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AFM studies of PBX systems

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Abstract

Polyeurathane and gel-bound PBX systems are studied using atomic force microscopy (AFM). Comparative images for the pure explosive crystals and the binders are taken and compared. The images reveal a complex structure for the polyeurathane-bound system in which there is a surprising diversity of features. The gel system appears to be simpler appearing as a two-phase system. In both cases, however, the stiffening effect of the crystals on the binder is emphasised. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Atomic force microscopy (AFM); PBX system; Polyeurathane

1. Introduction

Explosives have been used for many commercial and military applications throughout the industrial period. In many cases the energetic material needs to be poured or shaped into a well-defined form. While melt-pouring techniques are suitable for TNT-based compositions, for many more complex compositions this is not possible. One solution has been to use polymers to act as a binder for the explosive crystals, thus allowing systems to present superior impact safety over powders and also to possess good mechanical properties which allow them to be machined and even used as structural components. A further advantage is that the preparation of complex shapes and some systems can be poured into position and the polymer then cured, thus giving the safety of low temperature fabrication.

PBX mechanical properties are known to be dominated by the chemical and physical characteristics of the polymeric system and its interaction with the explosive crystal filler. It has been shown that the binder has a pronounced effect on the properties of the composite material even when the explosive loading is greater than 90 wt.% [1,2]. A basic knowledge of the ways in which the explosive and the binder interact is essential to understanding and predicting the behaviour of the composite systems. The development of finite element (FE) models for predicting mechanical properties based on knowledge of the microstructure is one area of increasing importance. It is one aim of these studies to provide data suitable for inclusion in such a model.

Atomic force microscopy (AFM) is one of the family of probe microscopies which are currently undergoing great development. In its basic form, the AFM technique consists of the sample being scanned by a miniature cantilever with a sharp tip (Fig. 1). The tip apex is in continuous contact with the surface and the cantilever flexes as it is moved over the sample. The degree of flexure is monitored and so surface topography is recorded. Materials such as silicon carbide, diamond and metals have all been used as the tip. The high resolution of AFM relies on

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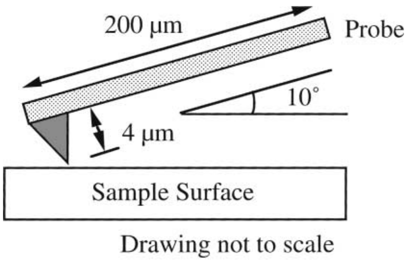

Fig. 1. The arrangement of AFM probe and sample surface.

the tip having a curve radius of the order of 25 nm, this has allowed atoms in a metallic matrix to be observed and the double helix of DNA to be directly detected.

For soft materials such as polymers and biological samples, the high contact forces cause the sample to be deformed, this can lead to sample damage as well as inaccurate images. This led to the development of the tapping mode of image acquisition [3]. In this mode, short intermittent contact is made between the tip and the surface by oscillating the cantilever. One additional effect of doing this oscillation is that the resonant frequency of the cantilever changes with the surface force acting on it. This produces a change in the phase of the cantilever and the oscillator driving the tip. In general, the magnitude of the force between sample and tip decays with tip sample distance differently for chemically distinct materials; this allows compositional variation to be detected. Reneker and Maganov have recently reviewed AFM studies of polymers [4]. The mechanical properties of polymers have been probed using the AFM tip as an indentation probe [5,6] and the damage produced by mechanical action has received attention [7].

Some studies have been performed with AFM on energetic systems, looking either at the fracture surfaces of TNT [8], nanostructures of RDX [9] or at impact-induced ignition sites in RDX [10]. Overall, energetic materials have not received a wide attention in the AFM literature, with few locations in the world performing such research.

2. Experimental

The materials used in this study consist of two types of polymer-bonded explosive. In the first case a polyeurathane-bound system in which the loading of HMX exceeded 90 wt.% is studied, thus representing a generic solid polymer system. The second material consists of a HMX loading of over 90 wt.% in a gel system representing a second generic class of PBX. Single-crystal HMX and samples of the pure binder materials were also studied.

