DSC 2010 Differential Scanning Calorimeter

TA Instruments
Thermal Analysis & Rheology
A Subsidiary of Waters Corporation

DSC: The Technique

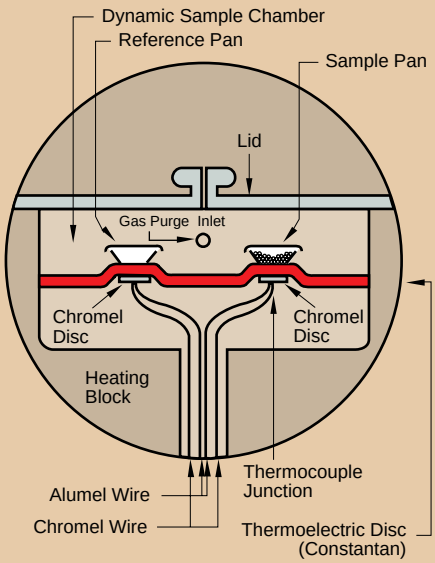
Thermal analysis is the generic name used to describe a series of analytical techniques which measure physical and chemical changes in materials as a function of temperature and time. The most widely used of these thermal analysis techniques is differential scanning calorimetry (DSC) which specifically measures the temperatures and heat flows associated with material transitions. Such measurements provide quantitative and qualitative information about endothermic (heat absorbed) or exothermic (heat evolved) processes, as well as changes in heat capacity. DSC is primarily used to characterize polymers and other organic materials, but is also applicable to metals, ceramics, and other inorganics.

What DSC Can Tell You

DSC provides important information that can be used to characterize materials, design products, select the best materials for a specific application, predict product performance, optimize processing conditions, and improve quality. Specific measurements made by DSC include:

- Glass transitions
- Melting points
- Crystallization time and temperature
- Percent crystallinity
- Heats of fusion and reactions
- Specific heat and heat capacity
- Oxidative stability
- Rate of cure
- Degree of cure
- Reaction kinetics
- Purity
- Thermal stability
- Boiling points

Figure 1.
DSC Cell Cross-Section



TA Instruments DSC 2010

The TA Instruments DSC 2010 is the result of more than 30 years of leadership in calorimetry and provides a series of features which make it ideal for laboratories that want a high quality DSC, but have a limited budget.

- *Excellent DSC performance* based on a proven heat flux design. The unit's high sensitivity (1μW), wide temperature range (-180 to 725°C) and superior baseline stability are equivalent to those normally associated with expensive research-grade instruments. Furthermore, the DSC 2010's heat flux design is extremely rugged, making it ideal for less experienced operators.
- *Compact design* which makes efficient use of valuable laboratory bench space.
- *Modular design* which provides a cost-effective initial system price, but still allows future expansion into other thermal analysis techniques if laboratory needs change.
- *Complete installation, training, and applications/service support* including a variety of training aids for new DSC users and immediate access to knowledgeable applications and service specialists by telephone.

Principle of Operation

A cross section diagram of the TA Instruments DSC 2010 cell is shown in Figure 1. The cell is based on a "heat flux" design which uses a constantan disk as the primary means of transferring heat to the sample and reference positions. The sample, contained in a metal pan, and the reference (an empty pan) sit on raised platforms formed in the constantan disk. As heat is transferred through the disk, the differential heat flow to the sample and reference is measured by area thermocouples formed by the junction of the constantan disk and chromel wafers which cover the underside of the platforms. Chromel and alumel wires attached to the chromel wafers form thermocouples which directly measure the sample temperature. This continuous direct measurement of sample temperature accounts for high transition temperature repeatability and accuracy not available with alternative heat flux or power compensation DSC designs which determine sample temperature by calculation. Constant calorimetric sensitivity is maintained throughout the usable temperature range of the cell by electronic linearization of the cell calibration constant. The temperature environment of the sample is controlled by a sophisticated feedback-control temperature programmer with its own thermocouple system located in the silver heating block. This allows the temperature of the sample to be held isothermal, or raised or lowered at a variety of preprogrammed rates. Purge gas is admitted to the sample chamber through an orifice in the heating block wall midway between the two raised platforms. The gas is preheated by circulation through the heating block before entering the sample chamber. The result is a uniform, stable thermal environment which assures excellent baseline flatness and exceptional sensitivity (signal-to-noise).

