TA Instruments

Thermal Analysis & Rheology

Characterisation of Surface Morphology Changes by Micro-Thermal Analysis

Introduction

The ability to measure the localised thermal properties of a sample is a powerful capability of Micro-Thermal Analysis as it enables the differences between bulk and surface properties to be studied. The surface properties have a critical bearing on the stability, reactivity and performance of a material. Often important surface properties are masked in conventional thermal analysis measurements as their influence is “averaged” over the bulk response of the material. Consequently, valuable information regarding the surface morphology of the sample is lost. Micro-Thermal Analysis provides a unique way to study the surface transition temperatures and to measure their changes across the surface of a material.

In conventional thermal analysis, a sample of known mass (typically a few milligrams) is placed in a furnace. The furnace surrounds the entire sample. The heating rate for such experiments is selected in accordance with the size of the sample, as well as the size of the furnace in order to minimise thermal gradients within the sample. For DSC experiment one would typically use 10 to 20 °C/min. For DMA experiments, where the sample (and therefore the furnace) is larger, heating rates of 2 to 3 °C/min are typical.

In Micro-Thermal Analysis a 5µm diameter platinum wire that acts as both the heater and the temperature sensor. Consequently, the mass of the “furnace” and sample are several orders of magnitude smaller than conventional thermal methods. This enables heating rates of 500 to 1000 °C/min to be used. Thus in Micro-TA a small “furnace” is brought into contact with the surface of (relatively speaking) an infinitely large sample. This type of measurement leads to a new type of thermal analysis Localised Thermal Analysis (LTA).

Localised Thermal Analysis experiments can be used to explore morphology changes across the surface of a material by measuring the localised transition temperatures. By measuring the displacement of the thermal probe attached to an atomic force microscope (AFM) while it is heated, Micro-Thermomechanical Analysis (µTMA™) experiments can be made. By measuring the amount of power required by the thermal probe to maintain the temperature program, endothermic and exothermic events can be measured. This technique is called Micro DifferentialThermal Analysis (µDTA™). Both of these techniques provide a means to measure the localised transition (softenin)

temperatures. By measuring the displacement of the thermal probe (attached to an AFM) while it is heated, Micro-Thermomechanical Analysis (µTMA) experiments can be made. By measuring the amount of power required by the thermal probe to maintain the temperature program, endothermic and exothermic events can be measured. This technique is called Micro Differential Thermal Analysis (µDTA). Both of these techniques provide a means to measure the localised transition temperatures (softening, melting, oxidation) of an area approximately 2 by 5 micrometers.

Unlike conventional thermal analysis, the sample size is not known in an LTA experiment and only relative transition temperatures can be reported. Care must be taken when comparing these localised transition temperatures with the bulk transition temperatures measured using conventional thermal methods. Often surface topography, oxidation or enrichment can lead to differences in the transition temperatures measured by conventional thermal methods and localised thermal analysis. Neither are wrong, one is measuring bulk properties, while the other is measuring surface properties. A similar effect is encountered when comparing the bulk and surface rheology of a sample.

Nylon 6/6

Figure 1 shows the localised thermal analysis data obtained at two different locations upon a single pellet of Nylon 6/6. The solid circles represent the µTMA and µDTA data for one location (Location 1), and the open circles represent the µTMA and µDTA for the other location (Location2).

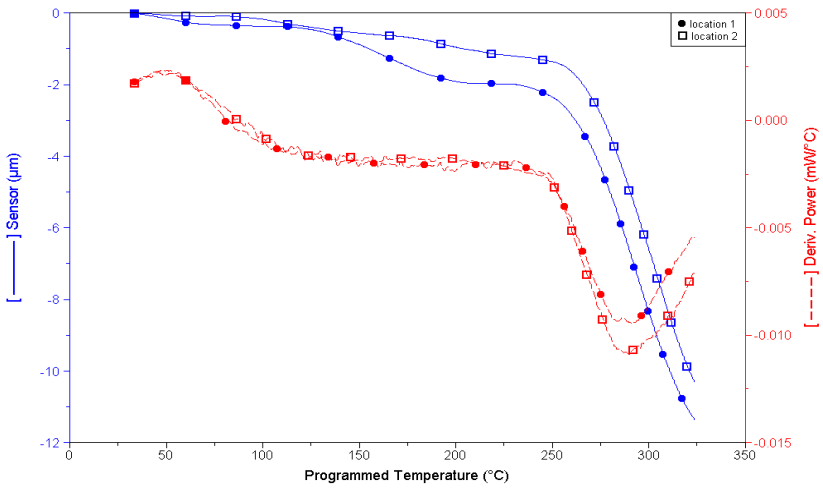

Figure 1. Localised Thermal Analysis data from two locations on a Nylon 6/6 pellet.

