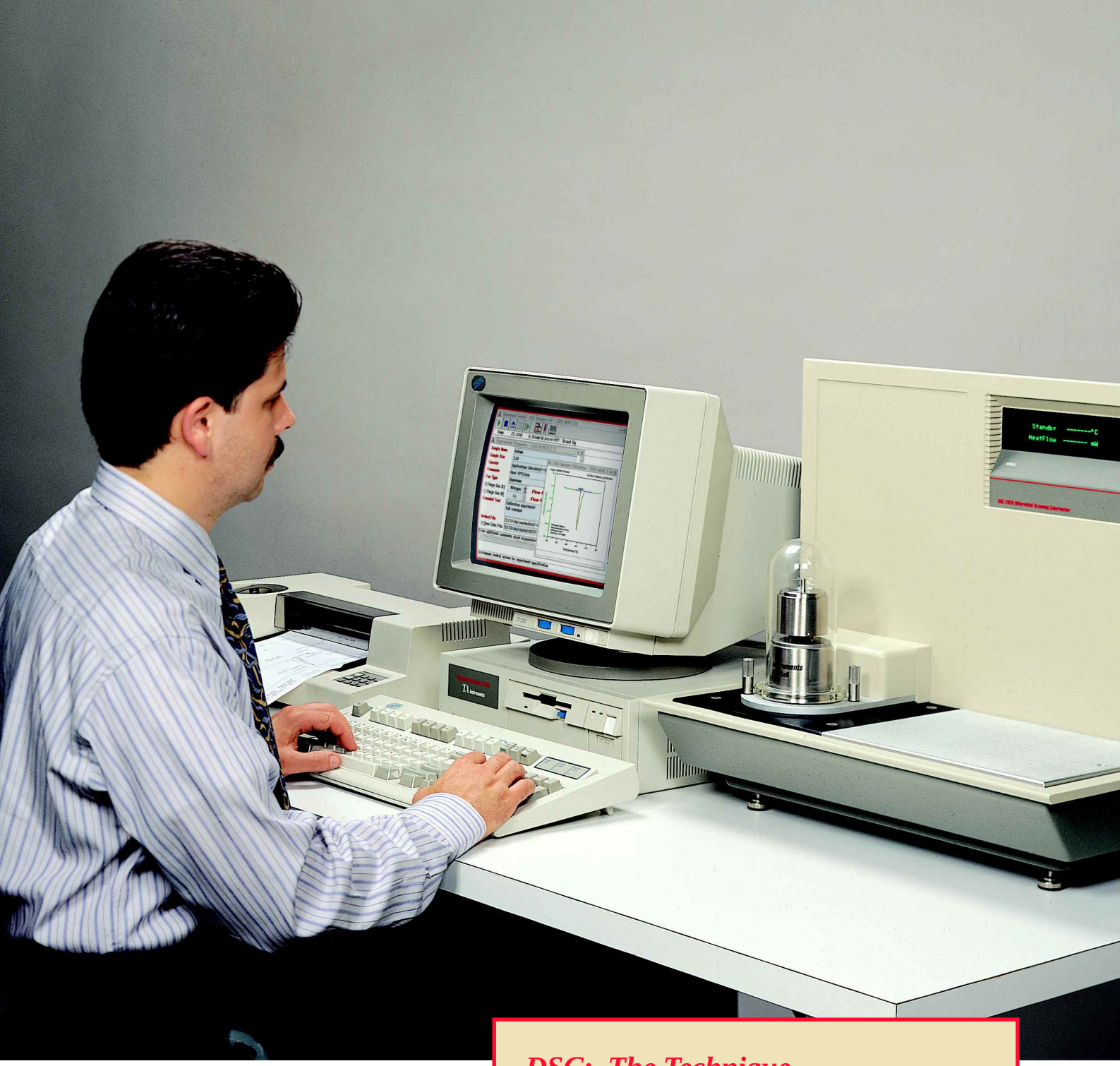
DSC 2920 Differential Scanning Calorimeter

TA Instruments
Thermal Analysis & Rheology
A Subsidiary of Waters Corporation



DSC: The Technique

Differential Scanning Calorimetry (DSC) measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature. Such measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity.

DSC is the most widely used of all thermoanalytical techniques. It is used primarily to characterize polymers and other organic materials, but is also applicable to metals, ceramics and other inorganics.

TA Instruments DSC 2920 Differential Scanning Calorimeter

The DSC 2920 is the product of more than 30 years of leadership in calorimetry. The instrument combines the features and benefits of a proven heat flux design with new cell mounting technology and enhanced electronics to provide a DSC that is more sensitive, more versatile, and easier to use than any of its predecessors.

The DSC 2920 is a plug-in module for the TA Instruments Thermal Analyst Controllers. A complete DSC system (Figure 1) consists of the DSC 2920 analysis module (base cabinet with interchangeable analysis cells), the Thermal Analyst computer-based Controller/Data Analyzer, and a data output device.

The 2920 is designed to operate a standard DSC cell, a pressure DSC cell, a dual sample DSC cell, and a high temperature 1600°C DTA cell.

These cells (described in more detail on the following pages) are mounted on the DSC 2920 base via a unique interconnect design which optimizes cell performance. In fact, the DSC 2920 offers the highest sensitivity (0.2 μW); temperature reproducibility (±0.05°C) and accuracy (±0.1°C); and widest temperature range (-180 to 725°C) of any commercially available general purpose DSC. In addition, the 2920 interconnect design allows rapid interchange of cells and "smart module" software further simplifies the interchange process. When a different cell is connected, the 2920 recognizes the cell type and automatically restores calibration parameters.

Compatibility with accessories for differential photocalorimetry and Modulated DSC™ as well as a 62 sample autosampler further broaden the versatility of the DSC 2920 making it the most complete research grade DSC available.

