MICRO-THERMAL ANALYSIS: A NEW FORM OF ANALYTICAL MICROSCOPY

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Introduction

Thermal methods have been for many years amongst the most widely used techniques for characterising morphology of, in particular, complex polymeric systems. The recent introduction of modulated temperature differential scanning calorimetry (MTDSC) [1-4] has considerably increased the ability of DSC to identify and quantify polymer phases and interphases making it, perhaps, the most powerful general method for these tasks. However, conventional thermal methods give no information about how these phases are distributed in space. For this microscopy must be used. Electron & optical microscopy - and also existing forms of analytical microscopy (IR, Raman, SIMS *etc.*) - can be successful in mapping the spatial distribution of phases. However, none of these techniques has achieved the status of a reliable, general, and simple-to-use tool for this application due to a variety of factors including resolution, specificity, difficulties in sample preparation and the amount of time required to acquire high resolution images. We are developing a novel form of analytical thermal microscopy, as an additional complementary method to these existing microscopies, with potential advantages for characterising the morphology of polymer composites and blends. Furthermore, a variety of other materials including pharmaceuticals, foods and even biological specimens could be analysed using this new technique.

Background

The most popular thermal method is differential scanning calorimetry (DSC) which measures the heat flow into or out of a sample subjected to a temperature ramp. In this way transition temperatures can be found and the enthalpies and heat capacity changes associated with them can be measured. Reading and co-workers introduced a few years ago a temperature modulation combined with a Fourier analysis of the resulting data [1-4]. This new technique is called modu-

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lated temperature DSC or MTDSC. This has the effect of significantly improving sensitivity and resolution for some transitions while also enabling their "reversing" or "non-reversing" character to be probed. Stated simply, multi-component polymer systems will exhibit the corresponding number of glass transitions, while crystalline systems will give melting endotherms. Observing and quantifying these transitions enables the sample's morphology to be characterised.

Another popular thermal method is thermo-mechanical analysis (TMA) where a probe is placed on a sample with a given force then, as the temperature is ramped, changes in dimension (such as accompany softening during melting) can be detected. In this way, thermal expansion coefficients and transition temperatures can be determined. For both of these techniques the sample is typically tens of milligrams or even, in the case of TMA, larger.

The starting point for Micro-Thermal Analysis (Micro-TA) is an atomic force microscope where the probe tip has been replaced with an ultra miniature resistive heater that also serves as a temperature sensor. This type of probe was first described by Dinwiddie et. al. who used it purely in an isothermal mode to simultaneously map topography and thermal conductivity [5]. We, in parallel with others [6,7] added a temperature modulation to improve the ability of sub-surface

Scanning Thermal Microscopy (SThM) to discriminate between detail seen at different depths. We then introduced the facility to position the tip on any feature in an image and then scan temperature - thus making possible, for the first time, localised thermal measurements - transforming thermal microscopy into a form of analytical microscopy [8].

In the SThM mode, three images are produced simultaneously as illustrated in figure 1. This shows a metal wire embedded in a polymer - although there is some topographic contrast at the interface between the wire and the substrate, the contrast is markedly different on the DC and AC thermal images. The DC image represents a convolution of the sample's thermal conductivity with its topography. Previously we have referred to the AC image as the "thermal diffusivity" image. However recent modelling studies have suggested that the contrast mechanism is more dependant on other factors so it is more correct to refer to it simply as the "AC thermal image". We will be publishing more on our theoretical work in the future.

Figure 2 shows typical results for a melting transition: the signals measured are deflection of the cantilever carrying the heated probe (equivalent to Micro-TMA [9]) and the DC power, AC amplitude and AC phase for the calorimetric measurement, called micro-Modulated Temperature Differential Thermal Analysis (micro-MTDTA) signals. We use the term "micro-MTDTA" rather than "micro-MTDSC" to indicate we are not yet claiming quantitative calorimetric measurements. Consequently, we do not relate the strengths of the signals directly to enthalpies for transitions (the capability to do this is the subject of ongoing work). However, often simply measuring the temperature of a transition is sufficient to identify a component and, in this case, all three signals clearly show the melting transition. We have also used a force modulation to provide two additional signals, the AC amplitude and phase for the position sensor (this is a micro-
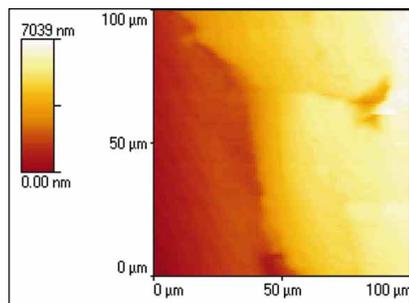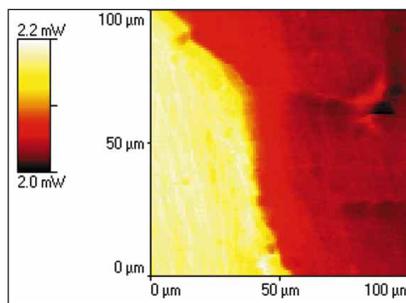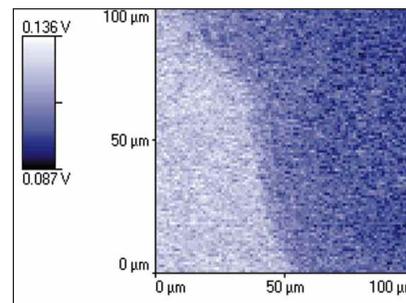

