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Thermal Properties of Polymers Part 1: Industrial Guide to Measurement by Differential Scanning Calorimetry (DSC)

In order to maximise their performance per unit cost, materials are increasingly required in situations that challenge the thresholds of their thermal capabilities. It is therefore important to understand material behaviour under a wide range of conditions relevant to industrial processing and use. Differential Scanning Calorimetry (DSC) can provide a variety of important information of use to the design engineer. In order to reduce the cost of processing polymers, increasing the speed of production is a valuable aim. To do this with confidence, an understanding of crystallisation behaviour or reaction rates is required. DSC can often provide the key to reducing the costs in this way. DSC measurement techniques can be used to analyse most materials in use today in a large number of applications such as elastomers, thermoplastics, thermosets, composites, coatings, adhesives, films, fibres, ceramics and metals and even biological materials and foods.

NPL is developing procedures based on various DSC techniques that can be used to design products based on existing materials, select the best material for a given application, predict its performance, optimise processing conditions, improve quality control, compare properties of similar or competitive materials and characterise newer research materials.

Figure 1. The NPL has carried out DSC work in support of Formula 1 racing.

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Differential Scanning Calorimetry

DSC measures the temperatures and heat flow associated with transitions in materials as a function of time and temperature. The technique provides qualitative and quantitative information about physical and chemical changes that give out or take in heat as well as changes in heat capacity using minimal amounts of sample (typically 20mg). It has many advantages including fast analysis time, typically thirty minutes, easy sample preparation, applicability to both liquids and solids, a wide range of temperature applicability (see table) and excellent quantitative capability. Some measurements that it can make are :

- Glass Transitions
- Boiling and Melting Points
- Crystallisation time and temperature

- Percent Crystallinity
- Heat of Fusion (latent heat)
- Specific Heat Capacity
- Oxidative Stability
- Rate and Degree of Cure
- Reaction Kinetics
- Percent Purity
- Thermal Stability

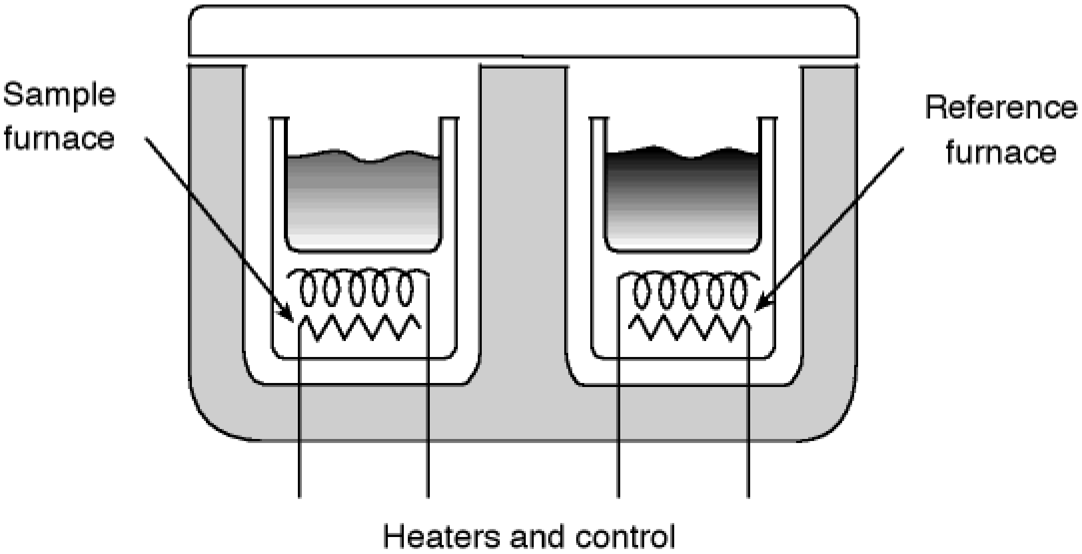

Figure 2. Schematic diagram of DSC

DSC allows accurate determination of temperatures associated with thermal events. The machine temperature measurement can be calibrated with respect to reference materials which allows highly accurate, precise and reproducible values. (Calorimetric precision ±0.1%, Temperature precision & accuracy: ±0.1°C)

The technique can reveal the thermal history imparted to thermoplastics as a result of different processing conditions. The information generated can be used to vary cooling rates to deliver the required degree of crystallinity.