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

Uses of DSC

Research and Development

- Theoretical research of new materials and processes
- New materials development
- Formula optimization
- Applications development
- End-use performance prediction
- Competitive product evaluation

Quality Control/Assurance

- Vendor certification
- Incoming/outgoing material consistency
- Process optimization
- Heat history tracking
- Finished product performance
- Troubleshooting

Figure 2
Standard DSC Cell

Standard DSC

The Standard (single sample) DSC cell measures the differential heat flow between a sample and an inert reference at atmospheric pressure. The sample and reference, placed in the cell on a high conductivity disk, are subjected to controlled heating or cooling in a controlled atmosphere. The resulting heat flow is measured and recorded for use in determining transition temperatures and heats of reaction.

Dual Sample DSC

The Dual Sample DSC makes the same basic measurements as the standard cell, but makes those measurements on two samples simultaneously. This multiple sample arrangement provides two important benefits, namely:

- Increased productivity - throughput in a specific period of time is doubled which effectively cuts the cost per experiment.
- Direct comparison of materials - both samples receive exactly the same thermal treatment during the experiment which is particularly useful when evaluating materials with different "as received" thermal histories.

Figure 3
High Pressure DSC Cell

Pressure DSC

The Pressure DSC cell also makes the same measurements as the standard cell with the additional capability for operating at pressures up to 7MPa (1000 psi) or at a vacuum as low as 1 Pa (0.01 torr). PDSC provides unique insights into physical transitions and chemical reactions involving volume changes including heterogeneous chemical reactions with a gaseous reactant, decompositions which produce volatile products, reactions overlapping with vaporization at ambient pressure (e.g. curing), and adsorption/desorption. Specific measurements made include heats of reaction, oxidative stability, rate and degree of cure, reaction kinetics, vapor pressure, and boiling point.

High Temperature (1600°C) DTA

The High Temperature Differential Thermal Analysis (HTDTA) cell is designed primarily for studying the effect of temperatures well above the range of the DSC cells. It is used to determine transition temperatures and to quantify endothermic and exothermic events in materials such as metals, ceramics, and glasses at temperatures up to 1600°C.

Figure 4
High Temperature DTA Cell

Accessories

A number of accessory devices are available to perform specialized functions important for some experiments. Several of those accessories are briefly described here. More complete descriptions and example applications can be found in specific individual product brochures.

Modulated DSC™

Modulated DSC (MDSC®)* is an extension to conventional DSC. In modulated DSC, a material is exposed to a linear heating method which has a superimposed sinusoidal temperature oscillation (modulation) resulting in a cyclic heating profile. Deconvolution (separation) of the resultant heat flow during this cyclic heating provides not only the "total" heat flow obtained from conventional DSC, but also

* U.S. Patent Nos. B1 5,224,775; 5,248,199; 5,335,993; 5,346,306; 5,439,291; 5,474,385
European Patent No. 0559362
Canadian Patent No 2,089,225

separates that "total" heat flow into its heat capacity-related (reversing) and kinetic (nonreversing) components. Thus, modulated DSC provides all the same benefits as conventional DSC plus several unique benefits including:

- Separation of complex, overlapping transitions
- Better sensitivity & superior baselines
- Direct heat capacity measurement in a single experiment
- Increased resolution without loss of sensitivity
- Measurement of thermal conductivity
- Characterization of simultaneous melting & crystallization

Differential Photocalorimetry

Differential Photocalorimetry (DPC) measures the heat absorbed or released by a material as it is exposed to UV/Visible radiation. The DPC provides measurement of physical properties before, during and after exposure to radiation. Such measurements provide information about the performance of light sensitive materials used as coatings, films, inks, adhesives and photo initiators. The DPC can be used in conjunction with the standard and dual sample DSC cells.

DSC Autosampler

The Autosampler accessory is designed to facilitate unattended evaluation of DSC samples, thereby increasing laboratory productivity and lowering operating costs. With the Autosampler (which accommodates up to 62 samples) and, autoanalysis software the operator can automate testing and analysis. The system is extremely versatile. The operator can choose from an unlimited number of experimental methods and analysis routines stored in memory. The resultant flexibility means that the samples being evaluated can all be different (ideal for use in a research & development laboratory) or the same (ideal for use in quality control).

The autosampler unit mounts on the DSC 2920 baseplate via a slide mechanism which has tight tolerances for reproducible alignment, allowing the autosampler unit to be slid away from the DSC cell so that a pressure DSC cell or high temperature DTA cell can be installed and run. Furthermore, the autosampler is compatible with the standard and dual sample DSC cells.

Cooling Accessories

Three cooling accessories are available for use with the DSC 2920 standard and dual sample cells. These are:

- *Quench Cooling Accessory*, for simple non-programmed rapid cooling, usually between experiments.
- *Refrigerated Cooling System (RCS)*, for controlled cooling between -70 and 400°C. The RCS is a self-contained mechanical refrigeration device and is ideal for long-term cyclic heat-cool-heat experiments as well as for modulated DSC.
- *Liquid Nitrogen Cooling Accessory (LNCA)*, for automated quench or programmed cooling to -150°C.

Gas Switching Accessory

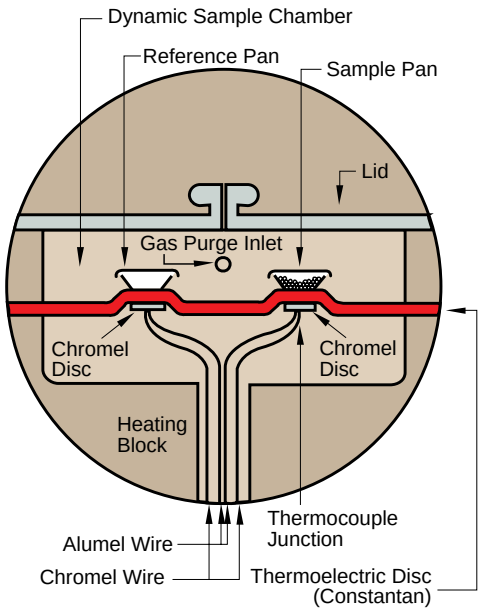
The Gas Switching Accessory facilitates programmed (automatic) switching of purge gases during or at the end of an experiment, such as in oxidative stability evaluations.

