Micro-Thermal Analysis of Polymers: Current Capabilities and Future Prospects

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Summary: The current state of development of micro-thermal analysis (micro-TA) and related techniques are briefly reviewed. Results for a PET/epoxy resin composite and a bilayer polymer film are given as illustrations. Details are given of a new interface that enables the micro-TA unit to be placed inside a conventional FTIR spectrometer to carry out photothermal IR microscopy. New results are presented for a micro-pyrolysis-mass spectroscopy technique. The limitations of the current instrumentation are discussed in terms of the overriding problem being one of spatial resolution. Images obtained using pulsed force mode AFM with a high-resolution heated tip indicate the scope for future development of this technique. The possibility of even higher spatial resolution with other forms of probe are discussed along with the potential for imaging micro-pyrolysis time of flight mass spectroscopy and even tomography. It is concluded that these methods offer excellent prospects for characterising a wide range of polymer systems.

Current Capabilities of Micro-TA

The technique of micro-thermal analysis (micro-TA) was introduced a few years ago by Hammiche et al. [1-5] and later Fryer et al. demonstrated their own version [6]. Micro-TA is an extension of scanning thermal microscopy (SThM) [7,8] which is part of the family of scanning probe microscopy (SPM) techniques. Micro-TA uses an atomic force microscope in which the conventional tip is replaced by an ultra-miniature electrical resistor. The present configuration employs the probe design described by Dinwiddie and Pylkki [9,10] (Figure 1). This is fashioned from Wollaston process wire which consists of a 75 μm diameter silver wire surrounding a 5 μm diameter core of platinum/10% rhodium alloy. The wire is bent to form a sharp loop and secured into shape with a bead of epoxy resin. The silver layer is then etched

away at the apex to reveal the platinum filament which forms the major electrical resistance element (approximately 2 Ω) in the assembly and acts as a temperature sensor and heater. A reflective mirror is glued on the wires to serve as a target for a laser spot which forms part of optical lever deflection feedback system of the microscope. The finished assembly is mounted on a carrier for mechanical and electrical connection to the piezoelectric scanner of the microscope.
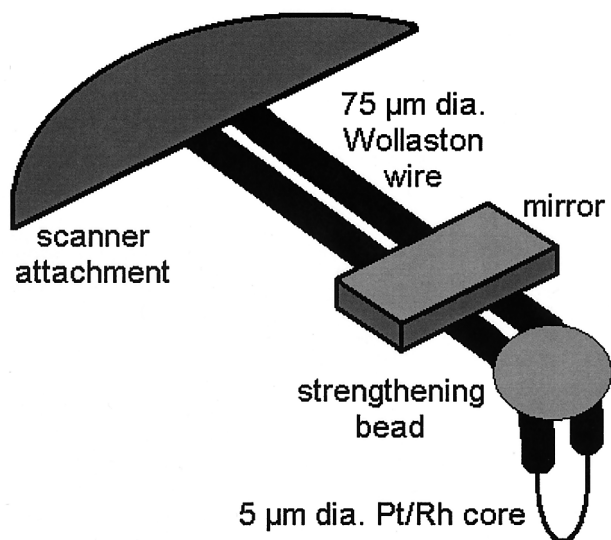

Figure 1.   Schematic diagram of thermal probe made from Wollaston process wire.

For imaging, the probe can be operated in a purely passive mode as a resistance thermometer in order to map temperature variations across a specimen. However, it is more commonly used in an active mode whereby current is passed through the resistance so as to maintain its temperature typically 10 to 20°C above ambient while the probe is rastered over the surface of the sample. By monitoring the electrical power required to achieve a constant tip temperature, an image of the sample may be acquired whose contrast is determined by the heat flux from the tip to the surface. Thus it is possible map relative differences in thermal conductivity across the specimen. In addition, a sinusoidal modulation of tip temperature can be superimposed upon the average constant value. This AC measurement is influenced by (amongst other things) spatial variations in the sample's thermal diffusivity. As these thermal measurements are made in contact mode using the usual force-feedback loop of the microscope, a map of topography is also obtained at the same time. Typically, therefore, an

