Micro-Thermal Analysis – An Holistic Approach to Materials Characterisation

Introduction

The measurement of transition temperatures, such as glass transitions and melting temperatures, can provide a great deal of useful information about the structure, and even the composition of polymer systems. More than one glass transition demonstrates a phase separated morphology, melting behavior provides information about crystallinity, a low glass transition temperature (Tg) for a cured system (compared to some standard) demonstrates lower and possibly inadequate cure. A broad glass transition indicates possibly inhomogeneous cure. Often structural information is inferred from the bulk measurement but these measurements can never directly provide structural details.

To obtain structural detail, some form of microscopy is needed. However, it is often difficult to interpret micrographs in terms of the distribution of phases because they provide insufficient compositional distribution information. Thus the microscopist is forced to infer this aspect of morphology.

In addition to thermal analysis and microscopy, characterization scientists often also use spectroscopic methods to obtain composition information and positively identify a material using a search library.

The ideal solution would be to create a tool that would combine all of the above aspects of visualization, characterization and analysis. A new technique called Micro-Thermal Analysis (µTA) has combined all of these capabilities in a single instrument, and provides the basis for a family of related techniques.

Micro-Thermal Analysis

Micro-Thermal Analysis is a collection of techniques that use probe microscope technologies to study the relationship between temperature and the properties of a material on a microscopic scale.

The µTA 2990 Micro-Thermal Analysis System can sequentially provide ***Structure*** (imaging) – ***Property*** (thermal analysis) – ***Composition*** (evolved gas collection) information on the same sample.

- **Micro-TA** can be used to ***image*** the distribution of components, materials, phases, domains and contaminants. The 2990 images a 100 x 100 µm region of the sample with sub-micrometer resolution

and measures surface topography, thermal conductivity (among others) images of the sample by scanning (rastering) the thermal probe over the surface of the sample

- **Micro-TA** can be used to make ***local thermal analysis*** measurements at any specific location on surface identified in the imaging step above. The calorimetric and mechnical properties of a breack 2 x 2 μm region can rapidly be measured as the small thermal probe and sample size permit heating and cooling rates of over 100 ºC/min to be employed.

- **Micro-TA** can be used to pyrolyse a region or area of the sample by heating the probe to a temperature above that of the samples decomposition temperature. The ***evolved gas collection*** of the decomposition products are then collected onto a sorbent material that - at a later time - can be thermally desporbed and analyzed by Gas Chromatography / Mass Spectrometry (GC/MS) to chemically identify the sample.

Problem Solving Using Micro-Thermal Analysis

Fig 1 shows the MDSC results from a polystyrene molded part that had failed in the field, although the material had passed the organisation's quality control checks prior to shipment. The quality control test for the polystyrene is the measurement of glass transition temperature using MDSC. MDSC is typically used to measure the Tg of the "as-received" material with the complex heat capacity signal is devoid of all non-reversible events.

A shift in the Tg can be an indication of non-conformance due to changes in molecular weight distribution. The complex heat capacity clearly shows the typical heat capacity step change at the glass transition region at ~100 °C typical of Polystyrene. From this MDSC data it is unclear why the component might be failing.

The polystyrene component was then analysed using Micro-Thermal Analysis.

