Article

High-Fidelity Mock Development for the Insensitive High Explosive TATB

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Abstract: Due to the violent reaction potential of high explosives, in tests where a reaction is not desired, it can be safe and convenient to use an inert mock that can mimic relevant properties of the associated explosive. Use of mock materials is well-established in explosives work, but most existing mocks are generally meant to mimic only one or two properties of a given explosive, potentially failing to match the explosive in other critical ways. Recently, there has been interest in developing robust thermomechanical mocks for many common explosives. Here, eleven materials are systematically chosen and investigated as potential thermomechanical mocks for TATB, the explosive component of PBX 9502. DSC, nanoindentation, and compression testing are used to narrow down to most appropriate mocks and identify their advantages and limitations. Hardness and elastic modulus are reported for the first time for the molecular crystals iodoanthranilic acid, hexamine, melamine, and trithiolane dioxide, and the crystal structure is reported for the first time for the molecular crystals iodoanthranilic acid and iodosalicylic acid.

Keywords: nanoindentation; explosive; mock

Citation: Burch, A.C.; Herman, M.J.; Woznick, C.S.; Nguyen, T.-A.D.; Scott, B.L.; Yeager, J.D. High-Fidelity Mock Development for the Insensitive High Explosive TATB. *Crystals* **2022**, *12*, 192. <https://doi.org/10.3390/cryst12020192>

Academic Editors: Jesús Sanmartín-Matalobos and Dinadayalane Tandabany

Received: 20 December 2021

Accepted: 26 January 2022

Published: 28 January 2022

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1. Introduction

2,4,6-triamino-1,3,5-trinitrobenzene (TATB) is an explosive aromatic organic molecule that is the majority component of Insensitive High Explosive (IHE) formulations [1,2]. Crystalline TATB (90–95%) is formulated with between 5 and 10% fluoridated polymer binder system, commonly Kel-F 800, to create a Plastic-bonded Explosive (PBX) whose primary benefits are increased resistance to insults such as shock, vibration, fire, and impact when compared to traditional 1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (HMX) or 1,3,5-Trinitro-1,3,5-triazinane (RDX) based PBXs [3]. While TATB-based IHEs are considered to be less vulnerable to insult than traditional explosive composite systems, IHEs still necessitate the same level of precaution during handling and characterization in some scenarios, resulting in higher experimental costs and throughput limitations. A practical solution that has been employed is to replace the explosive crystal with a surrogate or “mock” material in cases where explosive initiation are not required. These mock systems are generally used in calibration, new procedure development, and new experimental design before the introduction of live HE [4–6]. Historical mock materials for TATB-based composites, such as 900-19 and 900-24, were not intended for general experimental substitution, as they both require a talc filler to reach target density [7,8]. These mock materials were designed to capture one aspect of the HE material well, in this case density, but they do not represent the complete thermomechanical behavior of the live PBX, which prevents one-to-one replacement in critical testing situations [9]. In order to develop a new TATB mock composite, an inert organic crystal substitute with single crystalline properties,

such as elastic modulus, hardness, mechanical strength, and density similar to TATB ($\rho = 1.93 \text{ g/cm}^3$), must be identified.

Mock materials for TATB have been limited historically, and have been blends of materials intended to reproduce only the density of the PBX 9502 composite. Mechanical testing have been performed on mock 900-24, but as it was intended as only a density mock and is a blend of Cyanuric Acid and talc, the performance was found to be less than acceptable as a mechanical mock [10,11]. General thermomechanical mocks for other HE materials often use the same binder as the target PBX while substituting a single inert material for the HE crystal [9]. These type of high fidelity mock materials will replicate the most important physical parameters of an explosive, such as density, while approximating as many other thermal and mechanical properties of the parent PBX as possible. Our methodology of identifying new potential mock crystals has been detailed in a previous publication where HMX was the target, and we will employ similar methodology here for TATB [12]. Literature methods for selecting mock candidate materials fall into two general themes: (1) select an organic molecular crystal with similar chemical structure to the HE of interest [13–15]; or (2) identify inert materials which mimic a specific property of interest, and then select a candidate that most closely matches other secondary properties of interest [6,8,16]. Properties that we are specifically interested in for a TATB mock candidate are density, melting point, elastic modulus, and hardness.

