ZURÜCK

µTA™ - Innovative Surface Characterization by Combining AFM with Thermal Analysis

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Abstract

Micro Thermal Analysis (µTA™) combines the high resolution visualisation and positioning methods of scanning probe microscopy with the technology of thermal analysis. Equivalent to atomic force microscopy (AFM) the surface under investigation is scanned first to image its topography. Simultaneously contrasts in thermal conductivity and / or thermal diffusivity across the surface of the sample are acquired. Based on these images specific locations are then selected for further thermal analysis (µTMA and µMDTA as local counterparts to thermo-mechanical, TMA, and modulated differential thermal analysis, MDTA). Within this article the fundamental principles of atomic force microscopy and µTA™ will be explained. Following applications relevant to thermal analysis will be discussed to illustrate the abilities of µTA™.

Principles of Scanning Probe Microscopy

Since its first technical realisation about twenty years ago scanning probe microscopy invaded many fields of research due to its anormous flexibility and ease of use. In a scanning probe microscope the surface under investigation is probed by a sharp tip and the interaction between surface and tip is acquired. Depending on the design of the instrument this interaction can be, e.g., a force (as in Atomic Force Microscopy – AFM or in Scanning Force Microscopy - SFM) or tunnelling current due to a quantum mechanical phenomena (as in Scanning Tunnelling Microscopy – STM). All these interactions have in common that their values are varying strongly within a few nm distance between tip and surface. By introducing a feedback loop, which controls the tip to surface distance, the quantity of the interaction is then held at a pre-selected value while the tip moves across the surface. Acquisition of the vertical tip-position (z-axis) as controlled by the loop vs. the lateral position of the tip in an x-y – Raster is then used to generate a digital image. Typically the tip is stirred line by line across the surface to build up a square scan area.

During the first decade of SPM, the STM was the most widely used of all SPM techniques due to its comparatively simple mechanical design and its ability to achieve a resolution sufficient to image individual atoms on a surface. However, as STM is based on the measurement of a small current between a sharp metal tip and the surface, its operation is restricted to imaging conductive or at least semi-conductive samples. In contrast the operation of AFM is based on the measurement of forces and thus it is not bound to this limitation. In an AFM the sharp probing tip is attached to a small cantilever, which is sensitive enough to be significantly influenced by small forces down to the sub nN region, i.e. forces which are too small to dislocate single atoms on a sample surface. Depending on the configuration of the instrument and the used tip-cantilever system the tip senses repulsive Forces (electrostatic / Pauli Principle) as tip and surface are in immediate contact or the usually attractive van-der-Waals and hydrostatic forces acting at larger distances. Due to its flexibility AFM is the SPM technique most widely in use today and thus will be discussed in further detail.

In its most basic way of operation the probing tip is brought into immediate contact with the surface thus operating in the region of repulsive forces. While the tip is stirred across the surface changes in height within the topography will cause a deflection of the cantilever. This deflection change is optically magnified by observing the motion of a laser beam, which is reflected off the upper side of the cantilever (see figure 1 for comparison, where the laser beam is reflected off a small mirror attached to the cantilever). This motion is finally monitored and converted into an electrical signal in a four-zone photodetector. During the imaging process the feedback loop controls the vertical position of the cantilever mount to keep the deflection of the cantilever constant. Displaying this vertical position vs. the lateral position of the tip within the scan-area results in an image of the topography, in which all three dimensions are quantified. This is important for metrology applications or, e.g. studies of the roughness of a surface.

Further popular imaging modes are utilizing the change in resonance behaviour of a given tip-cantilever system as a function of tip-surface distance. This allows the image acquisition based on far ranging attractive forces. In these modes, commonly called non-contact modes, an immediate contact between tip and surface can be totally avoided. Depending on the operation parameters an intermediate stage between contact and non-contact mode can be accessed, in which the tip taps the surface during an oscillation cycle. As these modes lead to an undefined and permanently changing contact area between tip and surface they are not found to be useful for studies based on the thermal interaction between tip and sample and will thus not be discussed further in this article. It should be mentioned though, that there is a big potential for µTA™; within these modes as they can be combined with a stage allowing temperature control of the sample between -60°C and 300°C.

