Thermal Analysis

An Introduction
"A collection of techniques that measure the property of a material as a function of temperature"
Typical Properties Measured

- Weight
- Length
- Heat Flow
- Modulus
Thermal Analysis Techniques

- Differential Scanning Calorimetry (DSC)
- Differential Thermal Analysis (DTA)
- Thermogravimetric Analysis (TGA)
- Thermomechanical Analysis (TMA)
- Dynamic Mechanical Analysis (DMA)
- Dielectric Analysis (DEA)
What is a Thermal Analyser?

Diagram:
- Transducer
- Sample
- Furnace
- Temperature Programmer
- Experimental Method
- Sample Temperature
- Sample Property
Type of Polymers

- **Thermoplastic**
  - These polymers melt on heating and recrystallise on cooling. They can be processed and moulded.

- **Thermosets**
  - These polymers cross-link (cure) on heating and form a 3-dimensional rigid matrix.

- **Elastomers**
  - These are usually long chain polymers that are flexible at room temperature but brittle (i.e. below their Tg) at sub-ambient temperatures.

- **Blends**
  - Physical or Chemical mixtures of any of the above types
Thermoplastic Polymers

Semi-Crystalline Polymer

Crystalline Phase
- this will melt and give an endothermic peak in the DSC

Amorphous Phase
- this will soften and give a glass transition (Tg)
Slow cooling from the melt
- This will give more time for the polymer chains to orientate and crystallise giving a higher crystallinity. On re-heating a larger fusion peak will be observed.

Fast cooling from the melt
- This will give less time for the polymer chains to orientate and crystallise giving a lower crystallinity. On re-heating a smaller fusion peak will be observed.
Factors Affecting Polymer Transitions

- Heating Rate
- Sample Size
- Sample Form
- Sample Pan
- Thermal History
- Degree of Crystallinity
- Filler
Differential Scanning Calorimetry (DSC) & Modulated DSC
Differential Scanning Calorimetry

- A **calorimeter** measures the heat into or out of a sample
- A **differential calorimeter** measures the heat of a sample relative to a reference
- A **differential scanning calorimeter** does all of the above and heats/cools the sample with a linear/modulating temperature ramp
Differential Scanning Calorimetry

- Differential Scanning Calorimetry (DSC) is the most popular thermal analysis technique.
- DSC measures endothermic and exothermic transitions as a function of temperature:
  - \textit{Endothermic} heat flows into a sample.
  - \textit{Exothermic} heat flows out of the sample.
- Used to characterize polymers, pharmaceuticals, foods/biologicals, organic chemicals and inorganics.
- Transitions measured include T\text{g}, melting, crystallization, curing and cure kinetics, onset of oxidation and heat capacity.
DSC: Terminology

- **Amorphous Phase** - The portion of material whose molecules are randomly oriented in space. Liquids and glassy or rubbery solids. Thermosets and some thermoplastics.
- **Crystalline Phase** - The portion of material whose molecules are regularly arranged into well defined structures consisting of repeat units. Very few polymers are 100% crystalline.
- **Semi-crystalline Polymers** - Polymers whose solid phases are partially amorphous and partially crystalline. Most common thermoplastics are semi-crystalline.
- **Melting** - The endothermic transition upon heating from a crystalline solid to the liquid state. This process is also called fusion. The melt is another term for the polymer liquid phase.
- **Crystallization** - The exothermic transition upon cooling from liquid to crystalline solid. Crystallization is a function of time and temperature.
- **Cold Crystallization** - The exothermic transition upon heating from the amorphous rubbery state to the crystalline state. This only occurs in semi-crystalline polymers that have been quenched (very rapidly cooled from the melt) into a highly amorphous state.
- **Enthalpy of Melting/Crystallization** - The heat energy required for melting or released upon crystallization. This is calculated by integrating the area of the DSC peak on a time basis.
Sample: PET (Quenched from the Melt)
Size:  7.8680 mg
Method: RT-->300°C @ 10°C/min
Comment: He Purge=25mL/min