imaging experiment provides a map of the topography plus the underlying "DC" thermal image and two "AC" thermal images (the amplitude of the power required to modulate the tip temperature and the phase difference between applied modulation and tip/sample response). This is illustrated in Figure 2 for a microtomed cross-section of a sample of polyethylene terephthalate (PET) embedded in an epoxy resin. Such thermal images have been used to follow the process of phase separation in a polymer blend [4].
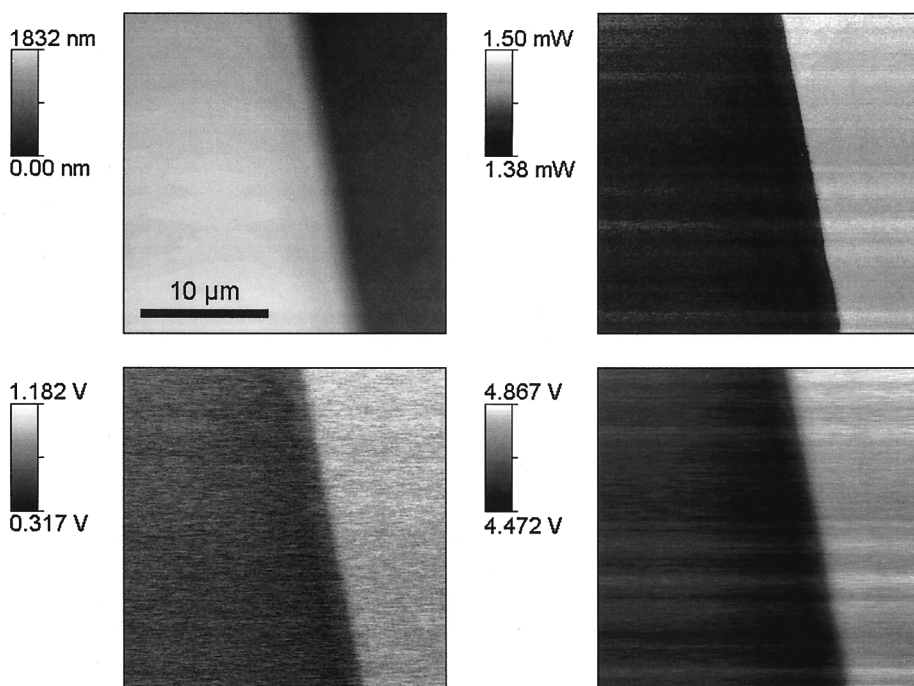

Figure 2.   Clockwise from top left: topographic, DC thermal, AC amplitude and AC phase images for a sample of poly(ethylene terephthalate) (PET) (right) embedded in an epoxy resin.

There are a variety of different types of analysis that can be performed using the thermal probe described above which exploit its ability to function as a heater/thermometer that may positioned over a specimen with high precision using the x,y piezoelectric actuators of the AFM scanner. The first of these is localised thermal analysis [1-3,5]. Using a previously acquired image as a guide, the tip is placed at a selected point on the surface and its temperature is ramped linearly with time, usually with a superimposed temperature modulation. This carried out in a differential configuration in conjunction with a reference probe that is normally suspended in air. The difference in electrical power supplied to the sample and reference probes is measured. This gives three calorimetric signals: the average or DC power required to achieve the underlying linear temperature rise and the amplitude and phase difference of the sample response to the superimposed modulation [11,12]. These measurements are often referred to as micro-modulated temperature differential scanning calorimetry (micro-MTDSC) or micro-modulated temperature differential thermal analysis (micro-MTDTA) by analogy to their counterparts in the field of "bulk" thermal analysis [13]. In addition to the localised calorimetry, the position of the cantilever is monitored using the microscope z-axis displacement detection system. When the probe is placed on the surface of the sample, the cantilever is bent to a predetermined extent so as to exert a controlled force at the tip. As the temperature is increased the sample will often soften as it melts or undergoes a glass-rubber transition. This leads to the tip indenting into the sample. During this measurement, the force-feedback loop of the microscope is disabled after applying the initial force so as to prevent the probe being driven through the sample as it softens. The change in deflection of the cantilever is monitored concurrent with the localised calorimetry described earlier. This measurement is usually referred to as micro-thermomechanical analysis (micro-TMA) [14,15].

