

Modulated Differential Scanning Calorimetry

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1. Introduction

Modulated Differential Scanning Calorimetry (MDSC) is a recently introduced technique that was developed in our laboratory and has several advantages over conventional Differential Scanning Calorimetry (DSC) ^(1,2). The method and the basic theory have already been described elsewhere ^(1,2). Essentially, the conventional isothermal or linear rising temperature ramp is modulated by some form of perturbation. A mathematical treatment is then applied to the resulting heatflow data to separate the sample response to the underlying temperature programme from its response to the perturbation. Currently, the type of perturbation used is a sinewave and the mathematical analysis is a combination of a Fourier Transform and an averaging process.

The underlying response is equivalent to a conventional DSC and from it, with appropriate calibration and baseline subtraction, the underlying heat capacity (C_p) can be calculated. From the response to the perturbation, the cyclic C_p is determined (again with appropriate calibration and baseline subtraction). The cyclic component can be separated into the in and out of phase components. The component in phase with the dT/dt modulation is called the heat capacity or the real part of the heat capacity and is associated with energy storage. The out of phase signal is called the kinetic component or the imaginary part of the heat capacity and is associated with energy loss or gain. Correct division of the cyclic C_p into these two components requires proper characterisation of the instrumental factors affecting the phase lag. This will be dealt with in a future article. Here we deal with measurements taken under conditions

where the out of phase component is small and can be neglected.

2. Irreversible Reactions

Fig.1 shows results for a sample consisting of 10:1 mixture of sodium bicarbonate and alumina. It can be seen that the underlying C_p shows two endotherms associated with the loss of water and the subsequent decomposition. The cyclic C_p "sees" only the heat capacity regardless of the energy associated with the chemical reaction, thus the difference signal shows the kinetic component. These signals can be expressed as heat flows by multiplying them by the underlying heating rate. When so expressed, the underlying signal is called the total heat flow, the cyclic signal the reversing heat flow and the difference the non-reversing heat flow. This demonstrates how processes that are, at the time and temperature they are observed, irreversible can be sep-

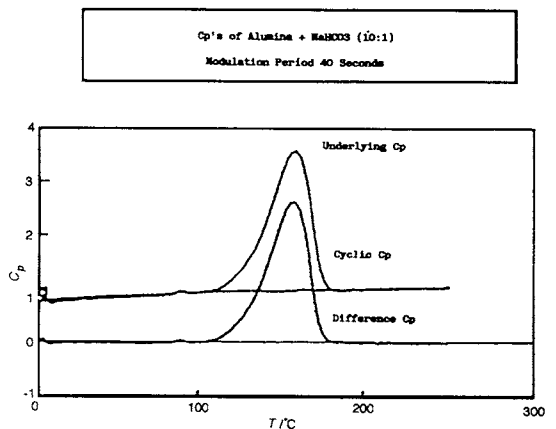


Fig.1 Separation of reversing and non-reversing processes.

Cooling Curves for Polystyrene for different MDSC Periods

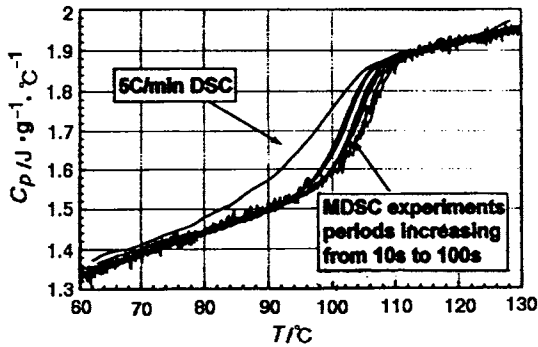


Fig.2 Glass Transition of polystyrene under various conditions showing Cyclic C_p for MDSC experiments.

arated from processes that are, at the time and temperatures they are observed, reversible.

3. Glass Transitions

Fig.2 shows the cyclic C_p 's from a series of MDSC

experiments on polystyrene carried out at different frequencies using a cooling rate of $1\text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The expected frequency dependence is seen. The apparent activation energy is $658\text{ kJ}\cdot\text{mol}^{-1}$. The C_p from a cooling experiment by conventional DSC at $5\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ is also shown for comparison. It can be seen that the shape of the transition is different from that given by the cyclic C_p . This means that the conventional DSC may not be equivalent to a single frequency, rather it is equivalent to a range of frequencies that are dependent on the degree of devitrification.

Alternatively, the cooling result is influenced by an enthalpic processes or possibly both of these two phenomena are required for a full explanation. These concepts will be explored in a future article.

Reference

- 1) M.Reading, *Trends in Polymer Sci.* p.248 (1993) .
- 2) M.Reading, A.Luget and R.Wilson, *Thermochim. Acta* **238**, 295-307 (1994)