Figure 5
DSC Autosampler

Figure 6
DSC Quench Cooling Accessory

Principles of Operation

Figure 7
DSC Cell Cross-Section



DSC

A cross-section diagram of the TA Instruments standard DSC cell is shown in Figure 7. 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 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).

Figure 8
Loading Dual Sample DSC Cell

Dual Sample DSC*

The dual sample DSC uses the same heat flux design as the standard DSC. The constantan disk, however, is separated into three measurement areas by isothermal boundaries which are integral parts of the heating block. This isolation of signals assures no heat flow interactions occur between the two samples. Purge gas is admitted to the sample chamber through an orifice in the heating block wall. The small internal volume of the cell assures rapid atmospheric equilibration so that both samples see identical conditions.

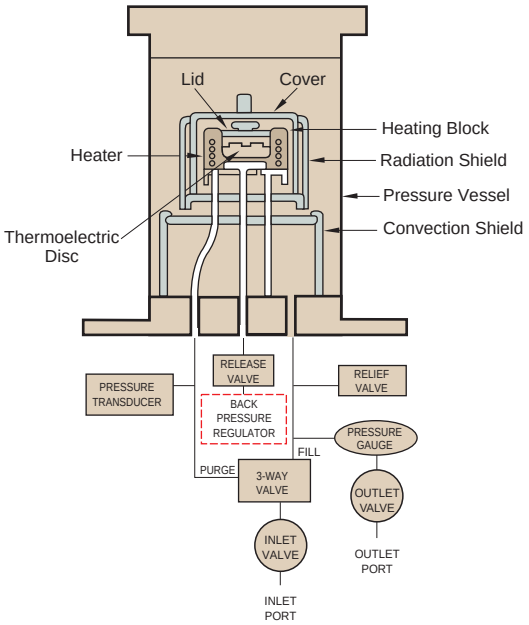
* U.S. Patent No. 4,350,446

Pressure DSC

In pressure DSC, the constantan-based heat flux measurement area shown in Figure 9, is surrounded by a pressure enclosure, consisting of a base, metal cylinder and top plate. This enclosure is designed to operate at a maximum working pressure of 7MPa and to attain a vacuum of under 1Pa with a good pumping system attached. A spring-loaded safety valve in the gas supply line in the base of the enclosure prevents overpressurizing. Purge gas enters the pressure cell through an inlet valve connected to a hole in the base plate, floods the internal volume of the enclosure, and exits through an outlet valve connected to the orifice in the heating block wall. This flow arrangement ensures rapid pressurization of the cell without displacement of the sample pans. Once pressurized, the outlet valve can be sealed for constant volume studies, or adjusted for a slight continuous purge to allow constant pressure studies. In addition, a purge switch on the front of the base provides rapid reversal of the purge gas flow path once the cell is pressurized so that specific applications such as oxidative stability, where it is desirable to have "fresh" purge gas continuously entering the sample area, can be accommodated.

A pressure transducer located in the flow path provides continuous readout of pressure (to within 5kPa) on either the DSC 2920 module display or on the controller signal control screen. The pressure reading from this transducer is automatically stored along with the other traditional DSC signals (heat flow, temperature, and time) for each data point collected, and can be displayed on subsequent data analysis plots.

Figure 9
Pressure DSC Schematic



High Temperature DTA

As shown in the cross-section drawing of the high temperature DTA Cell (Figure 10), the sample is contained in a platinum sample cup which rests on top of an insulated thermocouple pedestal. A reference cup rests on an adjacent thermocouple pedestal. The sample and reference, located 6mm apart, are surrounded by a furnace whose temperature is programmable and precisely controlled. The thermocouples detect the presence of transitions and measure the temperatures at which they occur. The thermocouples can be in direct contact with the sample and reference or isolated from them by the use of platinum or alumina cups (The latter arrangement is recommended because it prevents potential contamination of the thermocouples.) With these cups, semi-quantitative heat measurements, such as heat of fusion, can be made. The sample environment can be static gas or a sweeping purge gas at ambient pressure or under a modest vacuum.

Figure 10
DTA Cell Cross-Section

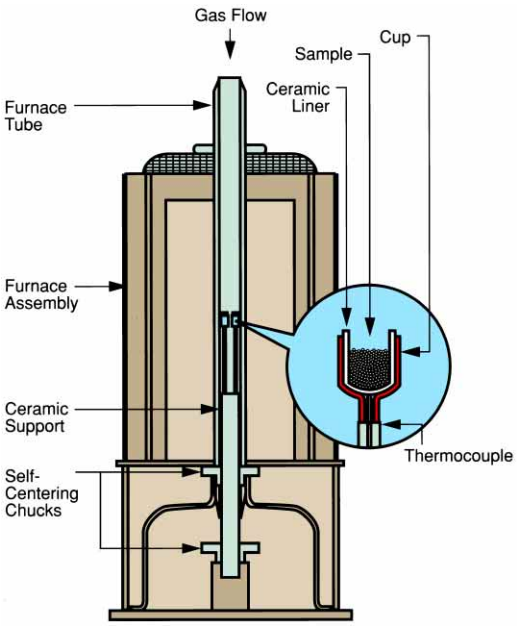


Figure 11
DSC 2920 Module Display and Keypad

Figure 12
Instrument Control Window

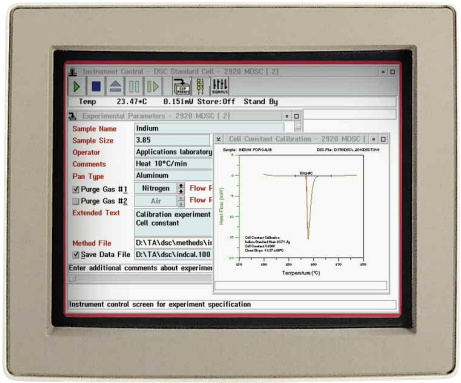


Figure 13
Sampling of Available DSC Pans

Features and Benefits

The DSC 2920 is designed to provide unequaled performance and versatility. In combination with a Thermal Analyst Controller, the DSC 2920 is the best 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. The DSC 2920 sensitivity (0.2 μW) and short-term noise (<0.1 μW) are significantly improved over earlier DSC's.