AFM is a surface technique, so sample preparation and handling is of great importance. The following scheme was used to prepare the samples. The sample, face area 1 cm^2, was first potted using Vari-set 20 (MetPrep Ltd.) cold moulding powder. The sample was mounted to be 1 mm above the potting surface to avoid simultaneous polishing of the sample and the potting compound, thus avoiding cross-contamination. A vibrational polishing machine using 0.6 μm grit (Silco Colloidal Silica MetPrep Ref. 15 99 97) was used. The polishing cloth was 12 in. (30 cm) diameter microcloth (Beuhler). The polishing pressure was between 3.2 and 7.5 kPa. The polishing was continued for 90 min using an orbital period of 30 s at 30 cm diameter. The samples were then cleaned in running water followed by blow-drying.

After following this scheme, the samples were handled only at the edges, using tweezers and the surfaces destined for imaging never touched by any object. Samples were placed in a Nanoscope III AFM and studied in tapping mode. Images were obtained covering areas from 50 μm × 50 μm down to 1 μm × 1 μm. It was found that at the greater magnification levels the structures surrounding the explosive crystals could be resolved.

3. Results

3.1. Images of polyeurathane bound PBX

Fig. 2 shows the topographic structure for a field of view of 50 μm × 50 μm. An explosive crystal occupies the top left-hand corner of the image, another crystal occupies the lower left-hand edge of the image. In the region between these two crystals, a region of smaller explosive crystals and binder is seen. The explosive crystals vary greatly in size and shape.

A closer examination of an explosive crystal was made and Fig. 3 shows the result. In this figure, the image on the left is the topographic image, the right-hand image is the phase map of the same area. The

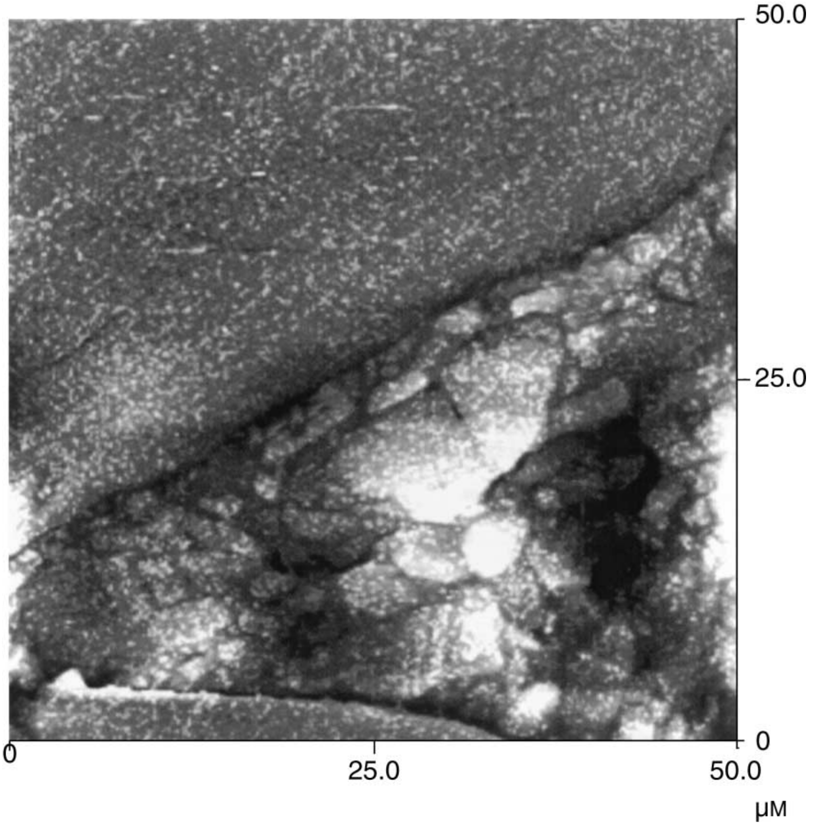

Fig. 2. Topographic image of a 50 μm × 50 μm area of polyeurathane HMX system. The surface is flat to 350 nm. This shows part of an explosive crystal at the top left-hand side while the edge of another crystal forms the lower left-hand edge of the image. The region flanked by these crystals is the binder-rich area.

lower image is a three-dimensional representation of the surface. Though the phase map contains zones of phase difference, these correspond to the regions seen in the topographic image indicating that only one material can be detected. The rounded shapes seen and the overall flatness indicate these shapes are probably left from the polishing of the surface.