Introduction to µTA™

The methods of thermal analysis are well established and commonly recognised techniques for the characterisation of morphological and compositional quantities of samples on a macroscopic scale. By acquisition of e.g. the enthalpy changes (in DSC or MDSC), the weight of a sample (in TGA), the dimension or hardness of a sample (in TMA) as a function of temperature information can be gained about the crystallinity, the amount of filler material or the cross-linking density of a sample. Samples with a complex structure or samples exhibiting local variations in thermal properties throughout the dimensions of the sample lead to results, in which measured values represent the average over the volume under investigation. The contributions of single components or layers to a measured signal can be recognised, if they can be identified and separated by characteristic transition temperatures (e.g. temperatures of glass transitions, melting or decomposition) or the transition behaviour (reversible vs. non-reversible heat flow in MDSC). With these methods however the spatial distribution of single phases, the thermal characterisation of their interfaces and the study of the relation between morphological features and thermal properties is not possible in general. Thus it is a quite promising approach to combine some methods of thermal analysis with the unique capabilities of scanning probe microscopy.

µTA™ - 2D Imaging

The most striking difference between µTA™ and a conventional AFM can be found in the different tip design: in µTA™ the AFM tip-cantilever assembly is replaced by a thin wire, from which cantilever and tip are formed (see figure 1). As wire material a so called Wollaston wire is chosen, which consists of a 5µm diameter Pt-core surrounded by a more than 100µm thick Ag coating. The immediate tip area is then freed from the coating, leaving only the small Pt-core exposed to form the tip. At the tip end this typically results in an area smaller than 1µm x 1µm, which will be in contact with a surface during the investigation. The tip can now be heated by an electric current flowing through the wire. The generation of heat will be pronounced where the ohmic resistance of the wire is large, which is the case at the very tip end. Here the wire lacks the thick silver layer leaving only Pt with its small diameter, furthermore the resistance will be increased at the position, where the Pt-core has been bend to form the V-shaped tip end. Finally the temperature of the tip itself is a function of its ohmic resistance, and thus it can be controlled by introducing the shown assembly into a Wheatstone bridge circuit.

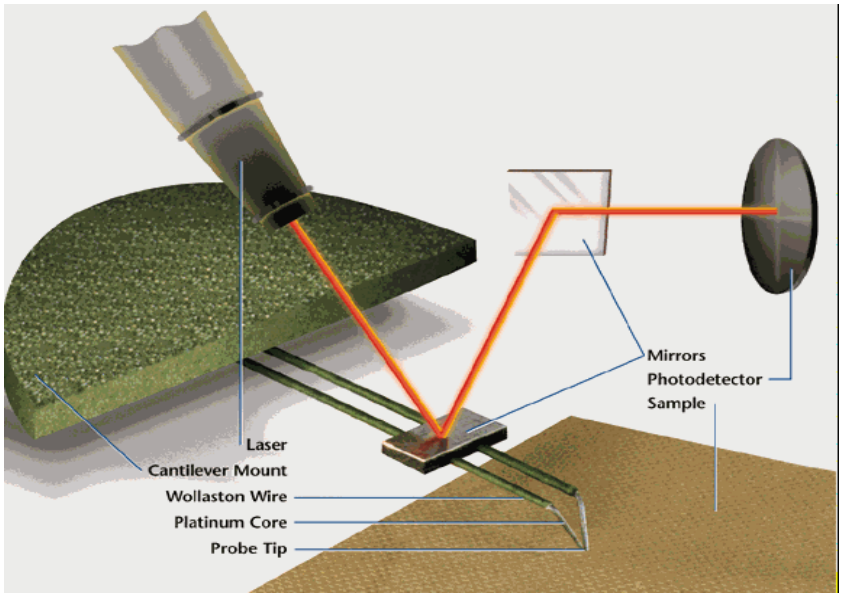
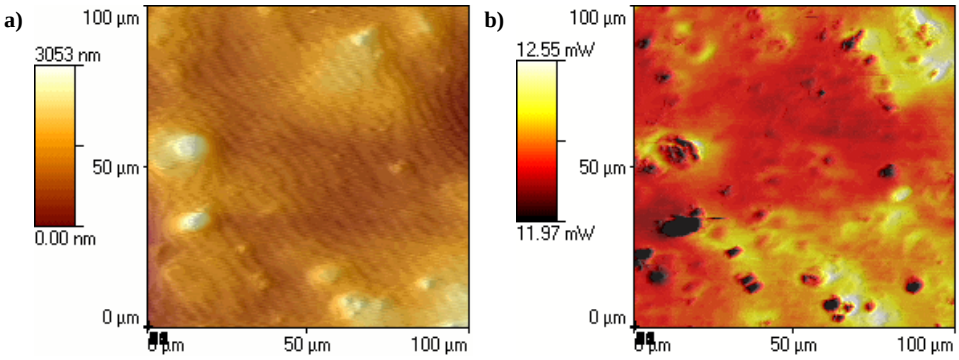


