



nano-TA™: Nano Thermal Analysis

Application Note #2

Analyzing Nanoscale inclusions within a Polymer Matrix

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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 an 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 understanding local thermal properties 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 characterize the nanoscale inclusions within two 50/50 polyolefin blends. Imaging these materials using a conventional AFM probe had revealed the scale and form of their phase-separated microstructures, but could not identify which polymer formed the matrix and which formed the occluded phase. Inclusions in compounded polyolefin resins are common in many applications. The final morphology in these multicomponent blends may be complex. Techniques such as nano-TA which correlate the morphological structure to thermal properties are crucial for product development. Nano-TA probes have the lateral resolution to enable the structure to be imaged and the key ability to measure the melting temperature of each phase. The samples were submitted in the form of sectioned sheet material.

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, and a polyolefin sheet material. 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-TMA. 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 samples, suitable target features were selected by contact mode AFM imaging using the same thermal probe.

Results and discussion

Sample 1

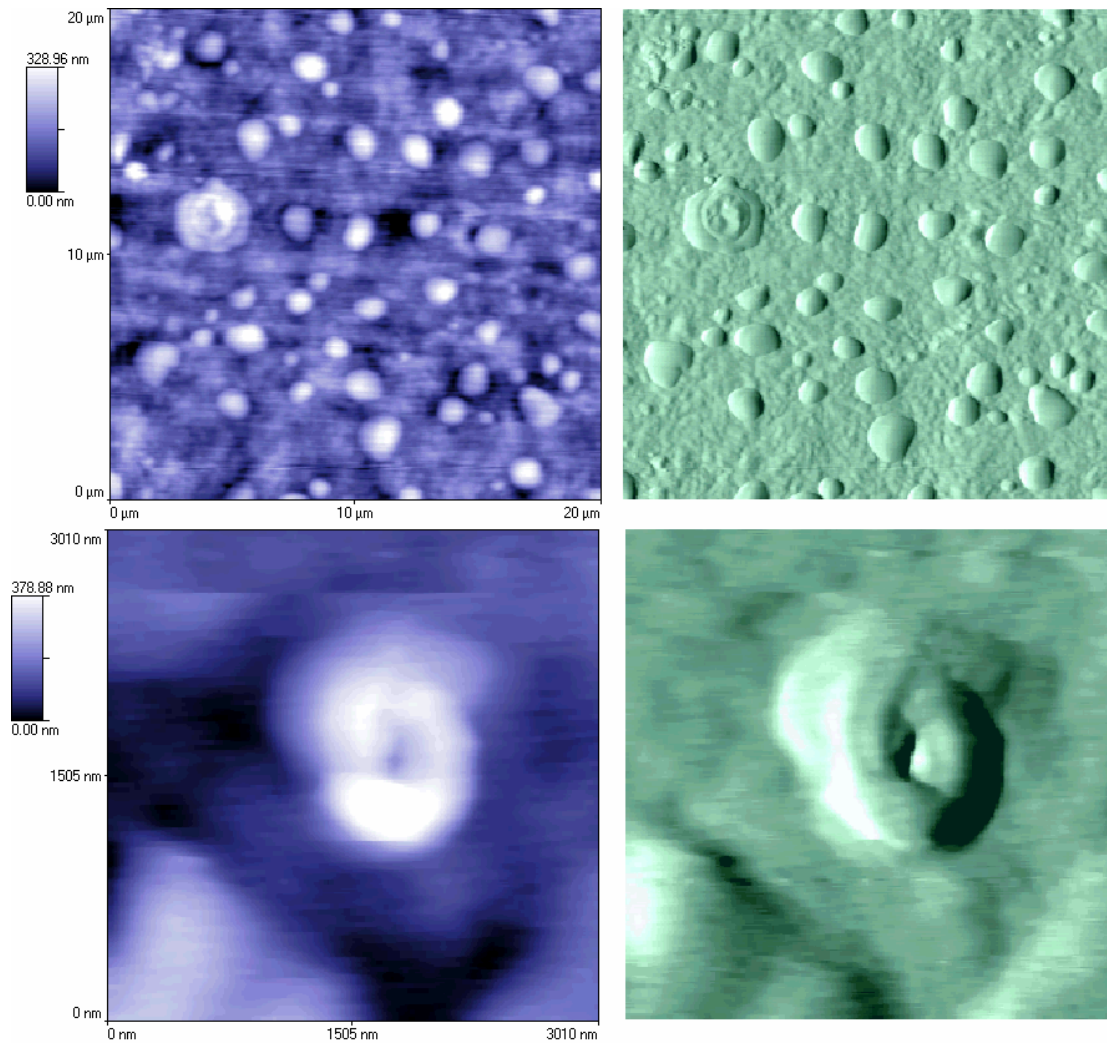


Fig. 1. Sample 1 - topographic (blue) & tip deflection (green) images of the surface before & after nano-TA. The bottom row of 3 micron scan size images shows a nano-TA hole in an occluded domain.

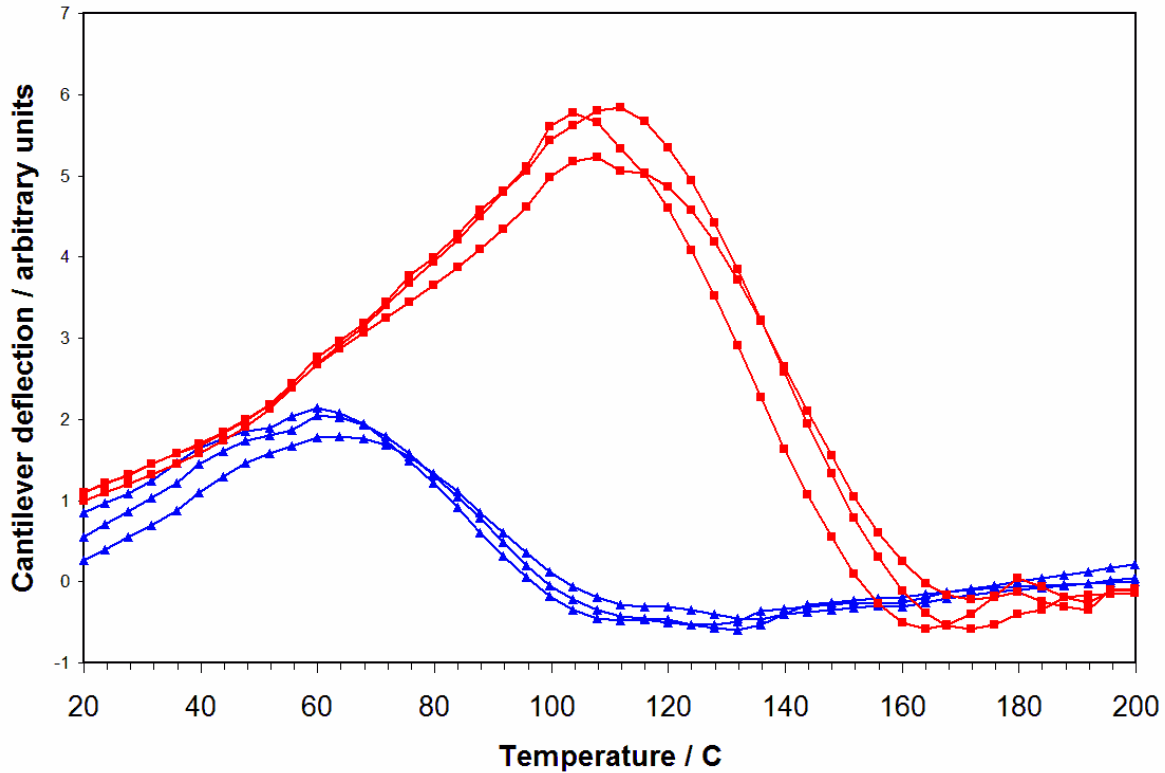


Fig. 2. nano-TA results for Sample 1. The continuous phase (squares in the fig) refers to the matrix and the occluded phase (triangles in the fig) refers to the inclusions.