The binder-rich region of the PBX is shown in Fig. 4. There are three features to be noted in this image: (a) the pebble-like structures on the surface, 50–100 nm long, some of which appear to be fractured, (b) the flat region between the pebbles and (c) the darker regions seen predominantly in the phase image.

There are several possible explanations for these structures. The most likely is that the pebbles are small, hard explosive crystals; the flat region is the bulk of the binder, and the dark regions in the binder are regions of soft binder, possibly a less cured area. It should be noted that these dark regions are seen in the phase image but are hardly noticeable in the topographic image and are an indication of a different chemical or mechanical nature. The fine-grained material is not the polishing medium, as this has been examined and found to be angular and is very much tougher than the relatively soft PBX surface.

The main result from this image is not the pebble-like material rather the softer material regions seen in the binder.

3.2. Gel–HMX system

Fig. 5 shows a region of explosive crystals and the mixture of large and small explosive crystals and

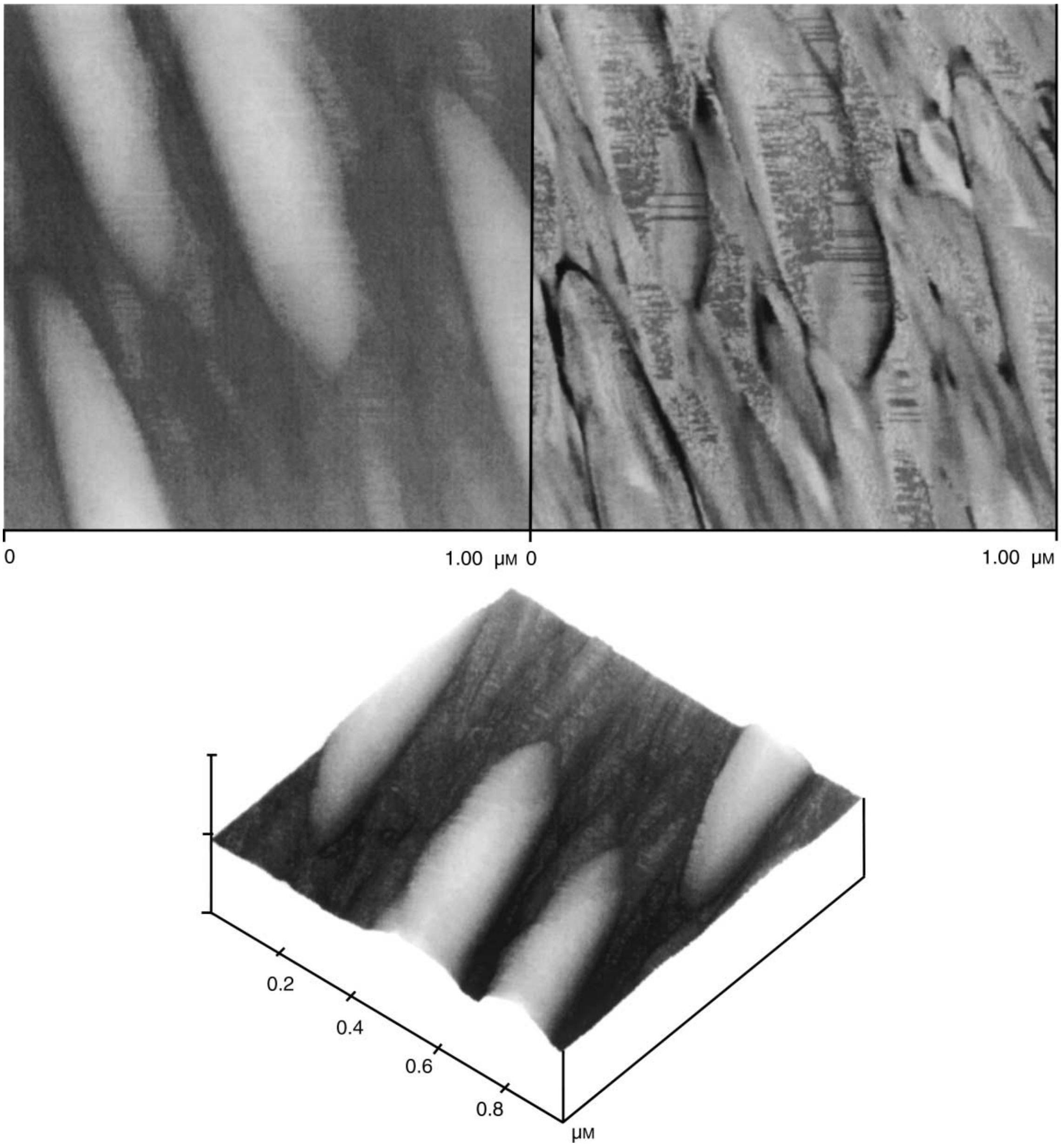

Fig. 3. Surface of an HMX crystal in EDC29. The area of view is 1 μm × 1 μm. The vertical scale is 200 nm per division in the lower image. The top left-hand image is the topographic image, the top right-hand image is the phase image, while the lower image shows a three-dimensional representation of the surface.

binder seen between these large crystals. The phase image shows no great difference from the topographic image. Closer imaging of the explosive crystal has shown it to have a flat featureless surface.

In the binder-rich region the gel has been removed from near the surface region during polishing and now is found between the explosive grains. This is shown in a three-dimensional representation in Fig. 6.