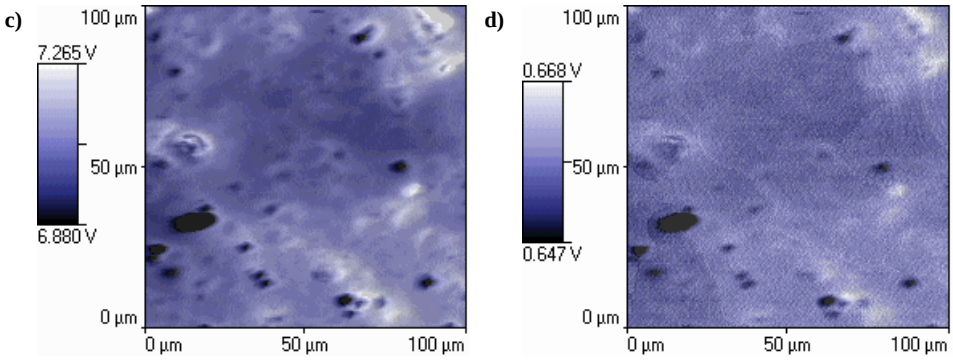
Figure 1: Shown is the design of µTA™. The AFM sensor is replaced by a thermal probe, which can be heated by an electrical current. The reflection of the laser beam is used to control the deflection of the cantilever.

With this assembly the topography of the surface can be imaged just as described above. Simultaneously the thermal properties of a sample surface can be acquired now as well: during the imaging process the tip is in direct contact with the surface. Changes in thermal conductivity across the surface result in a different heat flow between tip and sample. Thus changes in this property can be acquired by measuring the power level, which is necessary to maintain the tip-temperature at a constant, pre-chosen value. As this image is obtained isothermally the acquisition time is rather small, typically a scan is finished within a few minutes.

In addition to this constant temperature a small modulation can be added. For this purpose a small high frequency AC component is added to the electric current. During scanning the temperature response of the tip is then monitored by a lock-in amplifier. The response reveals information about the thermal diffusivity of the sample surface as it is a function of the thermal conductivity as well as the heat capacity. The frequency can be chosen to values of up to 50kHz, which is possible due to the small total heat capacities involved at the tip and at the affected sample area. The most striking and interesting aspect of this modulation technique can be found in the fact, that the depth of thermal information can be varied by tuning the modulation frequency. Low frequency signals as well as the isothermal measurement described before yield information depths of roughly 10µm in a typical polymer application. By increasing the frequency the signal becomes more surface sensitive limiting the depth to values even below 1µm at 50kHz on selected samples. Again, as the modulation frequency is high, the acquisition is rather fast allowing also an image to be completed within a few minutes.



Topography **Thermal Conductivity**



Thermal Diffusivity, 5 kHz **Thermal Diffusivity, 50 kHz**

Figure 2: Images of topography, thermal conductivity and thermal diffusivity obtained on a metallic paint film. The images of thermal conductivity and diffusivity measured at low frequencies display sub-surface particles, while the diffusivity image obtained with a high frequency exhibits only particles present at the surface.