Density and thermal properties of organic molecular crystals are commonly reported in the literature, making selection of a mock candidate on these two properties relatively easy. However, the mechanical properties of the crystals, along with the ease of dissolution/crystallization to specific particle ranges of interest, are infrequently reported for molecular crystals and necessitate investigation for mock candidate consideration. Nanoindentation is a powerful tool to determine the mechanical properties when attempting to quickly identify new mock candidates. The accuracy, repeatability, and small sample quantity need for nanoindentation make it an ideal test for HE crystalline materials, where the explosive hazard is directly correlated to the amount of sample being tested or handled during an operation. Nanoindentation has been previously used to determine the mechanical properties of many explosive crystals such as HMX, RDX, TATB, pentaerythritol tetranitrate (PETN), and others [12,17–21]. In addition to a candidate material's mechanical properties, the crystals must be able to be grown to a specific size range to best allow for mimicking the PBX microstructure in a mock composite system. Crystals with low solubility in common solvents, or that cannot be easily crystallized to a given size range ($>300 \text{ }\mu\text{m}$), are non-ideal as mock candidates. Additionally, the crystal must be able to later be processed by grinding and sieving in order to create the sieve cuts needed to mimic the particle size distribution of the PBX [22]. Crystal size and distribution play a critical role in the final pressed density, and mechanical performance of a mock HE composites [23–26].

In this work, eleven candidate materials, identified from Cambridge Structural Database (CSD) queries and literature searching, were subjected to crystal growth screening, thermal analysis, and mechanical testing [27]. 6-amino-2,4-dihydroxy-1,3,5-triazine (ammelide), 4,6-diamino-2-hydroxy-1,3,5-triazine (ammelene), 4-amino-1,2,5-oxadiazole-3-carboxylic acid (AOCA), 4-bromobenzoic acid (BBA), bis(trifluoroacetamido)pyridine (BTFAP), hexamethylenetetramine (hexamine), 5-iodoanthranilic acid (IAA), 5-iodosalicylic acid (ISA), 1,3,5-triazine-2,4,6-triamine (melamine), 2,6-bis(pentafluoropropanamide)pyridine (PFPAP) and trans-1,2,4-trithiolane-1,4-dioxide (TTDO) were all considered as candidate TATB mock crystals. All materials were received as powders, so when possible, crystals were grown from appropriate solvents to allow for nanoindentation. Indentable crystals were achieved with TTDO, Melamine, Hexamine, and Iodoanthranilic acid. These materials were further down selected through the mechanical comparison of crystalline hardness and elastic modulus, determined by nanoindentation, to the physical properties of TATB. Thermal properties (i.e., melting point) were determined by Differential Scanning Calorimetry (DSC) and were used to identify a candidate material with similar thermal behavior to TATB. These screening mechanical and thermal experiments allowed for the selection of one can-

didate mock material, Iodoanthranilic Acid, which was then formulation with the PBX 9502 binder polymer, Kel-F 800. Uniaxial compression testing was used to determine the mock composite's mechanical performance and our new mock material is compared with historic PBX 9502 mock performance data. Quantitative and qualitative comparison between the new Iodoanthranilic Acid mock to PBX 9502 are given and the impact and limitations of this new mock system is discussed.

2. Materials and Methods

2.1. Materials

6-amino-2,4-dihydroxy-1,3,5-triazine (ammelide), 4,6-diamino-2-hydroxy-1,3,5-triazine (ammeline), 4-amino-1,2,5-oxadiazole-3-carboxylic acid (AOCA), 4-bromobenzoic acid (BBA), hexamethylenetetramine (hexamine), 5-iodoanthranilic acid (IAA), 5-iodosalicylic acid (ISA), and 1,3,5-triazine-2,4,6-triamine (melamine) were purchased commercially and used without further purification.