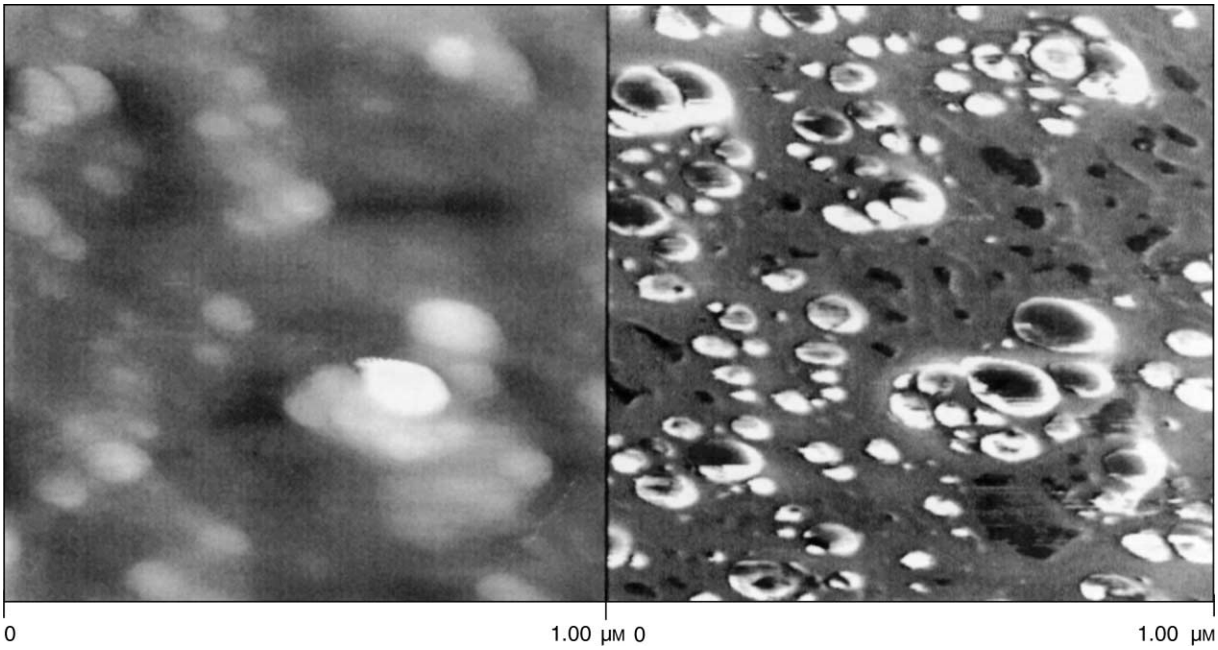

Fig. 4. A binder-rich area. Field of view 1 μm × 1 μm. Topographic image on the left, phase image on the right. The phase image indicates hard pebble-like inclusions along with softer regions in the binder matrix.

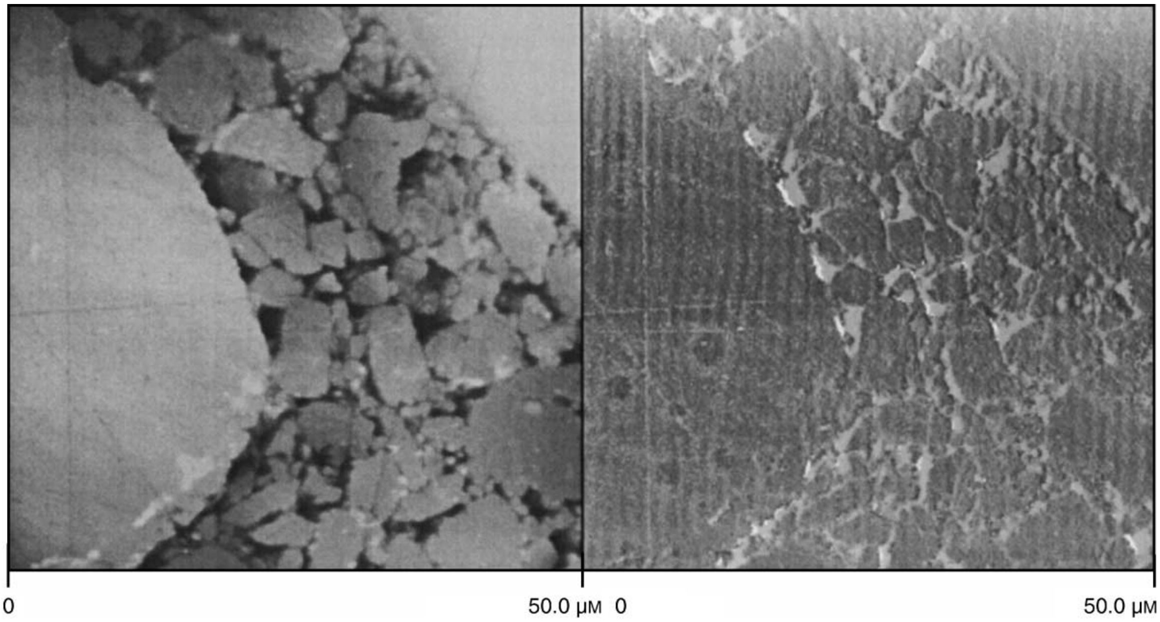

Fig. 5. The surface of a polished gel–HMX sample. 50 μm × 50 μm field of view. Topographic image on the left and phase image of the same area on the right. An explosive crystal forms the right-hand side of the image, and a zone of binder-rich material the central and left side.