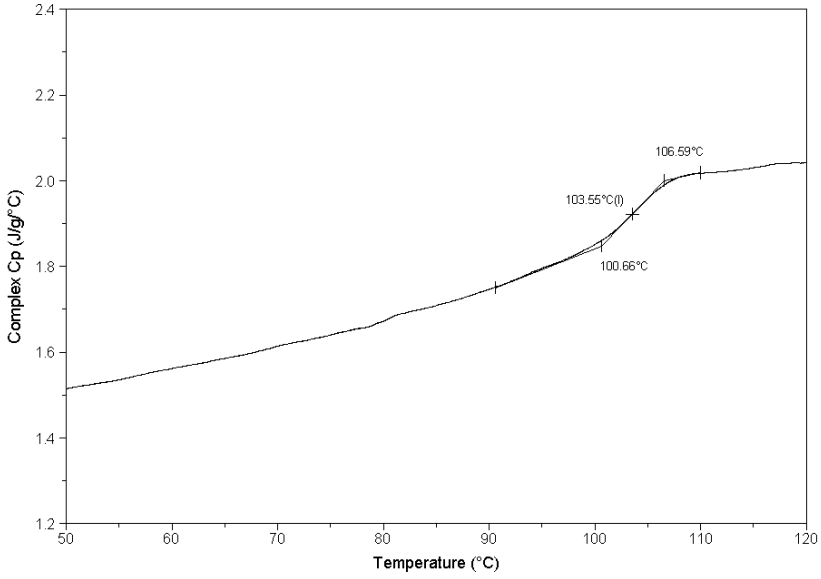


Figure 1. *Complex Heat Capacity signal for the polystyrene molded part.*

I) Visualisation – Structure

First the surface of the material is imaged. Although little detail is seen in the topographical image, the thermal conductivity image does show significant image contrast Fig 2. This image contrast is due to two phases with differing thermal conductivities being present in the sample.

The upper phase requires more power to maintain the thermal probe at a constant temperature as heat is being "pulled" away from the thermal probe by the sample. By comparison, the lower phase requires less power to maintain the probe at a constant temperature. From the image in Figure 2 it can be concluded that at least two components are present at the surface of the sample.

It is likely that the second component exists as a small contaminant, otherwise it would have affected the MDSC results shown in Figure 1. It is not possible to identify either of the components from the thermal conductivity image.

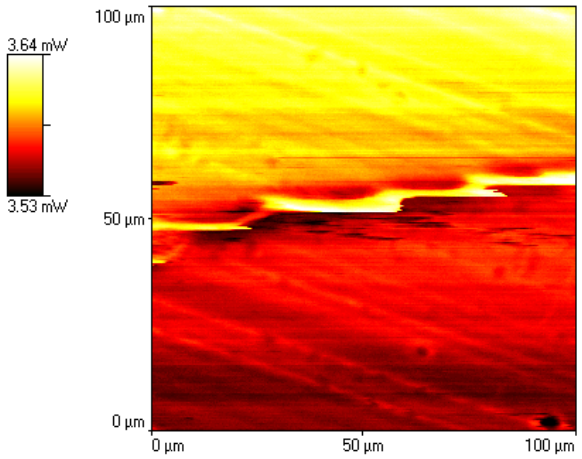


Figure 2. *Thermal Conductivity image of the polystyrene molded part.*

II) Characterization – Property

Local thermal analysis (LTA) experiments were than made on each of the "upper" and "lower" phases. For the LTA experiments, the thermal probe is brought to rest at a specific location on the surface and the probe heated. The position (height) of thermal probe is measured while heating and the resulting data are the "micro" equivalent of thermomechanical analysis. The Micro-TMA data from each phase are shown in Figure 3. The Micro-TMA data from the upper left hand corner of the image (25 x 75 um) is labelled with the solid circles (•), while the data from the lower right hand corner of the image (75 x 25 um) is labelled with the open squares (□). The upper phase is seen to soften around 100 °C, while the lower phase has a softening temperature around 25 °C lower at 75 °C.

Turning once again to the MDSC data in Figure 1, a broad glass transition can be seen around 30 °C lower than that in the polystyrene. The bulk sample appears to have a lower percentage of the material with a lower glass transition than is seen by the imaging of the surface. This would indicate that the majority of the lower Tg material is concentrated at the surface of the sample, rather than being evenly distributed within the bulk.