Bis(trifluoroacetamido)pyridine (BTFAP), trans-1,2,4-trithiolane-1,4-dioxide (TTDO), and 2,6-bis(pentafluoropropanamide)pyridine (PFPA) were synthesized at LANL. 1,2,4-trithiolane was prepared according to the previously reported procedure [28]. NMR spectral data for this compound were consistent with those reported in the literature. BTFAP was prepared according to the previously reported procedure [29]. NMR spectral data for this compound were consistent with those reported in the literature.

2.1.1. TTDO Synthesis

TTDO was prepared from 1,2,4-trithiolane (4.710 g, 37.91 mmol) by oxidation with 70–75% balance mCPBA and H₂O (18.856 g) according to the previously reported procedure to yield a crude product (10.7 g white powder), containing TTDO, the benzoic acid by-product, and other minor impurities [30]. The literature procedure did not describe the recrystallization method by which their material was purified. Our material was purified by recrystallization from a methanol solution. The crude white powder was dissolved by heating with stirring in methanol (600 mL). This solution was filtered while hot and allowed to evaporate slowly at room temperature for 5 d in a filter flask covered with a Kimwipe. Upon which, TTDO formed as a colorless crystalline solid along with a small amount of powder. The supernatant and powder were decanted from the TTDO and the product was washed with ethyl acetate. This material was air dried to provide TTDO as a white solid (1.84 g, 31% yield). Block crystals with a flat surface for nanoindentation were grown by slow evaporation over 50 d of a solution of TTDO prepared by heating TTDO with stirring in a mixture of primarily methanol and diethyl ether, with smaller volumes of ethyl acetate, ethanol and acetone until dissolved and subsequent filtration while hot. NMR spectral data for this compound were consistent with those reported in the literature. This synthesis is depicted in Figure 1.

Figure 1. Two step synthesis of TTDO.

2.1.2. PFPA Synthesis

Ethyl acetate (50 mL) was added to a flask charged with 2,6-diaminopyridine (2.007 g, 18.39 mmol) and stirred to form a brown slurry. Pentafluoropropionic anhydride (4.7 mL, 55 mmol) was added to the brown slurry, upon which the reaction became a clear brown solution. This mixture was refluxed for 4 h and then allowed to cool to room temperature. The excess pentafluoropropionic anhydride was quenched with a saturated sodium carbonate solution (30 mL), warming the solution and bubbling vigorously. The reaction was then transferred to a separatory funnel and shaken and allowed to separate. The organic

layer was brown and the aqueous layer was light yellow. The organic layer was collected and dried with anhydrous magnesium sulfate, filtered and the solvent was removed to yield a crude brown product. This crude material was purified by column chromatography on silica gel using 30% ethyl acetate in hexanes as eluent to isolate an off white powder that formed needles from slow evaporation of a concentrated chloroform solution (2.2 g, 30% yield). TLC (30% ethyl acetate in hexane): $R_f = 0.67$. NMR spectral data for this compound were consistent with those previously reported in the literature [31]. This synthesis is depicted in Figure 2.

Figure 2. Synthesis of PFPAP.

2.2. Characterization and Processing Methods

NMR spectra for TTDO and PFPAP were recorded on a Bruker Avance 400 MHz spectrometer at ambient temperature. Chemical shifts were referenced to the residual solvent signal.

Melting point and thermal decomposition temperatures were measured by DSC (TA Instruments Q2000 DSC) in hermetically sealed aluminum pans that contain a pinhole lid. A typical analysis utilizes approximately 1 mg of sample with 50 mL/min ultrahigh purity nitrogen purge gas at a thermal ramp rate of 10 °C/min. Each sample was run from 40 to 400 °C.

All commercially purchased materials were received as powders, so when possible, crystals were grown from appropriate solvents to allow for nanoindentation. Indentable crystals were achieved with three commercially purchased materials and one locally synthesized material: hexamine, IAA, melamine, and TTDO. Figure 3 shows optical images of the indentation surfaces of these four materials, and Figure 4 shows the molecular structure of each material.

