



# nano-TA™: Nano Thermal Analysis

Application Note #3

Multilayer Biaxially Oriented Polypropylene (BOPP) Films

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## **Introduction**

**BOPP Films:** Biaxially Oriented polypropylene (BOPP) films, both heat sealable and non-heat sealable are extensively used in the packaging industry. These films are uni or multi-layered structures having a typical total thickness of only 15-25  $\mu\text{m}$ . The simplest multilayer films correspond to three-layer structures: one thick core layer of polypropylene homopolymer sandwiched between two thin (usually close to 1  $\mu\text{m}$ ) skin layers. Each layer has its own contribution to the properties of the film. In the standard three-layer structures, the core layer mainly provides the rigidity of the film, whereas the skin layers provide sealing and/or surface properties [1].

The aim of this work was twofold:

1. To investigate the thermal properties of three-layer BOPP films and in particular to use nano-TA to investigate the transition temperature of the 1  $\mu\text{m}$  skin layer in cross-section for the first time.
2. To investigate the effect of ageing on the thermal properties of BOPP films. An additional goal was to compare the differences in measurement with a Wollaston wire probe (probe radius of around 2.5 micron by 25 microns) versus the nanoscale probe (probe radius of around 20 nm) in nano-TA.

**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. (a breakthrough in spatial resolution  $\sim 50\text{x}$  better than the state of the art, with profound implications for the fields of Polymers and Pharmaceuticals). 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.

### **Experimental Setup**

The results were obtained using an 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 sample was a BOPP film manufactured by Solvay. The “fresh” version of the sample corresponds to the BOPP film as produced while the “aged” version corresponds to the same film annealed at 60°C.

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](http://www.anasysinstruments.com).

### **Results and discussion**

The films were analysed in two configurations: The vertical or top-down configuration and the cross-section configuration.

#### **Top-Down Configuration**

The uppermost layer (the one that the thermal probe is placed on) of the BOPP film is the skin layer and it has a thickness of around 1µm or less. Below it is the core layer with a thickness of 15-25 µm and this is again followed by the skin layer.

Figure 1 shows the results of a micro-TA experiment (with a Wollaston wire probe) performed on the sample. The figure contain the results for both the “fresh” and the “annealed” or “aged” film and show the phase transition measurement on the skin layer.

Figure 2 shows the results of a nano-TA experiment (with the nanoscale probe) performed on the sample. The figure shows the differences between the “fresh” and “aged” sample in terms of the phase transition measurement of the skin layer.

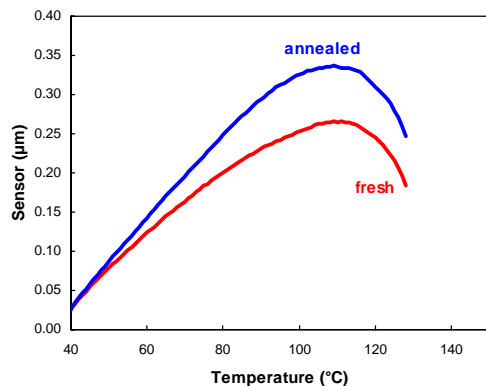


Fig 1: micro-TA on the sample

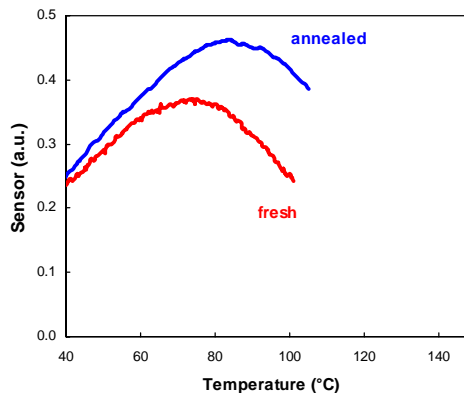


Fig 2. nano-TA on the sample

There are 2 aspects that clearly stand out when we compare Figures 1 and 2:

