LX-17 heated to cookoff conditions (unintentionally). We measured both

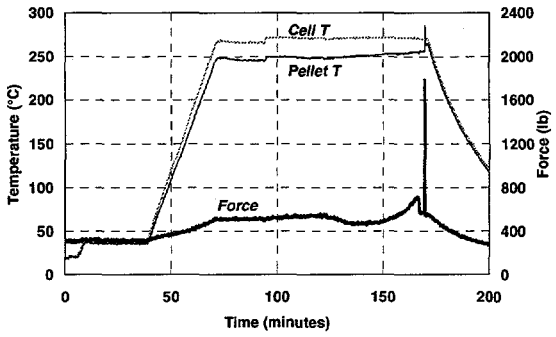

FIGURE 9. FORCE AND TEMPERATURE VS TIME FOR LX-17 HEATED TO COOKOFF CONDITIONS. TEMPERATURE AND FORCE EXCURSIONS SHOW THE TIME AT WHICH COOKOFF OCCURRED (170 MIN).

temperature and pressure excursions due to the cookoff. The result was clearly a thermal runaway and damage to the cell and pistons was significant – much more than a mere pressure rupture. We also observed cookoff with PBX 9502 under similar conditions, leading to similar violence.

We performed only a few tests on Al/AP/HTPB propellant. We encountered difficulties because of the highly reactive decomposition products. We observed significant relaxation of the material during the heat ramp, and only pressure vents from o-ring failure.

CONSTANT-LOAD EXPERIMENTS

Heating EMs in the constant-load configuration explored different environments and responses. The applied loads were lower than those used in the constant-volume configuration. Additionally, when reaction occurred the top piston moved to relieve the additional pressure. Thus, these experiments did not reach similarly high pressures. Results are shown in Fig. 10 for HMX heated in the constant load configuration. The temperature

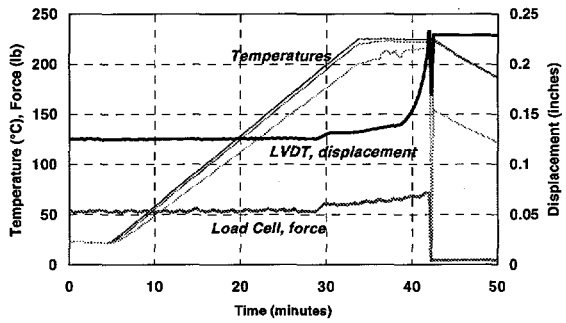

FIGURE 10. FORCE, DISPLACEMENT AND TEMPERATURE VS TIME FOR HMX HEATED IN CONSTANT-LOAD CONFIGURATION

conditions were the same as the T1 experiment shown in Fig. 3 for constant-volume heating. Near 30 minutes and 170 °C the β–δ phase transition occurred; the measured displacement accounted for a 6% volume increase. The experiment shown in Fig. 10 ended due to a violent cookoff, severely damaging the pistons, the cell, the load cell, the pneumatic cylinder and the plate that contacted the LVDT. The rapid movement of the piston just prior to cookoff indicated fast decomposition leading to volatile products that could expand against the applied load. Because of the damage done to the hardware, further tests were done without complete instrumentation (no load cell and no pellet thermocouple) and using some previously damaged parts. Nevertheless, an approximate repeat of the experiment shown in Fig. 10 cooked off within a minute of its time-to-event. Subsequent experiments, done at lower temperatures, still cooked off. Fig. 11 shows results from

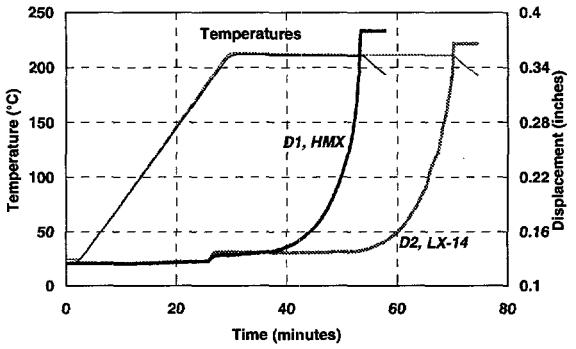

FIGURE 10. DISPLACEMENT (D) AND TEMPERATURE VS TIME FOR HMX (ρ = 1.79 g cm^{-3}) AND LX-14 (ρ = 1.84 g cm^{-3}) IN CONSTANT-LOAD CONFIGURATION. BOTH MATERIALS COOKED OFF.

both HMX and LX-14 heated to temperatures 12 °C below that of Fig. 10. (Only cell temperatures are displayed in Fig. 11, pellet temperatures were approximately 10 °C lower.) Again, both materials cooked off violently, although the times-to-event were not the same.