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

Direct measurement of sample temperature, assuring accurate and precise transition temperatures. Temperature precision is ±0.05°C. In addition, 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.

Modular design, with the economy and convenience of a single cell-base cabinet accommodating four different analysis cells-standard DSC, pressure DSC, dual sample DSC, and high temperature DTA. The dual sample cell provides the highest productivity available from a commercial DSC system.

Sample versatility, facilitating evaluation of organic or 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. In addition, the interchangeable pressure DSC and high temperature DTA cells extend the measurement range.

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). Unique segments are available for controlling the LNCA cooling accessory and stopping (aborting) a segment when a specific measurement signal is achieved. Temperature programming options include heating and cooling at rates from 0.01 to 200°C/minute, step heating and cooling, and isothermal operation. Data collection rate and threshold level can be adjusted to maximize data storage effectiveness. Furthermore, the DSC 2920 can be readily upgraded to perform Modulated DSC™ experiments.

Controlled atmosphere, with automated or manual programming of temperature-equilibrated inert or reactive gases. Pressure of the atmosphere (purge gas) is an additional operator-selectable parameter with the pressure DSC cell.

Automated operator-oriented features, providing increased productivity and reducing the requirement for a highly skilled operator. Special features include:

- Automated self-diagnosis and start-up procedures
- "Smart module" recognition of cell type and automatic reset of calibration parameters
- Easy sample loading and cell cleaning
- Automated temperature calibration
- Automated collection, storage, and display of data
- Automated data analysis (with optional software)
- Multi-tasking and multimodule operation

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

- *Quench Cooling Accessory:* for simple nonprogrammed rapid cooling.
- *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.
- *Autosampler Accessory:* for unattended evaluation of up to 62 samples.
- *Differential Photocalorimetry (DPC) Accessory:* for characterizing the photosensitive and physical properties of materials.

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 controllers 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 and DTA experiments. These programs include:

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

Figure 14
Liquid Crystal Transitions

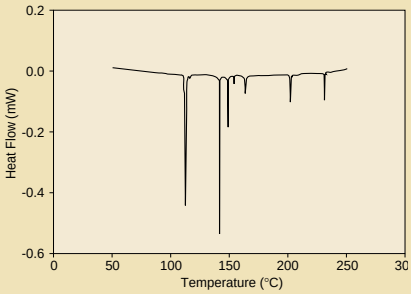


Figure 15
Temperature Calibration Standards

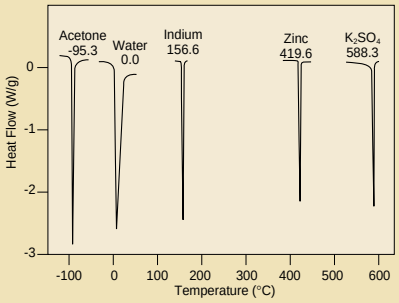


Figure 16
Transition Temperature Reproducibility

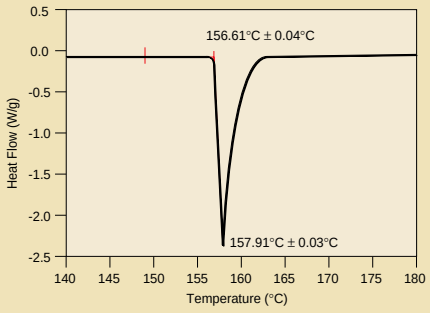
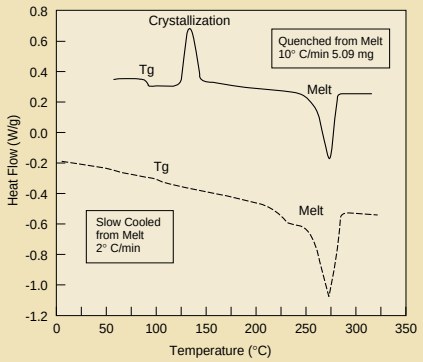


Figure 17
Thermal History Effects



Applications

The broad capability of the TA Instruments DSC 2920 for characterizing materials is illustrated by these representative applications. These examples also illustrate many of the benefits inherent in the DSC 2920 System.

Traditional DSC

Evaluation of Subtle Transitions

Sensitivity and resolution are two important parameters associated with obtaining precise and accurate DSC results. Generally, optimizing both of these parameters simultaneously is difficult because sensitivity is increased by larger sample sizes and faster heating rates, while resolution is improved by smaller sample sizes and slower heating rates. The exceptional sensitivity of the DSC 2920, because of low noise and a flat baseline, facilitates obtaining both good resolution and sensitivity simultaneously. Figure 14, which shows the multiple phase transition peaks for a liquid crystal, illustrates this capability. This curve was obtained using approximately 1 mg of material at 1°C/minute heating rate. The transition at 153°C is still detected and readily quantifiable even though the peak height associated with the transition is less than 20μW.

