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Mesoscale observations of the thermal decomposition of energetic composites under ultrasonic excitation

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Z. A. Roberts,[1,2,3] J. A. Wickham,[2,4] C. J. Sorensen,[1,2] T. D. Manship,[1,2] I. E. Gunduz,[1,2] S. F. Son,[1,2,5] and J. F. Rhoads[1,3,6,a)]

AFFILIATIONS

[1]School of Mechanical Engineering, Purdue University, West Lafayette, Indiana 47907, USA
[2]Maurice J. Zucrow Laboratories, Purdue University, West Lafayette, Indiana 47907, USA
[3]Ray W. Herrick Laboratories, Purdue University, West Lafayette, Indiana 47907, USA
[4]School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907, USA
[5]School of Aeronautics and Astronautics, Purdue University, West Lafayette, Indiana 47907, USA
[6]Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana 47907, USA

[a)]**Author to whom correspondence should be addressed:** jfrhoads@purdue.edu

ABSTRACT

Polymer bonded explosives (PBXs) have exhibited localized heating and, in some cases, subsequent reactions in response to ultrasonic excitation. The objectives of this work are to investigate the conditions for, and locations of, hot spot initiation of energetic crystals embedded within a polymer binder subjected to periodic mechanical excitation from a contacting transducer operating at 210.5 kHz. Crystal and binder interactions and events such as delamination, solid-solid phase change, and gas production were observed in real time via optical microscopy. We conclude that there are two main pathways of heat generation which are capable of driving an explosive to decomposition in the systems of interest: frictional heating from a delaminated and moving binder interface and viscoelastic heating in the binder near an embedded crystal. Formulations that address the vibration initiation sensitivity of PBX composites require knowledge of the key internal heat generation mechanisms. The results included here indicate that improving binder adhesion to energetic crystals or improving crystal morphology to reduce heating during cyclic loading may only address one of the available pathways of energy dissipation and that binder and crystal selection should be done concurrently. Furthermore, the results presented herein appear to indicate that rounded particles, in contrast to faceted crystals, with strong adhesion to the binder are expected to result in decreased heating rates under ultrasonic excitation.

I. INTRODUCTION

The initiation of solid explosives is commonly considered to be thermal in origin and energy from mechanical processes dissipated as heat can form localized areas of intense heating called "hot spots." Once formed, hot spots either lead to exothermic reaction or fail to create an ignition site due to thermal diffusion.[1] In other words, a hot spot will grow provided that the rate of heating from both mechanical insult and chemical reaction at the small volume is greater than the heat lost to the surroundings.[2] Impact-induced hot spots can be 0.1–10 μm in diameter and have durations of around 10^{-5}–10^{-3} s and temperatures of approximately 400–500 °C.[2–6] Others have estimated the size and critical temperature of hot spots arising from impact-induced or shock-induced loading to span 0.1–1000 μm in diameter inversely corresponding to 727–927 °C and durations of 10^{-8}–10^{-1} s.[1] Hot spots can be formed on longer time scales under high-frequency periodic loading, leading to accidental initiation. The focus of this current work is to investigate the mechanisms of energy dissipation causing hot spots in composite energetic crystal/binder materials subjected to ultrasonic insult.

Friction from sliding or impact, viscoelastic/viscoplastic heating within the binder, and the compression of trapped gas

spaces have all been considered internal heat generation mechanisms leading to the formation of hot spots in polymer bonded explosives (PBXs) under mechanical loading. Investigations into the heat generation mechanism of frictional heating have examined, for example, the minimum melting temperature of hard grit particles necessary to initiate the solid explosive pentaerythritol tetranitrate (PETN) during impact or rapid shearing.[5–8] High melting temperature and high hardness grit particles (both higher than those of PETN) were necessary to initiate reactions because the frictional heating reduced once melting of the grit particles occurred at the surface.[9] The mechanism associated with the compression of trapped gasses has been investigated via drop-weight impact testing of crystals arranged in an annulus. This work demonstrated initiation from the center, as well as from cavities (pores) in the binder and/or crystals collapsing from low strength shocks.[3,4,10–12] If extreme conditions exist such that there is a sufficient temperature rise, such as the case with very high impact energy, viscous heating of a flowing, plastically deforming solid explosive or binder can create hot spots.[5,6] High cyclic loading rates can also generate the necessary heat to reach a critical temperature in the binder or at crystal interfaces, which has been demonstrated via the thermal decomposition of HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocane) and RDX (1,3,5-trinitro-1,3,5-triazine) explosive crystals.[13–15] The modeling of periodic compressional plane waves interacting against a rigid spherical HMX inclusion showed that viscoelastic heating on short time scales can approach the same order of heating (55 °C/s) as situations considered to be frictional.[16,17]