The µDTA curves show an onset for the surface melting on the Nylon 6/6 to be ~250 °C with a peak maximum ~290 °C. As the size of the sample being heated is unknown, it is not possible to look at the area under the µDTA curve as a measure of crystallinity. However, as the measurements were made under identical conditions, the peak height may be used to assess the relative crystallinity at these two locations. Using the peak height to evaluate crystallinity is a typical measurement in conventional DTA

system. As Location One has a higher peak height in the μDTA curve, it is likely that there is higher level or orientation present at this location.

The μTMA curves also show the softening and melting of the Nylon 6/6 at~250 °C. However, Location 2 also shows an additional softening region between ~125 to 175°C. This additional softening may be due to the effect of localised water absorption upon the surface of the Nylon. Nylon is well known to readily absorb moisture and this can have a significant effect on its processing behaviour and this could well be the cause of the variation in surface morphology.

It should be noted that as the amount of sample heated in these LTA experiments is so small that the heating rate used was 600 °C/min. Also, as the platinum filament used to heat the sample is of such a low thermal mass it cools down to room temperature in a few seconds. The total time to make the measurements in Figure 1 was less than two minutes.

Gel Contaminants

One of the essential quality issues of thermoplastic films is their clarity and opacity. Understandably, the presence of imperfections often referred to as gel particles in the film is something to be avoided by the manufacturer of the thermoplastic film. These imperfections can arise from poor processing conditions, raw material feedstocks or contamination during production.

For example, if the molecular weight range of the polymer is not controlled during the polymerisation process, or if the level of branching increases gel particles may result when the polymer is used to make a film. Alternatively, gel particles may be formed in the film, even when using good feedstock due to poor cleaning of equipment between batches or from other forms of contamination.

Figure 2 show an optical micrograph of a gel particle taken from a polyethylene film. It measures less than 0.5 mm across. Although small, the presence of a significant number of gel particles in the film may lead to the customer rejecting the delivery of the batch.

Such a gel particle was analysed at multiple locations using the Micro-TA system. The data from four

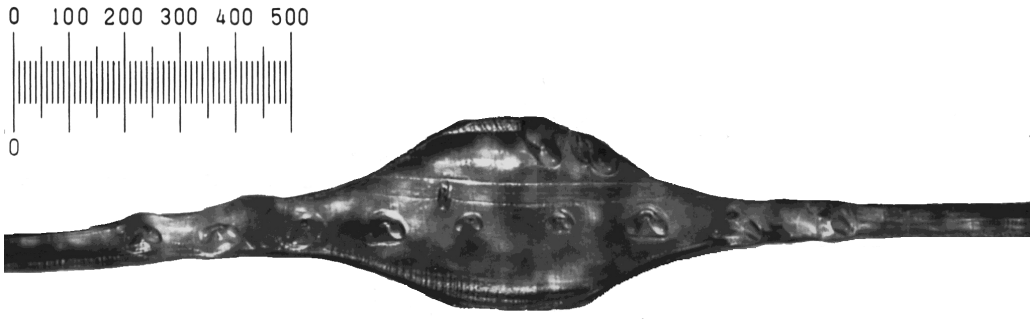

Figure 2. Optical Micrograph of a Gel Particle cut from a Polyethylene Film

of these locations are shown in Figure 3. Locations 1 and 4 are on either side of the gel particle and represent the bulk material, whereas locations 2 and 2 are at the center of the gel particle. The µTMA data shows that the gel particle is softening about ~20 °C higher than that of the bulk material. In addition, the thermal probe does not penetrate into the gel particle as deeply as it is in the bulk during the measurements, indicating that the imperfection has a higher molecular weight than the bulk. The µDTA data also show that the gel particle has a much lower crystallinity (due to the reduction in peak height) than the bulk. All of these results can be interpreted to indicate that the imperfection is due to unwanted cross-linking of the polyethylene film during production.