To illustrate the use of all three imaging modes the results of the investigation of a paint-film are displayed in figure 2. Shown is the surface of a metallic paint film, consisting of larger metal flakes, pigments and a polymer matrix. The area under investigation was 'shiny', compared to duller areas nearby. It is the goal of the investigation to show the differences between these areas. The topography image (a)) reveals with a height scale of just about 3µm only small changes in height within the displayed 100µm x 100µm scan. In parallel the image of thermal conductivity displayed in figure 2 b) was acquired with a temperature of 200°C at the tip. The thermal conductivity shows areas of bright colours (i.e. higher power) revealing the position of the metal flakes far below the surface. Also smaller features are shown in dark colours, indicating the positions of pigments in or close to the surface. Those sticking out of the surface can be assigned to protrusions in the topography image and cause quite large depressions of the imaged conductivity. Sub-surface particles show smaller depressions as the signal 'smears' out, but are still readily visible in the image. Within the images of thermal diffusivity (c)-d)) these sub-surface pigments disappear with the increase of modulation frequency. Some of the particles are still visible while measuring with an amplitude of 10°C at 5kHz, in contrast only the surface particles remain in the image when acquiring the data at 50kHz. Concluding it should be mentioned, that images of dull areas reveal a high increase in the number of pigments close to the surface.

µTA™ - Local Thermal Analysis (LTA)

Having imaged the surface and having identified features or phases of interest, the thermal properties of any specific point may be acquired in µTMA, µDTA and µMDTA experiments. For this purpose locations may be chosen within the image. The tip is positioned at these locations first and is then subject to a given temperature program.

µDTA curves display the power level necessary to keep the heating rate constant. The power is measured in comparison to a reference probe, which experiences the same temperature program. As in macroscopic DTA or DSC measurements, an endothermal transition like melting results in an increase of power consumption, as shown in the curves of figure 3. Displayed is the melting of a PET surface. In this case there is only a gradual change in power consumption throughout the temperature range, until melting of a surface phase occurs at a temperature of 257°C, consistent with the onset of the melting peak in macroscopic DSC measurements. Upon melting the power signal (here shown as a derivative) rises sharply followed by a decrease, when the tip does not penetrate into the melt anymore.

