

A High Resolution Multiple Analysis Approach Using Near-Field Thermal Probes

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Abstract. We have been developing new analytical techniques using resistive type thermal probes, as employed in scanning thermal microscopy (SThM), to implement different measurement mechanisms. The same active sensor is used to probe chemical, morphological and physical properties of the surface of materials with high spatial resolution. As well as providing passive (temperature) and active (thermal properties) mapping of the surface of a sample, the probe is used to perform localised thermo-mechanical measurement similar to that achieved by bulk techniques such as differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA). Photothermal infrared micro-spectroscopy and spatially resolved pyrolysis mass spectrometry are also implemented by interfacing a scanning probe microscope to a FTIR spectrometer and a mass spectrometer respectively. An approach to multiple analysis, based on proximal probe methodology and using the same sensor to obtain different information from precisely the same area is thus established. Effective data correlation and identifications of species is hence possible with high spatial resolution. The techniques, their implementation and continuous development are described and typical results obtained from measurements on polymeric materials are presented

INTRODUCTION

Modern materials technology is increasingly concerned with the control of materials at the mesoscale. The ability to add an extra dimension of, say, chemical composition information to high resolution microscopy, or microscopic information to spectroscopy, plays an increasingly useful part in applied research. To that effect, in a wide variety of new forms of analytical instrumentation we see one feature in common: quantitative analysis or physical characterisation is combined with the ability to record microscope images, and thus to choose individual regions of an inhomogeneous sample for analysis. Our research group is involved in the development of novel non-invasive proximal probe techniques which combine the high spatial resolution capability of near field scanning probe microscopy and other analytical techniques which in the present state of the art either lack spatial resolution,

can only be applied to bulk samples, require an elaborate sample preparation or a controlled environment.

A number of analytical techniques that normally operate on bulk samples to obtain macroscopic information may, in principle, be incorporated into the design of a scanning probe microscope. At the heart of such techniques will be a near-field operated probe. The source of excitation can be the probe itself or located in the far field. Similarly detection can be achieved by the probe itself or by a detector in the far field. The scanning probe device can be interfaced to another analytical instrumentation resulting in the creation of new forms of high spatial resolution analytical techniques. The concept can be further developed into a multiple analysis capability that permits different types of measurements from the exactly same area using the same near-field probe. This approach, based on the integration of more than one measurement mechanism within the same instrument, would involve multiple instrument integration, including a scanning probe microscope. A range of material properties including chemical, morphological and physical properties, can be probed from precisely the same area of the sample. Effective data correlation is thus possible which will greatly enhance the identification and characterisation of species with high spatial resolution.

We have first developed microthermal analysis [1,2], which probes local thermo-mechanical properties, followed by photothermal infrared micro-spectroscopy [3-5] with the aim of achieving IR spectroscopy at a resolution better than the diffraction limit. Pyrolysis mass spectroscopy was then developed as another means for chemical analysis in ambient environment [6].

EXPERIMENTAL

The probes

Miniaturised thermal sensors/sources are used. These are AFM type ultra-small cantilevered resistive probes that can be operated either as temperature sensor, by monitoring changes in resistance with temperature, or highly localised heat source via Joule heating. In the former case, when scanned across a sample, a surface temperature map is obtained. In the later case surface/near surface thermal properties are imaged: when maintaining the probe temperature constant, conductivity variations is mapped; when the probe temperature is modulated and diffusivity variations is mapped. It is also possible to obtain 3-D information about sub-surface features non-destructively, as the depth "viewed" by the probe may be controlled by varying the frequency of the temperature modulation. Two types of probes have been used: the Wollaston wire probe [7], after the type of silver-sheathed noble metal wire from which they are made, and more recently a high-resolution micromachined probe functionalised with a metallic constriction at the tip [8]. Scanning is achieved at constant force resulting in a topographical map to be obtained simultaneously. These purely thermal modes of imaging are complemented with localised analysis: Individual regions are selected from the image contrast. The probe is moved to a

location of interest, so as to add spatial discrimination, to established methods of chemical fingerprinting as described below.

