MICRO-THERMAL ANALYSIS: THE TECHNIQUE AND ITS APPLICATIONS TO POLYMERS

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The major difficulty with conventional thermal analysis techniques is that they measure the response of the whole sample. For example, if one observes a broad glass-rubber transition this could be due to a genuine effect in a homogeneous system or a series of overlapping responses from a heterogeneous system where there may be a difference in molecular weight or cross-link density throughout the sample.

Micro-thermal analysis (micro-TA) is a form of analytical microscopy that affords the ability to perform calorimetric and thermomechanical measurements in a localised way so as to characterise the nature and distribution of thermal transitions in a specimen [1-3]. Scanning probe microscope technology is used to move an ultraminiature heater/thermometer sensor across the specimen's surface so as to obtain images representing the sample's topography and apparent thermal conductivity. Other imaging modes are possible which can be used to generate image contrast on the basis of thermal expansivity or to obtain 3-dimensional tomographic mapping of buried structures. These images can then be used as a guide to position the sensor over areas of interest and record its vertical displacement and thermal flux whilst it is heated in contact with the sample. These measurements represent the micro-analogues of TMA and DSC and can be used to establish the temperatures of thermal transitions of a region less than 5 μm square. Localised forms of DMA and even TGA have also been demonstrated [4, 5].

The physical property measurements afforded by the above methods may, however, be insufficient to discriminate between different materials. We are therefore developing the means to add chemical analysis by using same device to pyrolyse small areas of the sample. The evolved gases may either be passed directly to a mass spectrometer or trapped, and subsequently analysed by GC-MS [6-7]. Alternatively the sample can be irradiated with IR radiation and the localised temperature rise produced by the absorbtion of IR radiation can be detected [8]. This is used to reconstruct the IR spectrum of the selected region with a resolution surpassing that available by conventional IR microspectrometry. This opens up

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the possibility of imaging a specimen and performing a wide range of physical and chemical characterisation using one versatile instrument.

Traditional forms of atomic force microscopy may also be employed for thermal analysis by changing the temperature of the whole sample rather than discrete locations. By the use of image analysis techniques we are then able to deduce the location of phases in polymer blends and networks to much higher spatial resolution than is currently possible with micro-TA [9]. The two approaches can be combined to perform subambient micro-TA for the measurement of thin adhesive coatings.

This presentation will review the design and operation of the instrumentation used. Different imaging and analysis modes will be illustrated with reference to various systems such as polymer blends, thermosets and composites. Drawbacks of the current approach will be discussed along with opportunities for future technique and application development.

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