The critical impact and shock conditions necessary for the hot spot initiation of solid explosives have been extensively explored but little work has focused on high-frequency contact loading.[18] Insight has been gained with ultrasonic experiments on "simplified" PBX samples consisting of discrete solid explosive inclusions within a block of elastomeric binder.[13,14,17,19–22] The longer duration hot spots and lower heating rates seen in ultrasonic experiments are useful for investigating the temperatures and locations of heating and also to approximate some of the loading conditions experienced during transportation and end use. Men *et al.*[22] exploited this fact to predictably capture the onset of a thermally induced explosion in single HMX and RDX crystals and found that reactive gases expanded a cavity within the polymer and subsequently ignited in a "second stage" due to the partial confinement provided by the binder. This work concluded that mechanical processes in the surrounding medium influence the chemical kinetics of explosions. The objectives of the current work are to more fully understand the influence of the previously delineated heat generation mechanisms in periodically insulted composite energetic materials, such as PBXs and solid propellants, by examining the evidence of hot spots (delamination, melting, phase change, and multiple stages of gas production) induced by heating from the motion of a polymer binder near various HMX crystal surfaces, and to identify the various steps which could be taken to mitigate against this heating.

II. EXPERIMENTAL PROCEDURES

Samples were prepared with BAE Systems grade B class 3 HMX sieved to 500–850 μm. The crystals were encapsulated in Sylgard 184 (polydimethylsiloxane), an optically transparent elastic binder suggested for use in PBXs,[23,24] in two steps. First, a 1 mm layer of Sylgard was mixed at a 10:1 base to curative ratio and cured at 60 °C for 12 h. Next, crystals were arranged on the surface of the 1 mm layer and encapsulated with approximately 3 mm of additional Sylgard before curing in the oven again. Care was taken to subject the embedded crystals to vacuum before final curing in order to draw bubbles away from the crystal interface and facilitate good binder contact. Finally, approximately 5×7 mm^2 Sylgard rectangles with encapsulated HMX 1 mm below the top surface were obtained using a razor blade.

In addition to production-grade β-HMX, the following three types of HMX crystals of the same size range were encapsulated: δ-HMX which was created by heating the material above 170 °C for several minutes before encapsulating and was characterized by a rough cracked surface due to the approximately 7% volume expansion accompanying the phase transition;[25,26] recrystallized β-HMX with few surface or internal defects; and recrystallized β-HMX which was agitated in acetone for 1 min to remove sharp corners and round the flat sides. Additionally, predelaminated production-grade β-HMX samples were created by manually compressing the cured Sylgard rectangles until the binder was observed to peel off of the crystal surface without damaging the encapsulated crystal. Images of representative HMX crystals of each type are shown in Fig. 1.

Recrystallization of the β-HMX was performed using a Soxhlet extraction process to remove impurities, immersion in cyclohexanone for 6 h to remove RDX contaminant (maximum 2% RDX per