File: C:\TA\Data\DSC\Dsc-pet.001
Operator: Applications Laboratory
Run Date: 10-May-1995 14:44

DSC File
Universal V4.1D TA Instruments
Two Major Types of DSC’s on Market Today:

Heat Flux DSC

and

Power Compensation DSC
HEAT FLUX DSC-PRINCIPLE OF OPERATION

\[ Q_s = \frac{T_s - T_{fs}}{R_s} \]

\[ Q_r = \frac{T_r - T_{fr}}{R_r} \]

\[ \Delta Q = Q_s - Q_r \]
HEAT FLUX DSC - EXPANDED PRINCIPLE OF OPERATION

\[ Q = \frac{T_s - T_r}{R} + A + B + C \]

- **A**: Thermal Resistance Imbalance
- **B**: Thermal Capacitance Imbalance
- **C**: Heating Rate Imbalance
Tzero™ HEAT FLOW TERMS

- $\frac{\Delta T}{R_r}$  
  Principal DSC Heat Flow

$\Delta T_0 \left( \frac{1}{R_s} - \frac{1}{R_r} \right)$  
  Thermal Resistance Imbalance

$(C_r - C_s) \frac{dT_s}{d\tau}$  
  Heat Capacity Imbalance

$- C_r \frac{d\Delta T}{d\tau}$  
  Heating Rate Difference

Q Series DSC’s
Tzero™ HEAT FLOW TERM CONTRIBUTIONS

- Principal heat flow provides main heat flow signal
- Thermal resistance and heat capacity imbalance terms improve baseline
- Heating rate difference term improves resolution and MDSC® performance
Tzero™ DSC Cell
DSC: Heat Flow/Specific Heat Capacity

\[ \Delta H = C_p \Delta T \]

or in differential form

\[ \frac{dH}{dt} = C_p \frac{dT}{dt} + \text{thermal events} \]

where:

- \( C_p \) = specific heat (J/g °C)
- \( T \) = temperature (°C)
- \( H \) = heat (J)
- \( \frac{dH}{dt} \) = heat flow (J/min.)
- \( mW = mJ/sec \)
- \( \frac{dT}{dt} \) = heating rate (°C/min.)

assuming work & mass loss are zero
Baseline Slope due to Heat Capacity
# DSC: Heat Flow Measurements

## Calorimeter Signals
- Time
- Temperature
- Heat Flow

## Signal Change
- Heat Flow, absolute
- Heat Flow, shift
- Exothermic Peak
- Endothermic Peak
- Isothermal Onset

## Properties Measured
- Specific Heat
- Glass Transition
- Crystallization or Cure
- Melting
- Oxidative Stability
DSC: Typical DSC Transitions

Temperature

Heat Flow -> exothermic

Glass Transition
Crystallization
Melting
Cross-Linking (Cure)
Oxidation or Decomposition
Modulated DSC®
Agenda

1. Understanding Heat Flow from DSC Experiments
2. Natural Limitations of DSC and How They Are Solved by MDSC
3. General Theory of MDSC
   - What Is Really Measured In MDSC Experiments
4. Calculation of MDSC Signals
5. Calibration
6. Optimization of MDSC Experimental Conditions
   - Practical Application of MDSC
     - Glass Transitions
     - Melting
     - Initial Crystallinity
     - Heat Capacity
     - Quasi-Isothermal Heat Capacity
Understanding Heat Flow from DSC Experiments

\[
\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)
\]

Where:

\[
\frac{dH}{dt} = \text{DSC heat flow signal; Watts = J/s}
\]

\[
C_p = \text{Sample Heat Capacity; J/°C}
\]

\[
= \text{Sample Specific Heat (J/g°C) x Sample Weight (g)}
\]

\[
\frac{dT}{dt} = \text{Heating Rate; °C/min}
\]

\[
f(T, t) = \text{Heat flow that is function of time at an absolute temperature (kinetic); J/s}
\]
DSC Heat Flow (cont.)

• For a given sample, the rate of heat flow (J/sec) due to heat capacity is linearly proportional to heating rate; Figure 1.

