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The Identification of Particles in a Polymer Film Using Nano-Thermal Analysis

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Introduction

Nano-TA is a local thermal analysis technique that combines the high spatial resolution imaging capabilities of atomic force microscopy (AFM) 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 ~50× better than previously reported, 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. The nano-TA probe enables a surface to be visualised at nanoscale resolution using the routine imaging modes of AFM. The user is able to select the spatial locations for the investigation of the thermal properties of the surface. Heat is supplied locally via the probe tip and the thermomechanical response is measured.

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' (ethylene vinyl alcohol), 'PP' (polypropylene) 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 an 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. Unless otherwise stated, the heating rate used was 20 °C/s.

The deflection of the cantilever (whilst the probe is in contact with the sample surface) is plotted against probe temperature. This measurement is analogous to the well established technique of thermo-mechanical analysis (TMA) and is known as nano-TMA. Events such as a melting point or glass transition that result in the softening of the material beneath the tip, produce a downward deflection of the cantilever.

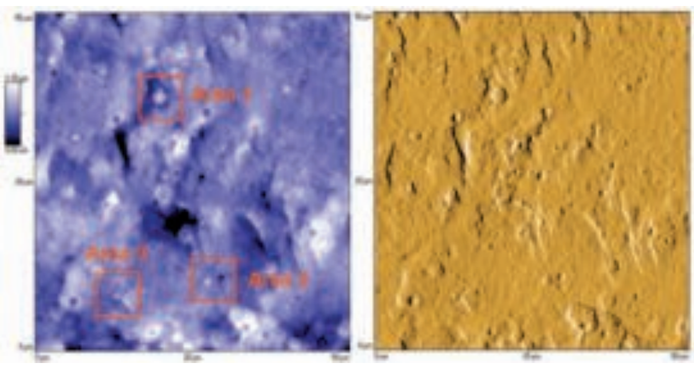

Figure 1. Cryo-fractured polymer film, 50 µm × 50 µm AFM topographic (left – blue) and tip deflection (right – gold) images. The three marked areas were selected for further imaging and analysis.

Prior to carrying out nano-TA on the sectioned film, suitable target features were chosen following contact mode AFM imaging. The feedstock materials were investigated using nano-TA at random locations on the surface of a pellet.

Results and discussion

Sectioned film

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.

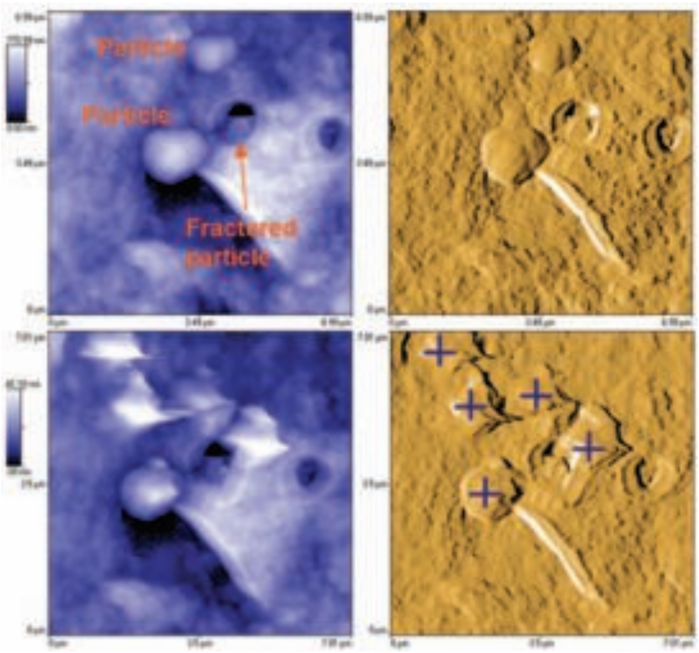

Figure 2. Cryo-fractured polymer film area #3, 7 µm × 7 µm AFM topographic and tip deflection images before (top row) and after (bottom row) nano-TA. It is noted that the lateral spatial resolution evident in these images is comparable with that obtained by a conventional AFM probe.

Selected nano-TA locations, typically a single particle and nearby areas of matrix, are marked with a cross. 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.

The results from the matrix show good reproducibility, with an obvious melting transition 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.

