



Fundamental studies of the adhesion of explosives to textile and non-textile surfaces



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ARTICLE INFO

Article history:

Received 18 August 2016

Received in revised form 30 January 2017

Accepted 9 February 2017

Available online 17 February 2017

Keywords:

Explosives

Detection

Adhesion

Analysis

Forensic

Explosions

ABSTRACT

This paper describes the use of atomic force microscopy (AFM) to investigate the interactions between explosives crystals and different surfaces. Crystals of TNT, PETN and RDX were mounted onto tipless AFM cantilevers and repeatedly brought into contact with a range of surfaces ($n = 15$), including textile and non-textile surfaces. The adhesion force during each contact was measured, and the results are presented in this work. The results suggest that explosives crystals display a higher adhesion to smoother, non-textile surfaces, particularly glass. This finding may be of use for forensic explosives investigators when deciding the best types of debris to target for explosives recovery.

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1. Introduction

The recovery of explosives evidence from textile surfaces can be vital during a forensic investigation. When constructing an explosive device, it is likely that traces of explosives will be transferred to the bomb-maker's clothing [1,2]. For example, traces of PETN were found on the clothing of the Oklahoma City bomber. Similarly, traces of explosives were found on the clothing of the foiled 'Millennium bomber' [2]. Other textile surfaces such as carpets have also been demonstrated to be a good matrix for retaining explosives, with nitrate ester explosives reported to have a particularly high affinity for such substrates [3]. As textile fabrics are ubiquitous and likely to be present at many post-blast scenes, they present good potential as sources for trace explosives evidence both at scenes or sites where explosive materials may have been constructed or transported.

Techniques for the recovery of explosives from non-porous surfaces typically involve the application of a cotton swab or polyester wipe, which may be either dry, or wetted with a solvent, to the surface of interest. Analysis is subsequently carried out on solvent extracts of the swab or wipe. A swipe

sampling technique is also commonly used in airports, with a dry swab (often made from glass fibre, Teflon or cotton, and coated with various polymers) wiped across passengers' hands, clothing and belongings [4].

Several techniques are in current use for the recovery of explosives traces from porous surfaces, although their recovery can be challenging [5]. Swabbing is also used to recover explosives residues from porous surfaces [1]. Compared to non-porous surfaces, solvent-swabbing is less successful. The use of solvents on fabrics may cause damage to the fabric in question. Additionally, when solvent-swabbing a piece of clothing, often only a general swab of the garment is taken, meaning that any sections containing high concentrations of explosives particles may be inadvertently passed over and not sampled [6]. Alternative methods for sampling porous surfaces include vacuum sampling [7,8], solvent extraction [1,9,10] and direct sampling methods such as Raman spectroscopy and DESI-MS [5,11–14]. However, these methods all have limitations. For example, vacuum sampling can only recover relatively large explosives crystals, solvent extraction may damage the surface of interest, and Raman spectroscopy requires an explosives crystal to be physically located on a surface before it can be analysed, which can be challenging due to the typically small size of explosives crystals. A recent promising candidate for sampling from textile surfaces is the contact heater [15], which heats a surface at the same time as drawing vacuum from it, with

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volatilised explosives captured within a sampling cartridge. This has proved successful for the recovery of TATP and EGDN from a variety of surfaces, including ceramic tiles, carpet and denim.

In order to improve the recovery of explosives from porous surfaces, a greater understanding is required of the fundamental interactions between explosives and these surfaces. Atomic force microscopy (AFM) provides an ideal means of assessing the interaction of explosives with different surfaces as it can measure the adhesive force between an explosives crystal and a surface of interest [4,16]. This can be achieved by functionalising the end of a commercially-available tipless cantilever using an explosives crystal. The use of tipless cantilevers which have been functionalised in this manner is termed colloidal probe microscopy [16].

Zeiri et al. studied the adhesion of explosives crystals to various self-assembled monolayers. They mounted a self-assembled monolayer (SAM) or an explosives crystal onto the end of a tipless AFM cantilever, then measured the adhesion between the mounted SAM and an explosive particle secured on a glass slide, or between the mounted explosive particle and a SAM secured on a glass slide. The monolayers contained a variety of end groups ($-\text{OH}$, $-\text{CH}_3$, $-\text{NH}_2$, $-\text{CF}_3$, $-\text{COOH}$, $-\text{C}_6\text{H}_5$, $-\text{C}_3\text{H}_4\text{SN}$), and they examined four explosives (TNT, RDX, HMX and PETN). The results of their study showed that the SAMs with $-\text{OH}$ and $-\text{C}_6\text{H}_5$ end groups showed the strongest adhesion towards the explosives analysed [4].