Single crystal X-ray diffraction data were collected on IAA and ISA using a Bruker microsource ($\text{MoK}\alpha = 0.71073 \text{ \AA}$) and Photon II detector. Data on ISA were collected at 100 °C using an Oxford 800 cryostream. Data on IAA were collected at room temperature due to a first order phase transition between room temperature and 100 °C. Structure solution, refinement, and creation of publication materials were performed using the SHELXTL software suite [32].

Figure 3. Optical images of: (a) Hexamine (b) IAA (c) Melamine (d) TTDO.

Figure 4. Molecular structures of: (a) Hexamine (b) IAA (c) Melamine (d) TTDO.

Single-crystal nanoindentation samples were mounted using the technique described by Maughan et al [33], in which crystals resting on a level surface are adhered to a 7 mm steel disc from above such that when inverted, a level face of the crystal is upright for indentation. Nanoindentation was performed using a Hysitron Triboindenter 950 with a Berkovich indenter probe. Loading profiles were quasi-static open loop with 30 s loading, 5 s hold, and 5 s unloading, chosen to resemble prior indentation studies [12,17,19], with peak loads chosen for each material so as to not exceed an indentation depth of 250 nm; this peak load was 300 μN for hexamine, 500 μN for IAA, 1000 μN for melamine, and 1000 μN for TTDO. To determine hardness and elastic modulus, the Oliver and Pharr method [34] was used, for which 7 indents were performed on hexamine, 8 on IAA, 10 on melamine, and 5 on TTDO.

IAA was chosen to formulate with a polymer binder for bulk composite mechanical testing. IAA was sieved to achieve a particle size distribution of 45–75 μm , chosen to resemble particle size distributions from the literature [35,36]. This IAA was formulated with Kel-F 800 binder with 95% IAA and 5% binder, as a one-to-one mock replacement for TATB in PBX 9502. This plastic-bonded IAA composite is called “Mock IAA”, as opposed to the pure crystalline material “IAA”. This Mock IAA was die-pressed into right cylindrical cylinders with a height of 19.1 mm and a diameter of 12.7 mm, and a target pressing density of 1.88 g/cm^3 . These pellets were used for quasi-static compression testing, which was done on an MTS Criterion C45.504E load frame with Bemco, Inc. environmental chamber. Strain was measured using two oppositely-mounted knife-edge extensometers, Instron model 2620-826. All tests were performed in crosshead control at speeds adjusted for the length of the specimen to achieve a near equivalent strain rate of 0.00222 s^{-1} , and all tests were performed at 50 $^{\circ}\text{C}$.

3. Results

3.1. Material Selection

The methodology used here to generate a list of mock candidates and choose a selection of those materials for further testing has previously been reported for HMX and PETN [9,12]. Eleven materials were initially chosen as potential mock candidates for TATB: ammelide, ammeline, AOCA, BBA, BTFAP, hexamine, IAA, ISA, melaine, PFPAP, and TTDO. Analytical testing and crystallization/nanoindentation in many cases occurred concurrently, so failing one metric did not preclude it from being included in the other. Physical property values used for this initial selection are listed in Table 1.

Table 1. Physical property values for TATB and each material initially under consideration as a thermomechanical TATB mock.

Material	Density (g/cm ³)	Crystal Structure
TATB	1.93	triclinic
Ammelide	1.71	
Ammeline	1.70	triclinic
AOCA	1.90	
BBA	1.88	monoclinic
BTFAP	1.82	
Hexamine	1.35	cubic
IAA	2.18	monoclinic
ISA	2.26	monoclinic
Melamine	1.57	monoclinic
PFPAP		
TTDO	1.93	monoclinic

The material that appeared most similar to TATB based on these properties was AOCA and, which was within 3% of TATB's density and had a characterized crystal structure that had the same degree of symmetry. BTFAP, IAA, ISA, melamine, and TTDO all shared a crystal structure that was of acceptably similar symmetry to TATB.

