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APPLICATIONS OF MICRO-THERMAL ANALYSIS

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Abstract

Micro-thermal analysis combines the imaging facility of scanning probe microscopy with the ability to characterize, with high spatial resolution, the thermal behavior of materials. A sample may be visualized according to its surface topography and also its relative thermal conductivity. Areas of interest may then be selected and localized thermal analysis (TMA and modulated temperature DTA) performed. Applications of this new technique to study semiconductors, polymer blends and biological specimens are described.

Keywords: modulated temperature DTA, scanning probe thermal microscopy, thermomechanical analysis

Introduction

Thermal methods such as differential scanning calorimetry (DSC), thermogravimetric analysis (TG), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) are well-established techniques for characterizing the morphology and composition of materials. It is often possible to identify substances by reference to their characteristic transition temperatures. By investigating the changes in the measured property (e.g. enthalpy, mass, length, stiffness, *etc.*) with temperature, one may be able to quantify the degree of crystallinity, filler content or cross-link density. Multi-phase systems will often give a combined response from which it is possible to estimate the amount of each component present. Conventional thermal methods give only a specimen-averaged response i.e. they cannot give any information regarding the distribution of phases – in order to obtain spatially-resolved information about a sample, the investigator must resort to microscopy.

Experimental

The development of the scanning probe microscope has opened up many new ways of visualizing surfaces to very high resolution [1, 2]. A typical instrument consists of a sharp tip mounted on the end of a cantilever which is scanned across the

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specimen by a pair of piezoelectric elements aligned in the x- and y-axis. As the height of the sample changes the deflection of the tip is monitored by an optical lever formed by reflecting a laser beam from the back of the cantilever into a segmented photodetector. The tip is then moved up and down by a feedback loop connected to a z-axis piezo which maintains a constant contact force thus providing the height of the sample at each x,y position. In addition to the topographic information from scanning the tip across the sample, other information can be obtained by measuring the twisting of the cantilever (lateral force microscopy) [3]. This provides image contrast based on the frictional forces generated from the sample-tip interaction. Other imaging modes, such as force modulation and pulsed force modes can indicate the stiffness and adhesive properties of the sample [4, 5]

This work is concerned with scanning thermal microscopy (STM). Here the conventional sharp SPM tip has been replaced by a miniature temperature sensor. This uses a Wollaston wire probe described by Dinwiddie [6] which consists of a silver wire with a fine platinum core which is bent into a sharp loop and etched to expose the core. The probe forms part of an electrical bridge and behaves as a small resistance heater as well as a conventional SPM tip. The power required to maintain the tip at a constant temperature can be monitored as it is scanned across the specimen and used to build up an image based on the variation in apparent thermal conductivity (concurrent with topographic image described above). AC heating of the probe generates image contrast related to the thermal diffusivity of the sample, the depth of view depending on the frequency of modulation [7].

The design of the probe readily lends itself to thermal analysis. The tip is used as one half of a bridge circuit, whereby the difference in electrical energy supplied to the probe (in contact with a point on the sample) is compared with that of a reference probe (not in contact with the sample) as both are scanned in temperature. Thus the device behaves as a micro-differential thermal analyzer (micro-DTA). We use the term 'DTA' rather than 'DSC' because the present system is not quantitative in measuring transition enthalpies. In a conventional DSC the instrument is large in comparison to the sample (which can be weighed) – in this equipment, the sample is large in comparison to the measuring head. Although the probe only measures a small area (a few square microns), the sample's mass is unknown therefore the measurements are currently only qualitative in terms of identifying transition temperatures. This is often sufficient for characterization purposes, and semi-quantitative information can be obtained by comparing different areas of the same sample. The small scale of the probe means that high heating and cooling rates of the order of tens of degrees per second can be used. AC heating can be used to operate the system in a modulated-temperature mode [7]. Modulation frequencies in the kilohertz region are also typical.

The z-axis deflection of the probe is monitored during the experiment. This is the microscopic equivalent of TMA [8]. The force feedback mechanism must be disabled during the experiment otherwise the z-piezo motion would drive the tip through the specimen as it softens. Thus four signals can be measured and displayed:

the sensor height position (micro-TMA), the differential DC power required to change the probe temperature and the differential AC power and phase (micro-MTDTA). By analogy with MTDSC, the DC signal is equivalent to the 'total heat flow', and the AC amplitude is equivalent to the 'complex heat capacity'. It is often convenient to plot the 'calorimetric' signals as their first order derivatives with respect to time or temperature.

The instrument used for this work was a TA Instruments μTA 2990 Micro-Thermal Analyser based on the TopoMetrix Explorer TMX2100 scanning probe microscope. Temperature calibration of the probe was carried out by measuring the melting temperatures of purified organic materials such as phenanthrene and caffeine. Modulated temperature DSC measurements were carried out on a TA Instruments MDSC 2920.