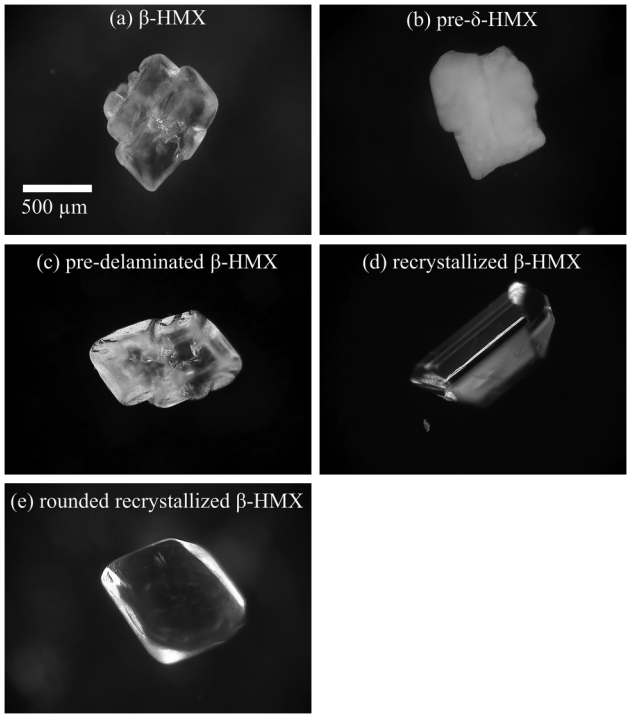

FIG. 1. Images of representative HMX crystals embedded in Sylgard.

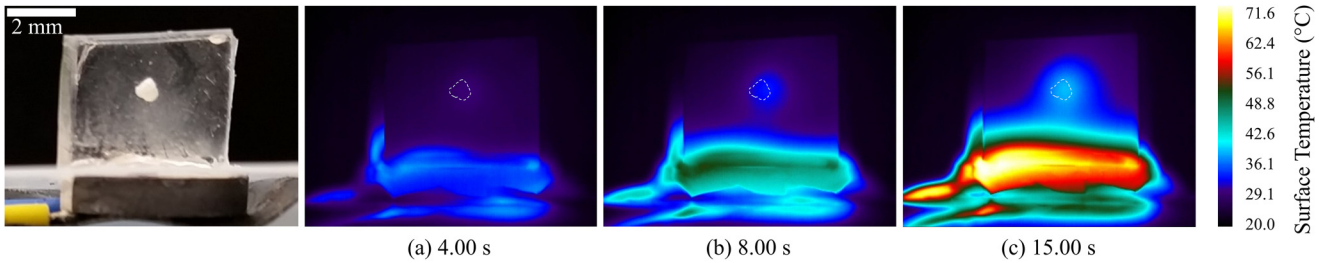

FIG. 2. Side view from a FLIR A325sc infrared camera of a predelaminated β-HMX sample which transitioned to the δ phase. The transducer is shown, as well as a white dashed outline around the crystal location. The sample was modified to have a particle embedded 1 mm from the sidewall to obtain a more differentiated temperature pattern. This image sequence was used to determine the end time of 15 s, about when the heat conducted from the transducer first tangibly influenced the ultrasonically driven heat at the particle location. The insets show the sample at 0 s; (a) 4.00 s; (b) 8.00 s; and (c) 15.00 s.

MIL-DTL-45444C), and finally the crystals were dissolved in 3:1 acetone:nitromethane and stirred for several hours before allowing slow evaporation and crystallization on the bottom of a glass container.

An Agilent N9310A RF signal generator and a Mini-Circuits LZY-22+ high power amplifier powered by a Keysight E3634A DC power supply, as detailed in Roberts *et al.*,[17] provided a 10 W sinusoidal signal at 210.5 kHz to a Steiner and Martins SMD10T2R111WL PZT transducer. Strong coupling between the piezoelectric transducer and the Sylgard sample containing the embedded HMX crystal was found to be extremely important to induce crystal/binder delamination and for high heat generation at the inclusion location. Cyanoacrylate (Loctite gel control superglue) was used to adhere the Sylgard sample to the surface of a