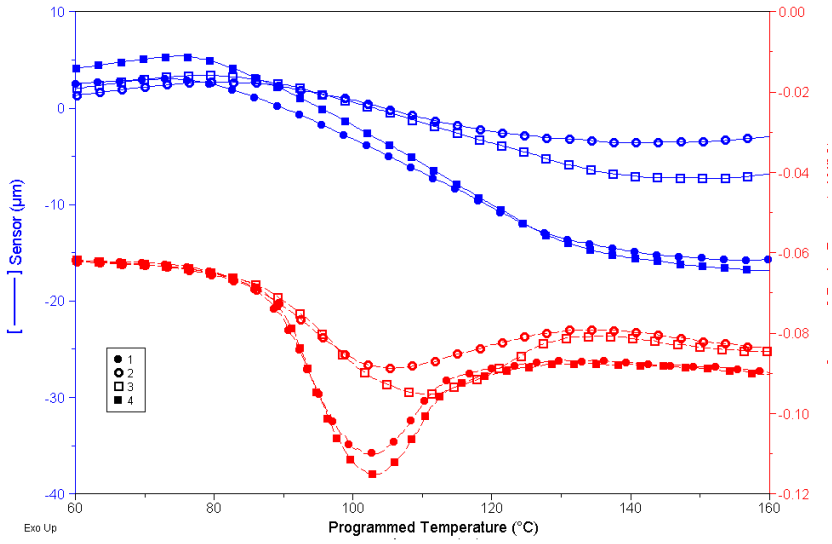

Figure 3. Localised Thermal Analysis data from 4 locations across a Polyethylene Gel Particle.

Prior to the availability of the Micro-TA system this problem was assessed using Gel Permeation Chromatography whereby multiple gel-particles would be cut out of the polyethylene film for analysis, a sample preparation technique that would take several hours to obtain enough material. The Micro-TA data shown above were collected in less than 15 minutes.

Micro-Thermal Analysis provides a useful tool for the characterisation of gel particles and to help differentiate between the various causes of their formation

Polymer Weld

The assessment of the quality of a polymer weld can simply be made by measuring the force required to pull the two parts away from each other. Visual inspection will then indicate the location of the failure. However, Micro-Thermal Analysis provides a way of assessing the “weak spot” in a weld before it is pulled apart.

Figure 4 shows two images obtained by scanning the thermal probe across the surface of a polymer containing an embedded metal wire. In this system the metal wire is inductively heated to to facilitate the welding of two pieces of material placed in contact with each other. These images show different views of the surface of the material. For a detailed review of how these images are obtained refer to the µTA 2990 brochure.

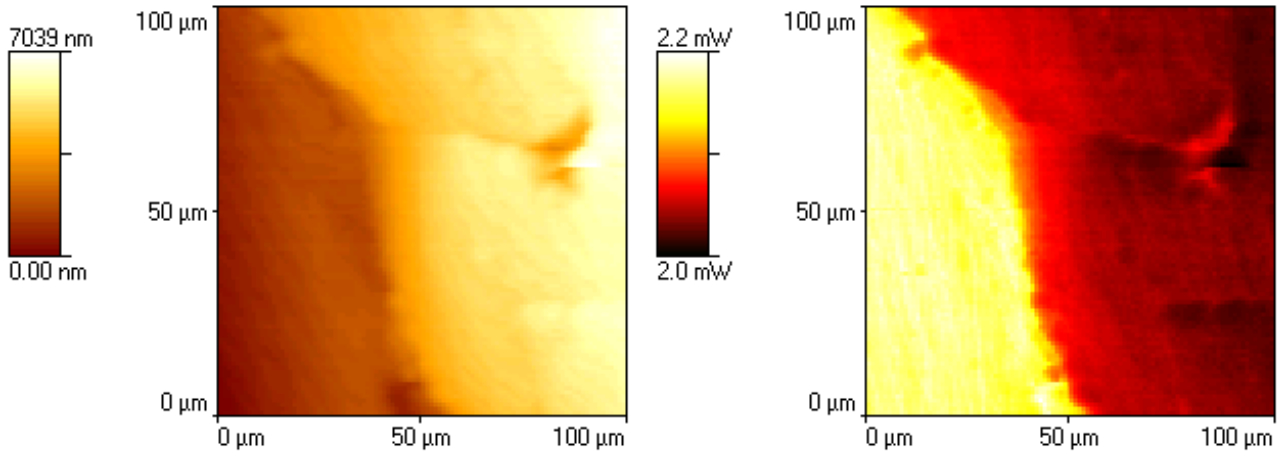

Figure 4. Topography (left) and Thermal Conductivity (right) images of a heater wire emdedded in a polymer substrate.