Accurate Determination of Transition Temperatures

The direct temperature readout provided by a thermocouple located under the sample pan in the heat flux cell design and the one to five-point temperature calibration of the DSC 2920 combine to provide high accuracy and precision when measuring the temperatures of thermal events. Single point calibration has the advantage of simplicity and is adequate for many applications. Additional calibration points increase precision and accuracy but require slightly more time. When more than two points are used, the DSC 2920 employs a cubic-spline method to calculate a third-order polynomial equation to determine the temperature correction anywhere on the measurement curve. Calibration standards commonly used (Figure 15) are acetone (-95°C), water (0°C), indium (156°C), zinc (419°C) and potassium sulfate (588°C). Figure 16, which shows the overlaid results of 5 separate indium melt evaluations, indicates the level of temperature precision and accuracy which results with proper calibration.

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 (ordered) or amorphous (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 17 shows the DSC heating profiles for two samples of a typical thermoplastic material, polyphenylene sulfide (PPS), 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 18. 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 (it's an 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 19 shows the DSC curve for an epoxy resin "as received". Also shown is the DSC cure 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.

Reaction Kinetics by DSC

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 20 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 2920 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 phenacetin sample are shown in Figure 21.

Evaluation of Metal Alloys

A variety of DSC sample pans are available so that samples which might interact with the typical aluminum pans can still be evaluated. Figure 22 shows comparative DSC curves for two different aluminum alloys run in graphite sample pans. Alloy A is a magnesium-aluminum alloy which shows a single melting peak located between the melting temperatures for the pure components. The DSC curves generated by running a series of alloys of different known compositions such as Alloy A provide the information needed to prepare phase diagrams. The DSC curve for Alloy B, which contains magnesium, aluminum and silicon, is more complex indicating the presence of two separate phases.

Figure 18
Polymer Crystallinity

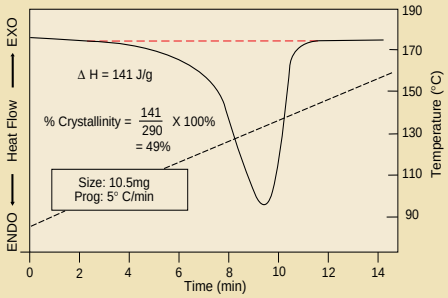


Figure 19
Thermoset Cure Determination

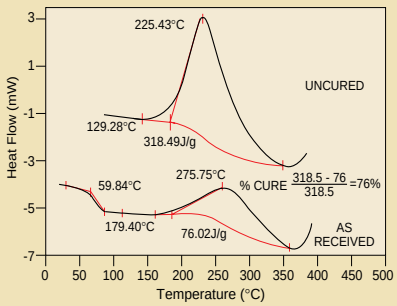


Figure 20
Relative Resin Reactivity

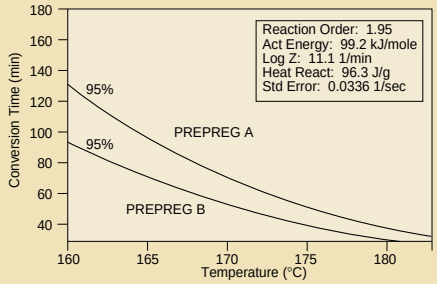


Figure 21
Purity of Pharmaceuticals

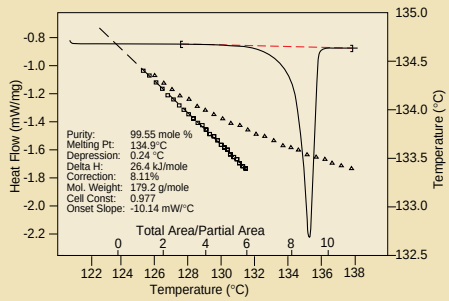


Figure 22
Low Temperature Alloy Evaluation

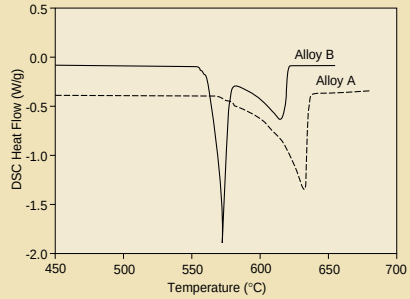


Figure 23
Stability of Water in Oil Emulsion

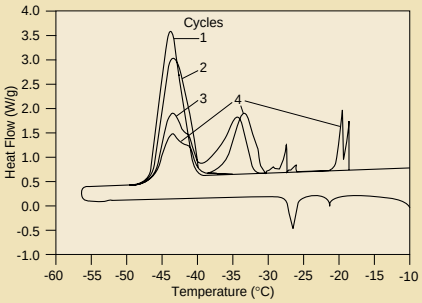


Figure 24
Grease Characterization

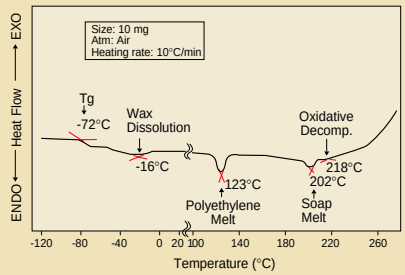
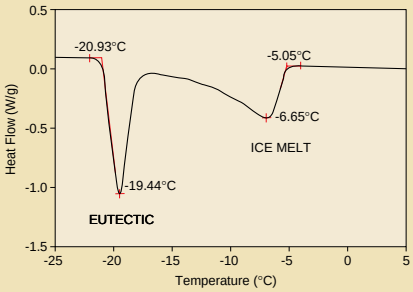


Figure 25
Pharmaceutical Lyophilization



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 23 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 phenomenon indicate a poor emulsion.

The Refrigerated Cooling System (RCS) which facilitates cyclic temperature programming of the DSC cell in the range -70 to 350°C is ideal for studies such as this one.