The main penetration of the skin layer is lower with nano-TA, around 80°C versus 120°C with micro-TA. The micro-TA does show a gradual penetration starting at approximately the same temperature as the main penetration of the nano-TA. This difference is most probably due to the difference in end radius and aspect ratio of the two probes. The micro-TA probe is significantly larger and lower aspect ratio and so requires more material to melt and move out of the way of the probe. Due to this, the nano-TA has a much higher sensitivity to smaller reductions in crystallinity (less material needs to melt for the probe to penetrate). It is known that the skin layer has a broad melting endotherm with the first onset of a small melting peak at around 50°C and a larger melting peak at around 110 °C. The micro-TA measurement is showing the onset of this larger melting peak while the nano-TA is sensitive to the smaller initial peak.

1. The measured  $T_m$  of the “fresh” layer is lower than that of the “aged” layer in the case of nano-TA while this distinction is not so clear in the micro-TA measurement. By annealing, the crystal lamellae become thicker and this increases their melting point. Again the higher sensitivity of nano-TA catches this distinction more clearly than the micro-TA.

### **Cross Sectional Analysis**

For this portion of the work, the BOPP films were embedded in epoxy resin and a cross-section

was made. Figure 3 below shows the cross-section of the BOPP film in the epoxy matrix.

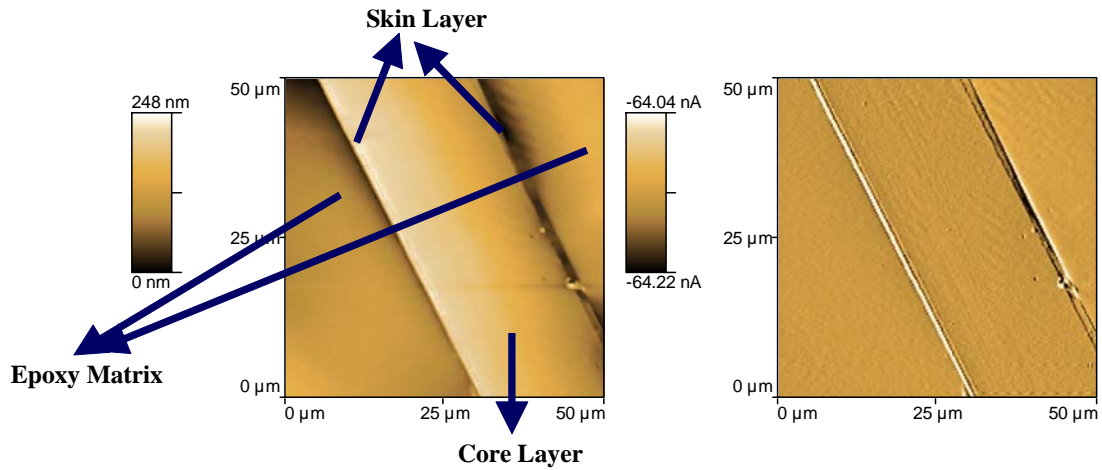


Fig. 3. Cross section of an embedded BOPP Film (Left Topography and Right Sensor Signal)

In the past, Barrel and co-workers (2) have attempted to measure transition temperatures of the skin layer in cross section but the lack of spatial resolution of the micro-TA technique prevented this from happening. The 100x improvement in spatial resolution of the nano-TA now allows this as shown in Figure 4 and Figure 5 below.