Although there is some topographical contrast at the interface between the wire and the polymer substrate, the contrast is markedly different in the thermal conductivity image. The highly thermal conductivity of the wire (bright area) is clearly visible in contrast the poorer thermal conductivity of the substrate (darker area)

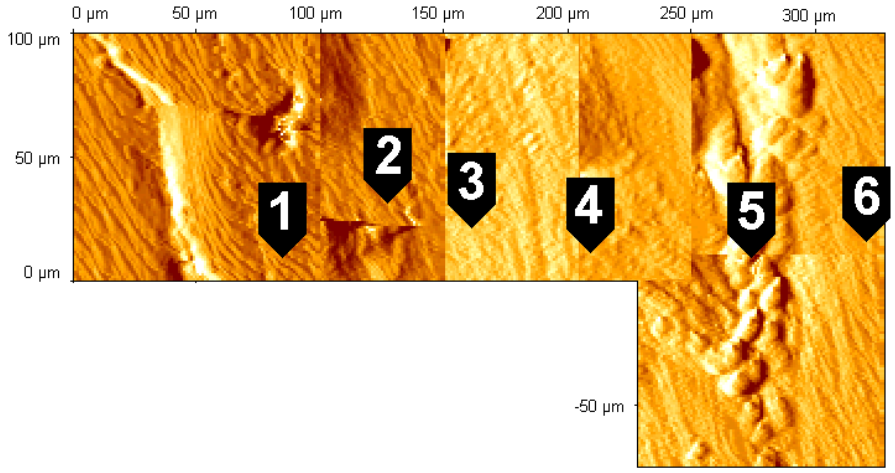

Figure 5. Composite Topography image of the polymer weld showing the locations of the Local Thermal Analysis experiments.

In order to examine a larger area around the heater wire, the sample was translated underneath the Micro-TA head and re-imaged. The resulting images were then overlaid to produce the composite picture shown in Figure 5. The heater wire can be clearly seen on the left of the image and the weld line runs vertically down the right of the image (interestingly about 200µm away from the heating wire)

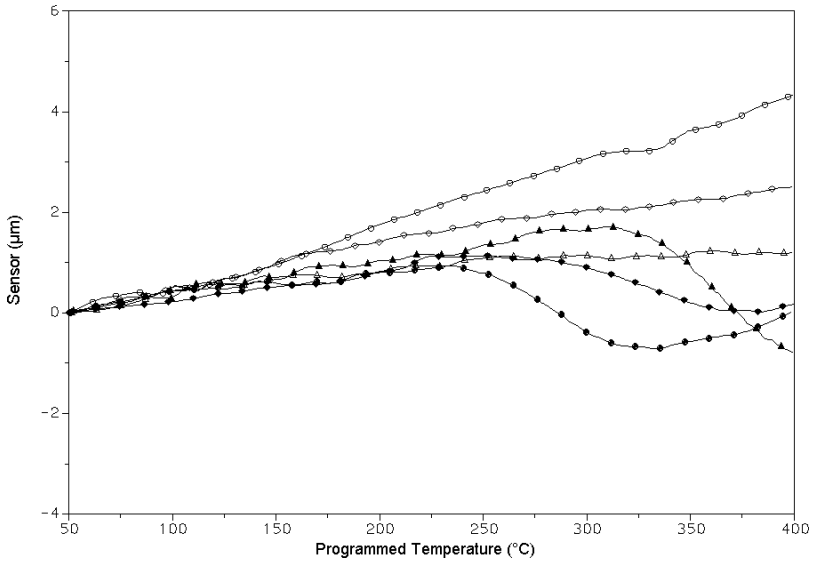

Figure 6. Micro-Thermomechanical Analysis data obtained from the surface of a polymer weld.

µTMA experiments were carried out across the surface of the polymer weld to measure any softening point temperature variations (Figure 6). The data for Locations 1 and 2 (close to the heater wire) show little or no softening up to 400 °C and indicate that the polymer is highly cross-linked in this area. As one moves away from the heater wire, towards the weld the localised softening temperature decreases (Locations 3 and 4) and then rises again (Locations 5 and 6). The polymeric material lying exactly on the weld line has a softening temperature in excess of 400 °C. Why this should occur in not clear it is speculated that mechanical vibration brought about by the AC heating of the wire may provide a localised source of heat along the weld line itself.

By providing a means to assess the localised transition temperatures across the surface of a weld line, it is possible to locate the “weak spot” of the weld. In this example, the weak spot is in-between the heater wire and the weld line, not as one might suspect the weld line itself. These tiny changes in localised properties are masked if a bulk sample is analysed by conventional thermal methods. It is said, “a chain is only as strong as the weakest link”. Micro-Thermal Analysis provides a means to locate the “weak link” in such situations.

Summary

These results clearly show the value of localised thermal analysis measurements in assessing changes in transition temperatures across the surface of a sample. Measuring these changes provide an additional tool to the thermal analyst to assess surface quality, contamination and mechanical properties.

The ability to measure localised transition temperatures and to map them across the surface of a sample provides a powerful tool in the material scientists problem solving armoury.