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The Effect of Hardness on Polymer-Bonded Pentaerythritol Tetranitrate (PETN) Explosive Impact Sensitivity

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ABSTRACT.

Handling sensitivity is an important property to assess when working with explosive samples, and can be measured using a variety of tests, including drop-weight impact sensitivity. There exists a longstanding interest in the explosives community on the importance of measurable chemical, physical, and mechanical properties of explosives in impact sensitivity. However, most recent work in this area has explored chemical attributes rather than physical and mechanical properties of explosives. In this study, we measure hardness of explosive samples of pentaerythritol tetranitrate (PETN) and Sylgard binder (XTX) during the curing process. The samples have been characterized for particle morphology through scanning electron microscopy (SEM) and handling sensitivity through drop-weight impact testing. The relative importance of states of cure, methods of curing, morphology, and age of material are discussed. The data indicate that although there is a notable difference in morphology and mechanical properties for the samples as the polymer-bonded mixtures cure, the resulting changes to mechanical properties have a minimal effect on the sensitivity of the XTX.

1. Introduction

The sensitivity of an explosive, which describes how prone it is to react in response to various input stimuli, largely determines the handling safety of explosive materials. Sensitivity is typically characterized for individual explosives by a suite of systematic tests; one such method of determining handling sensitivity is the drop-weight impact test[1–8], which has seen ubiquitous use amongst the explosives community over the past 60 years[2,5,7,9–15].

In a drop-weight impact test, a standard mass is dropped onto an explosive sample from varying heights, and in each trial, an audible reaction is recorded as a "go" and the absence of reaction is recorded as a "no-go". The series of go/no-go measurements for a variety of heights undergo a statistical analysis to determine the height at which the material is expected to have a 50% probability of reaction, reported as DH_{50}. A lower DH_{50} corresponds to a more sensitive explosive, and a higher DH_{50} corresponds to a less sensitive explosive. For example, the common initiating explosive pentaerythritol tetranitrate (PETN), which is used in commercial detonators, has a measured drop-weight impact sensitivity of approximately 12 ± 4 cm[7]. The DH_{50} reported can vary significantly depending upon the mass of the drop-weight used, the amount of explosive material used, and whether or not the sample was placed on grit paper[7]. When these factors are standardized, there can still be notable variation in the results that depend on the test operators, the apparatus, the state of wear of the equipment, the statistical analysis methods, and the method and thresholds for determining a go versus a no-go[3,4].

Extensive work has been conducted to determine if impact sensitivity correlates with measurable properties of explosive materials, including chemical, thermal, and mechanical properties[16–31]. Recent work by Wickham et al.[25] investigated mechanical properties on several explosive formulations; however, the explosive composite chemistry also varied in that study, making it difficult to unambiguously assign a relationship between mechanical properties and impact sensitivity. Hardness is a mechanical property that is easily and repeatably measured in solid materials, and can generally be easily measured on explosive materials without risk of reaction[32–35]. For these reasons, hardness is a convenient property to examine with respect to potential correlations with sensitivity and DH_{50}. In addition, cast-cure explosives are available in which hardness varies systematically depending on the state of cure. The examination of a single cast-cured explosive sample during the curing process also minimizes variations in composition, particle size, and sample preparation, in order to isolate for specific effects. One such material is the extrudable cast-cure explosive XTX 8003[29,36], a composite PBX (plastic-bonded explosive) made of 80% PETN and 20% Sylgard 182, an inert binder. XTX 8003 is most typically used in special applications that require explosives with small detonation failure diameters, as well as use in the LANL "Minimum Priming Charge" test. The uncured form of the material is a soft and malleable paste. It is kept in cold storage to prevent curing, and once brought to room temperature XTX 8003 will cure over a period of several days, hardening and losing all malleability. Impact sensitivity values were reported in the 1970's for cured and uncured samples of XTX 8003, with some changes in DH_{50}, with no further investigation on material properties or test details[37].