Heat evolved during cure can be related to the degree of cure in thermosetting materials. Percent conversion with time at a given temperature or for the same time under varying temperatures can be determined.

Reaction kinetics can be studied to determine Arrhenius parameters, Activation Energy (E), the pre-exponential term (Z), rate constant (k) and reaction order (n). Experiments can be carried out isothermally at temperatures of interest or at constant heating rate.

DSC finds application in the pharmaceutical and health care industry as a means to determine purity. The presence of an impurity leads to a decrease in melting point which can be related to percent purity. DSC is used to evaluate metal alloy properties and provide data required to prepare phase diagrams.

Greases and lubricants can be evaluated in terms of the transitions of interest, glass transition, wax dissolution and decomposition in a single run allowing the determination of life expectancy in service. Quantitative analysis of the different constituents can be made by measuring the areas under the different peaks.

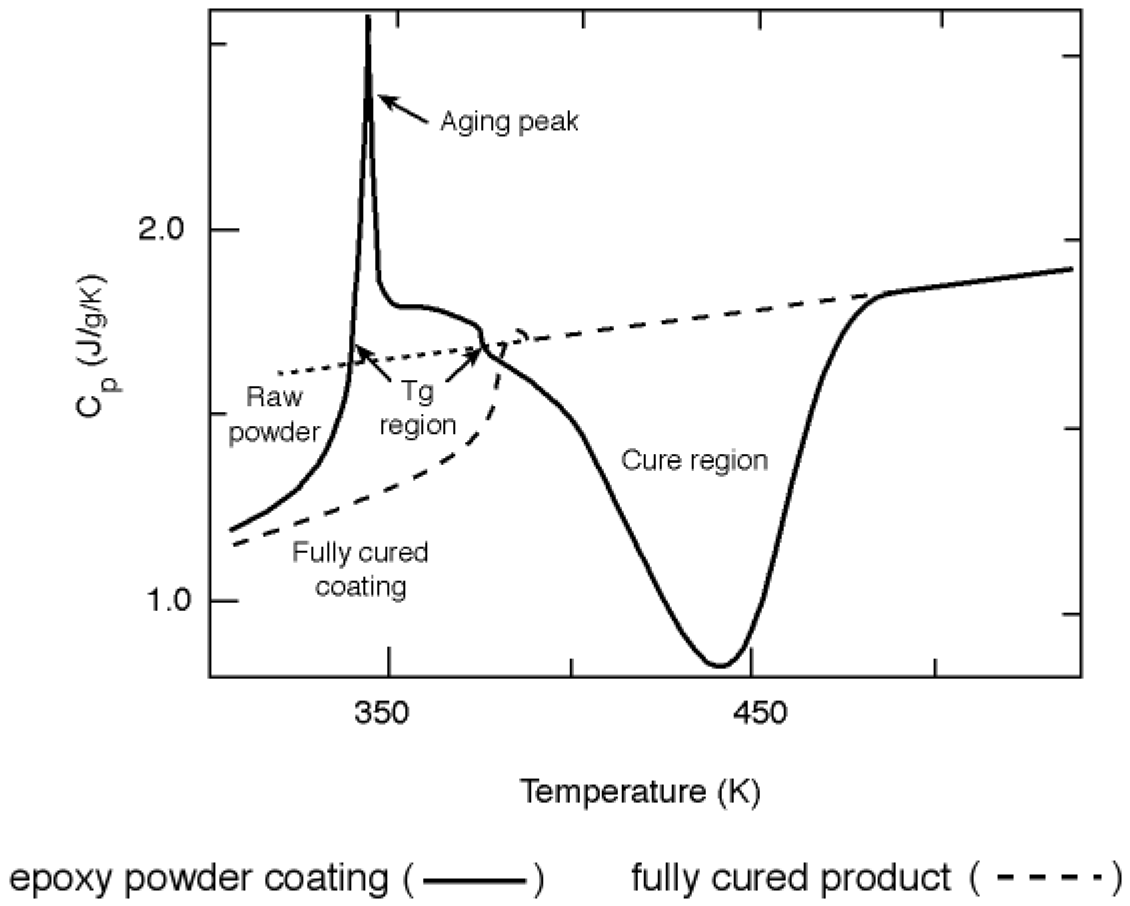

Figure 3. DSC curves showing the cure of an epoxy powder coating and the fully cured product.

Temperature Modulated DSC

TMDSC is a modification of DSC which allows the differentiation of overlapping transitions. In TMDSC, a sinusoidal modulation is overlaid on the linear heating ramp of the DSC. Depending on the underlying heating rate, the period and amplitude of modulation, the result is an improved resolution and sensitivity not possible in normal DSC. Fourier Transform analysis is then used to separate the resulting raw experimental heat flow into the heat capacity related (reversible) and kinetic (non-reversible) heat flows. Typical reversing events are glass transitions and crystalline melting and examples of non-reversing events are evaporation, thermoset cure and decomposition.

Complex transitions can be separated into simple, easily interpreted components. During thermoset cure, for example, relaxation of internal stresses generated during processing and glass transition (Tg) often overlap, making it difficult to interpret the transition. It is not possible to use the method of heating past Tg and rapidly cooling to remove thermal history and analysing the second heat up in this case since heating could result in further cure of the resin, changing the Tg.