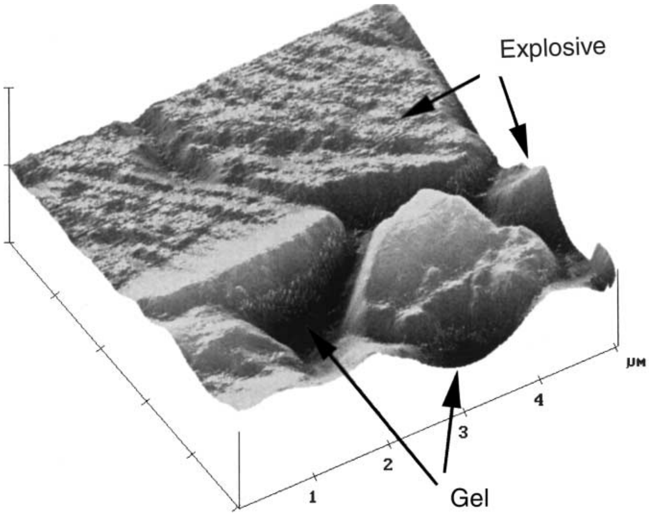

Fig. 6. The gel-rich area of the gel–HMX system. Image covers a 5 μm × 5 μm area, the vertical scale is 500 nm per division.

3.3. Images of HMX and binder

An image of a HMX crystal, 10 μm × 10 μm field of view is shown in Fig. 7. This crystal is unpolished and steps and facets are seen on the surface. When facets are examined closely, small granules are observed on the surface similar to the fine material found in the polyeurathane PBX system.

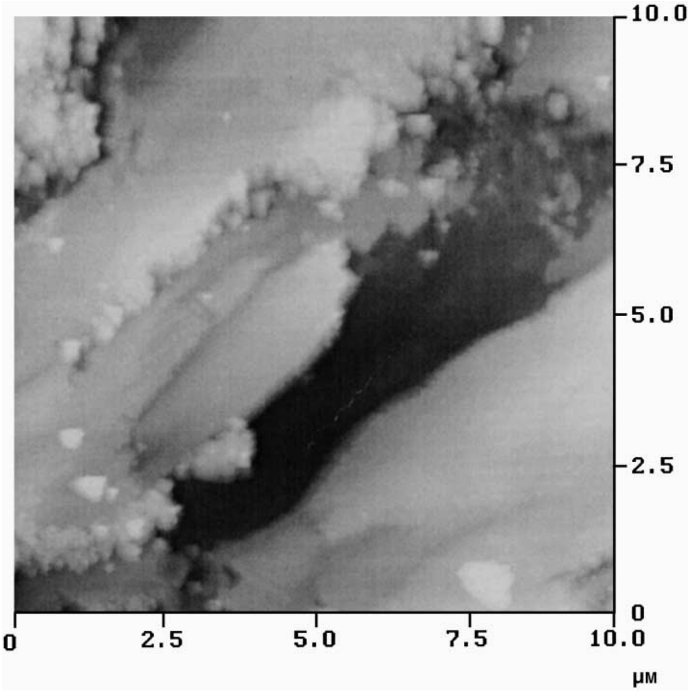

Fig. 7. Topographic view of a HMX crystal. Field of view 10 μm × 10 μm.

The pure binder materials could not be imaged under the same conditions as the PBX systems or explosive crystals. The reason for this was the softness of the binder material. The binder materials were polished in the same way as the PBXs and did not accumulate any appreciable polishing debris in their surface. The only image gained from these samples was a region where a very large piece of polishing agent had become engrained in the surface and stiffened it enough for the probe to image it. No evidence of fine-grained debris was found in this system.

4. Conclusion

This study has given high-magnification views of some of the key features seen in two types of PBX systems and has highlighted several points.

The binder materials on their own could not be imaged as they were too soft, yet they could be imaged in the PBX as in Fig. 4. This implies that the presence of the explosive crystals stiffens the binder appreciably. While many explanations for this exist, two of the more reasonable ones are; firstly, the binder layers are thin and if they adhere strongly to the crystals the interaction will produce a higher yield strength. Secondly, the inclusion of very small crystals, ‘‘fines’’, will stiffen the polymer in a similar way that a mortar (cement plus sand) is stiffened by the sand particles. This has obvious implications for the modelling of PBXs, since using the bulk binder properties clearly will give incorrect predictions.

In the polyeurathane system it is possible to see dark soft regions in the binder phase, possibly marking limits of the crystal's stiffening influence.

The images of the gel system show nothing unusual in the structure, a mix of explosive grain sizes and an apparently homogeneous binder.

This study will be complemented by nanoindentation studies across the images seen in the surface. This study is now in progress.

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