In this study, we measured drop-weight impact sensitivity and shore "A" durometer hardness of XTX 8003 at various states of cure in order to determine whether the hardness of cast-cure PBXs would influence drop-weight sensitivity values. We characterized the morphology of the materials using scanning electron microscopy (SEM). The relative importance of states of cure, methods of curing, morphology, and age of material are all discussed. By measuring material hardness, particle morphology, and impact sensitivity during the cure process with a single binder system, this study is unique in that it directly probes the importance of an explosive material's mechanical properties *without* inadvertently varying chemical properties. This is a critically important area of study, as it allows us to determine which material and morphology characteristics must be tuned in order to systematically adjust the safety of explosives.

2. Experimental

2.1 Sample preparation.

Two batches of XTX 8003 were used in this study, one produced on December 20, 2018 (XTX-1) and the other produced on March 15, 2021 (XTX-2). SEM imaging of the PETN powder used in each mix indicated that the particle size was generally < 20 µm, with a range of sizes spanning from < 1 µm – ~20 µm, including both spherical and longer rod-shaped particles. Measurements of specific surface area for each batch averaged to 4,100 ± 100 cm^2/g used in XTX-1 and 5,800 ± 200 cm^2/g used in XTX-2. To produce a 1 kg batch of XTX-8003, 200 g of Sylgard 182 (Dow Corning) A:B was mixed at a 10:1 ratio as a binder-only mixture. Within 5-10 minutes of mixing the Sylgard binder, 800 g of PETN was added to the

binder in a dual planetary remote mixer in order to wet the PETN with the Sylgard. Once wetted, the material had a wet sand consistency, and was then put through a roll mill 25 times in order to develop a paste-like consistency. This paste-like material was the final uncured product, and was stored at a temperature of -55˚C, allowing a usable lifetime of more than 6 months.

For the heat-cured samples, XTX-1 was held at a constant temperature of 60°C on a hot plate for approximately 72 hours (3 days) and XTX-2 held at a constant temperature of 60°C in an oven for approximately 168 hours (7 days). Ambient-cured samples were held at room temperature in a desiccator for approximately 500-550 hours (21-23 days). A second sample from 2018 was also included, XTX-1R, which underwent a long and slow ambient cure followed by a heated cure. Samples were characterized before testing using SEM imaging following standard methods, with a thin coating of conductive material deposited onto the surface to avoid charging. Each of the tests (SEM, hardness, and impact) used different samples from a given batch because hardness and impact testing were destructive and so could not be performed on the same sample. However, the large number of samples tested gives confidence in the similarity of samples taken from a given batch.

2.2 Hardness testing.

Hardness testing was performed using a Type A Shore Hardness Durometer on cylindrical XTX 8003 samples approximately 30mm in diameter and 7mm thick. All testing followed ASTM standard procedures[38]. Hardness testing was done on each sample at the uncured state and cured state. Ambient-cured samples were also tested at intermediate cure states. Hardness tests on all samples were repeated approximately 10 times.

2.3 Drop-weight impact testing

Impact testing was performed on an ERL Type 12 apparatus with a 2.5 kg drop weight and 0.8 kg striker[7]. For each drop, a 40±2mg sample on 150 grit paper was placed on the anvil with the striker resting on top of the sample, and the drop weight was dropped onto the striker from various heights. A go/no-go was determined by measuring sound level produced, measured by two microphones positioned within approximately 150 cm of the apparatus. An average sound level of 117 dB or above between the two microphones is considered a “go”, and any sound level averaging below 117 dB is considered a “no-go”. 15 drops were done for each set of conditions and results were analyzed using the Neyer *D*-optimal method. Results are reported as DH_{50}, the height at which the material is expected to “go” 50% of the time.

3. Results and Discussion

3.1. Sample morphology evolution with curing

Each of the XTX 8003 hardness samples were imaged with SEM at each of the three states of cure, as shown in Figure 1: uncured, heat-cured, and ambient-cured. There were noticeable changes in morphology between the samples. As the material cured, porosity seemed to increase and the facets of the PETN crystals became more pronounced.

