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Microstructural effects of processing in the plastic-bonded explosive Composition A-3

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HIGHLIGHTS

- A model explosive composite is characterized to describe the microstructure.
- Formulation of the composite involves emulsified plastic and explosive crystals.
- Key formulation chemicals remain in the composite after drying.
- The process affects the explosive crystal surface and crystal-binder interface.
- The interface is more complex than assumed by current mesoscale models.

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ABSTRACT

Multiscale model development for composites such as plastic-bonded explosives (PBXs) is critical for assessing structural integrity and behavior and for developing new materials. For models to be successful they must reproduce bulk material responses while incorporating important microstructural features. These features arise at the mesoscale during processing, and while they have commensurate effects on composite material response they are not easily identified or characterized. Here, we study Composition A-3 as a representative PBX, chosen both for relevance to the field and as a tractable formulation to model. Composition A-3 is formulated by mixing micron-scale explosive crystals with an emulsified polyethylene solution, then breaking the emulsion to form small crystal/polyethylene agglomerates suitable for pressing and machining. Key aspects of this formulation process that may potentially affect the microstructure were identified. Specifically, the emulsification chemicals in a model system were found to partially dissolve or degrade the explosive and create a diffuse interface between the crystal and binder. The diffuse interfaces, along with some of the chemicals that remain in the composite after manufacture, create a heterogeneous multicomponent system that likely influences adhesion, void formation, and crack formation. The observed interfaces may be difficult to model. These results are compared with previous interfacial studies in other PBX materials, and the necessity of including such data in mesoscale models is discussed.

1. Introduction

1.1. Microstructure and modeling of explosive munitions

Efforts to ensure reliability of current munitions and to develop new munitions require multiscale modeling of energetic materials from formulation to application. Integration of computational methods across the size scales of scientific and engineering interest, from atomistic through micro- and meso-scale to the continuum level, is an active area of research [1]. The ultimate objective is to be able to approach energetic material design problems with less reliance on trial and error approaches and the subsequent battery of expensive and time-consuming testing protocols. Models are particularly desirable for complex explosive formulations such as plastic-bonded explosives (PBXs) and their thermal/mechanical response throughout munitions' lifecycles leading up to detonation. In order to achieve this multiscale modeling objective, the models must account for both constituent properties and effects of processing on the composite. Incorporating all microstructural features in these multi-component formulations is not tractable, so

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key features must be identified for inclusion through multiscale characterization of structure-processing-property relationships.

PBXs are polymer-matrix composites, often highly loaded (>80% by weight) with micron-sized explosive crystals. Many microstructural parameters affect sensitivity (i.e. safety) and performance through mechanical and thermal reliability or shock response and detonation. Crystal properties (e.g. size, size distribution, morphology, purity) and binder properties (e.g. elastic–plastic behavior, chemical inertness) both affect these responses. Recently, the crystal-binder interface has come under scrutiny because crack propagation often proceeds along the interface [2]. Cracking not only affects structural durability but also intentional explosive initiation [3] and thermal cycling or aging [4]. Table 1 illustrates the inherently large surface area to volume ratios associated with various energetic composites and emphasizes the importance of interfaces. The materials chosen for Table 1 contain several different high explosives (HE) and exhibit significant variation in crystal weight percent and particle size [5–8]. This table is intended to provide estimates of HE surface area in PBXs for illustration, not as a rigorous calculation (note the assumptions regarding particle size and morphology). As a first order estimate, consider that typical small-scale PBX samples have a volume of 5–10 cm^3; such a sample likely contains several m^2 of crystal/binder interfacial area.

Our recent work has demonstrated that the interfacial properties of certain PBXs control small-scale mechanical properties [9]. Parameters such as interfacial strength [10–12], surface energy [13,14], and crystal-binder intermixing [9,15] have been characterized to various extents and should be captured accurately by multiscale modeling efforts. Related issues such as density gradients or void fraction, both of which could be a function of poor crystal-binder adhesion or surface coverage, have been shown to be problematic for PBX materials [16]. It is clear that small-scale structure and formation mechanisms drastically affect large-scale properties in these materials. This is especially important when linking formulation parameters to finished product microstructure and properties.