Features and Benefits

The DSC 2010 is designed to provide performance usually associated with research-grade instruments, but at a lower price. In combination with a Thermal Analyst Controller, the DSC 2010 is the most cost-effective general purpose DSC system available. Key features and benefits include:

High calorimetric sensitivity, permitting measurement of low enthalpy transitions and the use of small samples resulting in high resolution and optimum temperature accuracy.

Constant calorimetric sensitivity, permitting measurement of calorimetric properties over a wide temperature range, with an easy single-point calibration.

Direct measurement of sample temperature, assuring accurate and precise transition temperatures. Temperature calibration can be based on one to five standards assuring maximum temperature accuracy.

Superior baseline stability, facilitating measurement of weaker transitions and assuring reproducibility and reliability of the data.

Sample versatility, facilitating evaluation of polymers as well as organic and inorganic materials in solid, paste, or liquid form. A wide variety of sample pans ensure good heat transfer and eliminate undesirable sample-pan interactions. Only a few milligrams of material are needed because of the instrument's sensitivity.

Experimental methods versatility, permitting a wide choice of temperature programming (heating/cooling) and atmosphere conditions for obtaining maximum information from a single sample. An unlimited number of methods containing up to 60 segments each can be created using 18 available functions (segment types). Temperature programming options include heating and cooling at rates from 0.01 to 200°C/min, step heating and cooling, and isothermal operation. Unique segments are available for controlling the LNCA cooling accessory and for stopping (aborting) a segment when a specific measurement signal is achieved. Data collection rate and threshold level can be adjusted to maximize data storage effectiveness or the operator can accept default conditions optimized for general experiments.

Data analysis versatility, providing options which facilitate interpretation and report generation, including:

- Multi-tasking capability for increased productivity
- Ability to perform multiple analyses (e.g. glass transition, ΔH crystallization, and ΔH melting) on a single curve.
- Ability to analyze complex experiments (e.g. cyclic heat-cool-heat experiments) using only a single curve.
- Compatibility with a variety of data output devices.

Availability of specialized accessories, permitting specific experiments to be performed. These accessories include:

- Quench Cooling Accessory: for simple nonprogrammed rapid cooling (to -180°C).
- Liquid Nitrogen Cooling Accessory (LNCA): for automated or quench cooling, or programmed cooling to -150°C.
- Refrigerated Cooling System (RCS): a mechanical refrigeration device for controlled cooling to -70°C.
- Gas Switching Accessory (GSA): for programmed or manual switching of purge gases.

Compatibility with other thermal/rheology techniques, broadening the range of materials and the types of measurements which can be performed. These other techniques include thermogravimetric analysis (TGA), simultaneous TGA-DTA, thermomechanical analysis (TMA), dynamic mechanical analysis (DMA), dielectric analysis (DEA) as well as controlled stress and controlled rate rheology. These techniques can be run individually, or in multimodule configurations, by the Thermal Analyst controller to provide complete materials characterization.

Data Analysis Software

Universal Analysis

A versatile "general purpose" data analysis program is an integral part of the *Thermal Solutions* Software. This program analyzes files from all the core thermal analysis modules (DSC, DTA, TGA, SDT, TMA, DEA, and DMA) and provides the following analysis capabilities and features:

DSC Standard Analysis

- Temperatures of transitions
- % Crystallinity
- Degree of cure
- Oxidative stability & induction time

Generic Analysis Functionality

- Peak integration
- Partial areas
- Onset temperature
- Step transition
- Running area integral plots
- Data point value
- Tabular data report
- Results report
- ASCII file export
- PCX and HPGL file export
- Curve rotation
- File addition and subtraction
- Generic equation calculations
- X and Y linear transformation
- Curve overlay
- Saved analysis
- Saved session

Specialty Programs

In addition to Universal Analysis an extensive library of optional specialty data analysis program are available for interpretation, evaluation, and optimization of DSC experiments. These programs include:

- Dynamic Calorimetric Purity
- Borchardt & Daniels Kinetics
- Thermal Stability (ASTM E-698 and E-1231)
- Isothermal Kinetics
- Heat Capacity
- Autoanalysis