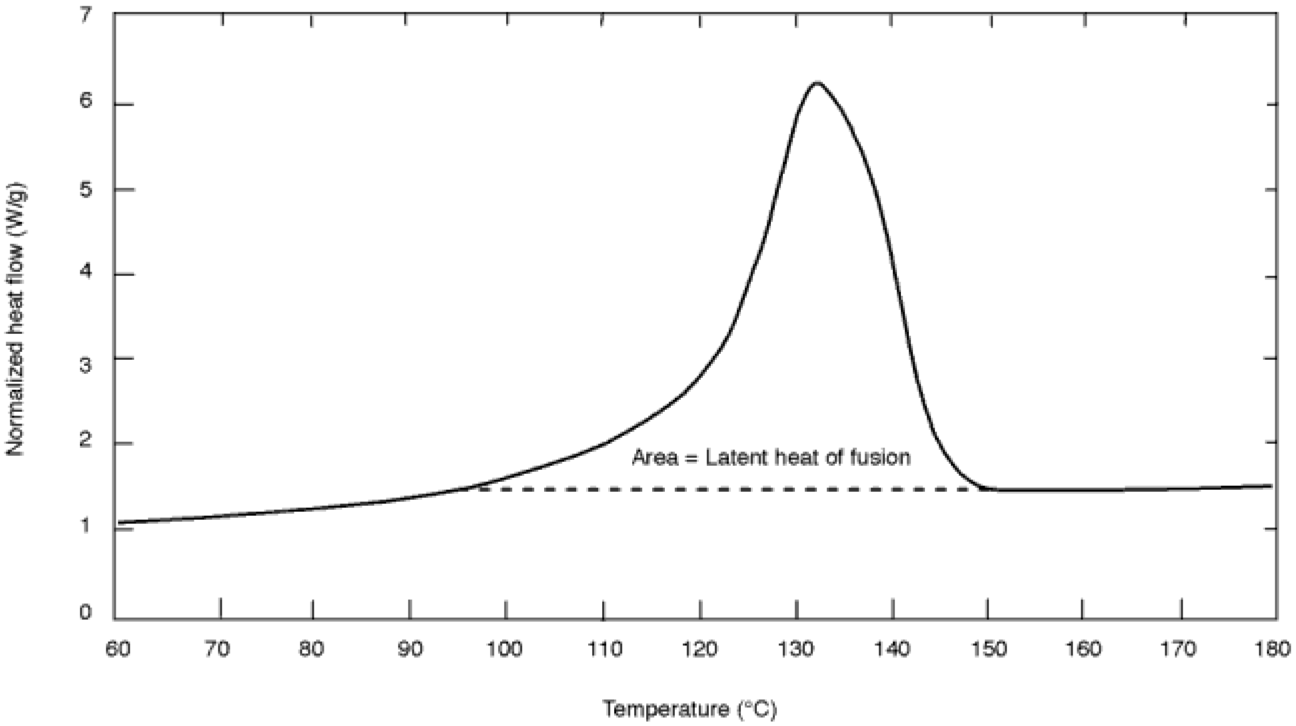

Figure 4. Typical DSC plot for an HD polyethylene.

High Temperature DTSC

High temperature DTSC measures temperatures and heat flows (semi-quantitative) for high temperature transitions. Primarily used for inorganic materials (glasses, metals, minerals). See table for temperature range.

Pressurised DSC

Pressurised DSC provides the same basic measurements as DSC but with a pressurised gas facility as an additional experimental variable. This can facilitate studies of heterogeneous chemical reactions with a gaseous reactant, decompositions which produce volatile products, reactions overlapping with vaporisation at ambient pressure (e.g. curing), and adsorption/desorption. The pressure range is 1.3 Pa to 7 MPa. Pressurised DSC can be used to reproduce more accurately actual processing conditions. For example in forming operations, where pressure plays an important part in material behaviour.

Some Commercial Examples

A leading supplier of lubricants for formula one racing needed accurate data on thermal properties to help formulate and optimise lubricant thermal properties.

A major chemical company needed thermal data on experimental grades to help decide which new grades to develop. DSC helped them to decide on the best material for the job.

Several suppliers of reactive polymers (thermosets, rubbers) needed data on the reaction kinetics of their materials. Data was provided so that simulation packages such as Moldflow, could predict how these materials process in a range of products.

The NPL Facilities

The NPL has state of the art instruments of all types including dual cell, pressure, high temperature DSC and the most recent advance; modulated DSC. With this extensive range of facilities accurate measurements can be made on a wide range of materials over an extensive temperature range.