Figure 1 shows topographic and tip deflection images acquired before and after nano-TA. The diameter of the crater shown is approximately 200 nm. It is worth noting that most of the surface damage is caused during retraction of the probe, due to the significant lateral movement of the tip during lift-off. The area analyzed during nano-TA and giving rise to the plots shown in Fig. 2 is therefore considerably less than 200 nm in diameter. These results clearly show that the occluded phase and matrix have different melting temperatures (as determined by the onset of probe penetration). The T_m of the matrix varies from 105 to 112 °C and that of the occluded domains from 60 to 68 °C

Sample 2:

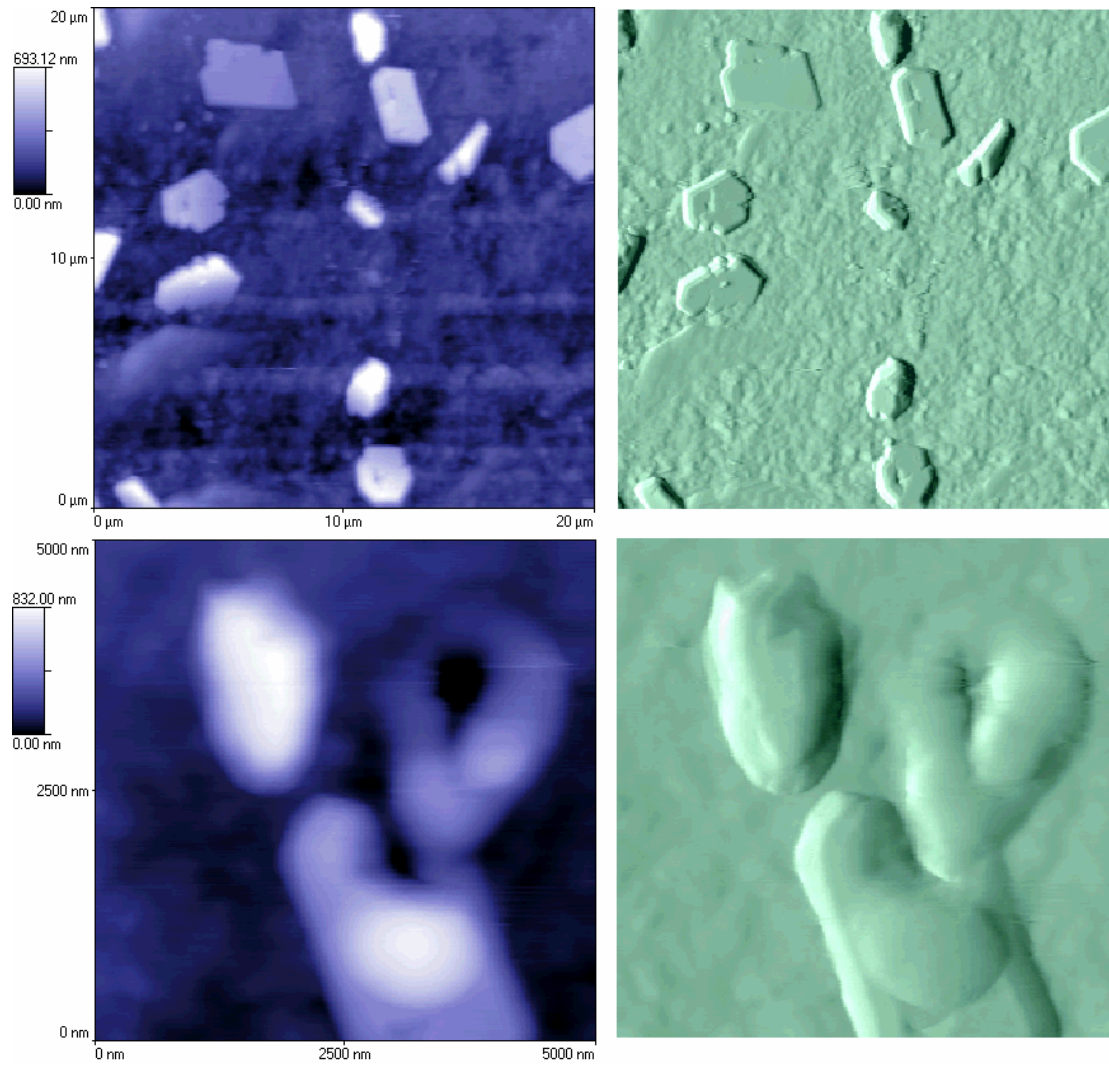


Fig. 3. Sample 2 - topographic (blue) and tip deflection (green) images of the surface before & after nano-TA. The bottom row shows nano-TA holes in an inclusion and the matrix in a 5 micron scan.