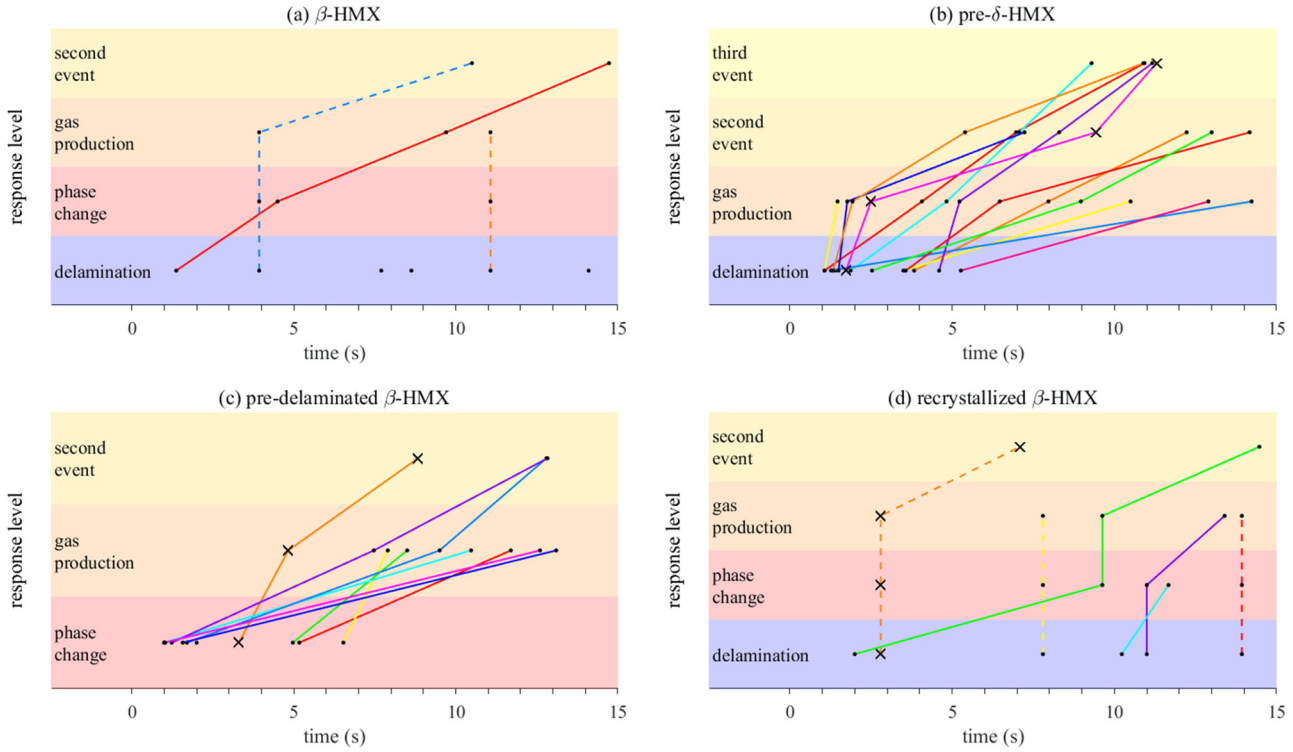

FIG. 3. The time of events observed during the 15 s duration tests for 15 of each embedded, single crystal HMX sample. Rounded recrystallized β-HMX had no responses within 15 s. The events beyond initial delamination, phase change, and gas production included resolidification, melting, and additional gas production before breaking out of the cavity/plane of casting. Dashed lines represent samples that had no visible delamination before gas production and "X" data are samples shown in the subsequent image sequences.