Microthermal analysis: Localised thermo-mechanical and calorimetric analysis

Any feature of interest may be heated in a manner similar to that used in conventional thermal methods, by placing the probe on this feature and using the tip to heat a small region of the sample using a temperature program. Induction and detection of phase transitions, such as glass transitions, melting and re-crystallisation in polymers for example, is achieved by ramping the temperature locally at rates up to 1500°C/min. Localised temperatures up to 800°C are achieved. The chief advantage of this method is that apart from the probed region, the rest of the sample is preserved in its original unheated state, avoiding the risk that it will be irreversibly altered (in which case it will be impossible to achieve the usual objective of microscopical examination, namely the characterisation of a material in its as-received state). Depending on the material, the volume of probed material can be as small as a few μm^3 . Domains in polymer blends, as small as a few μm , can be characterised. This capability transforms SThM into a powerful new form of analytical microscopy. Detection can be calorimetric or thermo-mechanical. We now have a new technique that combines the high spatial resolution capability of scanning probe microscopy (SPM) and conventional bulk differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA).

The probe is first pressed against a chosen region of the sample, leading to a deflection of the cantilever, with a given initial force. The temperature-calibrated probe is then heated so as to apply an upward and downward temperature ramp, and its deflection along the z-axis (perpendicular to the sample surface) is recorded. The force feedback mechanism needed for imaging is normally disabled during the experiment, otherwise the z-actuator motion would drive the tip through the specimen as it softens. If the material undergoes a phase transition, its mechanical properties vary (softening), so that the tip will indent the sample and the cantilever deflection will change. This change in deflection is monitored using the microscope z-axis displacement detection system. Hence, monitoring of the cantilever deflection permits the detection of phase transitions.

Simultaneously a calorimetric measurement is carried out in a differential configuration using a reference probe that is normally suspended in air. The temperature ramp will in general produce variations in the thermal conductivity and heat capacity of the sample, which may also undergo local phase changes. These changes affect the heat flow out of the probe, and thus the difference in electrical power supplied to the sample and reference probes. Although the observed response is also affected by elastic variations in the tip/sample contact area, as the sample moves from the glassy to the rubbery state.

Although the probe only senses a small volume (a few cubic microns), the sample's mass is unknown, so that at present the measurements are quantitative only in terms of identifying transition temperatures. This is often sufficient for characterisation

purposes, and semi-quantitative information can be obtained by comparing different areas of the same sample.

Here we demonstrate the suitability of the micro-machined probe for thermo-mechanical measurement. Melting temperatures were determined for three polymers, polycaprolactone (PCL) (60 °C) , nylon 12 (178 °C) and nylon 66 (267 °C) (Fig. 1).

