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Adhesive properties of some fluoropolymer binders with the insensitive explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)

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ABSTRACT

Adhesion between binders and explosive crystals is of critical importance for the mechanical performance of plastic-bonded explosives (PBXs). The surface properties of several prospective binders have been determined from static advancing contact angle measurements. The surface energies have been used to calculate theoretical work of adhesion to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), a common insensitive high explosive. The fluorinated terpolymer Oxy-461™, and Kel-F™ chlorotrifluoroethylene–vinylidene fluoride copolymers show the greatest potential for wetting TATB surfaces, and should promote the best adhesion to TATB in PBX formulations. In general, none of the fluoropolymer binders investigated here exhibit markedly superior adhesion to TATB. Thus, bulk physical properties are likely to be more important when choosing a binder.

1. Introduction

The use of polymers to “bind” high explosive crystals is paramount to the widespread, safe use of plastic-bonded explosives (PBXs). PBXs are a unique type of composite containing explosive crystals at high loading percentages (typically exceeding 85 wt.%) with the polymeric binder coating the individual explosive grains. The binder serves important roles in reducing the sensitivity of explosive charges to insults such as impact or friction, as well as improving charge mechanical stability. The selection of binders for use in PBX formulations, however, remains largely an iterative, trial-and-error process based on a handful of guiding principles, and limited by constraints dictated by the physical properties of the explosive being formulated (such as solubility, decomposition temperature, etc.).

While the thermomechanical properties of the binder have been shown to be important for manufacturing PBXs [1], binder-explosive adhesive properties have been linked to an ability to fabricate (machine) parts, maintain long-term durability, and inhibit failure. Bower et al. showed that thermomechanical properties such as glass transition temperature (T_g) and extensibility, as well as surface wettability of the binder, are critical for explosive performance and safety [2]. It has been posited that the most common, and limiting, mode of failure in plastic-bonded explosives under thermal or mechanical loads is crack formation and subsequent propagation along explosive crystal-binder interfaces [3–6]. For example, the mechanical properties of several PBXs were investigated by Palmer et al., revealing that even the most robust material failed by interfacial cracking at tensile stresses as low as 6.8 MPa [6]. Understanding the surface interactions between explosive crystals and polymeric binders is of great interest for potentially improving the production processes and failure limits of PBXs.

Here, the results of an experimental investigation of the adhesive properties of a number of fluoropolymer binders with the insensitive high explosive 1,2,3-triamino-2,4,6-trinitrobenzene (TATB) are reported. The TATB crystal is inherently anisotropic, with molecules adopting a $P_{\bar{1}}$ (triclinic) crystal structure in which the molecules are arranged in sheets in the a–b plane, Fig. 1. The a–b plane is alternatively labeled as the (0 0 1) plane in conventional crystallographic notation, while the edge of the a–b plane conventionally labeled (1 0 0). The (1 0 0) plane is referred to as the edge of the crystal arrangement here because the (0 0 1) planes tend to dominate when the crystal is grown from solution [7]. The edges of the crystal arrangement of TATB are highly oxygen- and amine-rich with strong intra- and intermolecular hydrogen bonding within the a–b plane, whereas in-between plane forces are dominated by π interactions associated with the benzene rings. The packing of planes in the TATB crystal results in an anisotropic crystal structure, leading to highly anisotropic thermal and mechanical properties. Indeed, a phenomenon of irreversible growth and dimensional changes, known as ratchet growth, occurs in temperature-cycled TATB formulations [8]. A review of of TATB properties can be found in Rice and Simpson [9].

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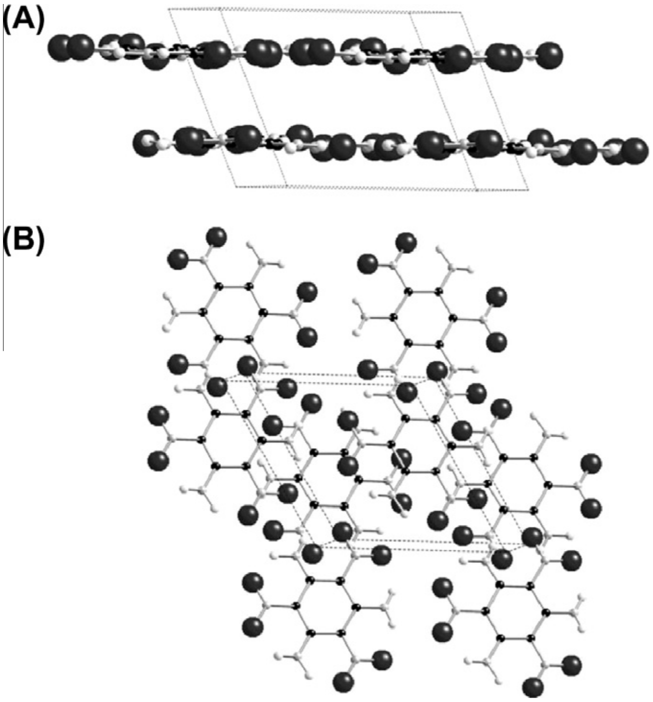

Fig. 1. Crystal structure of TATB shown parallel to the *a–b* plane (A), and perpendicular to the *a–b* plane (reprinted with permission from L. L. Stevens, N. Velisavljevic, D. Hooks, D. M. Dattelbaum, Hydrostatic compression curve for triamino-trinitrobenzene (TATB) determined to 13.0 GPa with powder X-ray diffraction, Propellants, Explosives, and Pyrotechnics 33 (4) (2008) 286–295. Copyright Wiley-VCH Verlag GmbH & Co. KGaA.).