3.2. Thermal Characterization

Thermal properties as measured by DSC are listed in Table 2. A suitable thermal mock will ideally be stable up to temperatures comparable to the explosive of interest, in this case over 250 °C for TATB, but not to temperatures so high as to exceed comparability. Materials that were determined to behave acceptably similarly to TATB thermally were BBA, hexamine, and IAA.

Table 2. Thermal property values of interest for TATB and each material initially under consideration as a thermomechanical TATB mock.

Material	Melt Temperature (°C)
TATB	>250
Ammelide	390
Ammeline	417
AOCA	191
BBA	255
BTFAP	183
Hexamine	273
IAA	221
ISA	197
Melamine	365
PFPAP	114
TTDO	158

3.3. Mechanical Characterization

A prerequisite for inclusion in mechanical characterization is the ability to grow suitable crystals. Many materials that were otherwise promising, such as AOCA, did not move on to the mechanical testing stage due to poor or no crystal growth.

Representative load–depth curves for nanoindentation experiments performed on IAA, hexamine, melamine, and TTDO, are shown in Figure 5.

Figure 5. Typical load–depth curves for hexamine, IAA, melamine, TTDO, and TATB, with maximum indentation loads chosen so as to not exceed a maximum indentation depth of 250 nm. Load–depth data for TATB from data set in [17].

Average elastic modulus and hardness values for each material are listed in Table 3, along with literature values for TATB [17]. While all of these materials were higher than TATB in elastic modulus, with TATB having a notably low stiffness, IAA was the closest, and additionally was especially similar in hardness with only a 7% difference. In comparison, the next closest material was hexamine with a 54% difference in hardness.

Table 3. Hardness and elastic modulus values for TATB and each mock candidate from which suitable crystals could be grown.

Material	Elastic Modulus (GPa)	Hardness (GPa)
TATB [17]	9.6 ± 1.5	0.41 ± 0.04
Hexamine	18.0 ± 0.5	0.19 ± 0.02
IAA	16.70 ± 1.2	0.38 ± 0.05
Melamine	25.8 ± 3.1	1.34 ± 0.19
TTDO	26.2 ± 3.9	1.04 ± 0.06

Incipient plasticity of IAA, hexamine, melamine, and TTDO were studied and compared to published data on incipient plasticity of TATB [17]. Incipient plasticity, or yield, is seen on a load–depth curve as a sudden increase in indentation depth without a corresponding increase in load, a feature typically referred to as a pop-in or excursion. Deformation up to this point can be considered elastic, following the Hertzian model [37], with the pop-in denoting the onset of plastic deformation. The load at which yield occurs can be generally indicative of defect density or defect formation in the material, as materials with high defect densities or materials that form defects easily will accommodate plastic deformation more readily; when plastic deformation occurs but no pop-ins are noted on the load–depth curve, this indicates a material with sufficiently high defect density or ease of defect formation to allow for plastic deformation from the onset of loading [38–42]. Figure 6 shows representations of typical pop-ins for each mock candidate that was indented, and Figure 7 shows a cumulative distribution of load at first yield. Based upon this cumulative distribution, it can be seen that IAA accommodates plastic deformation significantly more readily than any of the other three materials, with every indent exhibiting plastic deformation almost from the onset of loading and therefore an average load at yield of 0.5 μN . Melamine and TTDO had relatively similar yield responses to one another, with average loads at yield of 48.5 μN and 47.3 μN respectively (excluding outliers), and hexamine exhibited the highest average

load at yield, 90.0 μN . Average load at yield for TATB has been measured as approximately 26 μN (calculated from a reported shear stress at yield [17]), lower than all mock candidates besides IAA.

Figure 6. Typical yield behavior for hexamine, IAA, melamine, and TTDO. Load–depth data for TATB from data set in [17].

Figure 7. Cumulative distribution of load at yield for hexamine, IAA, melamine, and TTDO.