Figures 3 and 4 show typical results from the sample imaged in Figure 2 for areas located on the PET and epoxy resin areas. Heating rates over 500°C min^{-1} can be employed due to the small thermal mass of the system. In this way the transition temperatures can be determined in a localised way and differences in, for example, degree of crystallinity between the bulk and the surface of a sample can be determined [16]. The temperature response of the probe is calibrated using low molecular weight organic materials with certified transition temperatures such as biphenyl, benzoic acid and 2-chloranthraquninone [17]. Collectively the techniques described above are usually known as micro-thermal analysis (micro-TA).
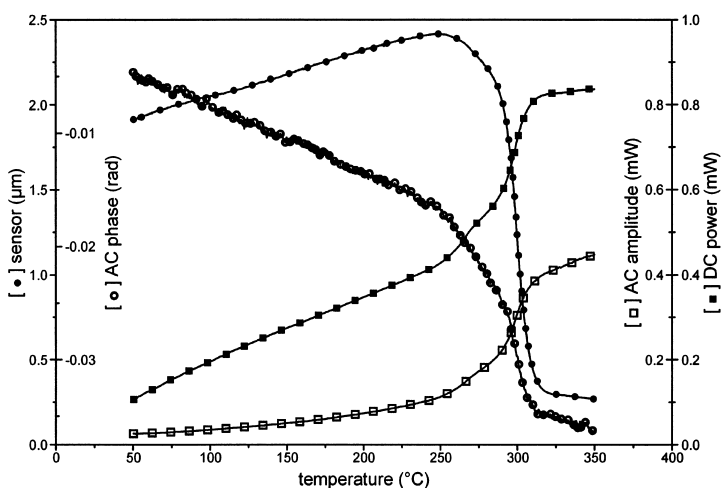
Figure 3   Localised thermal analysis data for an area from the top right of the images in Figure 2 showing the melting of the PET around 250°C (● sensor displacement = micro-TMA; ■ DC power, □ AC amplitude, ○ AC phase = micro-MTDSC). Heating rate 10°C/s with superimposed 5°C amplitude, 5 kHz temperature modulation. Initial force of surface 10 nN.
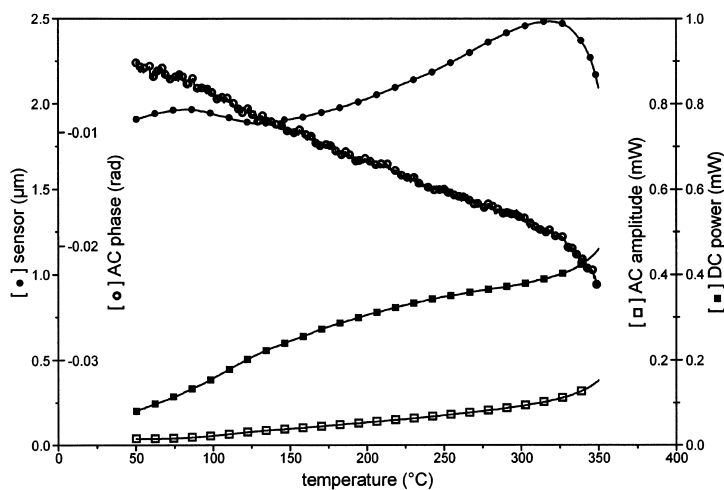

Figure 4   Localised thermal analysis data for an area from the bottom left of the images in figure 2 showing the response of the epoxy resin (glass transition around 75°C, thermal degradation around 300°C). Conditions and curve labels as for Figure 3.

In addition to the thermal analysis experiments described above, the tip may be heated to a temperature sufficient to bring about thermal degradation of most organic materials. This has the benefit of allowing the probe to be decontaminated between thermal measurements by simply burning off any residues. Furthermore, this facility can be used as an analytical method by rapidly heating the tip in contact with the specimen in order to bring about pyrolysis of the surface. Any evolved gases can be trapped by sucking them into a tube packed with suitable sorbent such as a activated charcoal or a molecular sieve placed close to the thermal probe using a micromanipulator. The sorbent tube can then be removed from the microscope and analysed by thermal desorption-gas chromatography/mass spectrometry (td-GC/MS) [12,18]. This affords the ability to perform localised chemical analysis of specimens in addition to physical characterisation by thermal analysis. Furthermore, we have shown that is possible to deliberately extract material from the surface of a specimen by using the heated tip to soften a region and then pull the tip away as it is cooling to leave a small sample adhered to the probe ("thermally assisted nano-sampling"). This could be removed from the tip by a solvent wash and subjected to a number of forms of analysis (e.g. nuclear magnetic resonance spectroscopy, size exclusion chromatography, etc.). How the sample on the tip decomposes with temperature after it has been removed from the surface can be studied by ramping the tip temperature while using the AC calorimetric signals as a measure of the amount of material remaining on the probe [19]. This experiment approximates micro- (or nano-) thermogravimetric analysis of the extracted sample.
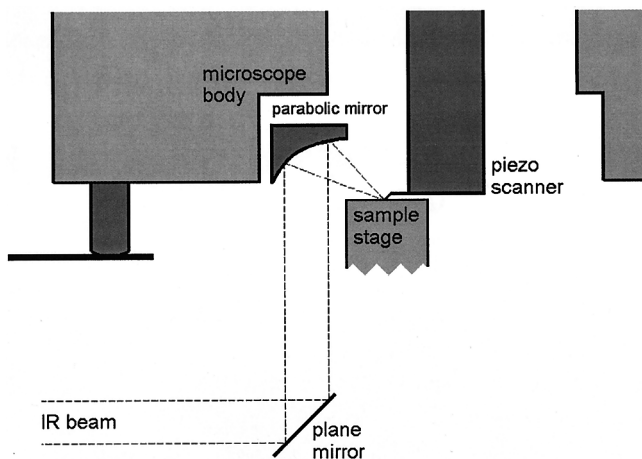

Figure 5.   Schematic diagram of interface that allows the microscope to be mounted in the compartment of a standard infra-red spectrometer.

