nano-TA: Nano Thermal Analysis

Application Note #1
Failure Analysis - Identification of Particles in a Polymer Film
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Introduction

Nano-TA is a local thermal analysis technique which combines the high spatial resolution imaging capabilities of atomic force microscopy with the ability to obtain understanding of the thermal behaviour of materials with a spatial resolution of sub-100nm. This breakthrough in spatial resolution of thermal analysis, which is ~50x better than the state of the art, has profound implications for the fields of Polymers and Pharmaceuticals where local thermal understanding is key.

The conventional AFM tip is replaced by a special nano-TA probe that has an embedded miniature heater and is controlled by the specially designed nano-TA hardware and software. This nano-TA probe enables a surface to be visualised at nanoscale resolution with the AFM's routine imaging modes which enables the user to select the spatial locations at which they would like to investigate the thermal properties of the surface. The user then obtains this information by applying heat locally via the probe tip and measuring the thermomechanical response.

The aim of this work was to identify the composition of contaminant particles present in a polymer film by comparing localized thermal analysis data (melting or softening temperatures) with those obtained from several feedstock materials. Several pieces of cryo-fractured polymeric film and four granular polymeric feedstock materials, labelled 'Adhesive', 'EVOH', 'PP' and 'Nylon', were supplied for the analysis.

Experimental Setup

The results were obtained using a Veeco Explorer AFM equipped with an Anasys Instruments (AI) nano-thermal analysis (nano-TA) accessory and AI micro-machined thermal probe. The nano-TA system is compatible with a number of commercially available Scanning Probe Microscopes. The probe was calibrated for temperature by melting samples of

polycaprolactone, paracetamol, nylon 6 and polyethylene terephthalate of known melting temperature. Unless otherwise stated, the heating rate used was 20 °C/s.

The nano-TA data presented are of the probe cantilever deflection (whilst in contact with the sample surface) plotted against probe tip temperature. This measurement is analogous to the well established technique of thermo-mechanical analysis (TMA) and is known as nano-TA. Events such as melting or glass transitions that result in the softening of the material beneath the tip, produce a downward deflection of the cantilever. Further information on the technique can be obtained at www.anasysinstruments.com.

Prior to carrying out nano-TA on the sectioned film, suitable target features were selected by contact mode AFM imaging. The feedstock materials were subjected to nano-TA at random locations on the surface of a pellet, without prior imaging.

Results and discussion

Sectioned film

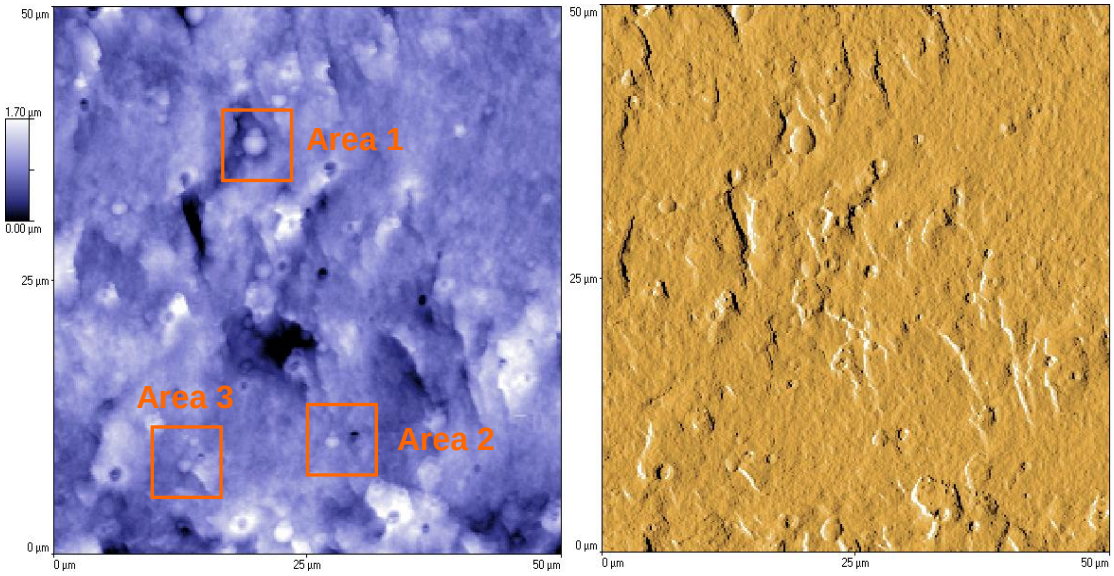

Fig. 1. Cryo-fractured polymer film, 50 µm × 50 µm AFM topographic (left – blue) and tip deflection (right – gold) images. The three marked areas were selected for further imaging and analysis.

