New Aspects of Temperature Modulation in Thermal Analysis

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Modulated Temperature DSC is a variant of conventional DSC in which the conventional linear heating program has a modulation superimposed upon it. It was introduced by Reading and co-workers in 1992. The modulation is typically sinusoidal but can be a combination of sine waves (which, in certain combinations, will result in a square or triangular wave). The modulation in heating rate results in a corresponding modulation in heat flow. The response of the sample can then be considered to be made up of two components, the response to the underlying linear heating rate and the response to the modulation. These two components can be separated by use of an averaging procedure combined with a Fourier transform. This results in three signals, the underlying or average response that is equivalent to a conventional DSC at the same underlying heating rate, the amplitude of the modulation and the phase lag. The phase lag can be used to separate the response to the modulation into an in and out of phase component if desired.

For transitions other than melting, the modulation enables the reversing heat capacity to be measured which can be transformed into a reversing heat flow by multiplying it by the average heat rate. The term reversing means reversible at the time, temperature and frequency at which the measurement is made. By subtracting the reversing heat flow from the underlying heat flow the non-reversing heat flow can be determined (non-reversing meaning not reversible at the time, temperature and frequency at which the measurement is made). In this way enthalpies of reactions can be separated from heat capacity changes occurring at the same time. Also enthalpy recovery at a glass transitions can be separated, with due allowance for the effective frequencies of the measurements, from the change in heat capacity at the glass transition.

This ability to separate reversing and non-reversing phenomena brings a number of advantages for studying curing systems and blends. Briefly, in curing samples the progress of the cure reaction can be separated from the progress of vitrification. Under some circumstances, phase separation induced by the reaction can be detected. When studying amorphous blends, the reversing signal has a much higher signal to noise and greater resolution than conventional DSC to the glass transition. The fact that this signal is approximately independent of thermal history also simplifies the detection and quantification of different phases.

Melting transitions can give a variety of complex responses. The reversing signal becomes sensitive to rearrangement processes that may occur on heating that are largely undetected by conventional DSC. This fact assists in measuring initial crystallinity correctly. Reversible melting can be detected. The interpretation of other aspects of MTDSC for melting transitions remains somewhat controversial but it may be possible to probe the kinetics of melting and rearrangement.

In summary, MTDSC offers a number of advantages over conventional DSC for studying curing systems, blends and semi-crystalline polymers.

Recently the interest in modulation functions other than a single sine wave has increased and stochastic variations in frequency have been introduced. Furthermore, the use of methods of analysis other than Fourier Transforms has come to the fore. These approaches have advantages and disadvantages and these will be discussed. There are also methods of dealing with the non-

linear response that is encountered, in particular, during melting events and these will be outlined.

Scanning probe microscopy (SPM) is a key technique in modern characterisation science and an important variant of this technique is scanning thermal microscopy (SThM). This is a method of imaging thermal properties by using a thermal probe that has an ultra-small resistive heater at or near the tip. In one mode the temperature of this heater is held constant while the tip is rastered over the surface of the sample. The amount of power supplied to the tip changes as a function of the thermal conductivity of the material beneath it. Temperature modulation can be used in which case the measurement is sensitive to the sample's thermal diffusivity. An important feature of using temperature modulation is that the depth that the measurement 'sees' into the sample is controlled by frequency and so depth information can be obtained. A lateral spatial resolution of tens of nanometers can now be achieved for these types of measurement. An extension of this technique is micro or nano thermal analysis which involves placing the tip on a selected point of interest and ramping its temperature in a way similar to conventional bulk thermal analysis. A form of local thermomechanical and calorimetric analysis, including modulated temperature calorimetry, then enables local transitions to be studied. Initially limited to a spatial resolution of microns, recent breakthroughs mean these measurements can now be made on the nano-scale. Other measurements that can be made with this type of instrument include IR photothermal spectroscopy. Using different modulation frequencies creates temperature waves that travel with different degrees of attenuation as a function of distance. As in the case of AC thermal imaging, discussed above, this means depth information can be obtained about the chemical nature of materials. Thermal probe techniques offer unique capabilities for characterising materials and temperature modulation plays a significant role in this.