A further form of chemical analysis that can be carried out by the apparatus is localised infrared (IR) spectroscopy [20]. IR radiation from a standard FTIR spectrometer is focused onto as small a spot as possible with the thermal probe located in the area of highest flux. The temperature change of the surface arising from the absorption of infrared radiation is detected (photothermal effect) and used as the input into the spectrometer. Figure 5 is a schematic diagram of a recently constructed interface that allows the microscope to be mounted in the compartment of a standard spectrometer. Infrared radiation from the source of the spectrometer is focused into a spot (typically of the order of 500 μm in diameter) on the surface. The tip is then used as the detector and the spectrometer is operated in the normal way.

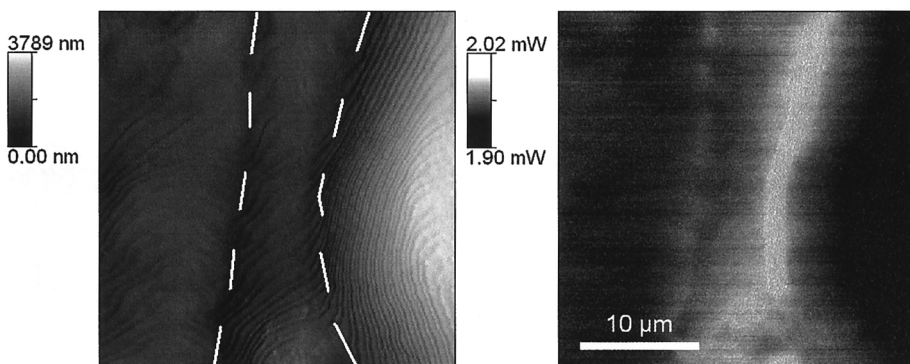Figure 6.   Cross-section though a sample of polyethylene-coated styrene-butadiene rubber film embedded in an epoxy resin. Left: topographic image, right: DC thermal image. Broken lines drawn on topographic image indicate boundaries between the rubber/polyethylene/resin.

An example of the characterisation of polymer system is shown in Figures 6-11 for a sample of a styrene-butadiene rubber film coated with a thin layer of polyethylene. Topographic and thermal conductivity images of a cross-section through the film embedded in epoxy resin are shown in Figure 6. The images indicate that the outer layer is only 5 μm in thickness. Thermal analysis of this layer indicates that it melts around 120°C - typical for polyethylene (Figure 7). The infrared spectrum of the outer layer, obtained using the thermal probe is shown Figure 8 supports this assignment (although some bands from the substrate are visible at low wavenumbers since the depth of penetration of the IR radiation depends on frequency in a similar fashion to conventional attenuated total reflectance spectroscopy).
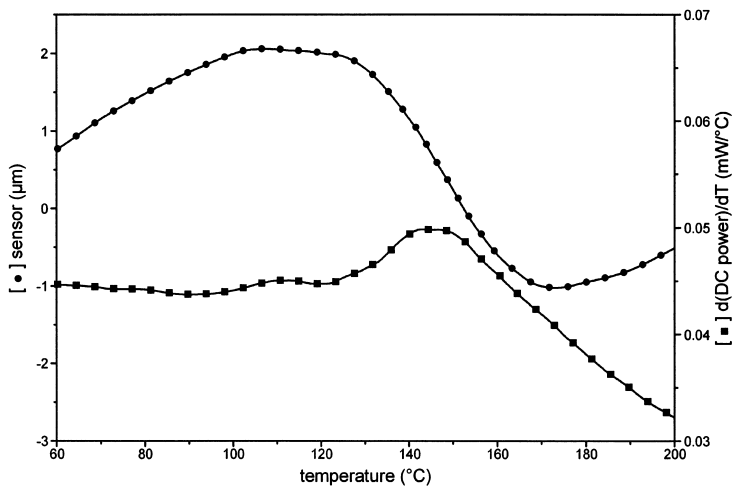
Figure 7.   Localised thermal analysis of top surface of the film in Figure 6 (• sensor signal; ■ derivative of DC power with respect to temperature). The melting of the polymer is observed to occur around 120°C. The first derivative of the calorimetric signal is plotted to enhance the sensitivity – AC signals omitted for clarity.
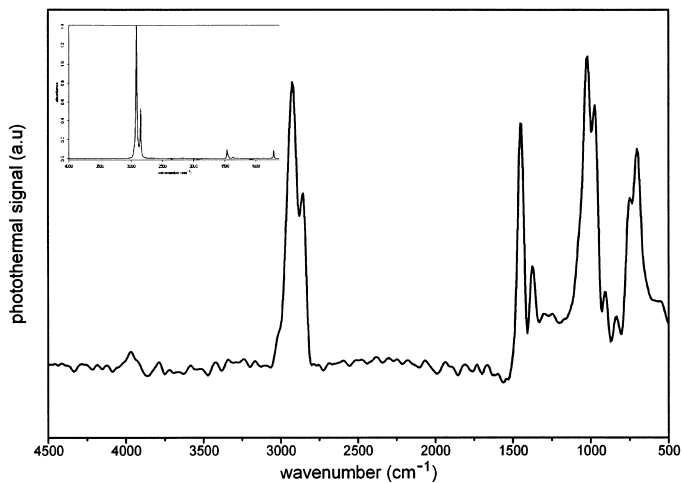