Figure 1 shows AFM images of the sectioned polymer film. The surface is characterized by well scattered micrometer-scale particles and holes. The three marked areas containing obvious particles were subjected to higher magnification imaging in order to select locations for nano-TA to be carried out. Images acquired before and after nano-TA are shown in Figure 2 below.

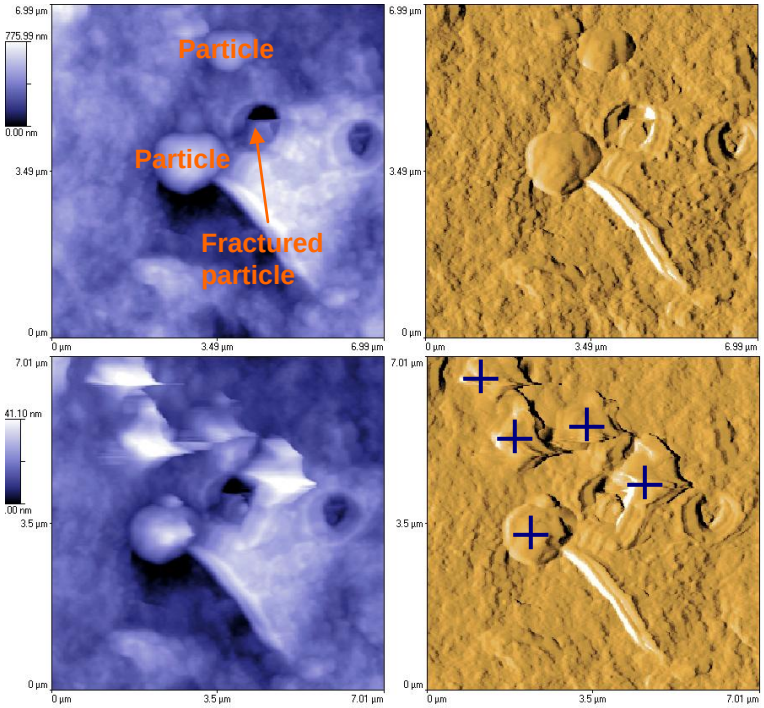

Fig. 2. Cryo-fractured polymer film area 3, 7 µm × 7 µm AFM topographic and tip deflection images before (top row) and after (bottom row) nano-TA. It is noted that the lateral spatial resolution evident in these images is comparable with that obtained by a conventional AFM probe.

Selected nano-TA locations, typically a single particle and nearby areas of matrix, are marked with a cross (note that not all matrix locations are shown). Figure 2 also shows a location inside a hole that was thought to contain a fractured particle. Nano-TA results from eight locations in the matrix and five particles, including the fractured one, are shown in Figure 3.

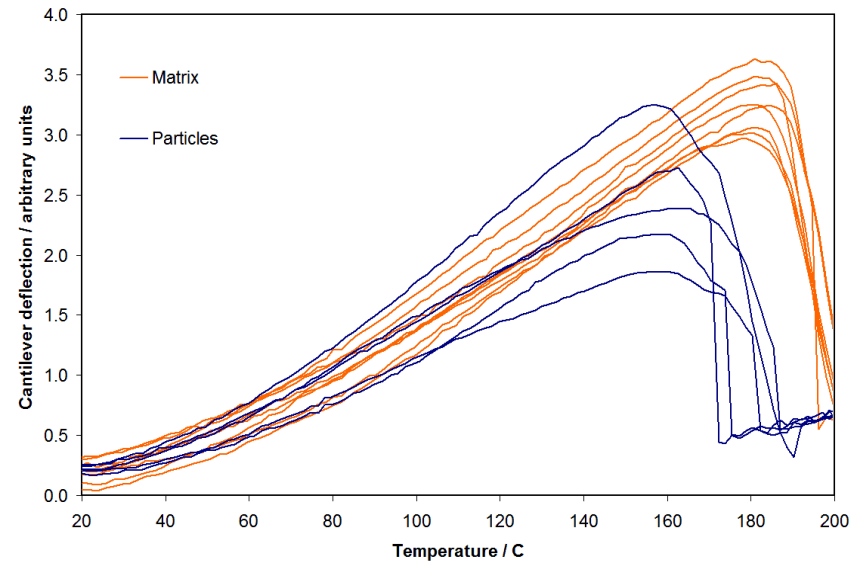

Fig. 3 Cryo-fractured polymer film. nano-TA results for particles and the matrix.

The results from the matrix show good reproducibility, with an obvious melting transition starting in the range 183-188 °C. The results from the particles exhibit more variation in the

rate of thermal expansion and the melting transition is somewhat less sharp than that of the matrix. The onset melting temperature varies from 161 °C to 165 °C. The rate of descent of the probe tip after melting is somewhat lower and more variable than produced by the matrix.