Fig 1a

Fig 1b

Fig 1c

Figure 1.   (a) topographic, (b) DC thermal and (c) AC thermal (2 kHz) images of a wire embedded in a polymer substrate.

equivalent to dynamic mechanical analysis), but this is not currently routinely available [10].

Micro-TA has been used in a preliminary study of phase separation of polymer blends and of crystallinity variations of different branched polyethylenes [11]. To further illustrate the use of this approach we shall use two examples: the first is a packaging film of the type used to make toothpaste tubes. This is made up of several layers of polyethylene. A thin layer of poly(ethylene-vinyl alcohol) copolymer (EVOH) is incorporated in order to provide adequate gas and flavour barrier performance. Different grades of polyethylene (PE) such as low density polyethylene (LDPE), medium density polyethylene (MDPE) & high density polyethylene (HDPE) are also used in the final construction. The type of polyethylene used in films is well known to affect their properties, however identification of the grade of polymer, particularly for commercial films, remains difficult. Bulk analytical techniques such as nuclear magnetic resonance spectroscopy (NMR), and differential scanning calorimetry (DSC) - whilst very sensitive to structure - are only able to give a specimen-averaged picture of the properties of the sample. More elaborate chromatographic techniques such as temperature rising elution fractionation (TREF) can, in favourable cases, separate the constituents of a multi-component film but afford no information regarding the original location of each fraction [12]. Infra-red microscopy is able to give more localised information of spectral properties, but (in this instance) it is not easy to distinguish between different grades of polyethylene.

The second example is a welded-joint produced by heating a wire embedded in the polymer just below the surface of one side of the joint. The temperature rise at the interface is sufficient to soften and fuse the two surfaces together. However, too much heat can cause cross-linking and thermal degradation of the polymer. In this case, we would like to study the morphology of the sample across the weld region - an application ideally suited to thermal measurements on this scale.

Experimental

The instrument used for this work was a TA Instruments μTA 2990 Micro-Thermal Analyser based on the TopoMetrix Explorer TMX2100 scanning probe microscope. In this work, we will concentrate on Micro-Thermomechanical measurements (Micro-TMA, see above); in this mode, the displacement of the tip is measured as it is heated in contact with the sample - as the temperature is raised a point is reached where the sample softens under the applied load causing a downwards deflection of the cantilever. At the end of the experiment, the probe is heated to the maximum scanned temperature and raised clear of the surface. Imaging of the sample after micro-TA shows cratered areas where the tests were carried out. Because of small thermal mass of the probe, high heating rates (typically 10°C/s or more) can be used. The low thermal conductivity of polymer samples means that only a small region ($10\ \mu m^3$) is examined.

The packaging film was prepared cutting 20 μm thick slivers of material using a microtome which were then mounted on a metal stub so that