Results and discussion

The applications of this technique are illustrated by considering three examples:

1. A semiconductor component.
2. A phase separated polymer blend.
3. The waxy coating on a leaf.

Semiconductor

Figure 1 (left-right) shows the topography, DC and AC (@ 30 kHz) thermal images of a light emitting diode. The scratches in the center of the topographic im-

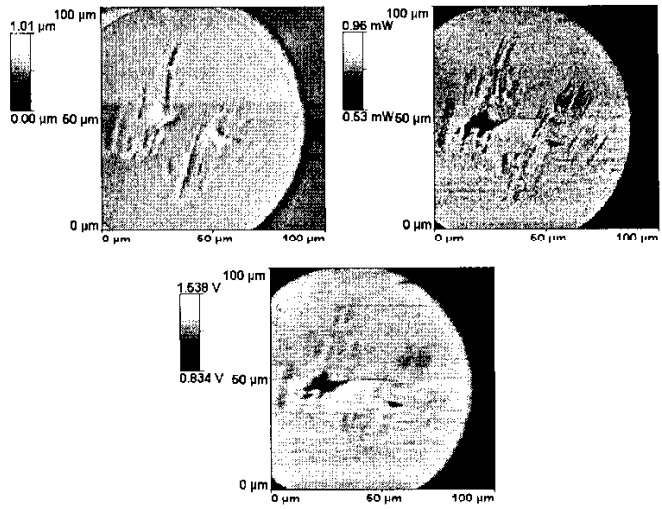

Fig. 1 (Left-right) topographic, thermal conductivity and modulated temperature (at 30 kHz) images of a light emitting diode

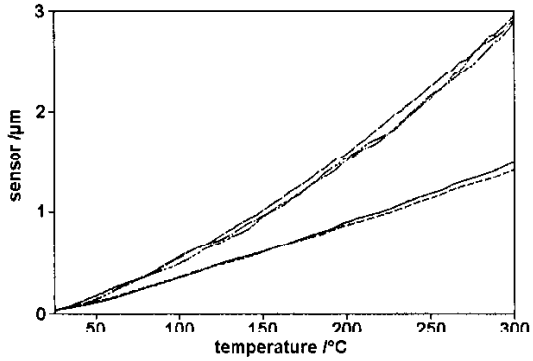

Fig. 2 Micro-TMA curves of LED from Fig. 1: lower two curves represent points on the outside right of images, top three curves from points within circular region

age are due to the removal of a gold contact wire – these create artificial contrast in the thermal images due to sharp changes in relief which affect the thermal contact area. However, both thermal images also show marked differences in contrast between the center of the image and the outside. These differences cannot be attributed to the surface roughness and were investigated by performing micro-TMA measurements at five different positions on the sample (Fig. 2). The sequence of scans took only a few minutes. These show the difference in thermal expansion coefficients of the component parts of the diode. Measurements on top of the scratches were the same as the surrounding material suggesting that no metal remained on the surface. Interestingly when a different LED was examined, no thermal image contrast was observed – although a similar topography was obtained. Micro-TMA confirmed that the surface was homogeneous and further investigation discovered that this component had been coated with a protective layer.

Phase separated polymer blend

Figure 3 shows the first derivative of heat capacity with respect to temperature of a two component polymer blend. Using the approach of Song *et al.* [9] a curve fitting procedure was used to separate the response of the sample into two peaks which can be compared with the individual components. The areas under these peaks represent the change in heat capacity of each component as it devitrifies (ΔC_p) and the peak position identifies the glass-rubber transition temperature. This result confirms that the system is immiscible and gives the composition of the blend (70:30 by mass) but does not indicate the spatial distribution of the phases.

Figure 4 shows the thermal conductivity contrast image of the same material – dark regions of low thermal conductivity can be seen within a matrix of higher thermal conductivity material. From the compositional analysis determined by MTDSC, it would be expected that the dark regions are the minority, higher T_g component. This is confirmed by micro-MTDTA measurements that show the spatially-resolved

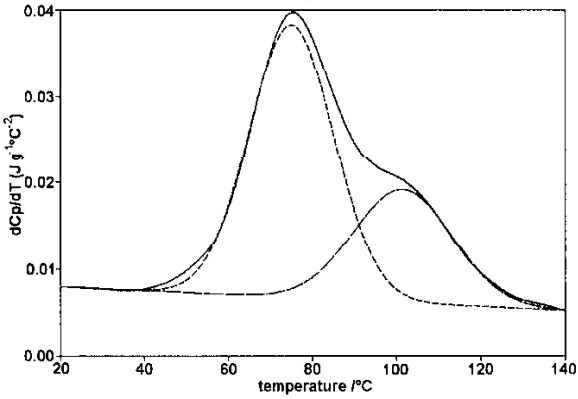

Fig. 3 First derivative of heat capacity with respect to temperature for two component polymer blend (solid line – raw data, dashed lines – fitted data to individual components)