1.2. Current approach

A complete, physics-based description of the microstructure is necessary for simulations spanning from mesoscale or grain level packing [17] to continuum micromechanics and fracture [18]. Recent efforts in the development of mesoscale models for PBX materials have incorporated features such as crystal-binder surface interactions [19], anisotropic elastic–plastic deformation of the crystal [20], and void distribution [21]. Typically, interfacial phenomena are simulated with numerical or analytical continuous zone models, but Tan et al. have shown that current PBX models fail to account for softening effects during debonding [22]. A recent numerical study found that interface debonding was a key damage mode in a generic PBX material, more so than transgranular cracking, even when the only parameters used to simulate the interface were friction, tensile strength, and cohesive strength [23]. Current mesoscale modeling efforts often incorporate experimental data that is extracted or inferred from macroscopic measurements. Values for key properties such as interfacial size, composition, and toughness are often estimated or ignored altogether. For example, a recent *ab initio* study of crystal-binder interactions used only pair potentials and ignored any possibility of crystal-binder interdiffusion or intermixing, let alone surface roughness effects [24].

Mesoscale simulations must address these limitations while remaining tractable. It is clear that the constitutive properties of the HE crystals and binder are essential but less obvious how to consider the composite. In most PBX materials, the HE crystals are the bulk constituent and so their properties are relevant. The binder is present in much lower percentages and exists as thin layers between crystal interfaces, creating large surface area to volume ratios. In this situation it is unclear whether bulk binder properties are representative of the thin layers in PBXs and if interfacial effects, such as adhesion, are more important. This question is difficult to answer because PBX formulations are complex and the interfaces and thin binder layers are non-ideal for characterization. To circumvent this problem, we have begun efforts where we make simplifying assumptions about what formulation processes are most important. We then reproduce those processes to create idealized samples that allow direct measurements of interfacial structure and resulting properties [9,25]. This allows us to make hypotheses about effects of processing on properties to probe the structure-processing-property relationships.

Here, we characterize the PBX "Composition A-3" in order to define important interfacial parameters. Composition A-3 was chosen because an abundance of large scale experimental data exists and the composition includes materials tractable for model development. Composition A-3 contains cyclotrimethylene-trinitramine (RDX) crystals coated with a low molecular weight oxidized polyethylene (OPE) wax. The RDX crystals comprise 91% of the composite by weight and have a broad but well-characterized particle size distribution with median size of 200 μm. The particle size of 140 μm quoted in Table 1 was determined by analysis of recovered munitions, indicating that the formulation and pressing processes alter the particle size. The wax is coated onto the crystals via an emulsion process. Depending on the manufacturer, the wax is emulsified in water with a combination of oil acids (primarily oleic and linoleic acids) and morpholine and/or morpholine derivatives. The RDX crystals are suspended in water and agitated with the emulsion for some time at elevated temperature (e.g. for 30–60 min at 95 °C [26]). Drying of the mixture to a formable solid can occur in several ways but usually requires removal of the liquids by adding dilute acids or applying heat in conjunction with suction [27–29]. The resulting product is a granular mixture, with each granule ("prill") consisting of RDX crystals held together with the binder. The prills can then be pressed to size and shape.

We present an investigation of Composition A-3, including the raw materials, formulated prills, and idealized samples to characterize bulk composition, surface properties, and effects of processing. We use desorption/pyrolysis–gas chromatography–mass spectrometry (D/P–GC–MS) and Fourier transform infrared (FTIR) spectroscopy to identify chemicals from the formulation process that may affect the finished composite, and surface energy measurements and neutron reflectometry to characterize the crystal-binder interface as in our previous work.

Table 1
Interfacial parameters for several example energetic materials.

Energetic material	HE/binder[a]	HE wt%	HE particle size[b] (μm)	HE surface area per composite volume[c] (1/cm)
Composition A-3	RDX/OPE Wax	91	140 [5]	343
PBX 9501	HMX/Estane	95	150, 10 [6]	365
XTX 8003	PETN/Sylgard	80	100 [7]	407
Generic propellant #1	AP/HTPB	75	80 [8]	432
Generic propellant #2	AP/HTPB	40	80 [8]	231
Generic propellant #3	AP/HTPB	40	15 [8]	1231

[a] HMX: cyclotetramethylene-tetranitramine, AP: ammonium perchlorate, PETN: pentaerythritol tetranitrate, HTPB: hydroxyl-terminated polybutadiene.

[b] PBX material calculations used PBX density, HE density, and particle size analysis from the literature. Propellant calculations were made from typical values found in the cited source. For these first order calculations, average particle size was used instead of size distribution, except for a weighted average in the case of PBX 9501.

[c] Calculation assumes spherical particles and no impurities or voids.