Figure 8.   Photothermal spectrum of outside surface of film in Figure 6. Inset shows reference spectrum of polyethylene by conventional FTIR spectroscopy.
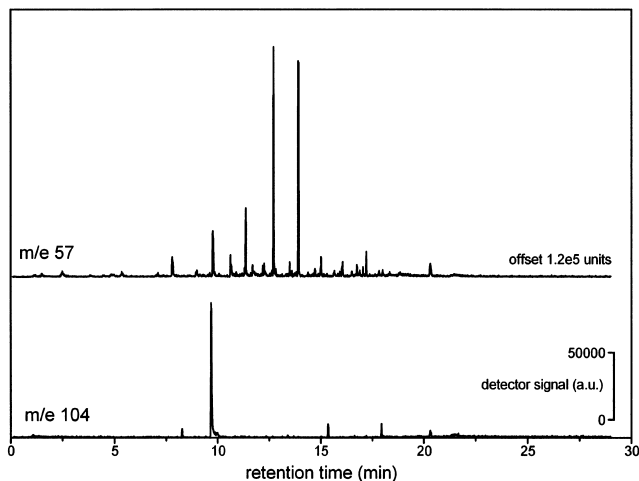
Figure 9.　　Localised pyrolysis-GC/MS data for top layer of film showing single ion chromatograms for m/e 57 ($C_4H_9^+$) and m/e 104 (styrene) (to same scale).

Pyrolysis of the outside surface of the free film (laid flat under the tip rather than in cross-section) in air yields mainly a mixture of hydrocarbons. These are identified in the GC/MS data by single ion monitoring of the $C_4H_9^+$ ion (m/e = 57) which is a major product in the fragmentation of higher alkanes (Figure 9). This confirms the structure of this outer layer. Also shown in Figure 9 is a single ion chromatogram for styrene (m/e 104) which would arise from some breakdown of the substrate underneath.

Figure 10 shows corresponding single ion chromatograms for a repeat measurement on the same location measured during the first pyrolysis experiment. The polyethylene layer has now been largely ablated by the earlier measurement and degradation products from the rubber substrate now dominate the results. Also detected in the GS/MS data are peaks due to butadiene dimer and trimer expected from the degradation of this polymer (not shown). The photothermal spectrum of this layer is shown in Figure 11.
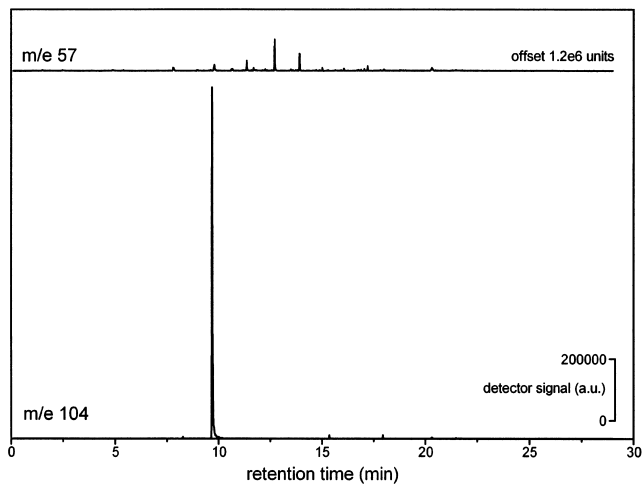
Figure 10.   Localised pyrolysis-GC/MS data for film substrate following initial pyrolysis experiment shown in figure 9.
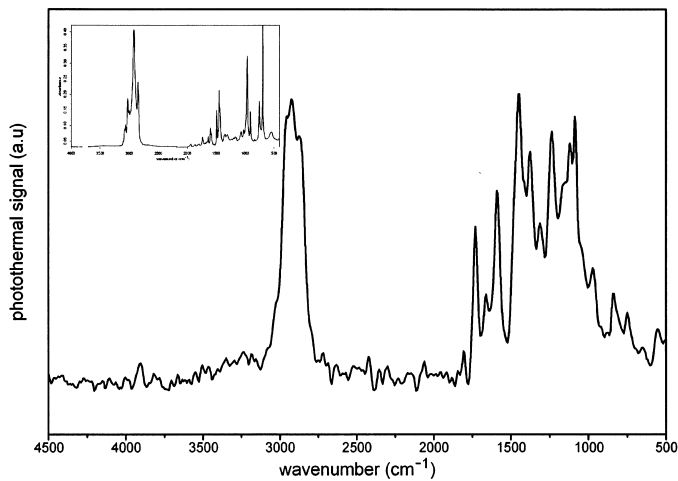

Figure 11.   Photothermal spectrum of film substrate in Figure 6. Inset shows reference spectrum of styrene-butadiene rubber by conventional FTIR spectroscopy.