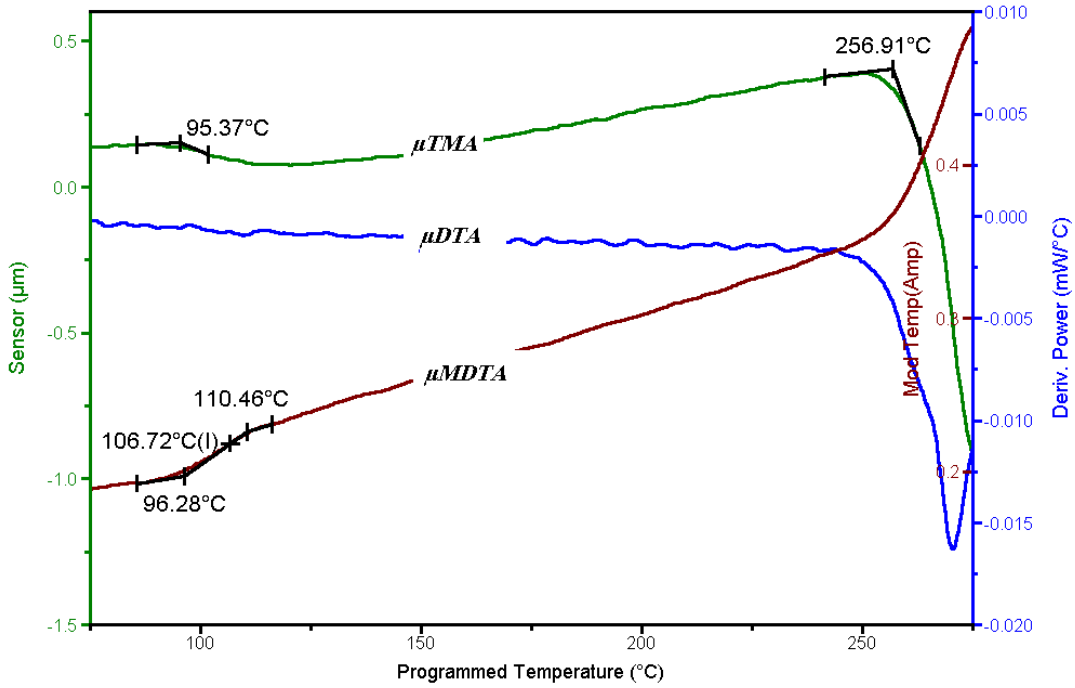


Figure 3: µTMA, µDTA and µMDTA signals as obtained on a PET sample. The surface melts at 257°C, resulting in a sharp peak in the µDTA signal. The µTMA signal increases as the sample expands, until the tip sinks in upon melting.

The µMDTA curve reveals the amplitude of the AC power required to maintain a selected temperature modulation at the tip. The respective curve is also included in figure 3, showing a sharp transition during melting. This signal is especially useful during the study of those phase changes, which require only small amounts of power but cause a larger change in heat capacity, as can be seen for the glass transition above 100°C.

Finally µTMA curves display the change of the vertical displacement of the cantilever as a function of tip temperature. An expansion of the sample causes an increase in the value, and indeed the TMA signal rises before melting occurs in the curves displayed in figure 3. The value decreases if, e.g., the sample softens during melting with the result that the tip sinks into the sample. This signal is always obtained simultaneously with the µ(M)DTA signals, and the parallel interpretation makes it well possible to distinguish between different types of transitions.

Being finished with the investigation of a selected location, the tip is automatically raised from the surface, heated to a high temperature to decompose contamination, and positioned at the following selected area of interest. Last not least it should be mentioned that realised heating rates are rather high with typical values ranging between 2 K/s and 10 K/s (i.e. 120 K/min up to 600 K/min!) due to the low heat capacity involved at tip and sample. Typically sample areas with diameters ranging between 2 and 10 µm are affected during LTA depending on the studied transition itself as well as on the acquisition parameters (force, final temperature, ...).

Applications

Following possible areas of applications will be discussed. Due to the flexibility of the instrument µTA™ has gained widespread use and in this contribution only selected applications can be discussed to illustrate the typical use of the instrumentation. For further interest a list of recent publications is added to this article. Thus the further discussion will focus on two applications:

- measurement of glass transition temperatures at the interface between toner particles and a low viscosity (‘oil’) film on an overhead transparency.
- analysis of the cross-section of a three layer paint film.

Studies of the thermal properties of polymer blend materials are of interest as they reveal information about the properties of the material within the phases. As an example the topography and thermal conductivity images obtained on a PE/PP film are shown in figure 4. The topography image reveals height changes across the surface which are related to the different blend components. The different phases can also be easily identified as areas of different thermal conductivity in the thermal image. These images allow then to position the tip on individual particles for further LTA. The results are summarised in figure 5, where µTMA-curves obtained on the different phases of the film are shown. The melting temperature observed on the matrix of the film equals the melting range of PP with 165°C. The melting temperature drops to 110°C on the embedded blend component, revealling this material to be low-density PE.