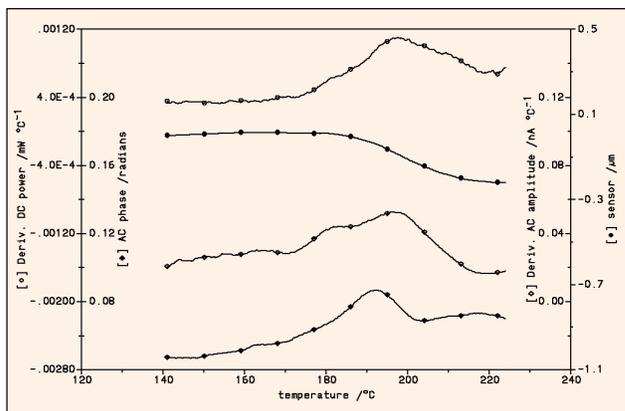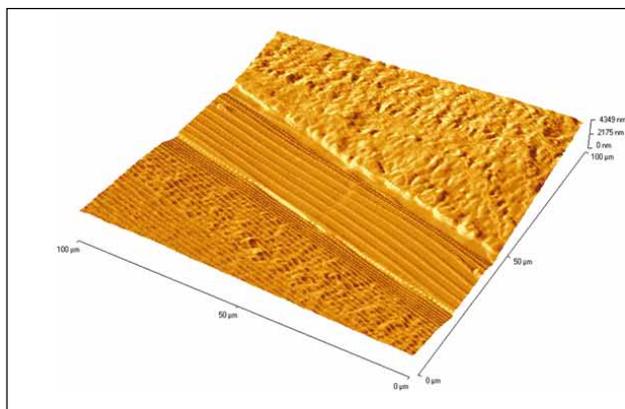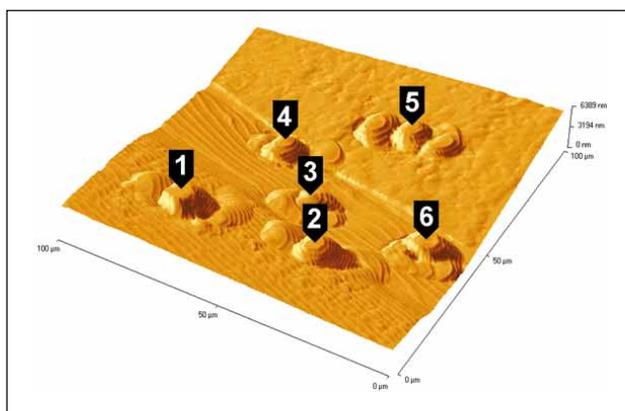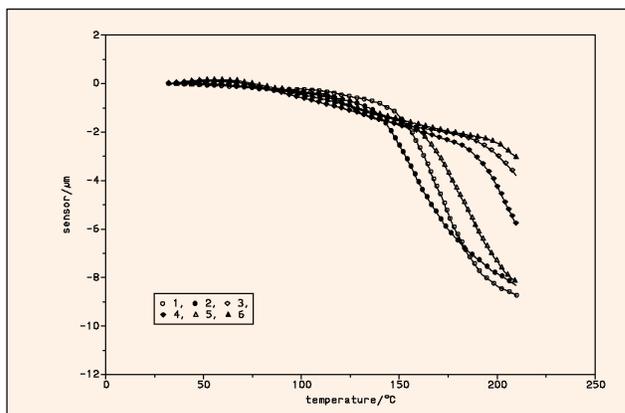*Figure 2. Typical Micro-Thermal Analysis results for the melting of a polymer.*

Fig 2

Figure 3. Three-dimensional image of barrier layer region of film before Micro-Thermal Analysis.

Fig 3

Figure 4. Three-dimensional image of barrier layer region of film after Micro-Thermal Analysis - labels refer to sequence of scans.

Fig 4

Figure 5. Micro-TMA plots for the scan locations shown in figure 4.

Fig 5

a cross-section could be presented to the microscope for imaging and subsequent thermal analysis. The welded joint was simply cut open using a saw and carefully polished to the required smoothness.

Results & Discussion

Packaging Film

Figure 3 shows a three dimensional representation of the gas barrier layer in the packaging film - it is clear from the topography that there is a central layer of polymer flanked by two outer layers with possibly an intermediate tie layer. Micro-TMA was carried out at six selected positions across the sample. The effect of tests are clearly seen in figure 4 which illustrates the damage craters (approximately 20 µm by 10 µm) caused by the test. The regions affected by the measurements appear large because the molten polymer flows away from the probe to cover the adjacent area. We estimate that the area characterised by the onset of probe penetration to be of the order of a few square microns. Plots of sensor response (obtained from the photodetector feedback circuit in the microscope head) versus temperature are shown in figure 5, these correspond to the locations indicated in the earlier figure. The softening temperatures are indicative of the polymer present in the film: curves 1 & 5 are typical of HDPE, curves 3 & 6 correspond to the EVOH layer, curve 2 (the tie layer) has a lower softening point than HDPE and is probably MDPE, curve 4 is located on the EVOH/tie layer interface and the thermal response is a combination of both. The entire sequence of tests took less than four minutes. This example shows that it is quite possible to quickly correlate the composition of a complex structure with its thermal behaviour.