As an alternative to analysis of evolved gases by GC-MS, mass spectroscopy by itself can be used. This has the disadvantage of lacking the specificity given by the chromatographic separation but the advantage of considerably reduced time for analysis. Figure 12 shows some initial results from this technique on the polyethylene/rubber film described above. The open end of a fine capillary transfer line is placed near the probe - this leads directly to the ion source of the mass spectrometer. It takes only a few seconds for the gas to travel to the detector. One mode of operation is to depth profile by gradually pushing the hot tip further into the sample as a smooth function of time. In Figure 12 we see a plot of 2 ions (selected to identify the polyethylene and rubber (via their decomposition products)) against time (which is then related to depth). It can be clearly see how the $C_4H_9^+$ (m/e 57) fragment ion (from the polyethylene degradation) is seen first followed by the styrene (m/e 104) fragment (from the rubber) as the probe goes deeper.
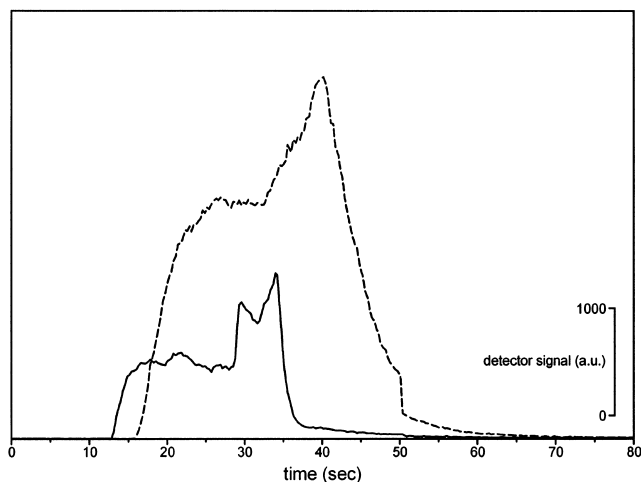

Figure 12.   Single ion intensities for m/e 57 ($C_4H_9^+$ - solid line) and m/e 104 (styrene - broken line) versus time as a heated tip (nominal temperature 700°C) is brought into contact with a polyethylene-coated styrene-butadiene rubber film.

Using the micro-TA unit it has, therefore, been possible to measure the physical and chemical properties of the two layers via thermal analysis, pyrolysis-GC/MS and IR microspectrometry. Furthermore, a depth profiling experiment by pyrolysis-MS confirms the chemistry and structure of the film. All of these measurements are made with the same instrument and the same probe. It should be noted that the equipment also functions as a conventional atomic

force microscope and thus the morphology of samples can be studied in addition to the localised characterisation afforded by micro-thermal analysis.

Other Micro-Thermal Analysis Modes

Although not yet available as a routine tool, localised dynamic mechanical analysis has been demonstrated [5,21,22]. Either the whole sample can be heated [21] or the temperature of the tip may be scanned [22]. Early indications are that it is possible to detect both primary and secondary transitions. Both oscillation normal to the surface and lateral oscillations have been used [22].

An imaging mode that has recently been demonstrated is thermal expansion microscopy where the temperature of the tip is modulated and the resulting modulation of the z-position of the probe is measured [22]. This modulation comprises a contribution from the thermal expansion of the probe itself and from the thermal expansion of the sample. The thermal diffusivity of the sample influences the amount of sample that is heated and therefore the resulting thermal expansion of the surface. In principle calibration could disentangle these various contributions. Even without this further refinement this mode of imaging has been shown to give good contrast between different polymers.

Current Applications of Micro-Thermal Analysis

Micro-TA has been used to study a number of polymer systems in addition to those described above: multi-layer packaging materials, polymer welds, defects in polymer films, interphase regions in composites [11,14,23,24]. A number of applications have also been demonstrated in biology, pharmacy and the electronics industry [14,24-26]. The range of problems that can be tackled using these tools should be as broad as their parent macroscopic techniques.