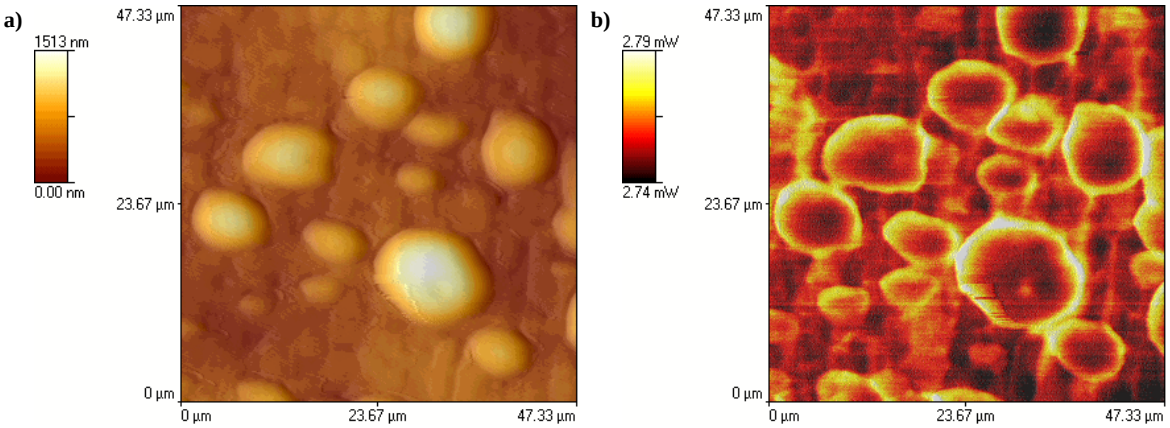


Figure 4: Topography (left) and thermal conductivity (right) of a PE/PP blend. The topography as well as the contrasts in thermal conductivity reveal the presence of two phases at the surface.

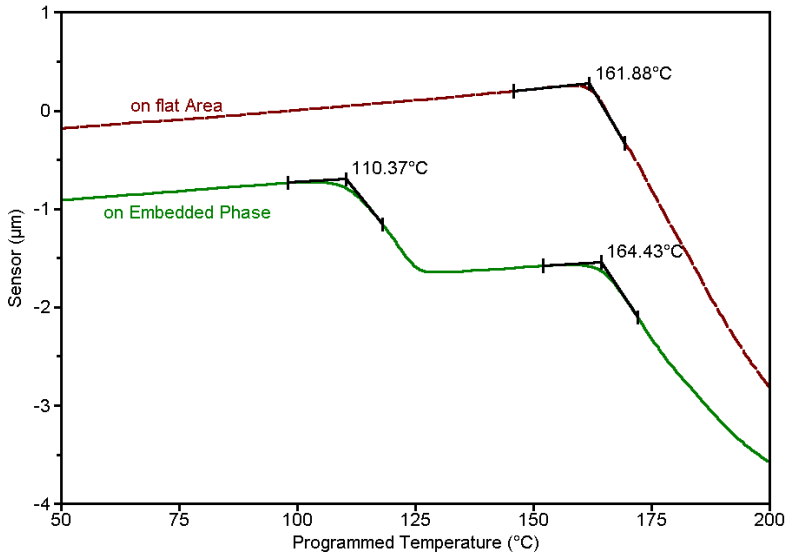


Figure 5: µTMA Curves measured on top of the embedded component as well as on the embedding medium.

The cross-section of a multilayer paint film is shown in figure 6. The layers were cut by a saw and thus the topography image reveals a rough surface. However the thermal conductivity image shows a good contrast between the individual layers. For a further analysis, the tip is then placed on each individual layer and the temperature is raised in each case until the layer begins to soften. The individual layers can then be characteriszed by their gradients in softening temperature towards the center layer, which can be identified by the high thermal conductivity, shown as bright color in the thermal conductivity image of figure 6. As can be derived from figure 7 the softening temperature of the outward layers drops towards the center layer with the relatively high Tg at 136°C. The temperature change within the outward layers covers just 7°C with a drop from 110°C to 103°C at the interface. In contrast the temperature change within the lowest layer is much more pronounced with a decrease of the temperature below 80°C. Such changes can in this case be traced to an enrichment of polyphosphates in the lower layer, which are evolving from the treatment of the wood prior to painting.

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Outlook

In this contribution the capabilities of µTA™ have been introduced and some applications have been discussed. Based on an AFM itself µTA™ links the characterisation of the Nano- and Microworld to the quantitative analytical power of macroscopic thermal analysis. New applications will evolve with the availability of a temperature controlled sample stage allowing the analysis of low temperature transitions in e.g. rubber materials. Also decomposition can be well characterised by the coupling of µTA™ to GCMS, which has been introduced recently.