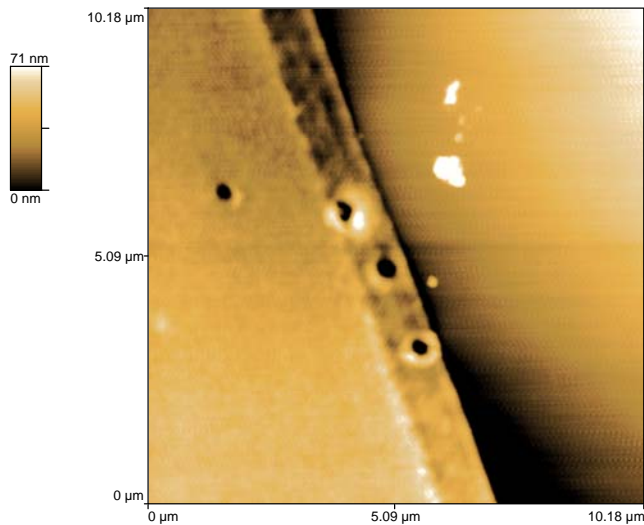


Fig. 4. Zoom in of the epoxy, skin and core layers showing the nano-TA indents in the skin layer and a nano-TA indent in the core layer.

Figure 5 below shows Local Thermal Analysis performed using nano-TA on the epoxy, core and skin layers. The melting temperature of the skin layer correlates well with the top-down measurements.

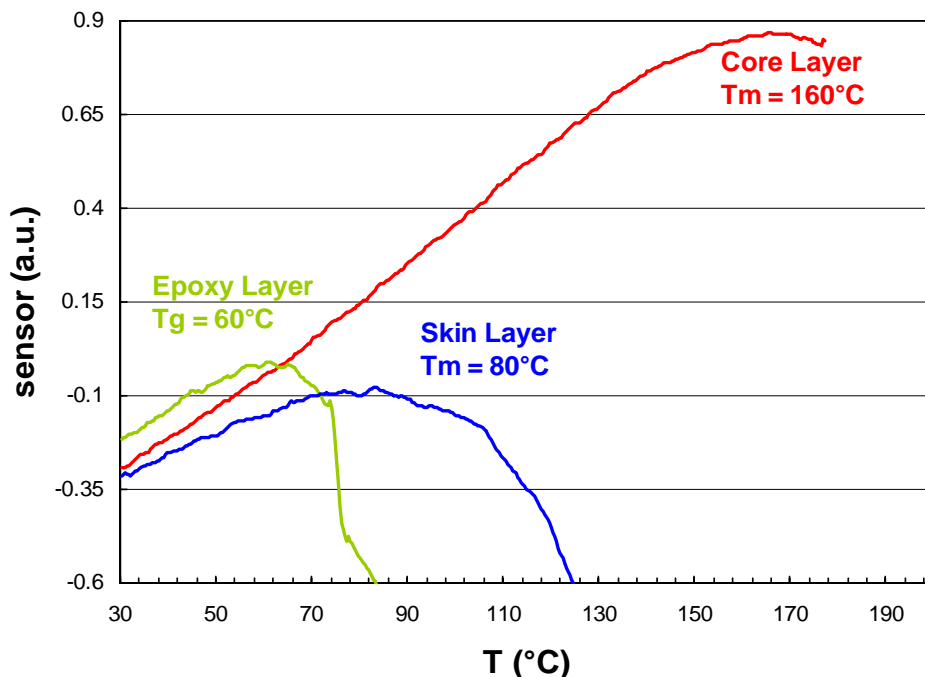


Fig. 5. Transition temperatures on the 3 layers measured using nano-TA.

## **Conclusions**

The sub-100nm thermal analysis capability of the nano-TA system has enabled transition temperature measurements of the skin layer in the cross section of BOPP films for the first time. It is clearly demonstrated that the nano-TA system is more sensitive than the micro-TA system in measuring onset temperatures and showed more distinct differences in transition temperatures for the fresh and the annealed BOPP films.

## **Acknowledgements:**

Dr. Antoine Ghanem of Solvay is kindly acknowledged for providing the BOPP samples.

## **References:**

- [1] Van Assche G., Ghanem A., Lhost O., Van Mele B., Polymer 2005; 46(18): 7132-7139
- [2] Abad M., Ares A., Barral L. et al, J. Appl. Polym. Sci. 2002; 85(7): 1553-1561