Future prospects for micro-thermal analysis

The main drawback of current micro-TA instruments is insufficient spatial resolution. The commercially available thermal probe described earlier, has a spatial resolution for imaging of about 1 μm, a few micrometres square for local thermal analysis and a few tens of micrometres square for localised pyrolysis-GC/MS. The limit of resolution for the photothermal IR measurement has not yet been established, but calculations suggest it will

ultimately be < 1 μm [20]. A micro-machined probe has recently been developed in which the resistance element is deposited across the apex of a silicon nitride pyramid similar to a conventional AFM tip [27].   Results obtained using a micro-machined thermal probe for imaging and micro-TA suggest that an order of magnitude improvement over the Wollaston wire probe [16]. A spatial resolution on the scale of tens of nanometres for thermal imaging has been realised using passive thermocouple tips [28]. Such devices could be adapted for use in an active mode by passing current through them. There would seem to be no fundamental reason, therefore, why micro-TA will not ultimately achieve a resolution of a few tens of nanometres. It may even prove possible to collect IR spectra with this resolution.
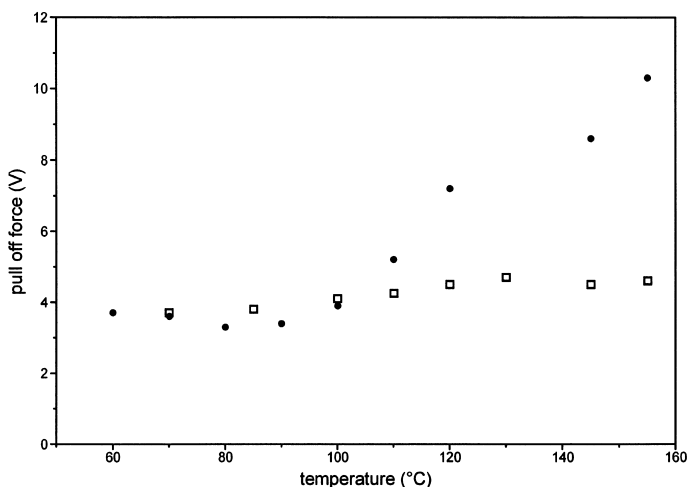

Figure 13.   Pull off force vs. temperature for polystyrene (●) and poly(methyl methacrylate) (□).

However, if the capability for thermal imaging is abandoned, then heated tips with the resolution of conventional AFM probes have been manufactured which are able to measure mechanical properties as a function of temperature with sub-nanometer resolution. Recently we have used pulsed force mode (PFM [29-31]) with a temperature stage to study how pull-off force varies as a function of temperature for individual polymers and polymer blends [32]. Figure 13 shows the data for polystyrene (PS) and poly(methyl methacrylate) (PMMA). The sharp increases in this quantity that are observed at specific temperatures are attributed to changes in the rheological properties of the samples as the temperature is raised and are, therefore, a measure of the viscoelastic response of the polymer. Krotil et al. have used PFM

data obtained at various temperatures to measure the glass-rubber transition temperature of polystyrene [31]. Changes pull-off behaviour can be used to make phase separation apparent and to identify the phases. Recent work using PFM microscopy in combination with a variable temperature sample stage has been used to study the morphology of PS/PMMA blends and several phase separated segmented polyurethane elastomers [32].
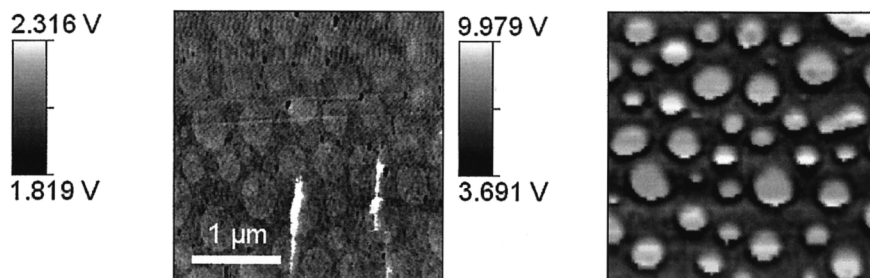

Figure 14.   Pulsed force mode (pull off force) images of a phase separated polystyrene/ poly(methyl methacrylate) blend using a micro-machined thermal probe. Probe temperature 30°C (left) and 150°C (right). The higher adhesion between the heated tip at 150°C and the occluded phase (bright) identify it as polystyrene. The light streaks in the image at 30°C are due to the presence of contamination.