The differences in morphology observed with SEM were most likely due to structural changes in the composite which occurred during binder curing. The polymer binder in XTX 8003, Sylgard 182, is a two-part system that cures into a flexible elastomer. After the roll milling formulation procedure, according to Gibbs and Popolato, XTX 8003 has a shelf life of 24 h at 25°C and storage at -30°C increases the shelf life to 8 months[36]. Traditionally, curing or polymerization is achieved by exposure to 65°C for 8-12 hours. Figure 2 depicts these two components as well as the chemical composition of the resulting cured elastomer[39,40], with SEM images of how the morphology of XTX-2 changed as a result of this reaction; however, as shown in Figure 1, both the pre- and post-cure appearance can be highly variable.

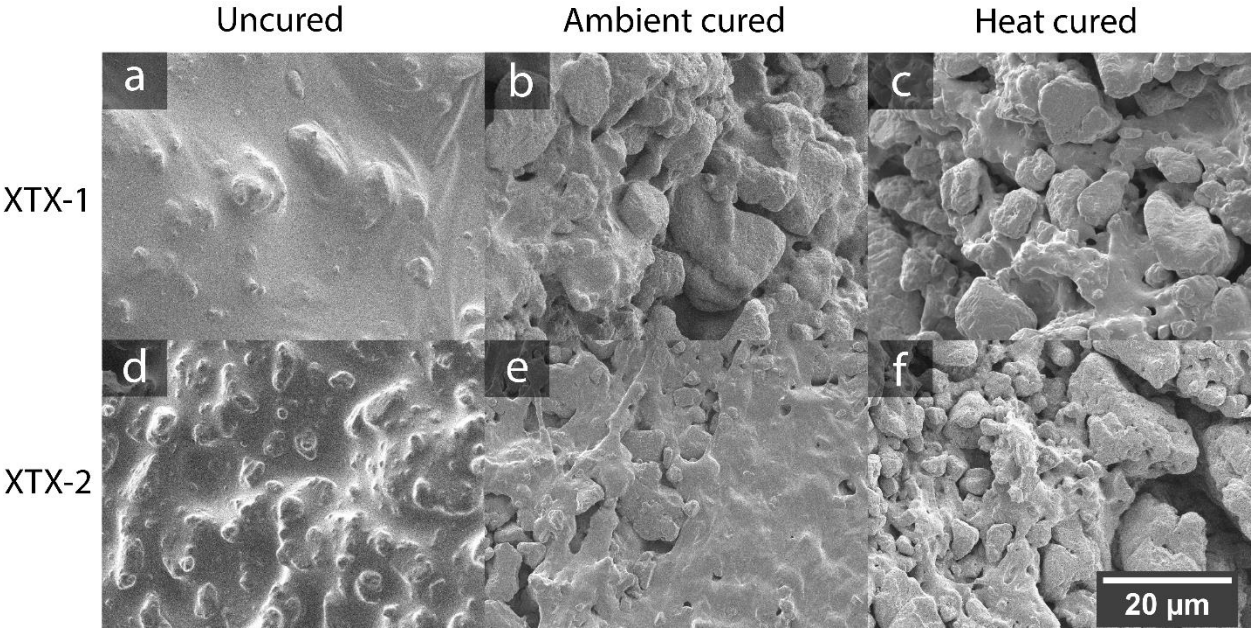

Figure 1: *SEM images of each XTX 8003 sample in the state at which impact and hardness testing were performed: (a) XTX-1 uncured, (b) XTX-1 ambient cured, (c) XTX-1 heat cured, (d) XTX-2 uncured, (e) XTX-2 ambient cured, and (f) XTX-2 heat cured.*