Sample Pans

Figure 2.
Evaluation of Thermal History in Polyester

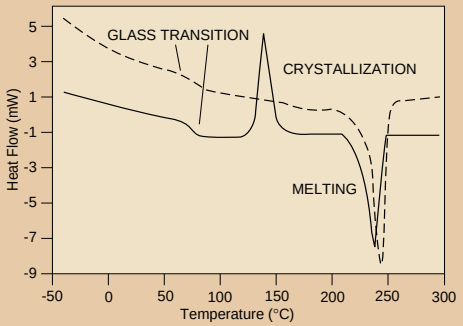


Figure 3.
Polymer Crystallization in Polyethylene

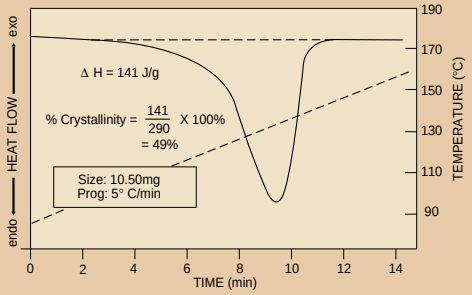


Figure 4.
Cure Determination in High Temperature Thermoset

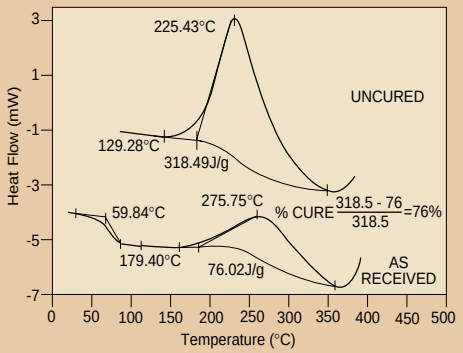
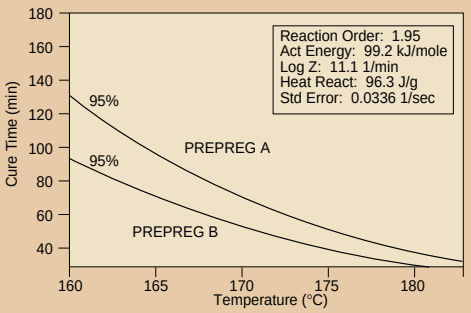


Figure 5.
Thermoset Cure Prediction



Applications

The broad capability of the DSC 2010 for characterizing materials is illustrated by these representative applications.

Thermal History of Thermoplastic materials

The internal structure of thermoplastics is strongly affected by the thermal history imparted during processing. In particular, the rate of cooling from the melt can result in either a crystalline (more ordered) or amorphous (more random) internal structure. The presence of a glass transition in DSC indicates that some amorphous structure exists, while the presence of an endothermic melting peak indicates that some crystalline structure exists. Figure 2 shows the DSC heating profiles for two samples of a typical thermoplastic material, polyethylene terephthalate (PET), that were previously subjected to different thermal histories. The solid curve represents the material after quench cooling from the molten state. The broken curve represents the material after slow, controlled cooling. The quenched material exhibits a totally amorphous internal structure (as indicated by a strong glass transition) which rearranges on heating to the more stable crystalline structure with an associated exothermic crystallization peak and subsequent melting peak. The slowly cooled material, on the other hand, yields a highly crystalline structure as evidenced by the presence of only a melting peak and a very weak glass transition on reheating. As these results indicate, DSC provides a convenient method for evaluating the effects of different processing conditions (thermal history) and is a valuable aid for choosing optimum processing conditions for obtaining a specific product.

In addition, the amount of crystalline structure (% crystallinity) can be quantified directly from the DSC melting endotherm by comparing the measured heat of fusion with that for a standard of known crystallinity. Typical results for polyethylene are shown in Figure 3. Alternatively, in polymer blends it is often possible to quantify blend composition based on the relative size of the crystalline melting peaks, provided thermal history effects are constant. Blends of polyethylene and polypropylene are a typical example.

Thermoset Cure Evaluation

Thermosets are another broad class of polymers which initially are powders or liquids, but which undergo a chemical reaction with time and temperature to form rigid, final materials. This chemical reaction process is called curing and involves crosslinking-that is, formation of new bonds in the material. Once curing occurs, thermosets, unlike thermoplastics, cannot be melted and reformed.