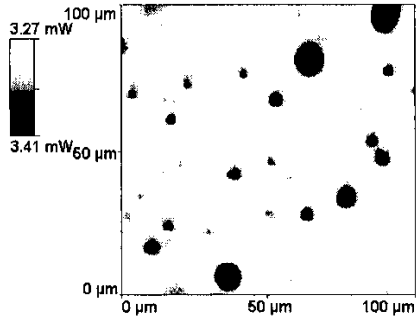

Fig. 4 Thermal conductivity contrast image of immiscible polymer blend (dark areas represent regions of low thermal conductivity)

differences in glass transition temperatures from the step change in the first derivative of the power applied to the probe (Fig. 5).

The waxy coating on a leaf

All plant leaves are covered by a waxy film which serves to protect the leaf and prevent moisture loss from the cells. This is particularly important for cacti and succulents which are adapted to live in arid climates [10]. A leaf from a specimen of crassula argentea was examined by localized thermal analysis. The resulting micro-TMA and MTDTA curves are shown in Fig. 6. The melting of the wax layer (ca 1 µm thick) is indicated by the penetration of the probe into the specimen and by an endothermic peak in the derivative power curve. At higher temperature an exothermic

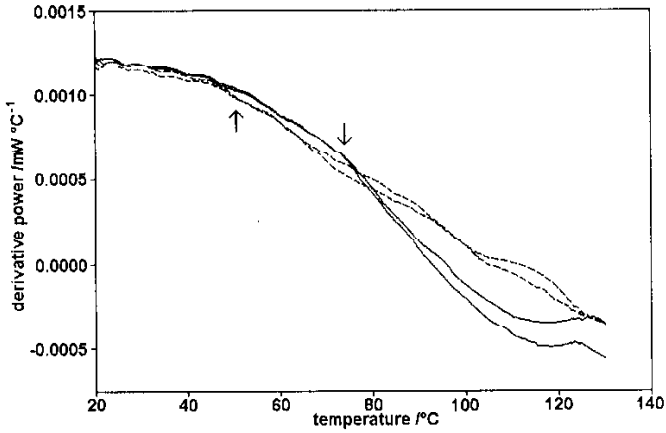

Fig. 5 Micro-MTDTA curves of dark (solid lines) and light (dashed lines) regions from Fig. 4. Arrows indicate onset of glass-rubber transition

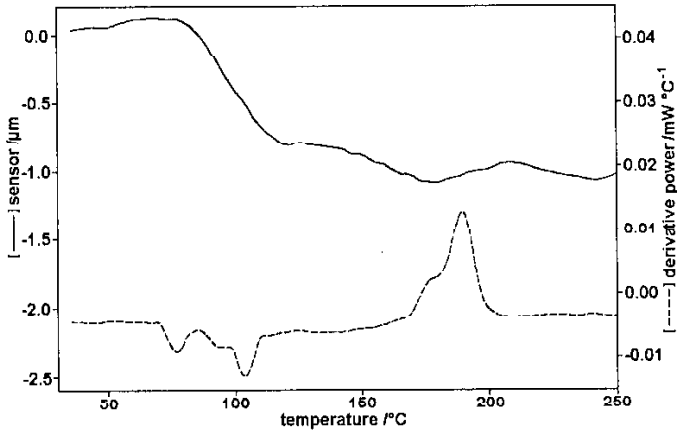

Fig. 6 Micro-TMA (solid line) and MTDTA (dashed line) of surface of leaf. Exothermic changes in the derivative power response indicated in a positive direction

process occurs which shifts to a higher temperature with an increase in heating rate suggesting that it is a kinetically controlled process. The melting of the wax is unaffected by heating rate.

A localized form of dynamic mechanical analysis has been demonstrated using the same probe to heat the sample [11]. The tip may also be used as a pyrolysis de-

vice for localized evolved gas analysis or as a detector for near-field infrared spectroscopy.

Conclusions

The combination of the scanning probe microscopy and thermal analysis opens new areas for the study of a material's properties at a very small scale. Case studies on a semiconductor component, a polymer blend and a biological specimen illustrate the wide variety of applications of this technique. It is possible to visualize the topographic and heat transport properties of a surface with high resolution. Selected locations may be characterized by thermal analysis (TMA and modulated temperature DTA) so as to investigate sample heterogeneity, composition or simply to examine specimens which are too small (e.g. thin coatings or minority constituents in a matrix) to examine by conventional techniques.

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