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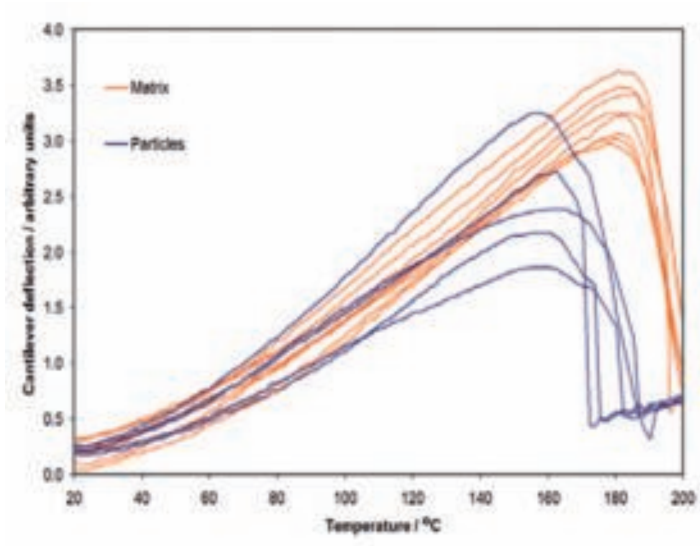

Figure 3. Cryo-fractured polymer film. nano-TA results for particles and the matrix.

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

Fig. 5. Overlay of selected nano-TA results from polymer film matrix and all four feedstock materials. This 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 was unnecessary for the present study as the differences in the maximum upward deflection of the probe between the pellet and the particles can be explained 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.

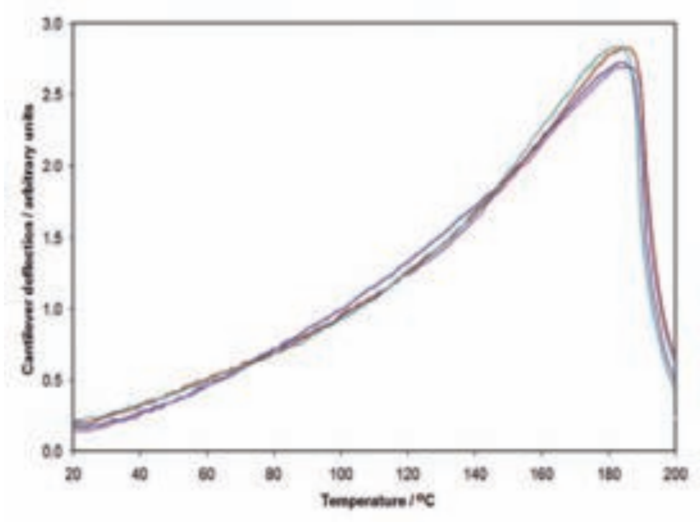

Figure 4. EVOH pellet nano-TA results.

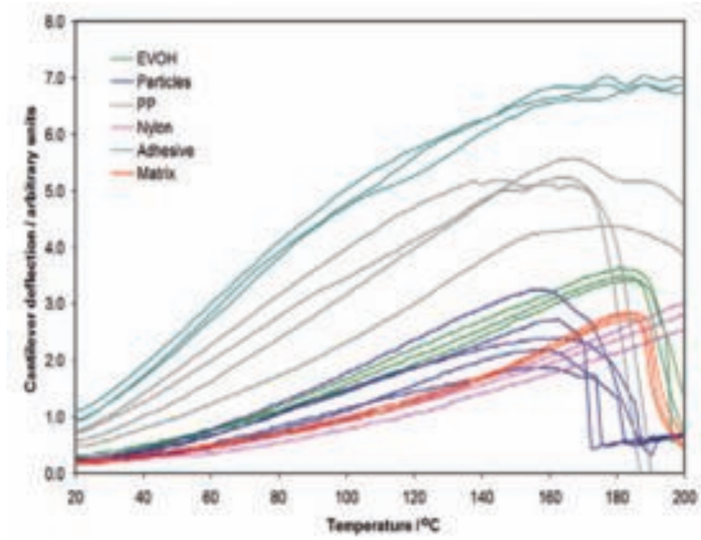

Figure 5 is an overlay of results from the film matrix and all four feedstock materials.

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 to control the probe temperature over a broad range allows analysis of polymer samples on the sub 100nm scale. ■

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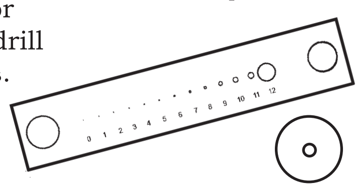

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