Preliminary measurements using a micro-machined thermal probe in PFM are illustrated in Figure 14 for a phase-separated PS/PMMA blend. In this experiment it is the tip rather than whole sample that is heated, but the same type of behaviour is observed. As the temperature is increased, the pull of force for the polystyrene increases dramatically before any change occurs for the PMMA thus identifying the occluded phase as polystyrene. The advantage of heating the tip over heating the whole sample are that the experiments can be performed much more quickly and easily over the same area, the chances of the thermal treatment altering the sample are greatly reduced, and micro-TMA (or micro-DMA) experiments can be performed to confirm any identification. Work with probes designed to make pits in a polymer coating as a means of data storage indicate an area as small as 20 nm are affected by such local experiments [33]. These or similar probes could also image using PFM or other modes that are sensitive to local mechanical properties, such as phase imaging [34-36]. How these properties change as a function of temperature could then be studied by successive images at different tip temperatures rather than changing the temperature of the whole sample as has been done elsewhere [37,38]. In this way phases could be visualised and identified with a spatial resolution

similar to that of conventional atomic force microscopy. Similar high-resolution probes might well also make it possible to ablate pits of a few tens of nanometres with the evolved gases being analysed by time-of-flight mass spectrometry. As this process would be very rapid, it should be possible to generate images using this technique and even carry out tomography as successive layers of the sample are ablated away with the probe being able to precisely map the changes in topology that occur as the surface is eroded. An illustration of this concept is shown in Figures 15 and 16 where a conventional Wollaston wire probe was used to image across the boundary between a sheet of PMMA glued to a sheet of PS (Figure 15).
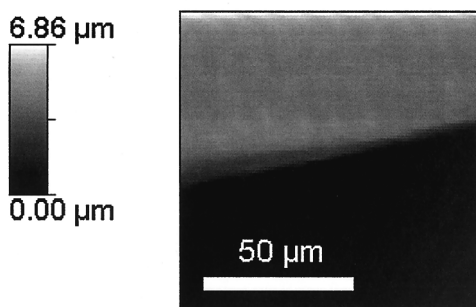

Figure 15.   Topography of the interface between a sheet of poly(methyl methacrylate) (top) and polystyrene. Image size: 100×100 μm.

Localised pyrolysis-MS measurements were then carried out in a down-up zig-zag pattern from the top left to the bottom right of the image whilst monitoring for the ions corresponding to the monomers of each polymer: m/e 100 (methyl methacrylate) and m/e 104 (styrene). The tip was heated at 25°C/s from 50°C to 600°C in air whilst in contact with the surface. The sequence of peaks in Figure 16 corresponds to the composition changing between the different layers and pyrolysis products from both polymers are detected at the interface between the PMMA and PS. The small peaks after the main pyrolysis products were detected are a result of cleaning the probe tip by heating it to 1000°C well away from the surface in order to remove any contamination from the filament. The observation of small amounts of residual material adhering to the tip is an example of "thermally assisted nano-sampling" described earlier.
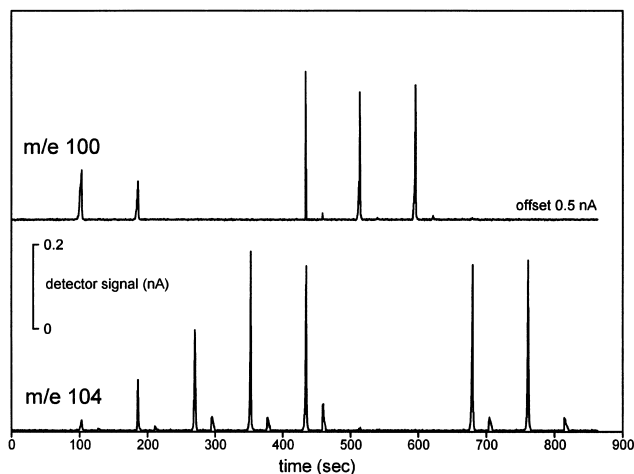
Figure 16.   Sequence of nine pyrolysis-MS measurements of the area shown in Figure 15 with single ion monitioring for m/e 100 (methyl methacrylate) and m/e 104 (styrene) (to same scale). The locations are (0,100), (0,50), (0,0), (50,0), (50,50), (50,100), (100,100), (100,50) and (100,0) in the order left-right. Small peaks after the main peaks are due to the tip cleaning procedure between measurements.

Conclusions

Thermal analysis is an essential tool for polymer characterisation. It is used to study cross-linking, crystallinity and structure in blends. However, it does not supply spatially-resolved information. With the advent of micro-TA, thermal methods have entered the domain of microscopy just as many other techniques such as IR and Raman spectroscopy have in the recent past. The ability to measure localised transition temperatures has a wide range of applications in polymer science as well as other fields such as pharmaceuticals. This is especially true when we add the capability of chemical analysis through local pyrolysis-GC/MS, pyrolysis-MS and high-resolution photothermal IR spectroscopy. Looking more broadly, using temperature as a variable with a wide range of SPM imaging modes, offers the potential for obtaining a great deal more information than is possible using only ambient temperature imaging. In general, heating the tip is preferable to heating the sample because the experiments can be performed much more quickly and easily over the same area, the chances of the thermal treatment altering the sample are greatly reduced and localised

characterisation can be performed to confirm any identification. As high-resolution probes become more widely available, micro-TA could become the technique of choice for tackling a wide range of academic and industrial problems in polymer science.

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