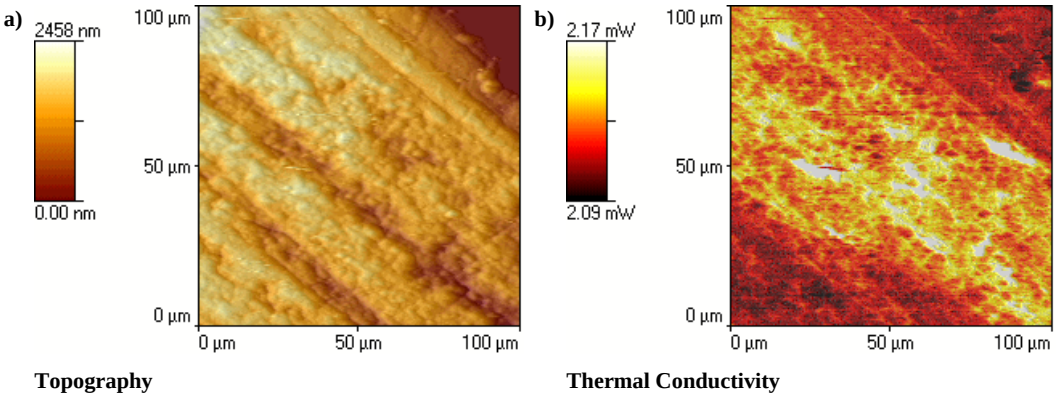

Figure 6: Topography and thermal conductivity imaged in the cross-section of a multilayer paint film system. The different layers can be clearly distinguished by their differences in conductivity, with the center layer being clearly identifiable by its high thermal conductivity.

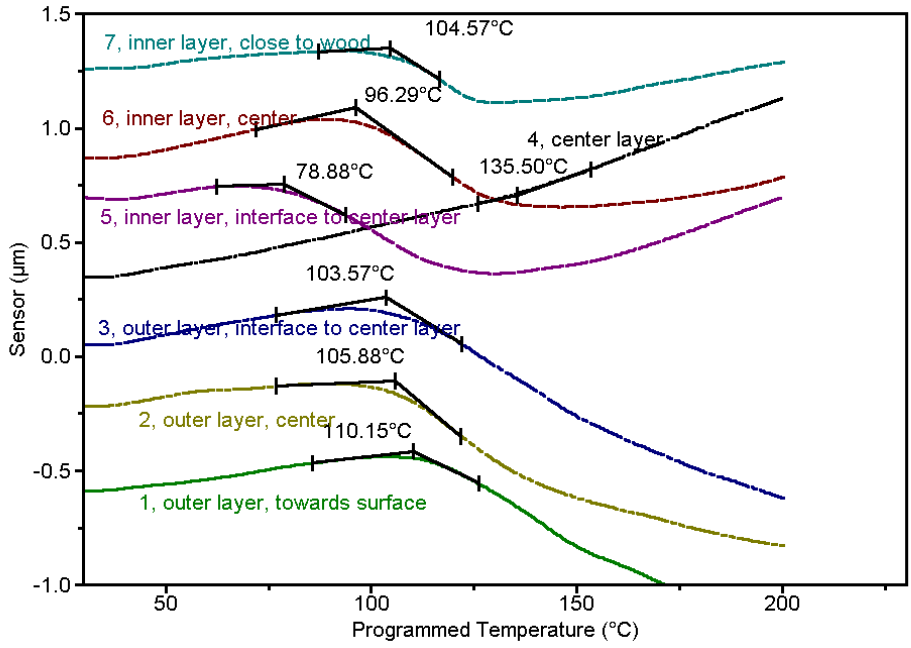

Figure 7: µTMA curves obtained on different areas of the layers displayed in the cross-sectional image. The softening transitions can be clearly identified can be clearly identified as the signal decreases if the tip sinks into the surface.

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