Characterization of Greases & Lubricants

Greases, which are typically 80-90% lubricating oils with an added gelling agent such as lithium stearate metal soap and high temperature thickeners such as polyethylene, provide an excellent example of the diversity of useful information available from a single DSC experiment as seen in Figure 24. For this grease, five transitions of interest are observed - the glass transition, wax dissolution, polyethylene melt, soap melt, and decomposition. For greases, the soap melt defines the highest useful temperature limit and the glass transition defines the lowest useful temperature limit. In addition, the percent composition of the polyethylene and soap can be determined from the areas under their respective melt peaks.

Optimizing Drying in Lyophilized Materials

In developing parenteral products, the drug candidate being formulated often exhibits poor solution stability. In those cases, the liquid formulation is usually lyophilized into a dried dosage form which has enhanced stability. Then, prior to use, the product is reconstituted with water to form the desired solution. In lyophilization (freeze-drying), the product is initially cooled to low temperatures (generally - 40°C or lower) where it becomes frozen or solidified. Then, primary drying is initiated by applying a modest vacuum and warming the freeze-dryer shelves to remove the bulk of the water present through sublimation. Once the majority of the bulk water has been sublimed, secondary drying is initiated to remove sorbed or residual water from the product by further increasing the shelf temperature and reducing the chamber pressure. During the primary drying process, the rate of sublimation can be accelerated by increasing the temperature of the product. Since the lyophilization time, and hence the cost associated with the lyophilization process, is mainly influenced by the primary drying process, processors would like to perform this step at the highest temperature possible which still retains product integrity. In materials that crystallize or form a eutectic on cooling, DSC provides a rapid method for determining the optimum drying temperature. Figure 25 shows the results for a 10% w/w sodium chloride solution. The peaks at -19.4 and -6.7°C represent the melting of the sodium chloride/ice eutectic and the depressed melting of ice respectively. In this case, the former is the maximum lyophilization temperature.

Dual Sample DSC

Direct Comparison of Materials

As described previously, the DSC results obtained for many materials, particularly polymers, are influenced by their thermal history. Hence, the ability to run materials simultaneously under identical conditions is valuable when trying to detect subtle differences. In amorphous polymers such as polyethyleneterephthalate (PET) an enthalpic relaxation peak occurs just above the glass transition which increases in size with longer aging times at increased temperatures. Quantitation of this relaxation provides valuable insight into aging effects in PET used for carpet fiber and packaging applications. Figure 26, for example, shows comparative results obtained using dual sample DSC for two PET materials aged for different amounts of time at 55°C.

Increased Productivity for High Volume Testing

When a large number of repetitive DSC evaluations are required for situations such as statistical quality control or rapid screening of new product formulations, dual sample DSC becomes a valuable productivity enhancer. Oxidative stability determinations (Figure 27) are a typical illustration. Addition of a DSC autosampler further increases productivity by allowing the DSC to be run unattended overnight.

Pressure DSC

Identification of Pressure-Sensitive Transitions

DSC is most commonly used to determine transition temperatures for glass transitions, melting, boiling, and decomposition. Of these transitions, only boiling is pressure-dependent in the presence of an inert purge gas. Nevertheless, varying pressure can aid in identifying the type of transition observed. Figure 28 compares the ambient pressure (solid line) and elevated pressure (700 Pa) DSC curves for benzoic acid. The pressure dependence of the higher temperature transition indicates the transitions are probably melting (121°C) and boiling (250°C). This conclusion is confirmed by TGA results which indicate that weight loss occurs only at the 250°C transition. The pressure dependence of boiling can also be quantified to obtain vapor pressure values.

Evaluation of Metal Catalysts

The efficient reduction of numerous organic compounds depends upon the activity of precious metal catalysts such as platinum and palladium. These metals are normally deposited on inert, porous substrates, such as carbon and silica. Catalyst activities are generally evaluated by one or both of two methods. The first measures the volume of hydrogen adsorbed by the catalysts under pressure as an indication of the active sites available. The second method measures the volume of hydrogen consumed during the reduction of a test compound added to the catalyst. Both methods require six hours or longer and use large samples in a pressure autoclave. They are therefore time-consuming, expensive and hazardous to personnel and equipment. However, since chemisorption and catalytic reduction are both exothermic reactions with the heat evolved being directly related to the hydrogen consumed, pressure DSC using increased pressures of hydrogen offers, a viable alternative to traditional tests. Results (Figure 29) are typically obtained in less than 15 minutes. [Note: A pressure DSC cell modified for use in hydrogen is available for these studies.]