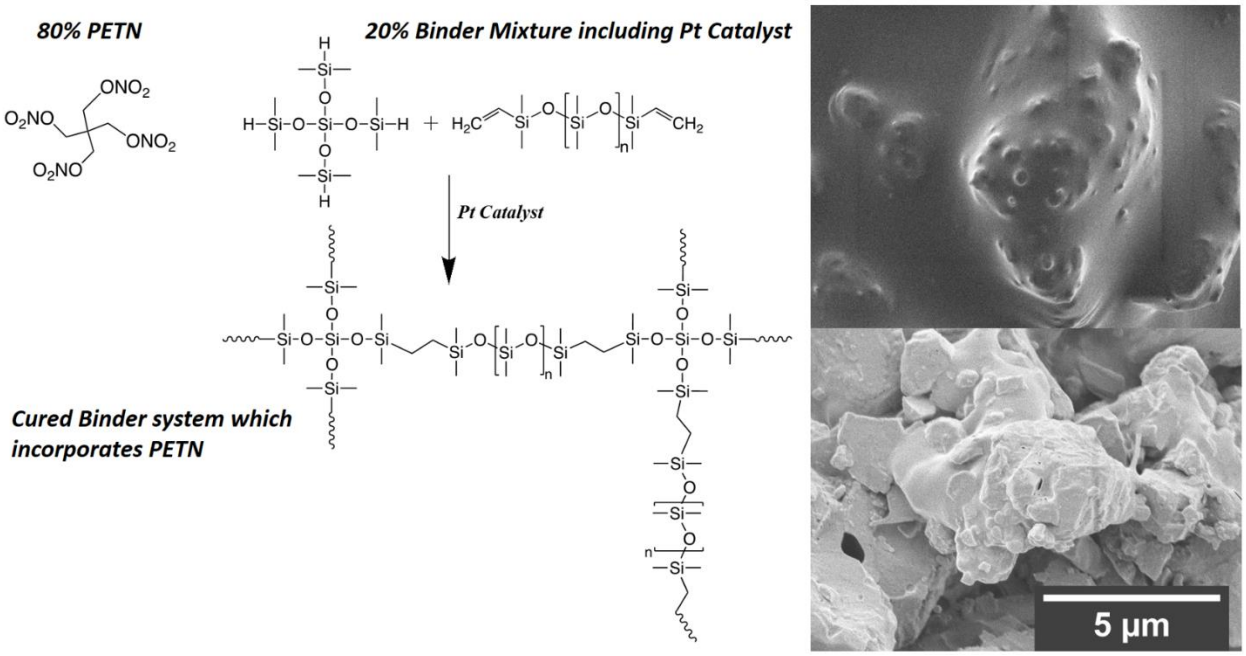

Figure 2: *Molecular structures of PETN and Sylgard uncured (top) and cured (bottom) with SEM images of the corresponding morphology in XTX-2.*

3.2. Hardness Testing

Figure 3 shows the results of Shore A testing vs. the curing time of the tested sample. A rapid increase in hardness was observed over approximately the first seven days of curing for both ambient- and heat-cured, after which point hardness does increase nominally for ambient-cured samples but at a much more gradual rate. Heat-cured samples reached a fully cured state after 5-7 days, and ambient-cured samples appear stable after approximately 15 days. The average hardness value for XTX-1 was 68.2, and the average hardness value for XTX-2 was 75.0. The lower hardness measurements for the older samples were consistent across all samples and all states of cure.