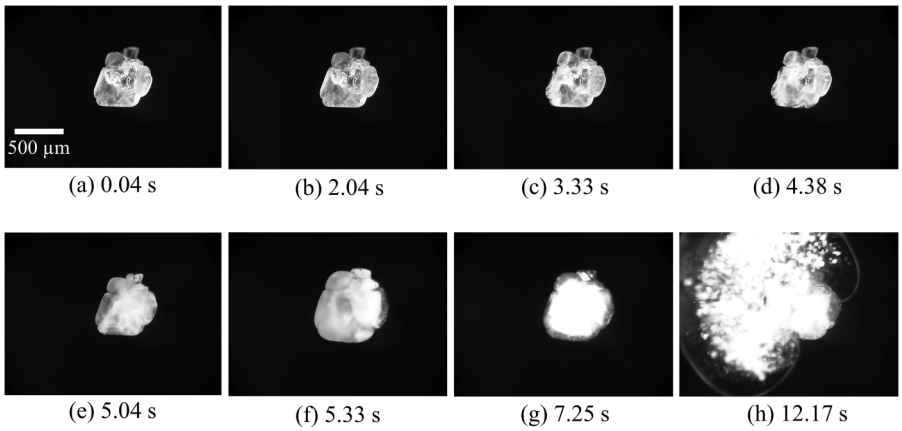

FIG. 4. An image sequence taken from a video (24 fps) of the top view of a single embedded predelaminated β-HMX crystal during excitation. (a) and (b) The delaminated binder moved rapidly against crystal interface; (c) and (d) the β-δ phase change began at the left edge of the crystal with an accompanying volume increase; (e) and (f) the initial gas production expanded the cavity of casting; (g) the gas production ceased and the cavity shrank slightly; and (h) a second gas production event occurred and broke out into the plane of casting. Multimedia view: https://doi.org/10.1063/1.5088153.

transducer that had been blackened with a permanent ink marker (Sharpie). A Hirox KH-8400 optical microscope with 140× lens recorded video at 24 fps with a resolution of 800 × 600 pixels. Due to the inexact start time of the recordings, excitation began tens to hundreds of milliseconds into each video. Tests were terminated after 15 s, about when heating from the transducer begins to influence the ultrasonically driven heating at the particle location (Fig. 2). Microscope videos were captured from a top view with the blackened transducer oriented behind the crystals. Side view videos were typically of lower quality due to the increased depth of the binder and did not reveal information about whether the delamination first took place on the near side of the crystal to the transducer or at surface asperities exclusively.

III. RESULTS AND DISCUSSION

The initial time of events observed in each of the 15 samples among the 4 sample types during the course of excitation is given in Fig. 3. The fifth sample type, rounded recrystallized β-HMX, had no response in any of the 15 samples within the 15 s tests. The point markers indicate the times at which the various samples showed evidence of delamination, as characterized by a visibly moving binder against the crystal; the β-δ phase change, as indicated by an increase in size and opacity of the crystal; gas production seen as an expansion of the cavity and bubbles forming in an HMX melt within the Sylgard; and any additional gas production events, which occurred up to three times in some of the tests. Note that the variation introduced by using distinct transducers for each sample as well as the variation in strength and uniformity of the coupling (super glue) between each Sylgard block and the blackened transducer surface were partially responsible for the variability of response level timing among the samples of a single crystal type. Additionally, both the individual crystal morphologies and the crystal locations and heights within the Sylgard contributed to the time dependence of reaction initiation by affecting the likelihood of delamination at stress concentrations as well as the crystal locations within the acoustic field, respectively. The occurrence of hot spots is inherently random, and 15 samples of each type were chosen to provide a sufficient picture of possible events.

The scarcity of events in the production-grade β-HMX samples in Fig. 3(a) was contrasted by the predelaminated β-HMX samples shown in Fig. 3(c). A delaminated and moving binder

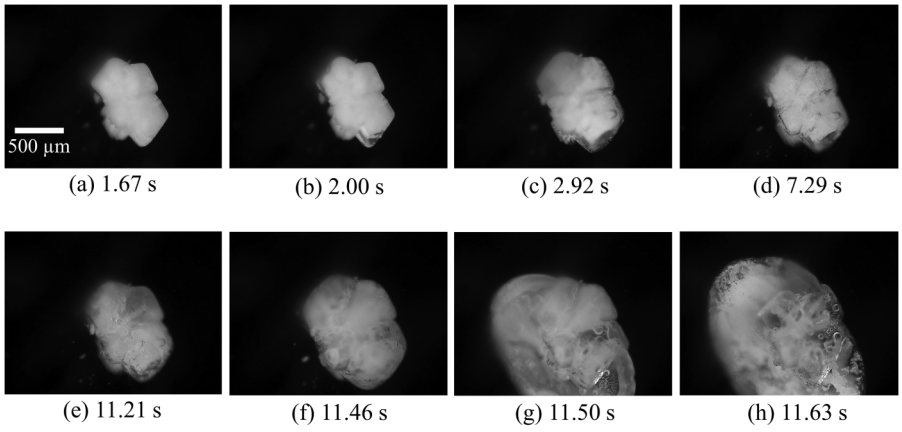

FIG. 5. An image sequence of the top view of a single embedded pre-δ-HMX crystal during excitation. Note the opaque white color of the crystal. (a) The initial δ-phase crystal, (b) the first sign of delamination and binder motion, (c) the first gas production event, (d) and (e) the cavity shrank and additional surface motion was recorded, and (f) and (h) the second gas production event and growth of the cavity until breakout. Multimedia view: https://doi.org/10.1063/1.5088153.