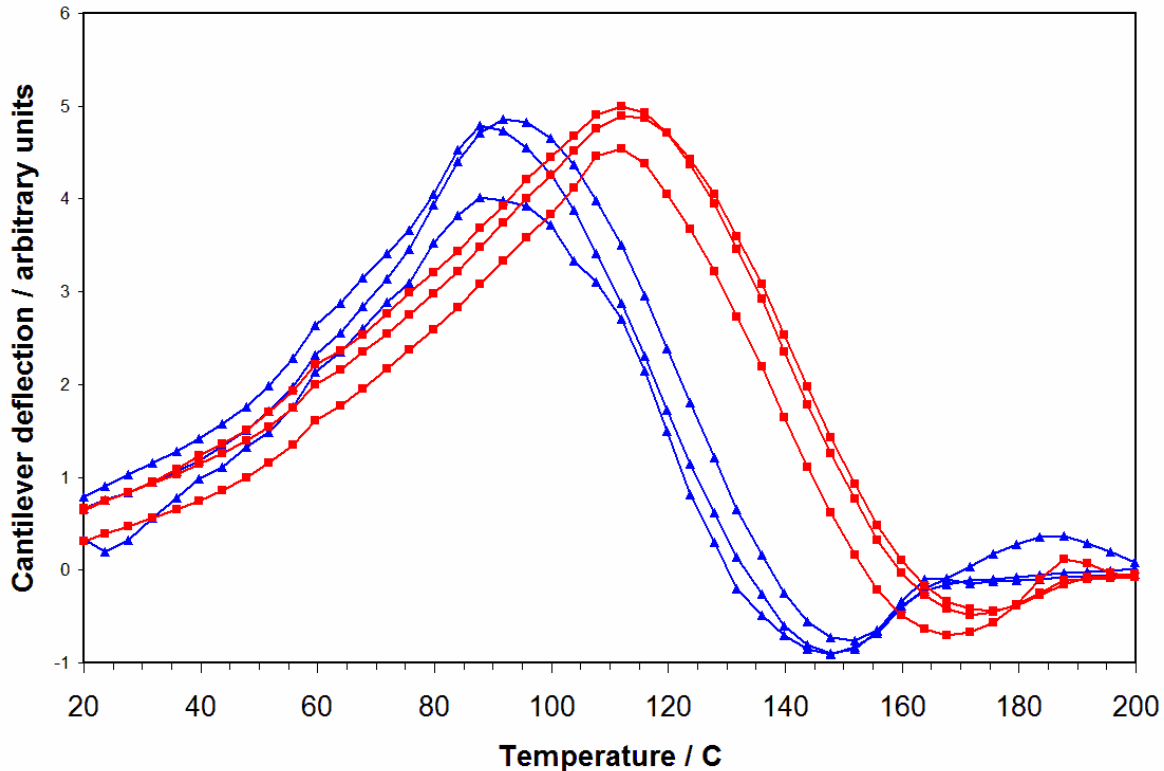


Fig. 4. nano-TA results for Sample 2. The continuous phase (squares in the fig) refers to the matrix and the occluded phase (triangles in the fig) refers to the inclusions.

Figure 3 shows topographic and tip deflection images acquired before and after nano-TA. The nano-TMA plots in Fig. 4 show that the T_m of the matrix is consistent at 112 °C and that of the inclusions varies from 88 to 92 °C.

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 thermal probe has a spatial resolution for imaging of sub-30 nm which can clearly reveal microstructural morphology as well as a conventional sharp AFM tip (in intermittent contact modes, if necessary). Nano-TA then enables the scientist to distinguish the phases by a measurement of their melting points. 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 allows analysis of a broad range of polymer samples.