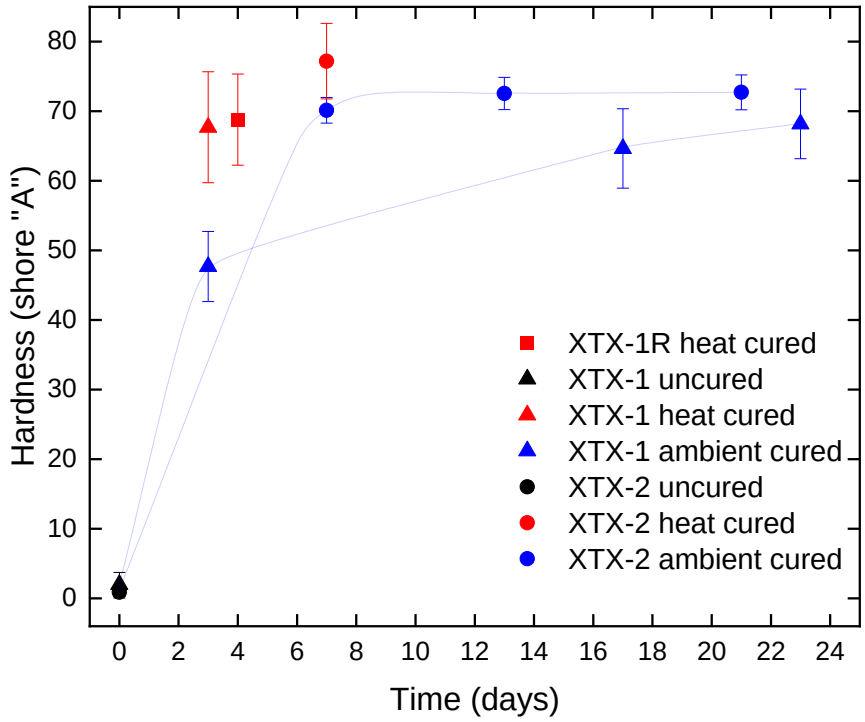

Figure 3: *Hardness of XTX 8003 samples as a function of cure time. Lines indicating change over time of ambient cured samples are qualitative and intended to guide the eye.*

3.3. Drop-Weight Impact Testing

Figure 4 shows the drop-weight impact test results for the samples as a function of cure time. Unlike the hardness results, the DH_{50} results do not show dramatic changes over time. The initial uncured results do appear to be slightly lower, meaning that they are slightly more sensitive. The difference between ~24 cm for the uncured and ~27 cm for the cured is close to the standard deviation of ~2 cm, and it is unlikely that this small difference is statistically significant[7]. Recall that the DH_{50} value is a statistical average, and the maximum scatter is naturally greater than the standard deviation. In other words, at least a few uncured samples showed higher sensitivity than at least a few cured samples. Similarly, Dobratz reported DH_{50} measurements of uncured and cured XTX 8003[37] with respective DH_{50} values of 21 and 25 cm using a 5kg drop weight and type 12 tooling (which uses grit paper). Overall the small change in impact sensitivity is relatively surprising when considering the large structural and porosity changes apparent in the SEM imaging.

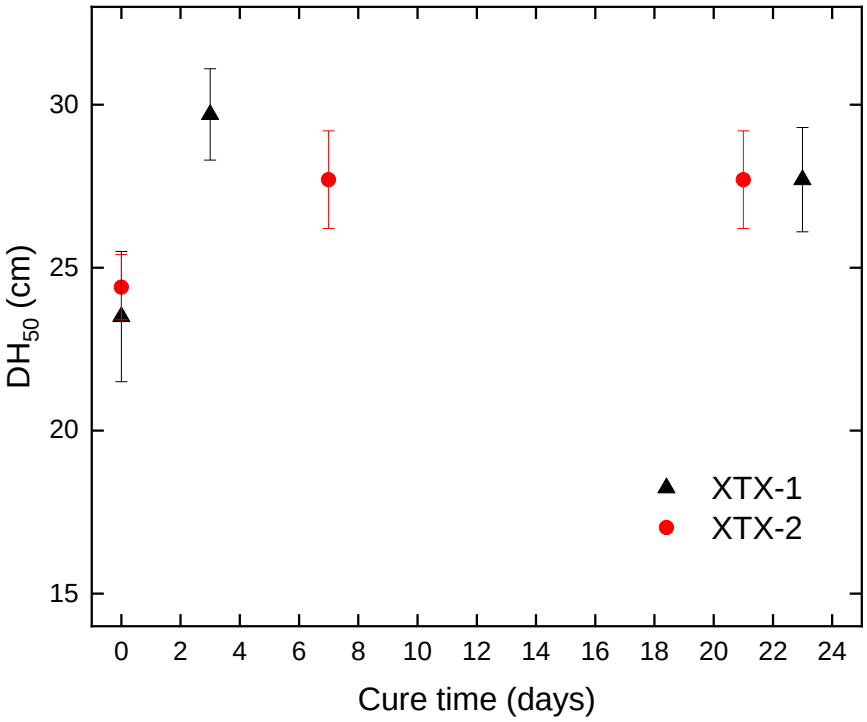

Figure 4: *Drop-weight impact sensitivity of XTX 8003 samples as a function of cure time.*