Beaudoin et al. [16] used AFM to investigate the adhesion between TNT, RDX and PETN and three coated aluminium surfaces, bearing an acrylic melamine clear coat, a polyester acrylic melamine white coat or a green military-grade finish, of differing roughness. The authors found that the roughness of a substrate has a strong effect on the adhesion of an explosive crystal, with rougher surfaces tending to give lower adhesion than smoother surfaces. From this, it was concluded that the roughness of a surface has a much stronger contribution to any observed adhesion than the inherent chemical composition of such a surface [16].

Adya et al. used AFM to periodically analyse fibres exposed to different environmental conditions, to see how the surface texture changed over time [17]. They studied cotton, wool and viscose fibres exposed to various environmental conditions. However, although work has been independently performed using AFM to look at the adhesion of explosives to non-textile surfaces, or the morphology of textile fibres, to date no research has examined the adhesion of explosives crystals to a wider variety of surfaces, including textiles.

Although, as outlined here, a number of techniques are available with which to recover explosives residues from different surfaces, there is no fundamental research detailing the nature of the interaction of explosives with these different surfaces. This work enhances current knowledge and understanding through the determination of the fundamental, molecular-level interactions of three explosives (TNT, PETN and RDX) with a large variety of surfaces, including a number of textiles. Through this approach we provide an increased understanding of the interactions of explosive crystals with a range of different surfaces, facilitating a deeper understanding of the optimal target surfaces for sampling following an explosion. This knowledge may also enable the development of new methods with which to recover explosives from such surfaces.

2. Materials and methods

2.1. Fabrics

All fabrics analysed in this work were obtained from Spotlight Fabrics, Perth, Western Australia. The following fabrics were investigated in this work: rayon, silk, polyester stretch fabric,

acetate, cotton jersey, wool, denim, calico natural cotton, mercerised cotton and polyester fleece.

2.2. Non-textiles

Aluminium foil was Confoil heavy duty catering foil brand; topography and adhesion measurements were performed on the matte side of the foil. A glass microscope slide (Biolab plain microscope slides, precleaned) was used for topography and adhesion measurements with glass. A Multix plastic lid was used as a source of polypropylene plastic for measurements. White and metallic orange car paint were obtained from car panels donated by Prestige Sunroofs WA sunroof fitters. The panels were close to factory finish.

2.3. AFM instruments

Topography and adhesion measurements were performed on a WITec alpha 300 SAR. A $20\times$ ($\text{NA}=0.4$) objective was used with this instrument. Data was collected using WITec ControlFOUR software. Cantilever functionalisation using explosives crystals was performed using a custom Nanoscope program using a Digital Instruments Dimension 3100 Atomic Force Microscope.

2.4. AFM analysis: topographic measurements

2.4.1. Sample preparation

Textile fibre samples were prepared by laying a fibre across a piece of black double-sided adhesive tape (Stylus tapes brand) stuck to a clean glass microscope slide. The fibre was then taped at each end using a piece of adhesive tape, ensuring the fibres were not stretched during their preparation. Sample preparation for the non-textile surfaces was performed as follows: for the car paints, the paint surface was cleaned using ethanol then ultra-pure water, then dried using a lint-free tissue. A small chip of paint was removed using a scalpel, and stuck down to a piece of black double-sided tape stuck to a glass microscope slide. Aluminium was treated in a similar manner: the matte surface was cleaned using ethanol and ultra-pure water, dried using a lint-free tissue, then a small piece stuck down to a piece of double-sided tape on a glass microscope slide. For the adhesion to glass studies, a glass microscope slide was cleaned using ethanol then ultra-pure water, and dried with a lint-free tissue. A small piece of polypropylene plastic was cleaned using ethanol then ultra-pure water and dried with a lint-free tissue, before being placed directly on the sample stage for analysis, clipped in place by two microscope stage clips. A photomicrograph was taken of each surface prior to topographic measurements. This was performed using a $20\times$ ($\text{NA}=0.4$) objective and the WITec alpha300 SAR.

2.4.2. AFM probes used for topographic measurements

The topographies of all surfaces (with the exception of wool) were measured using WiTec AFM arrow cantilevers, reflex-coated, contact mode, nominal spring constant 0.2 N/m , 14 kHz . The topography of wool was obtained using a WiTec AFM arrow cantilever, reflex-coated, NC (AC) mode, spring constant 42 N/m , 285 kHz .

2.4.3. Topography measurements

All topographies were measured using contact mode AFM, with the exception of wool, which was measured in intermittent contact mode. For each textile fibre, the topography was measured at three separate regions along the length of the fibre. For the non-textile surfaces, the topography was measured at three distinct regions of the surface. An area measuring $16 \times 10\ \mu\text{m}$ was selected on each

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