Figure 26
Polymer Aging Effects

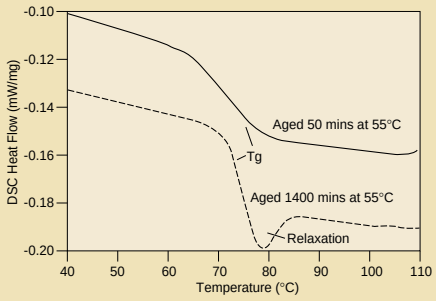


Figure 27
Polyethylene Oxidative Stability

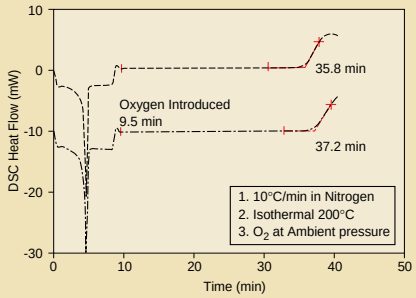


Figure 28
Pressure Effects on Benzoic Acid Transitions

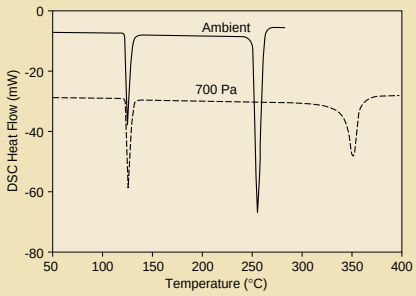


Figure 29
Heat of Catalyst Reduction

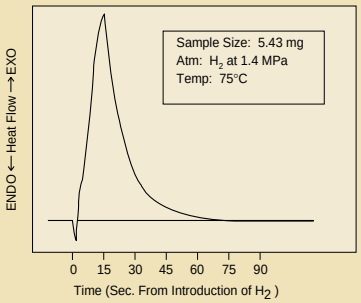


Figure 30
Comparison of Clays

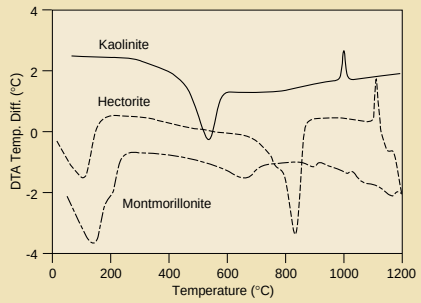


Figure 31
Palladium Melting Reproducibility

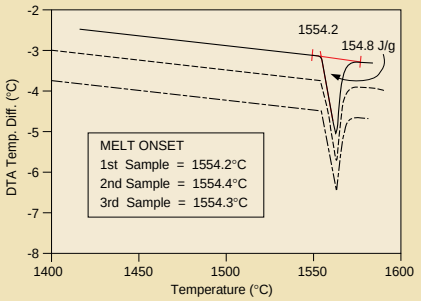


Figure 32
Effect of UV Exposure on Thermal Characteristics

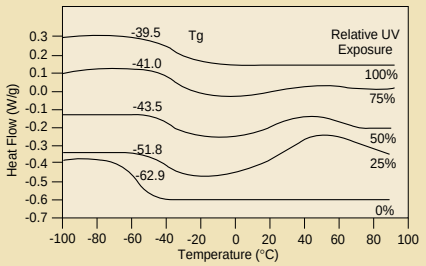
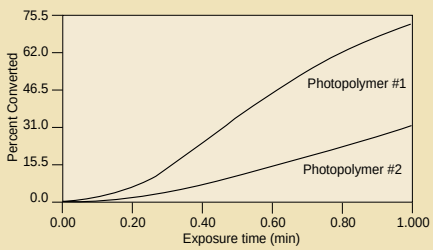


Figure 33
Comparison of Photopolymer Conversion Rates



High Temperature DTA

Identification of High Temperature Materials

Materials such as ceramics, glasses, clays and minerals, and metals often exhibit transitions at temperatures above the limit of DSC. High temperature DTA provides a viable alternative for evaluating those materials. For example, Figure 30 shows the DTA profiles for several clays commonly used in cement manufacture. Kaolinite which contains mainly alumina and silica is the most desirable clay for the production of white cement. It is easily separated from montmorillonite and hectorite by its endothermic dehydration between 450 to 530°C and exothermic crystalline transition at 980°C.

Measurement of Heats of Transitions

In addition to providing transition temperatures for high temperature materials, DTA with suitable calibration provides semi-quantitative measurement of the heats associated with those transitions. Figure 31 shows the overlaid results for three palladium melting curves. Even though this melting peak occurs close to the upper temperature limit of the cell, reasonable accuracy and precision can be obtained for both the temperature and heat of fusion.

Differential Photocalorimetry (DPC)

Characterization of Photosensitive Polymers

Differential photocalorimetry provides an additional mechanism for characterizing polymers, supplementing information obtained from traditional thermal methods. Since the DPC accessory attaches directly to the DSC 2920 cell without changing the characteristics of the cell, it provides ready measurement of photo-induced reactions as well as the thermal characterization of the polymer. For example, the physical properties of the photopolymer can be measured before and after exposure to light. The combined physical and light-sensitive properties provide information on rate of cure as well as the effect of cure on the physical properties of the material. Figure 32 shows DSC data on five different samples which were exposed to UV light for different lengths of time. The sample indicated by 0% received no exposure, while the one marked 100% was exposed long enough to reach complete cure. Results show that the glass transition temperature increases with exposure time, going from -62.9 to -39.5°C with 100% cure. In addition, once exposed, the sample is thermally sensitive and can cure with heat. This is seen as an exothermic peak, which is most apparent in the 25% sample, beginning as low as -10°C. Such studies can also be used to determine the effects of additives, such as pigments, stabilizers, antioxidants and plasticizers, on the photo-chemical and physical properties of polymers.

Quality Control Evaluations

The DPC provides fast, sensitive and reproducible measurements of the heat of reaction as a function of temperature and time. Characteristic features of these measurements, such as induction time, peak maximum time, percent conversion at peak, and kinetic parameters, are distinct for each material and extremely sensitive to differences in the chemical or physical nature of the sample. As a result, these parameters provide ideal specifications for quality control of a material or quality assurance of a finished product. The properties of two photopolymer resins, represented by the curves in Figure 33, for example, were indistinguishable by traditional QC tests but are clearly defined by DPC as having different sensitivity to light.

Modulated DSC™

Increased Transition Sensitivity Using MDSC®

Typically glass transition measurements in highly filled, reinforced, or highly crystalline polymers are difficult by conventional DSC. This is because these measurements by DSC are based on detection of a heat capacity change, and the addition of fillers and reinforcers or increased crystallinity dilutes the change being measured. Modulated DSC's high sensitivity, on the other hand, permits the detection of weak or subtle glass transitions. Figure 34, for example, shows the MDSC results for three Nylon samples exposed to different moisture levels prior to evaluation. The glass transition, as expected, shifts by more than 90°C between the sample dried in a desiccator and the sample pretreated by submersion in water. These results can not be obtained by conventional DSC because of the high crystallinity of Nylon. Other subtle transitions are also resolved in the MDSC results. The endotherm at 0°C in the wet sample is probably due to surface moisture. The step change at about 60°C (slightly above Tg) in the dried sample indicates a decrease in heat capacity at the cold crystallization of the material.