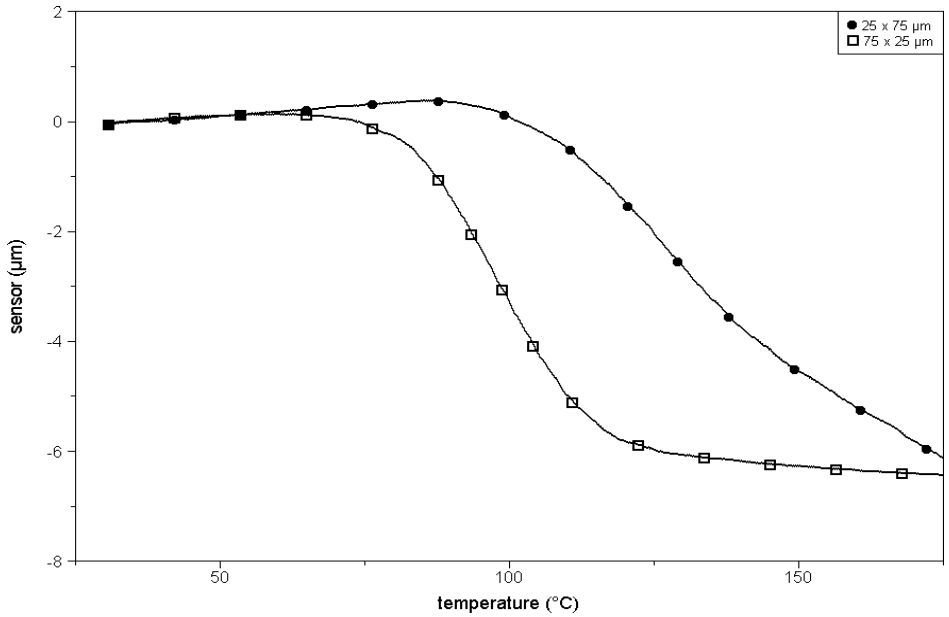


Figure 3. *Micro-TMA results for each of the phases present in the polystyrene moulded part.*

III) Analyze - Composition

To establish the composition of each phase, the decomposition products obtained from heating the thermal probe to 600 °C for 5 seconds were collected for both the upper and lower phase. This micro pyrolysis experiment creates small craters upon the surface of the sample that can be seen by imaging the topography of the surface (Figure 4.) The decomposition products are collected into tubes containing a sorbent material.

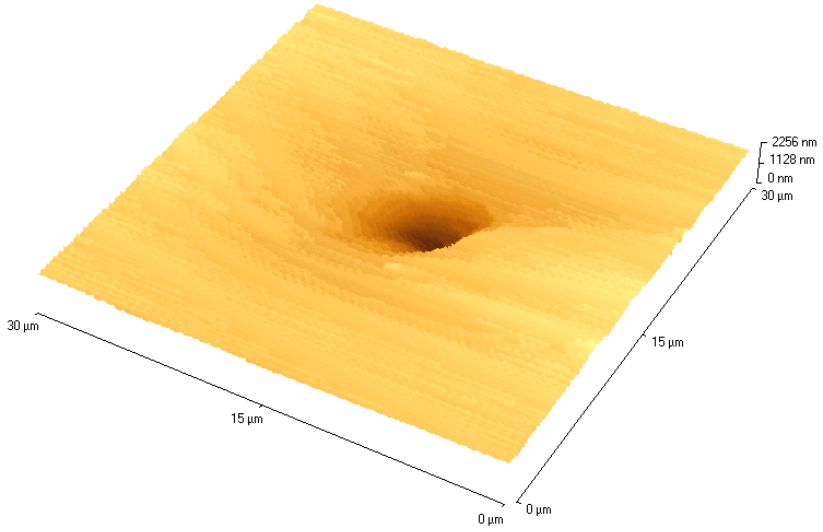
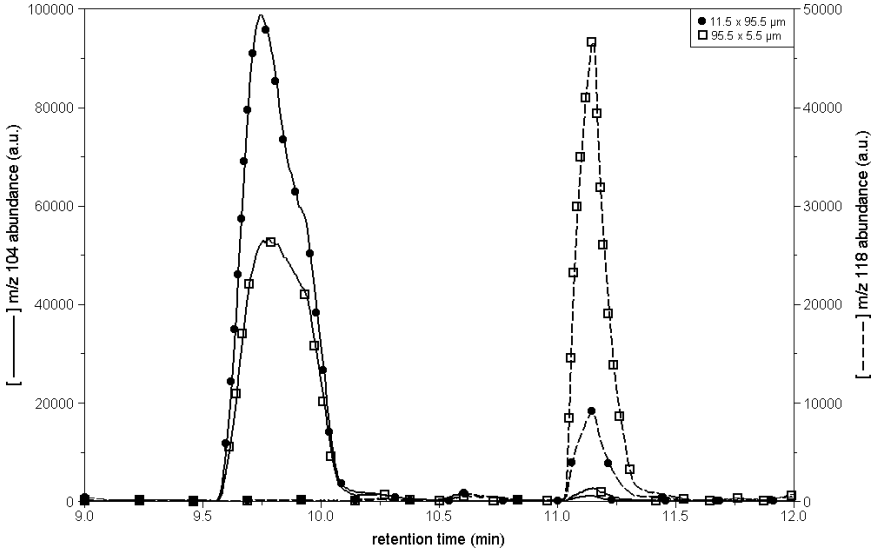


Figure 4*. Crater left after pyrolysing the surface of the polymer molded part with the thermal probe for 3 seconds at 600°C.*

The collected decomposition products were then released by heating the collection tube to thermally desorb the trapped decomposition product in the Evolved Gas Collector (EGC). It is then separated by capillary gas chromatography and identified by mass spectrometry.