3.4. Relating Impact Test Results to Hardness and Morphology

Figure 5 plots the drop-weight impact sensitivity as a function of hardness. Because the hardness changed dramatically during curing (as expected), clear distinctions or groupings can be seen between cured and uncured material. As indicated earlier, the hardness clearly changes with cure time while the sensitivity only changes slightly. Table 1 lists the full data for hardness and impact test values.

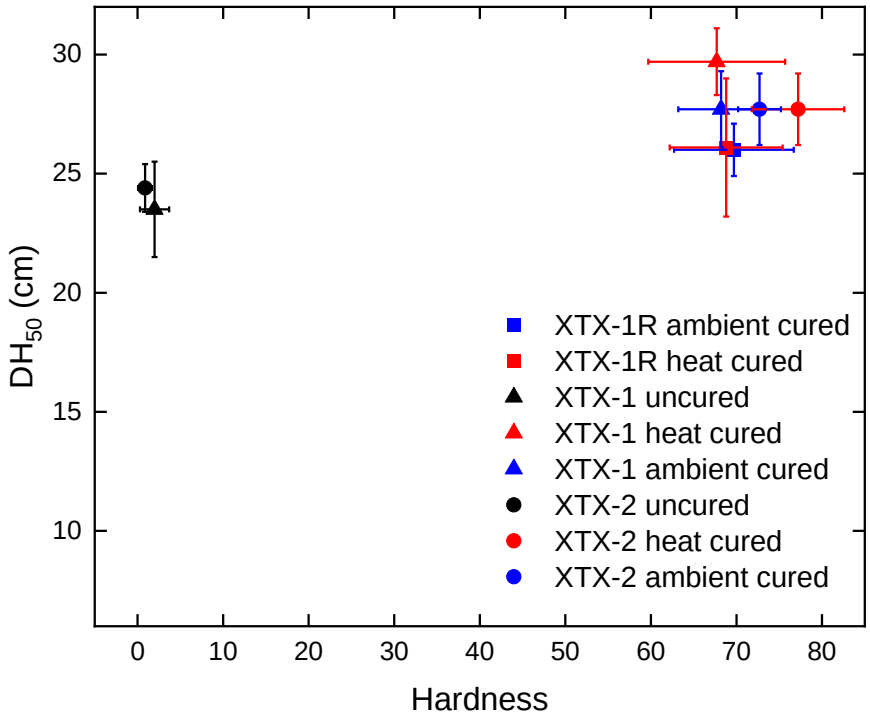

Figure 5: *Drop-weight impact sensitivity of XTX 8003 as a function of hardness.*

Table 1: *Hardness and impact sensitivity of XTX-1R, XTX-1, and XTX-2*

Sample	*Shore "A" Hardness*	*DH_{50}*
XTX-1R heat cured	68.8	26.1
XTX-1R ambient cured	69.7	25.9
XTX-1 uncured	2	23.5
XTX-1 heat cured	67.7	29.7
XTX-1 ambient cured 3 days	47.7	-
XTX-1 ambient cured 17 days	64.7	-
XTX-1 ambient cured 23 days	68.2	27.7
XTX-2 uncured	0.9	24.4
XTX-2 heat cured	77.2	27.7
XTX-2 ambient cured 7 days	70.1	-
XTX-2 ambient cured 13 days	72.6	-
XTX-2 ambient cured 21 days	72.7	27.7