Figure 35 illustrates another example of MDSC's sensitivity, even at extremely low heating rates. Sodium nitrite ($NaNO_2$) is an inorganic salt known to undergo a two-step ferroelectric phase transition around 165°C. The transitions occur less than 2°C apart, and are thus very difficult to resolve in standard DSC using conventional heating rates. Modulated DSC allows for extremely slow heating rates, without loss of sensitivity. In Figure 35, the $NaNO_2$ sample was analyzed at an underlying heating rate of 0.05°C/min, and the two-step process is clearly resolved in the heat capacity signal. Conventional DSC would not be able to detect or resolve these transitions at 0.05°C/min, as sensitivity is a function of heating rate.

Separation of Complex Transitions

Modulated DSC deconvolutes total heat flow into two constituents: heat capacity-related (reversing) heat flow and kinetic (nonreversing) heat flow. This deconvolution allows for the separation of complex and overlapping transitions, and thus facilitates a further understanding of these complex events. Figure 36 shows the MDSC results of a quenched 40% (w/w) aqueous sucrose solution. The sucrose is plasticized by the water and the glass transition of the sucrose is moved into the subambient region. However, at Tg the bound water is released and crystallizes, masking the heat flow of the glass transition. MDSC separates the crystallization into the nonreversing (kinetic) heat flow, which allows for easy identification of the Tg in the reversing (heat capacity) heat flow.

Quantifying Polymer Blend Composition

The blending of two or more polymers is becoming a common method for developing new materials for demanding application such as impact resistant parts and packaging films. Since the ultimate properties of blends can be significantly affected by small changes in blend composition, suppliers of these materials are interested in rapid tests which provide verification that the correct amount of each polymer is present in the blend. DSC has proven to be an effective technique for characterizing and quantifying polymer blends based on the presence of multiple glass transitions or melts. However, overlapping transitions of one component can sometimes interfere with the ability to detect the glass transition of another, necessitating multiple experiments and decreased sample throughput.

The ability of modulated DSC to resolve overlapping transitions solves this problem. Figure 37 shows the first heat on a molded part made from a blend of PET and ABS. In a standard DSC experiment, the Tg of the ABS is obscured by the cold crystallization of the PET in the first heat. A subsequent cooling and second heat experiment are required. On the other hand, MDSC separates the overlapping events in the first heat of the material, allowing for quantification and eliminating the need for additional experiments.

Figure 34
Effect of Moisture on Nylon

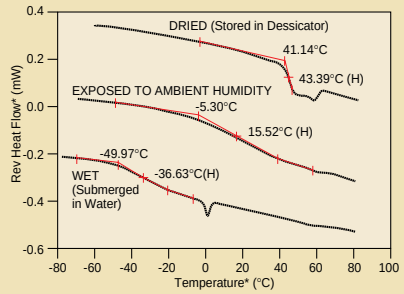


Figure 35
Sodium Nitrite Phase Transitions

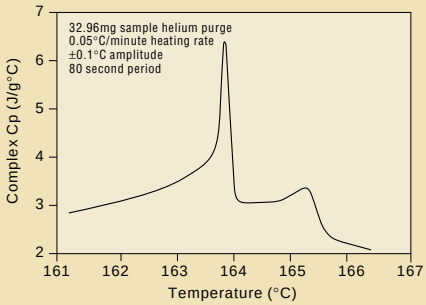


Figure 36
Quenched 40% (w/w) aqueous sucrose solution

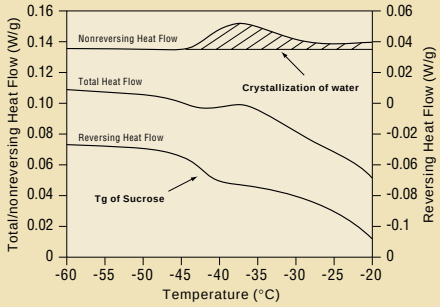
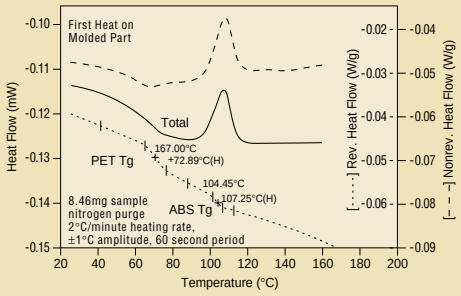


Figure 37
Separation of Polymer Blend Components



Specifications

Standard DSC Cell System

Atmosphere: non-corrosive inert, reducing or oxidizing
Dynamic Gas Purge (preheated): up to 100 mL/min at pressures from 300 Pa (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: 0.2 µW (2:1 signal-to-noise)
Calorimetric Precision: ±1% (based on metal samples)

Pressure DSC Cell System

Atmosphere: non-corrosive inert, reducing or oxidizing at 1.3 Pa to 7 MPa (0.01 torr to 1000 psi) at constant pressure or constant volume
Dynamic Gas Purge (preheated): up to 100 mL/min
Temperature Range: - Inert atmosphere: ambient to 725°C
- Air/oxygen: ambient to 600°C
Temperature Accuracy (using metal standards): ±0.1°C
Temperature Reproducibility (using metal standards): ±0.05°C
Calorimetric Precision: ±1% (based on metal samples)

1600°C DTA Cell System

Sample Volume: up to 75 µL
Atmosphere: Static or controlled flow with inert gas or air
Pressure: Atmospheric to 300 Pa (2 torr)
Temperature Range: ambient to 1600°C
Temperature Accuracy: ±1°C or 1%, whichever is greater
Temperature Reproducibility (using metal standards): ±0.5°C
Programmable Heating Rate: 0.01 to 200°C/min
ΔT Sensitivity: 0.004°C

TA Instruments Commitment

The DSC 2920 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.

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