Figure 5 shows the Single Ion Monitoring (SIM) data from the decomposition products collected at two different locations on the sample. The gases from the upper left hand corner of the image (11.5 x 95.5 um) are labelled with the solid circles (•), while the data from the lower right hand corner of the image (95.5 x 5.5 um) are labelled with the open squares (□).

Figure 5. *GC/MS data from the decomposition products collected at two locations on the polystyrene moulded part.*



The upper phase can be confirmed as polystyrene by monitoring the mass to charge (m/z) ratio of 104 ion (the molecular weight of styrene monomer) with a retention time of ~10 minutes within the gas chromatograph. The gases from the lower phase are dominated by the m/z 118 ion with a retention time of ~11.25 minutes.

Looking at the entire mass spectra at 10 minutes and 11.25 minutes show the gases to be styrene and alpha methyl styrene monomer respectively (Figure 6).

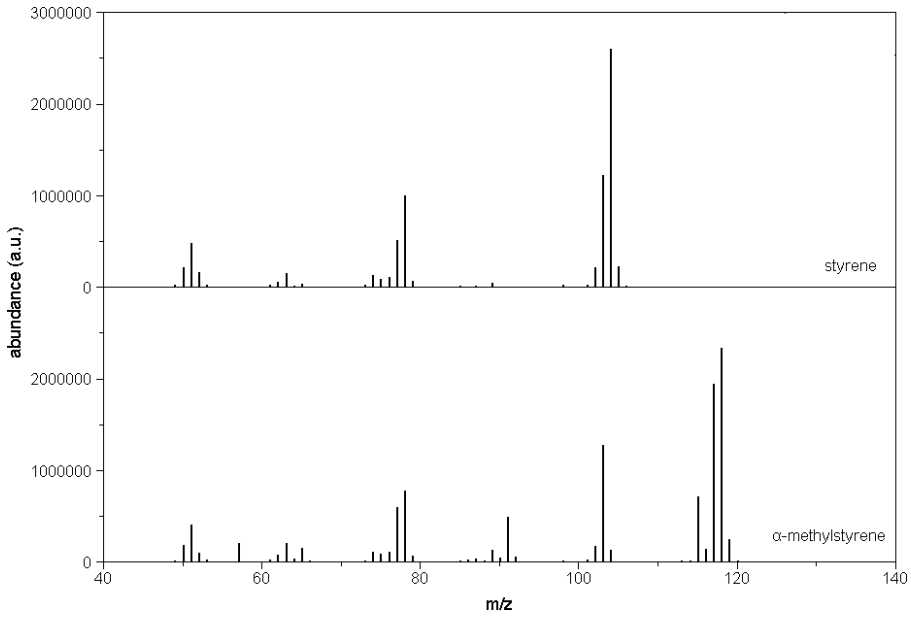


Figure 6. *Mass Spectra of the primary decomposition product from the upper phase (styrene monomer) and lower phase (methyl styrene monomer) of the polymer molded part.*

The upper phase, which has the softening point of 100 °C, primarily decomposes to give styrene monomer. This conclusively proves that the phase with higher thermal conductivity is polystyrene. The other phase decomposes to yield primarily alpha-methyl styrene, indicating that the surface contaminant is poly (methyl styrene).

The glass transition temperature for poly (methyl styrene) is around 25 °C lower than that for polystyrene. Hence we observe a lower softening temperature in the Micro-TMA data for the lower phase.

Conclusion.

It appears that the polystyrene moulding component has been contaminated with poly (methyl styrene). This was not detected by the original MDSC data as the small amount of contaminant was "swamped" by the polystyrene. Here the MDSC would average out the response from the poly (methyl styrene) over the total mass of the sample. By using Micro-Thermal Analysis and obtaining information about the Structure-Property-Composition of the sample it has been possible to understand the cause of failure of the product and positively identify the contaminant.