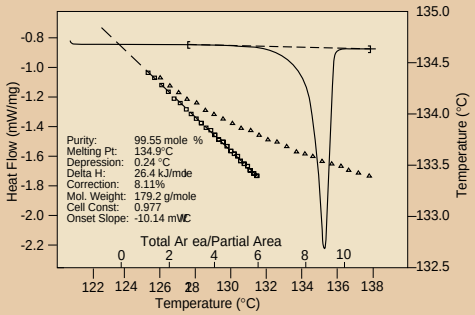
Since thermoset curing is accompanied by the evolution of heat (exothermic reaction), DSC can be used to evaluate partially or fully cured thermosets. This is important because thermosets are often processed initially to a low level of cure (B- stage) to facilitate storage and handling, and then later completely cured into the desired final form. Figure 4 shows the DSC curve for an epoxy resin “as received”. Also shown is the DSC curve for a completely uncured sample of the same epoxy. By measuring the heat evolved by the uncured material (in this case 318 J/g), it is possible to determine the degree of cure for the “as received” resin by comparing its remaining heat of cure to the uncured material’s. As shown in the Figure, the “as received” material is 76% cured. Notice that the partially cured resin exhibits a glass transition at 59.8°C. For thermosets, this glass transition temperature can also be used to determine the degree of cure provided suitable calibration curves are run.

In addition to measurement of temperatures and heats of reaction, DSC provides information about the rate (kinetics) of reaction. Three different kinetic software programs are available so that situations as diverse as curing and thermal hazard analysis during manufacture and storage can be accurately modeled. All three kinetic approaches (Borchardt & Daniels, Thermal Stability (based on ASTM E-698 & E-1231), and Isothermal) produce a series of quantitative parameters including activation energy (E), pre-exponential factor (Z), rate constant (k), and reaction order (n), as well as comparative curves such as those shown in Figure 5 for epoxy prepregs. Comparison of glass transition temperatures and residual heats of cure did not allow differentiation of these two similar prepreg formulations. The isoconversion curves to reach complete (95%) cure, however, clearly show that the two materials will process differently.

Determining the Calorimetric Purity of Pharmaceuticals

Using calorimetric purity software, the DSC 2010 can accurately determine the purity of highly pure (>97 mole % pure) chemicals. The technique is based on the principle that the concentration of impurity in a material is inversely proportional to its melting point; thus, an increase in the sample's impurity content decreases the melting point and broadens the melting range. Only a few milligrams of material are needed for an accurate determination without the need for pure reference materials. The analyst simply selects the baseline points, then the software calculates the mole percent purity. Results of an evaluation of a benzoic acid sample are shown in Figure 6.

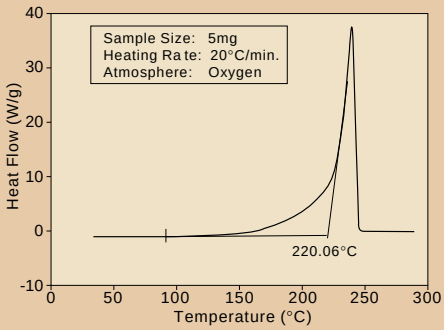
Figure 6.
Purity of Pharmaceuticals



Oxidative Stability of Materials

Oxidative stability is an important in-use property for a wide range of materials including plastics, oils and lubricants, and foods. Although other factors such as temperature and exposure to ultraviolet light can adversely affect a material over a long period of time, attack by oxygen in the atmosphere is usually the key factor in determining the material's lifetime. Special compounds, called antioxidants are often added to a base material to improve its resistance to attack by oxygen (its oxidative stability). Suppliers of the base materials are interested in comparing the effects of different antioxidants, as well as different levels of the same antioxidant, so that they can achieve the best compromise between increased lifetime of the base material and cost. Since oxidative stability is an exothermic process, DSC provides a convenient way to determine when significant oxidative degradation and material failure begins as shown in Figure 7 for a lubricating oil.

Figure 7.
Oxidative Stability for Lubricating Oil

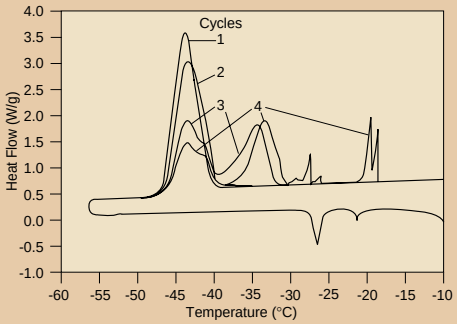


Development of Water in Oil Emulsions

In the development of water in oil emulsions, the structure of the emulsifier, the emulsion formulation and the process for making the emulsion are all critical to the final product's quality. DSC provides a rapid method for evaluating water in oil (W/O) emulsions based on following the freezing point depression of the water present. Figure 8 shows the cyclic DSC heating and cooling curves for a typical W/O emulsion. All four cooling cyclic curves are shown, whereas only the initial heating curve is shown, because the cooling curves are more sensitive to the emulsion quality. The peak at about -45°C is the exothermic crystallization (freezing) peak for the water in the emulsion. The temperature at which this peak occurs can be used to quantify the amount of added surfactant, while the shape of this peak provides information about emulsion stability. The presence of a single well-defined peak indicates that the emulsion is well-dispersed and all water droplets are essentially the same size. Multiple peaks (as occurs in this example), on the other hand, indicate different droplet sizes. The appearance of additional peaks at -35°C (after 3 cycles) and at -19°C (after 4 cycles) indicates the presence of a bimodal distribution of water droplet size and "water breakout" respectively. All of these latter phenomena indicate a poor emulsion.