In sum, the XTX 8003 samples exhibited clear trends of increasing hardness and porosity as a function of cure time, but there was little to no corresponding increase in impact sensitivity. A recent study by Wickham et al[25] measured impact sensitivity of 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX)-based cast-cure explosives with the goal of varying elastic modulus and the work of adhesion of HMX using various

binder systems. Their results indicated that the work of adhesion did not correlate with impact sensitivity for that system of materials, however the elastic modulus somewhat correlated with the impact sensitivity. Hardness, measured here, is a measure of resistance to *plastic* deformation, whereas elastic modulus is a measure of resistance to *elastic* deformation. Overall, materials with relatively higher stiffness tend to also have higher hardness, so based on the conclusions of that work we would have expected to see a significant increase in DH_{50} with increasing hardness. However, most of the observed DH_{50} values fell between 17 and 23 J, within 30% of each other. In general, we believe that it is difficult to draw strong conclusions from small changes in DH_{50}, as the standard deviations of these measurements are often fairly large. For example, we recently discovered that the variability of PETN impact test values approaches a multiplicative factor of 1.5[7]. Additionally, Wickham et al studied different binder systems, which necessarily had unique chemistry properties. Here, we attempted to keep chemical properties as consistent as possible (using the same explosive and binder chemical substituents) in order to better isolate the relationship between hardness material properties and handling sensitivity. In this system, although we observed significant changes in both particle morphology and hardness after curing, these differences did not influence the drop weight impact sensitivity outside of our measured standard deviations. It is possible that a different explosive or binder system could exhibit a correlation between handling sensitivity and material properties, however, we have yet to successfully find a connection between particle morphology and impact test results with recent testing in our labs on erythritol tetranitrate (ETN)[31], HMX[2], and 2,4,6-trinitrotoluene (TNT)[27].

While it is well known that the shock sensitivity of explosives depends sensitively on porosity and the shape and quality of the energetic grains[5,41], the evidence for the hot spot ignition of explosives via void collapse in drop weight testing is much less convincing. For instance, Rae and Dickson[6] highlight that the results of drop weight impact tests are fairly insensitive to initial particle size and shape because the samples are heavily deformed by the impact prior to ignition. In addition, the transparent anvil experiments of Field et al[42] showed that ignition tends to occur after the samples have melted and in the fast radial flow of material between the striker and anvil. Finally, our use of the Type 12 tool, which uses fine grit paper on the anvil, includes the additional ignition source associated with friction between high melting temperature grit particle and the steel anvil and striker[43]. The weak dependence of DH_{50} on both hardness and sample porosity seen in this study is therefore fully consistent with our current understanding of the ignition and propagation of reactions in drop weight impact tests.

Conclusions

In this study we sought to determine how explosive handling sensitivity varies with systematically-tuned mechanical hardness properties. Using an explosive composite with one consistent binder system, we were able to specifically evaluate the relationship between drop-weight impact sensitivity and hardness in XTX 8003.

There is a notable difference in XTX 8003 appearance and texture depending on the level of the curing process, and this visible difference in SEM imaging is not necessarily consistent between samples – the ambient cured XTX-2 appears visibly different from the heat cured XTX-2 as well as from the ambient cured XTX- 1. Generally, ambient-cured samples retain more of the smoothness of texture that the

uncured samples possess, whereas heat-cured samples appear more granular. We expected that the samples with additional porosity would be more sensitive to impacts owing to the well-known role of the adiabatic collapse of small gas spaces on the ignition of explosives[44–46]. However, none of the apparent changes in morphology correlated with any changes in handling sensitivity.

Hardness measurements stabilized, indicating complete curing, after approximately one week for heat-cured samples and after approximately two weeks for ambient-cured samples. Uncured samples did not have a measurable hardness value (<2), and fully cured samples had an average shore "A" hardness value ranging from 68-77. The average hardness value for XTX- 1 was 68.2, and for XTX- 2 was 75.0.

Impact sensitivity did not vary significantly with hardness or time, which match well with historical data reported in Gibbs and Popalato[36]. The small range of values (26.5 ± 3 cm) are well within the ~50% standard deviation expected from impact tests, as demonstrated by Marrs et al[7]. ***When composite chemistry is held constant, we observe that the level of cure, method of curing, and resultant changes in morphology and mechanical properties all have minimal effect on impact sensitivity.***

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Conflict of Interest Statement.

The authors claim no conflict of interest.

AIP Publishing Data Sharing Policy.

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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