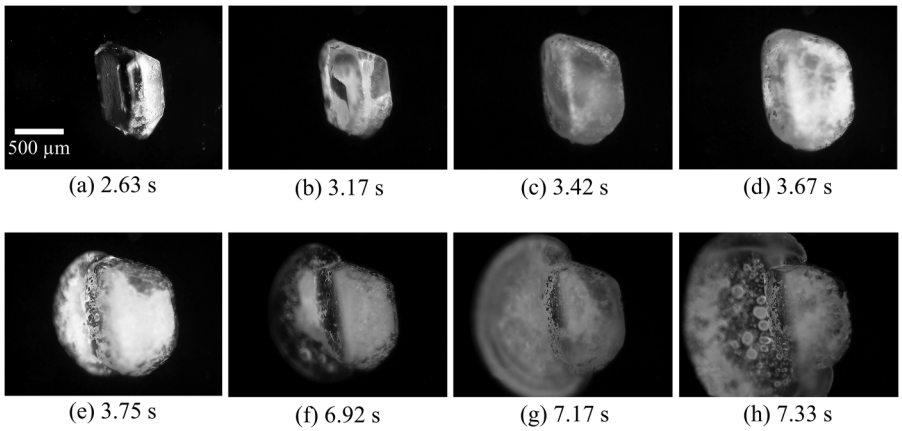

FIG. 6. An image sequence of the top view of a single, embedded, recrystallized β-HMX crystal. Note the flat facets, sharp corners, and clear initial appearance of the low-defect crystal. (a) No delamination or movement was observed for approximately 3 s; (b) the initial delamination and melting occurred almost simultaneously; (c) and (d) the gas was produced which expanded the cavity of casting; (e) the gas products broke out into the plane of casting; and (f)–(h) after approximately 3 s of additional excitation, the crystal melted and produced gas for a second time. Multimedia view: https://doi.org/10.1063/1.5088153.

interface was characteristic of energy dissipated frictionally or by the compression of created voids. Heat generated at the outer surface locations on a crystal was sufficient to drive the HMX to thermal decomposition, as evidenced by the melting and gas production of the predelaminated β-HMX shown in Fig. 4 (Multimedia view). Gaseous products expanded the cavity of casting and in some cases broke out of the binder in the plane of casting after one or more gas production events, sometimes audibly. It was not always the case that the binder was observed to delaminate and move rapidly against the crystal surface before the HMX underwent the β-δ phase change characteristic of reaching 170 °C, or thermal decomposition, which occurs at 290 °C at slower heating rates.[26]

Defects in crystal morphology provided nucleation points for binder delamination[27] in the pre-δ-HMX samples which exhibited a rough cracked surface. A pre-δ-HMX sample is shown in Fig. 5 (Multimedia view), and all of the observed events for samples of this type are shown in Fig. 3(b). Most of the δ-phase crystal/binder interfaces delaminated immediately upon excitation, and gas production events were more prevalent with these samples than with any of the varieties of β-HMX samples. The second and third events after initial gas production appear to be attributable to the HMX solidifying after having melted and then remelting and producing gas again. This could happen multiple times during a 15 s test and was usually terminated when the gas broke out into the plane of casting, quenching the reaction. This was further evidence that friction was a main heat generation mechanism because once having melted, friction between the moving binder and the crystal would be significantly reduced, allowing the temperature to drop enough for the HMX to resolidify before starting the process again. Had significant viscoelastic heating been present in the rapidly deforming binder, heat conduction likely would have still been able to reach the melted HMX and continue to drive the reaction (though obviously the changing nature of the acoustic scatter complicates this conclusion).