The Refrigerated Cooling System (RCS) which facilitates cyclic temperature programming of the DSC cell in the range -70 to 400°C is ideal for studies such as this one.

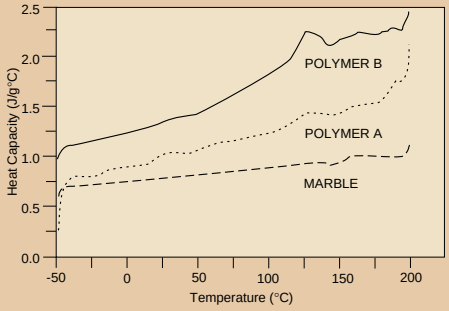
Figure 8.
Stability of Water in Oil Emulsion



Heat Capacity of Materials

Heat capacity is a measure of the energy required to raise the temperature of a material and is an important parameter for chemical engineers involved in heat transfer calculations, civil engineers involved in heating and cooling questions, scientists interested in energy storage, and civil or mining engineers interested in thermal conductivity and insulation properties. Measurement of heat capacity, a structure sensitive property, can be achieved using the DSC between -100 and 725°C. The measurement is made by heating a test sample at a fixed heating rate over a designated temperature range. The resulting heat flow response, normalized to sample mass and heating rate, is directly proportional to the sample's heat capacity. Figure 9 shows the comparative heat capacity results for two construction materials used to simulate marble. These results were used to choose Polymer A for the intended application.

Figure 9.
Heat Capacity



Specifications

Atmosphere:	non-corrosive inert, reducing or oxidizing
Dynamic Gas Purge (preheated):	up to 100 mL/min at pressures from 300Pa (2 torr) to atmospheric
Temperature Range:	- Inert atmosphere: ambient to 725°C - Air/oxygen: ambient to 600°C - With quench cooling can: -180 to 725°C - With Refrigerated Cooling System: -70 to 400°C - With Liquid Nitrogen Cooling Accessory: -150 to 725°C
Temperature Accuracy (using metal standards):	±0.1°C
Temperature Reproducibility (using metal standards):	±0.05°C
Programmable Heating Rate:	0.01 to 200°C/min
Maximum Sensitivity:	1μW (2:1 signal to-noise)
Calorimetric Precision:	±0.1% (based on metal samples)

Specifications are subject to change

TA Instruments Commitment

The DSC 2010 Differential Scanning Calorimeter is designed and engineered to assure easy, reliable, trouble-free operation. It is supported by a full range of services, including an applications laboratory, publications, training courses, seminars, training and applications CD's, an Internet website and a telephone Hotline for customer consultation. Highly qualified service personnel, specialized in thermal analyzer/rheometer maintenance and service, are available throughout the world. All of these items reflect TA Instruments commitment to providing thermal analysis & rheology products and related services that deliver maximum value for your investment.

For information or
to place an order, contact:

TA Instruments, Inc.
New Castle, DE USA
Telephone: 1-302-427-4000
Fax: 1-302-427-4001

TA Instruments N.V./S.A.
Gent, Belgium
Telephone 32-9-220-79-89
Fax: 32-9-220-83-21

TA Instruments, Ltd.
Leatherhead, England
Telephone: 44-1-372-360363
Fax: 44-1-372-360135

TA Instruments S.A.R.L.
Paris, France
Telephone: 33-01-30489460
Fax: 33-01-30489451

TA Instruments GmbH
Alzenau, Germany
Telephone: 49-6023-30044
Fax: 49-6023-30823

TA Instruments Japan K.K.
Tokyo, Japan
Telephone: 81-3-3450-0981
Fax: 81-3-3450-1322

Internet: http://www.tainst.com
e-mail: info@tainst.com

TA Instruments
Thermal Analysis & Rheology
A Subsidiary of Waters Corporation

TA-093C PRINTED IN THE U.S.A.