Other EMs that were heated in the constant-load configuration included PBX 9502 and an Al/AP/HTPB propellant. The PBX 9502 showed only modest reaction and no indication that cookoff was imminent. The propellant did cook off and showed a significant reaction rate increase after the AP phase transition near 220 °C.

MECHANICAL RESPONSE OF HOT HMX

We also used the constant load configuration to investigate the mechanical response of HMX at various temperatures by applying arbitrary loads and measuring displacement. Figure 12 shows results for HMX heated to above the phase transition temperature. Briefly, the HMX was heated under an initial low load. The displacement at 30 minutes tracks the phase transition of the material. After the pellet equilibrated the load was increased and the

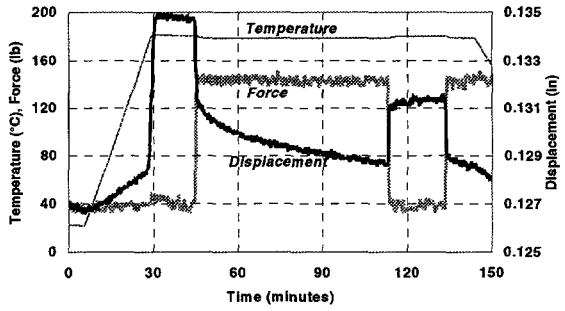

FIGURE 12. DISPLACEMENT, FORCE AND TEMPERATURE VS TIME FOR HMX (ρ=1.774) TO DETERMINE MECHANICAL RESPONSE

pellet was compressed, quickly at first (at 45 minutes) and then more gradually (from 45 to 110 minutes). A high load was then reapplied. Similar experiments were performed for various HMX samples at different temperatures, both below and above the phase transition temperature. The practical limit was that temperature at which measurable decomposition occurred, between 190 and 200°C, depending on how long the experiment ran.

DISCUSSION

HMX AND HMX-CONTAINING MATERIALS

The results presented above constitute a status report of work in progress. One important discovery from 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 shown and described in Fig. 3. The relaxation observed during the heating ramp (before the phase transition) is most likely due to mechanical creep under these high applied loads (above 6,000 psi). This creep appears to be a temperature and load-dependent process. It is also probable that creep is facilitated by small particle sizes. 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 could accommodate a complete phase transtion of all the 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 is 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 affects and is affected by the mechanical response of HMX. Referring to Fig. 4, it is clear that, after the final temperature is achieved, the gas pressure rises while the force measurement (combined gas pressure and mechanical response) falls. This coupled behavior is convincingly shown by the step-wise change in both measurements at 105 minutes. These observations lead us to believe that the relaxation after the phase transition is 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. Evidence of the void formation was shown in Fig. 5. 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 affects 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; refer to the LX-14 response shown in Fig. 6. We believe that the relaxation may result from the material, at elevated temperature, becoming more compressible. The PBX 9404 cookoff, also shown in Fig. 6, surprised us because it occurred well after the o-rings failed. Other tests on PBX 9404 showed that the recovered pellets were very sticky and rubbery. It is likely that a pocket of material within the pellet was sufficiently sealed by self-confinement to allow an ignition site to build. This behavior is directly related to the reaction and material properties of the nitrocellulose binder and the tris-beta chloroethylphosphate (CEF) plasticizer at these temperatures. Binder migration, as shown in Fig. 7b could lead to a material with a more rapid burn rate, even in the absence of significant decomposition. The resulting porosity is inherently connected, enabling the transition from laminar to convective burning. Such materials may give more violent cookoff events.