Comparison of nano-TA results from the fractured film and the feedstock materials

The results from four random locations on the surface of an EVOH pellet are shown in Figure 4.

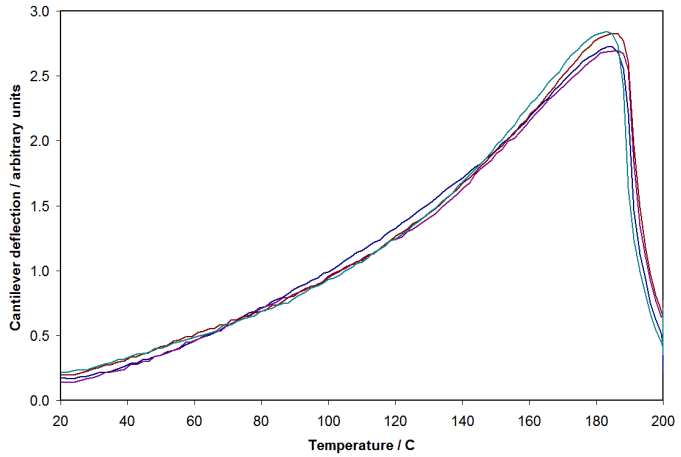

Fig. 4. EVOH pellet nano-TA results.

There is good agreement between the curves, with an obvious sharp melting transition whose onset temperature varies from 184 °C to 188 °C.

The figure below shows an overlay of results from the film matrix and all four feedstock materials.

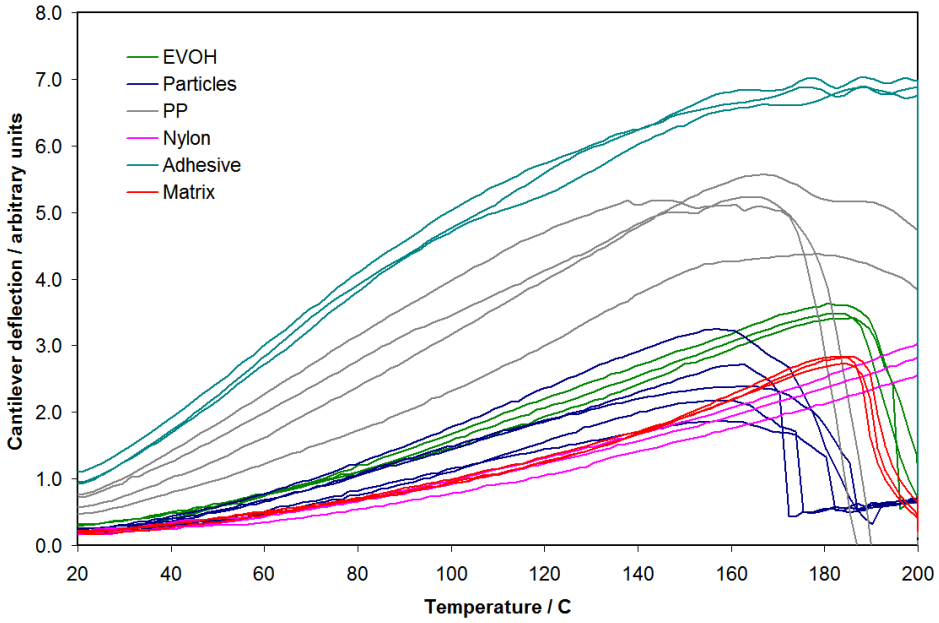

Fig. 5. Overlay of selected nano-TA results from polymer film matrix and all four feedstock materials.

Fig 5. clearly shows that the results from the polymer film matrix and the EVOH pellet are almost identical. Provided that the matrix can only be one of the supplied feedstock materials, the results show that it must be EVOH. The only feedstock material with a melting temperature in the same range as that of the particles is PP (the adhesive can be discounted as its overall behaviour is so different). There is some variability in the PP results from the pellet sample which is most probably due to sample roughness. This could perhaps be reduced by producing a flat section from a PP pellet. This is, however, considered unnecessary for the purposes of the present study. The considerable differences in the maximum upward deflection of the probe between the pellet and the particles can be accounted for by the very different nature of the samples – one a large rough pellet, the other a micrometer-sized particle. With the proviso that the particles cannot originate from a source other than the feedstock materials supplied, it can be deduced with a high degree of confidence that the particles must, therefore, be PP.

Conclusions

This sample analysis shows the benefits of adding the nano-TA capability to a Scanning Probe Microscope that is used for the study of polymers. The topography information from the SPM clearly shows the presence of micron scale contaminant particles, but without the thermal analysis of the nano-TA system these particles cannot be identified. The ability to position the probe with high resolution due to the sharp tip radius of these novel thermal probes and the ability to control the probe temperature over a broad range allows analysis of a range of polymer samples.