To obtain quantitative and accurate data all the instruments are calibrated over the working range with reference materials, where available (ref 1) and the tests carried out to ISO 9001 procedures and ISO/FDIS 11357 standards (ref 2).

The NPL is unique in offering to industry a complete DSC service over a wide range of materials from -170°C to 1570°C.

DSC Instrument	**Temperature range (°C)**	**Typical Test Materials**	**Typical Purpose**
Power compensated	-170 to (+730)	Polymers, foods, ceramics, metals, oils	T_m, T_g, enthalpy specific heat, crystallisation and reaction kinetics
Temperature Modulated, (heat flux)	-60 to (+300)	Composites thermosets semi-crystalline polymers	T_m, T_g, complex overlapping transitions
Pressure, (heat flux)	ambient to (+725)	Polymers	Heat of reaction, oxidative stability, vapour pressure
Heat flux, (DTSC)	600 to (+1500) 1100 to (+1570)	Metals, alloys, ceramics	specific heat, enthalpy, reaction kinetics

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The assistance of C.S. Brown, S. Gnaniah and D.R. Mulligan (all NPL) is greatly appreciated. This research was supported by the *DTI Materials Measurement* programme

References

1. Reference materials supplied by the Laboratory of the Government Chemist
2. ISO/FDIS 11357 draft standard at present.

The NPL conducts underpinning research on measurement methods such as heat transfer in polymer processing, viscoelastic measurement for polymer melts and improved PVT measurements for polymer processing.

For further information on DSC or to find out more about the NPL measurement service contact:

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