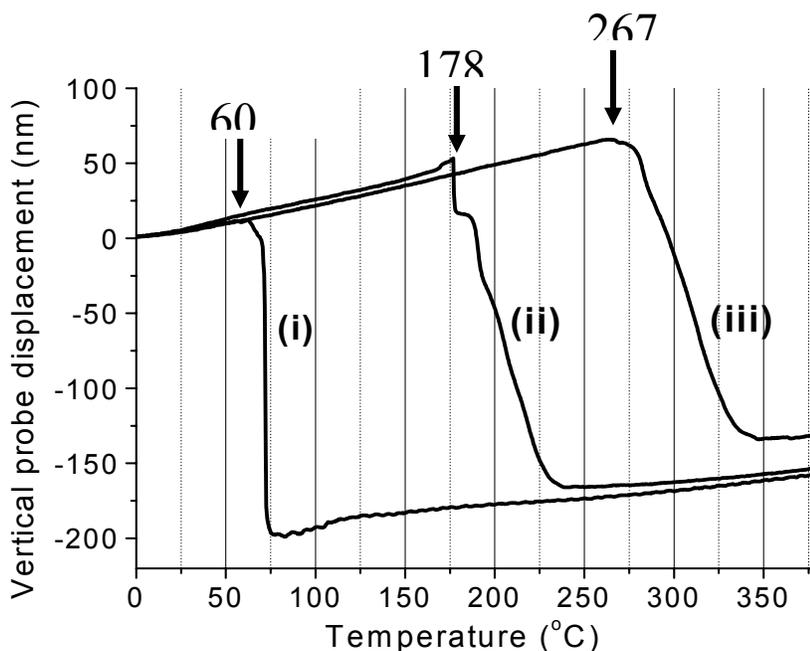


FIGURE 1. Localised thermo-mechanical measurements of melting transitions of polycaprolactone (i), nylon 12 (ii) and nylon 66 (iii), observed in the vertical probe displacement, as the tip is heated at a rate of 1500 °C/minute

The temperature was ramped at 1500 °C/minute. Surface expansion of up to 50 nm followed by indentation into the materials down to 200 nm was observed. After probe retraction, imaging revealed craters of the order of 500 nm in total lateral extent.

Using a Wollaston wire probe, true calorimetric measurement is performed on a microscopic sample of picric acid (Fig. 2). The sample was picked up by the probe and measurement performed with probe and sample free standing. The temperature program consisted of a ramp with superimposed modulation. The temperature ramp initiated two explosive events with resulting very energetic exotherms. These exotherms are clearly detected in the second harmonic of the ac signal across the probe.

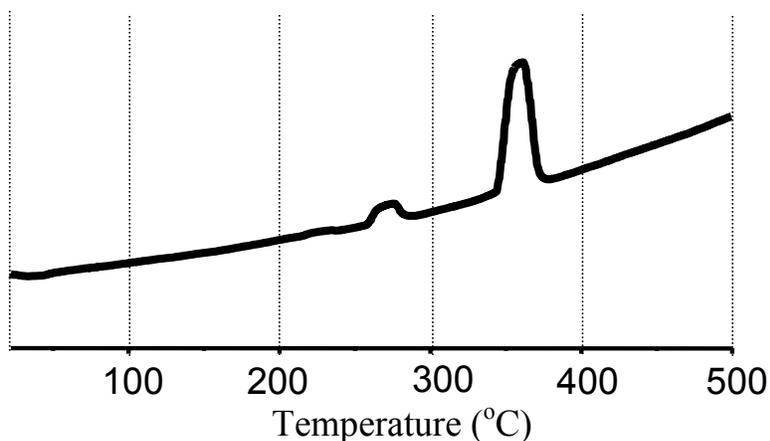


FIGURE 2. Calorimetric detection of exotherms from a microscopic sample of picric acid as explosions are induced by a rapid temperature ramp ($10^{\circ}\text{C}/\text{second}$). The temperature program includes a 1 kHz modulation as well. The vertical axis represent the amplitude of the second harmonic of the modulated voltage across the probe

Near-field infrared micro-spectroscopy

High resolution chemical analysis was then developed based on vibrational spectroscopy. The same probe, again operated as a thermometer, is used to record Fourier transform infrared absorption spectra. The technique has been further developed by interfacing two commercial instruments. An Explorer model SPM from Veeco inc. is integrated with a FT-IR spectrometer (Vector 22, Bruker UK Ltd.) (Fig. 3) by means of an optical interface developed by SPECAC Inc.

This consist of a planar mirror and a concave mirror, machined in a block of aluminum, which acts as condensing optics to focus the flux at the sample surface. The sample is mounted on a stage attached to an X-Y-Z micrometer-based translator. With the probe attached to the scanner, the microscope can be moved so that the probe tip is positioned at the focal point of the IR radiation. As the sample absorbs the IR radiation, it heats up. The associated temperature rise is measured by the probe whose amplifier output is fed into the external input of the spectrometer. The Fourier transform algorithm is performed on this signal after digitisation. Peaks on the resulting spectrum represent peaks of absorption by the sample across the wavelength range of the IR radiation. Coherent averaging using coadding is used for signal to noise improvement.