Fluoropolymers are attractive as binders in PBX formulations due to their high densities, high temperature and chemical stabilities, and history of favorable performance [10–12]. Examples of such fluropolymers are Kel-F 800™, a statistical copolymer of chlorotrifluoroethylene and vinylidene fluoride (75:25 ratio by weight), or FC-2175™, a hexafluoropropylene and vinylidene fluoride copolymer. Fig. 2 shows a scanning electron micrograph of prills of 95 wt.% TATB/5 wt.% LFC-1™/FC-2175™ obtained by precipitation from acetone solution. The prills are well-coated by the binder, indicating favorable surface interactions between the fluoropolymer and TATB.

Evaluation of the surface properties of polymers may be a useful tool for screening potential binders for TATB in the preparation of plastic-bonded explosive formulations. Here, we compare the surface properties of Kel-F 800 with related fluoropolymers that differ by their monomer chemistry, using contact angle measurements to measure the surface energies or surface tensions of polymer films.

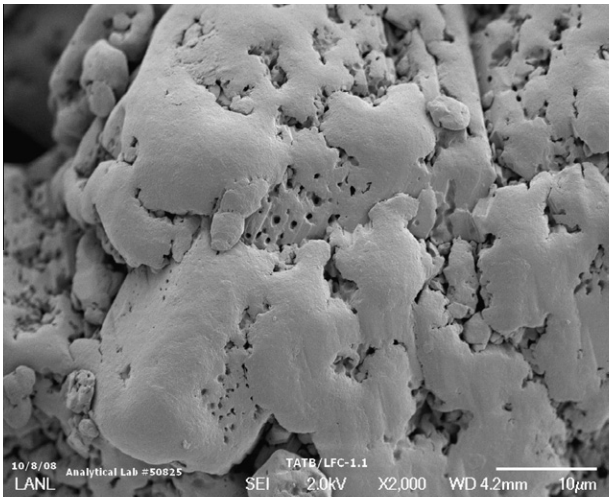

Fig. 2. Scanning electron micrograph of TATB-binder "prills" that are commonly pressed to produce plastic-bonded explosive charges (micrograph from E. Hartline, LANL).

1.1. Surface energy

Surface properties, including the dispersive and polar components of the surface energy, are relevant for evaluating adhesion between the explosive crystal and polymeric binder. The polar component of the surface energy arises from hydrogen and dipole interactions, while the dispersive component consists of London force interactions [13]. Thermodynamically, the work of adhesion is defined as the increase in free energy from creating two surfaces, and can be defined for liquid–solid interfaces by:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} \tag{1}$$

where γ is the surface energy or tension, and the subscripts refer to the solid (S), the liquid (L), and the vapor or atmosphere (V) [14]. This expression was originally derived from Young's equation for equilibrium of a droplet on a surface,

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL} \tag{2}$$

where θ is the angle the droplet makes with the surface [15]. Zisman discovered that a reasonable value for the critical wetting surface energy of a solid could be found by plotting liquids of known surface tensions against the cosine of their contact angle, then linearly extrapolating back to the "perfect wetting" value of $\cos\theta = 0$. However, the critical surface energy was pointed out by subsequent researchers, and Zisman himself, to be different than the thermodynamic quantity of surface energy [16]. Indeed, researchers have found that the Zisman method consistently underestimates the true surface energy [17]. To correctly measure the surface energy, both polar and dispersive contributions are important, and any determination of surface energy must use liquids with a large range of these components [16–20].

Considering both polar and dispersive components, the surface energy of a solid surface can be calculated using the geometric mean method, shown in Eq. (3) [16], where the solid–vapor energy has two components, as noted in Eq. (4):

$$\gamma_{LV}(\cos\theta + 1) = 2\left(\gamma_{LV}^{d}\gamma_{SV}^{d}\right)^{1/2} + 2\left(\gamma_{LV}^{p}\gamma_{SV}^{p}\right)^{1/2} \tag{3}$$

$$\gamma_{SV} = \gamma_{SV}^{d} + \gamma_{SV}^{p} \tag{4}$$

where the superscript "*d*" stands for dispersive, and "*p*" stands for polar. In order to find the two unknowns, γ_{SV}^{d} and γ_{SV}^{p}, $\cos\theta$ must be measured for at least two liquids with known γ_{LV}, γ_{LV}^{d} and γ_{LV}^{d}. Eq. (3) is then solved for the two liquids simultaneously, allowing for γ_{SV} to be calculated with Eq. (4). However, it is common for three or more liquids to be used in order to ensure accuracy [20–22].

It should be noted that contact angles can be measured in a variety of ways, all of which have been shown to produce slightly different results [23]. Generally, contact angles are measured either advancing (wetting) or receding (dewetting), while in motion (dynamic) or while stable (static). Each measurement technique typically yields a different angle, and thus comparison with the literature must be done carefully. In this study, an advancing contact angle is measured to represent the wetting of polymers on TATB during processing. The angle is measured statically as a compromise between ease of measurement and accuracy.