Prior to conducting the constant-load experiments with HMX we anticipated that longer times would be required to reach the same state of decomposition compared to tests conducted at constant volume. The lower applied load and the pressure relief possible by displacing the piston meant that reactions would not reach the same high-pressure conditions achieved when the piston was fixed. Because reaction rates tend to accelerate with increasing pressure we thus assumed a slower decomposition. Consequently, the first cookoff we observed (Fig. 10) came as a surprise, both because of its violence and because of how soon it occurred. The nature of the confinement, however, allowed for different physical and chemical processes. In the constant-load experiments we performed we were able to measure the piston displacement accompanying the phase transition. We know, therefore, that all the contained HMX transitioned to the more reactive δ–phase. Also, because the piston could move, the pellet's density could more readily decrease during heating and decomposition. Gas products could deconsolidate the pellet or accumulate above the pellet between it and the piston. It is likely, therefore, that ignition occurred in the gas phase and that the violence was enhanced by the high porosity of the thermally degraded HMX. Binder appeared to slow the decomposition (see Fig. 10) and increase the time-to-event of the cookoff, but the violence was similar. Because we were unsure of the handling safety of these EMs heated in the constant-load configuration, we have not yet attempted to halt experiments prior to cookoff to recover samples for postmortem examination.

We initially attempted to model the response of the HMX using a preliminary hydrostatic stress-strain constitutive model for decomposing energetic materials under various loading.[1,2,5] This Reactive Elastic-Plastic (REP) constitutive model was founded on the collapse and growth of internal inclusions resulting from physical and chemical processes such as forced displacement (preloading), thermal expansion, and/or decomposition. Stress was determined for any change in strain, temperature, and/or fraction of solid converted to gas. The REP constitutive model did not consider the effect of phase change. Results of this modeling led us to realize that a more detailed constitutive model was needed.[1] In particular, since it considers only hydrostatic forces REP could not describe the observed relaxation processes. The experiments (see Fig. 12) that measured the mechanical response of the hot (but unreacting) HMX were an initial step at providing data for the development of a constitutive model in which we could later include chemical decomposition. Such a model must contain thermal expansion, viscoelastic behavior, temperature and pressure-dependent volumetric and deviatoric creep and phase transition. We are still improving the experimental technique to refine the accuracy of the data, and to measure and account for thermal inhomogeneities in the experiment. Similar experiments will be performed on plastic-bonded EMs.

TATB AND TATB-CONTAINING EMs

We performed only a few experiments on TATB and plastic-bonded TATB. PBX 9502 and ultrafine TATB (both ρ=1.8 g cm^{-3}) showed significant relaxation during the heating ramp, essentially due to *in situ* hot-pressing. (See Fig. 8.) Samples that had been heated to 200 °C and then immediately cooled showed no relaxation during a re-heat experiment. The relaxation observed in Fig. 8, (F2) near 150 minutes is probably a pressure-induced creep response. As the material decomposed, the resulting gas pressure exerted a force to collapse the solid bed.

Unlike HMX, TATB materials showed no indication of nearing cookoff conditions in the constant-load experiment. It is likely, therefore, that the controlling

reaction rate enhancement leading to cookoff is pressure-dependent. Thus, the only cookoffs observed for TATB materials were in the constant-volume experiment, and only after significant decomposition. (See Fig. 9.) We plan to redo these experiments with the pressure-transducer to allow a separate measure of the gas pressure. The cookoffs from both PBX 9502 and LX-14 were less violent than the response of HMX in the constant-load cookoffs, but were not very different from the constant-volume cookoff of PBX 9404.

Al/AP/HTPB PROPELLANT

Only preliminary experiments were performed on propellant systems. We will redesign the cells and pistons to be more corrosive resistant. The main result of note in the work done to date is that, similar to HMX, the propellant cookoff was facilitated by the AP phase transition.

CONCLUSIONS

Thermal degradation leading to cookoff is a complex process with coupled chemical and mechanical behavior. It is important to evaluate EM response in configurations representative of how the materials are used in practice; constant-volume conditions are not equivalent to constant-load. Reaction leading to cookoff appears to be facilitated by solid-solid phase transitions in HMX and Al/AP/ HTPB propellant, and is enhanced by high-pressure reactions for TATB.

Future work will focus on characterizing the mechanical response of hot (but unreacting) EMs for developing a realistic constitutive model. We are also developing spectroscopic and acoustic probes for real-time monitoring of phase and morphology changes. Measurement of gas-product generation will be used to develop kinetic models of decomposition. We expect that these will provide inputs into both burn experiments and models that will help elucidate the processes that control violence of reaction for cookoff.

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REFERENCES

1. 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).

2. 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).

3. 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).

4. 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).

5. 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).

6. Gibbs, T. R., Popolato, A., LASL Explosive Property Data, University of California Press, Berkeley, CA (1980).

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).