In addition to nanoindentation, quasi-static compression testing of plastic-bonded IAA (called “Mock IAA” in the plastic-bonded form) was performed and compared to existing data on PBX 9502. Stress-strain curves for these tests are shown in Figure 8. Mock IAA was weaker and more compliant than PBX 9502, with an ultimate compressive strength of approximately 6 MPa compared to PBX 9502’s 14 MPa. This difference could be caused by a few different factors. One of these is that because the IAA crystal has a higher density than the TATB crystal but the composite parts were pressed to the same bulk density, this

resulted in the Mock IAA samples having a slightly higher porosity (about 10% higher). Another contributing factor is that these Mock IAA samples were die-pressed at a lower temperature than PBX 9502 is typically pressed at (50 °C vs. over 90 °C) which could have impacted the ability of the polymer binder to flow during pressing. A higher pressing temperature for the Mock IAA, allowing better binder flow, could improve performance. Strength of polymer composites can also vary based on strength of adhesion between the binder and the crystal, a relationship that at present is not characterized for this system of materials.

Figure 8. Stress–strain data for quasi-static compression of Mock IAA and PBX 9502.

4. Discussion

The results of these tests and selection criteria, namely density, crystal structure, DSC, nanoindentation, and compression testing, showed IAA to be the most consistently promising material as a mock for TATB in PBX 9502. IAA had a crystal structure of similar symmetry, a melting temperature within approximately 15% of TATB, and an indentation hardness within 7%, all of which are within acceptable range. While IAA had a notably higher elastic modulus than TATB, it was more similar than any other candidate, and similarly the two materials had rather different indentation yield strengths but the same could be said for all candidates, so neither of these factors detracted from IAA being the most suitable single-crystal candidate.

Upon the determination that IAA was the most suitable material to mock TATB as a single crystal, the subsequent question was whether this similarity continued in polycrystalline plastic-bonded composites. The formulation “Mock IAA” was made by substituting IAA for TATB in Kel-F 800, the PBX 9502 binder, and quasi-static compression testing was performed on the Mock IAA and compared to existing PBX 9502 results. Mock IAA did not perform as well in this test as would be desired for a high-fidelity mock, but it is expected that this performance could be improved and possibly brought within acceptable range by adjusting pressing parameters, specifically by increasing pressing temperature.

Of the other mock candidates considered here, some could be used to mock specific properties of TATB (such as AOCA for density or hexamine for thermal stability), but of the other ten mock candidates very few were successful in producing usable crystals, and those that did failed to match TATB mechanically within an acceptable range. Only IAA had acceptable levels of success in all criteria.

5. Conclusions

Of the eleven mock material candidates considered here as new high-fidelity surrogates for TATB, IAA was the most suitable. IAA was a good match for TATB in crystal structure, thermal stability, and indentation hardness. Further mechanical testing of die-

pressed plastic-bonded samples showed some difference from TATB, but it is expected that this could be improved by adjusting pressing parameters.

Author Contributions: Conceptualization, J.D.Y. and A.C.B.; synthesis, T.-A.D.N.; structural characterization, B.L.S.; mechanical characterization, A.C.B. and C.S.W.; data analysis, A.C.B., M.J.H., C.S.W. and J.D.Y.; writing, A.C.B., M.J.H., C.S.W., T.-A.D.N., B.L.S. and J.D.Y.; funding acquisition, J.D.Y. All authors have read and agreed to the published version of the manuscript.

Funding: Funding for this work was provided by the Delivery Environments Program at LANL under the direction of Antranik Siranosian. Los Alamos National Laboratory, an affirmative action equal opportunity employer, is operated by TRIAD National Security, LLC, for the National Nuclear Security Administration of the U.S. Department of Energy under Contract No. 89233218-NCNA000001.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Deposition numbers CSD 2129259 (ISA) and CSD 2129260 (IAA) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgments: The authors gratefully acknowledge David Bahr for graciously providing additional TATB data and insight. This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science.

Conflicts of Interest: The authors declare no conflict of interest.

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