The recrystallized β-HMX in Fig. 3(d) was characterized by flat facets; sharp edges and corners; and a clear low porosity crystal. Some videos of the recrystallized β-HMX showed no visible delamination before the crystals transitioned to the δ-phase, melted, and produced gas, as early as 2.80 s, as shown in Fig. 6 (Multimedia view). The lack of visible binder motion before melting and gas production provided evidence that there was another pathway for heating, such as viscoelastic heat generation in the binder near the crystal, enough to drive the HMX to thermal decomposition, as supported by Mares *et al.*[16] Two β-HMX samples, indicated by dashed lines, also achieved gas production without prior crystal-binder delamination being observed. Rounded recrystallized β-HMX lacked any delamination, phase change, or gas production events and again highlights the influence of crystal morphology on either frictional heat generation from a delaminated and moving binder or localized viscoelastic heat generation without visible delamination. The smooth cornerless surface did not allow delamination to initiate or propagate or allow for the concentration of stress in the binder near any sharp crystal points, as may be the case for other types of β-HMX.

IV. CONCLUSIONS

These experiments show evidence of both frictional and viscoelastic heat generation mechanisms contributing to the decomposition of HMX crystals embedded within Sylgard 184 binder and subjected to ultrasonic excitation. Production-grade β-HMX crystals did not typically delaminate or heat enough to undergo decomposition unless the crystal/binder interface had been damaged (mechanically predelaminated), which has been shown previously.[17]

Crystals which were thermally damaged before encapsulation, called pre-δ-HMX here, showed rapid motion of the binder immediately upon excitation due to the many delamination nucleation points on the crystal surface, which led to rapid debonding. The impact sensitivity of δ-HMX is known to be higher than that of β-HMX due to chemical rather than physical differences alone,[25] and δ-HMX is seen to form just before ignition.[28,29] In the present situation, δ-HMX appears also to be more sensitive to ultrasonic excitation leading to decomposition earlier because of the propensity to delaminate, and β-HMX crystals appear to change phase to δ-HMX and melt just before decomposition. It is expected that frictional heat generation

from the binder motion contributes largely to the melting and gas production in the pre-δ-HMX and predelaminated β-HMX samples because viscoelastic heat generation in the binder would require conduction to heat the crystal, and an intermittently contacting binder or melted interface may decouple this particular source. Additionally, δ-HMX had up to three gas production events during a single test, which, in agreement with the current literature stating that the binder confinement influences the chemical kinetics of the explosion,[22] also suggests that heating slows or terminates upon interfacial melting of the crystal, indicative of a frictional mechanism.

Recrystallized β-HMX decomposed in as quickly as 2.80 s without any visible binder delamination, which is indicative of viscoelastic heating forming a hot spot in the binder next to the crystal possibly near sharp corners. This was contrasted by the rounded recrystallized β-HMX samples in which no events were recorded, highlighting the significance of surface morphology on initiating binder delamination and possibly influencing viscoelastic heat generation and localization. Correlations could be made between the less sensitive rounded low porosity HMX presented here and reduced sensitivity RDX (RS-RDX) seen to be less sensitive to shock stimuli in cast PBX configurations. RS-RDX has similar rounded characteristics, as shown in SEM images, although Lochert *et al.*[30] indicate that there remains to be an analytical technique to identify and classify RDX as insensitive other than measuring the shock sensitivity of cast PBXs or examining how reduced shock sensitivity translates to other reduced sensitivity benefits.[31]

The results presented herein indicate that formulations that address the initiation sensitivity of PBXs to contact ultrasonic insult by increasing binder adhesion to mitigate heating may only address one of the available pathways of energy dissipation. Additionally, the counterintuitive results that rough morphology creates nucleation points for delamination rather than helping with adhesion, and that the low-defect recrystallized β-HMX could react even without visible delamination, indicate that crystal and binder selection should be a concurrent design decision. Rounded recrystallized β-HMX appears to be largely insensitive to initiation for these ultrasonic excitation conditions and times. It is important to note that frictional heating at interfaces will remain an important mechanism of heat generation in higher solid loaded systems. A single crystal study was deemed to be a necessary step before proceeding to structures with layers of crystals, which will be more directly correlated to the PBX behavior. Future work will focus on identifying the location of initial ultrasonically initiated delamination with respect to transducer orientation and exploring other energetic crystals having different melting temperatures, decomposition temperatures, and morphologies.

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