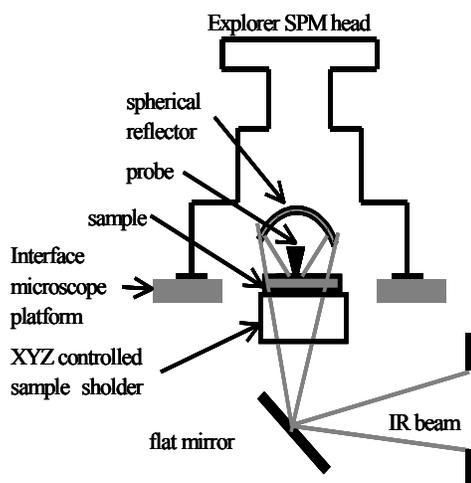


FIGURE 3. Schematic diagram of the photothermal FTIR micro-spectroscopy technique implementation. The microscope is mounted inside the sample compartment of the FTIR spectrometer

5 μm diameter polystyrene microspheres, suspended in a solution of surfactant and distilled water at 1% solids (from PSI supplies), were deposited on a glass slide. After surfactant evaporation, a few spheres were picked with the Wollaston probe (Figure (4-a)) and a spectrum taken with probe and spheres free standing in the air, the glass substrate having been removed. A strong signal with good signal to noise ratio is recorded resulting in a very clean spectrum as shown in Figure 4-b-i. The main absorption bands are clearly resolved as can be observed when the spectrum is compared to that found in databases (Figure 4-b-ii)

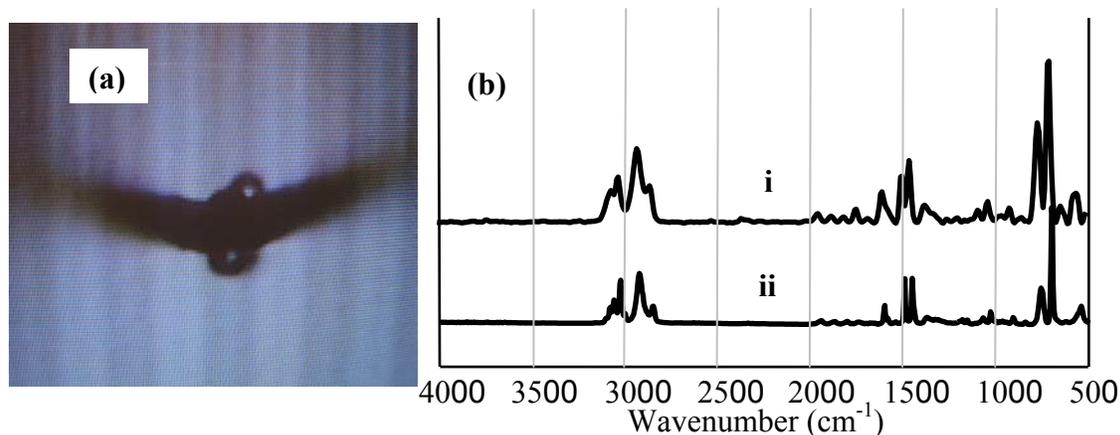


FIGURE 4. 5 μm polystyrene spheres on the tip of a Wollaston wire probe (a) and resulting absorption spectrum (b-i). A spectrum taken from a database (b-ii) is shown for comparison