Weld joint

The topography, thermal conductivity and modulated temperature images of the region around the heater wire were shown in figure 1. In order to examine a wider area using the microscope, the sample was moved under the head after each set of images (before and after Micro-TMA) and thermal scans had been collected. The resulting images were then overlaid to produce the composite map shown in figure 6. 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. As in the previous example, Micro-TMA was carried out in order to measure the softening temperature of the polymer (figure 7). As expected, the curves corresponding to positions closest to the source of heat show that the polymer had been cross-linked to such an extent that its softening point is above 400°C. As one moves further way from the heater, the softening temperature drops (curve 3) then rises again. Polymer lying on the weld line has a softening temperature above 400°C. Why this should occur is not clear - we speculate that mechanical vibration brought about by AC heating of the wire may provide a localised source of heat along the weld line itself. Further work is required to measure the softening temperatures of polymer with known thermal history so that we can determine the actual processing conditions seen by the sample.

Conclusions

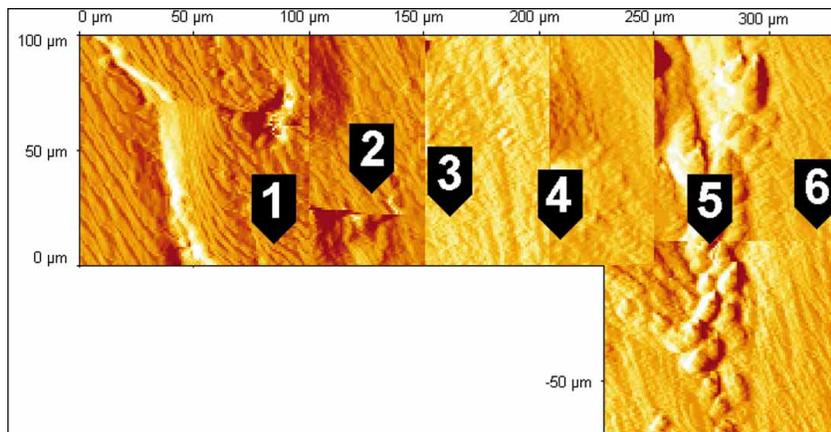The above examples illustrate some of the practical potential of the technique - we have concen-

Figure 6.   Composite shaded topographic image of weld joint - Micro-TMA scan positions shown.

trated here on the examination of articles in cross-section using Micro-TMA: other applications include the characterisation of polymer surfaces such as coatings and printed material. Future developments will include the exploitation of the frequency dependence of the AC thermal imaging technique to derive depth specific information about the sample. It is possible to use the thermal probe as a very sensitive infrared detector so as to achieve IR microscopy at very high resolution ñ well below the diffraction limit of conventional IR microscopes [13]. There is also the potential to perform localised pyrolysis-mass spectrometry using the probe to volatilise specified areas of the sample. High-resolution thermal probes are currently under development in order to enhance the spatial resolution of the technique. By combining scanning probe microscopy with thermal methods it is now possible to visualise and characterise a material, in the future it will be possible to analyse it too.

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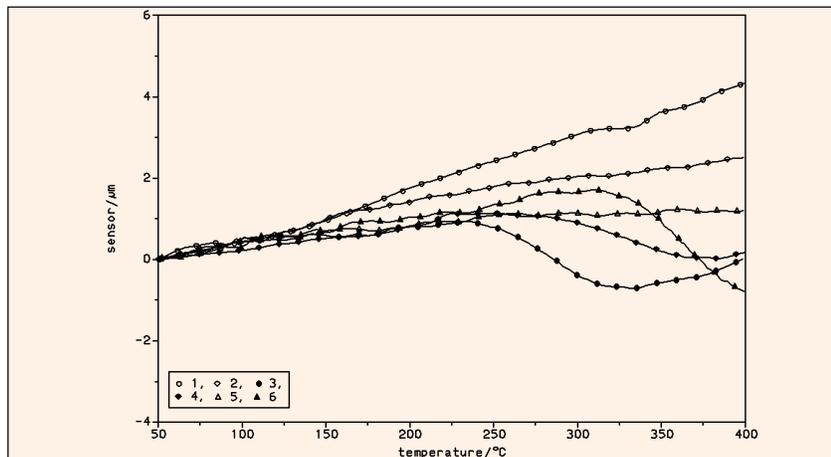
Figure 7.   Micro-TMA plots for the scan locations shown in figure 6.