Pyrolysis mass-spectroscopy

Another means to add chemical fingerprinting is to use the same probe to pyrolyse small volumes of the sample and analyse the resulting evolved materials by mass spectroscopy. Implementation is achieved using a TA Instruments 2990 Micro-Thermal Analyzer fitted with a Wollaston wire thermal probe. The probe is heated rapidly and repeatedly to temperatures up to 800 °C. The evolved gases resulting from thermal decomposition of a small region of material can be identified by mass spectroscopy (MS) or gas chromatography-MS (GC-MS). In the later case, the evolved gases are trapped in a specially designed tube packed with a mixture of Tenax and Carboxapack. The tube ends in a short section of hypodermic tubing (0.8 mm o.d., 0.4 mm i.d.), the open end of which is placed immediately adjacent to the heated thermal probe using a micro-manipulator. As the tip is heated, a pump is used to draw gas through the tube which is then placed in a thermal desorption unit (TA Instruments Evolved Gas Collector) for analysis of the trapped volatiles by GC/MS (Hewlett-Packard 6890 Gas Chromatograph with HP5973 Mass Selective Detector). The GC was fitted with a HP-5 MS capillary column (30 m x 0.25 mm i.d. x 1.0 μ m d.f.). The oven program consisted of a 5 minute hold at 40°C following desorption and then a ramp to 250°C at 15°C min⁻¹ followed by a 10 minute hold at this temperature. Mass spectra (m/z 45-350) were acquired every 0.5 s. A blank desorption run was carried out before and after each experiment to confirm the cleanliness of the detection system. One drawback of GC-MS is the time taken for analysis (up to 30 mins). One way around is to dispense with the trapping and separation stages by continuous sampling of the atmosphere around the probe. This was carried out using a 1 m length of 25 μ m i.d. capillary tubing as a transfer line to the ion source of a ThermoStar™ quadrupole mass spectrometer (Pfeiffer Vacuum). The capillary also acted as a single-stage pressure reduction device in order to bring the operating pressure for gas sampling down to that which the detector could accommodate.

This opens up the possibility of imaging surfaces by evolved gas composition. Spatially resolved elemental chemical characterisation is thus achieved, in ambient environment, permitting identification of microscopic features such as contaminants or phases in a complex system.

This imaging capability using on-line analysis is demonstrated on a model polymeric sample consisting of a 300 μ m thick polystyrene film sandwiched between two PMMA slabs and microtomed. A 6 by 6 array of measurements, spaced 20 μ m apart, were made across the interface PMMA and PS. The ions corresponding to the masses of the molecular ions from the respective monomers m/z 100 (methyl methacrylate) m/z 104 (styrene) were monitored and integrated to reconstruct an image showing the location of each polymer (figure 5).

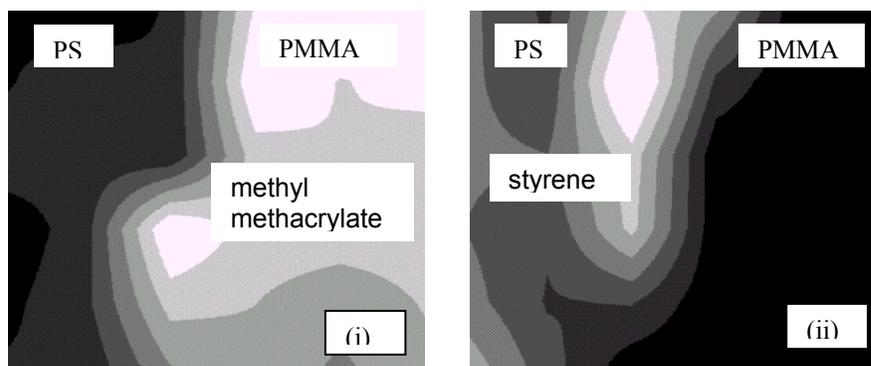


FIGURE 5. Compositional mapping using direct micro-pyrolisis mass spectroscopy of a polystyrene/poly(methyl methacrylate) composite sample. The ions corresponding to the masses of the molecular ions from the respective monomers m/z 100 (methyl methacrylate) (i) and m/z 104 (styrene) (ii) were monitored to reconstruct an image showing the location of each polymer.

CONCLUSION

We have demonstrated an approach to multiple analysis based on the integration of scanning probe microscopy with other analytical methodologies, using near-field active thermal probes for localised interaction. Future work will involve integrating the four methodologies described here (scanning thermal microscopy, thermo-mechanometry and calorimetry, IR micro-spectroscopy and pyrolysis mass spectroscopy) within the same instrument.

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