• At a heating rate of zero, the heat flow due to heat capacity is also zero.

\[
\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)
\]

• Any heat flow detected at a zero heating rate must be due to kinetic processes \( f(T,t) \) in the sample; Figures 2 – 4.

• The purpose of MDSC is to separate the total heat flow into the part that responds to heating rate and the part that responds to absolute temperature; Figures 5 – 6.
Figure 1

Sample: PMMA
Size: 10.0400 mg
Method: Heat@2,5,5,10,20
Comment: DSC@ 2.5,5,10&20°C/min

DSC
File: C:\DATA\DSC\W-pmma.001
Operator: Thomas
Run Date: 20-Jan-00 09:58

Heat Flow (mW)

Temperature (°C)

-0.8402mW
2.5°C/min
-1.857mW
5°C/min
-3.313mW
10°C/min
-6.620mW
20°C/min

Exo Up
Figure 2

Sample: Aged Epoxy
Size: 10.4000 mg
Method: Epoxy
Comment: DSC@10°C/min H-C-H

DSC

File: C:TA1DATA1DSCW-epoxy.001
Operator: Thomas
Run Date: 1-Feb-2000 12:08

- Heat Flow (mW)
- Temperature (°C)

First Heat of Aged Sample
Second Heat to 100°C
Figure 3

Sample: Annealed Epoxy
Size: 6.3300 mg
Method: MDSC 16860@1
Comment: MDSC 0.5A, 60secP @ 1°C/min

DSC

File: C:\MDSCMDSCepoxy001
Operator: Thomas
Run Date: 23-Mar-2000 15:56

Heat Flow at the Lowest Heating Rate
Heat Flow at the Highest Heating Rate
Modulated Temperature
Modulated Heating Rate
Modulated Heat Flow (mW)
Deriv. Modulated Temp (°C/min)
Temperature (°C)
Figure 4

Sample: Aged Epoxy
Size: 6.3300 mg
Method: MDSC .159/60@1
Comment: MDSC 0.5A, 60secP @ 1°C/min

DSC

File: C:\MDSC\MDSCepoxy.001
Operator: Thomas
Run Date: 23-Mar-2000 15:56

Heat Flow at the Lowest Heating Rate
Heat Flow at the Highest Heating Rate
Modulated Temperature
Figure 5

Sample: Aged Epoxy
Size: 6.3300 mg
Method: MDSC .159/60@1
Comment: MDSC 0.5A, 60secP @ 1°C/min

DSC
File: C:\MDSC\MDSCepoxy.001
Operator: Thomas
Run Date: 23-Mar-2000 15:56

Complex Cp (J/g°C)
Second Heat to 100°C (Sample Annealed)
First Heat of Aged Sample

Temperature (°C)
Figure 6

Comparison of Nonreversing Signals from Aged and Annealed Epoxy Samples

- MDSC Nonreversing Heat Flow (Kinetic Signal)
- Second Heat (Sample Annealed)
- First Heat of Aged Sample
Section 2: The Natural Limitations of DSC and How They are Solved by MDSC

1. It is not possible to optimize both sensitivity and resolution in a single DSC experiment.
   - In order to increase the sensitivity of DSC, where sensitivity is defined as the ability to detect transitions in the sample, it is necessary to increase sample size, heating rate or both.
     \[
     \frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)
     \]
   - Although increased sample size or heating rate improves sensitivity, they decrease resolution by causing a larger temperature gradient within the sample (see Figure 7 and Table 1).
   - MDSC solves this problem because it has two heating rates: the average heating rate can be slow to improve resolution, while the modulated heating rate can be high to improve sensitivity (Figure 8).
Figure 7

Sample: PMMA
Size: 10.0400 mg
Method: Heat@2,5,5,10,20
Comment: DSC@ 2,5,5,10&20°C/min

File: C:\TAIDATA\DSC\W-pmma.001
Operator: Thomas
Run Date: 20-Jan-00 09:58

DSC

Temperature (°C)

Heat Flow (mW)

2.5°C/min
5°C/min
10°C/min
20°C/min

95.91°C
96.95°C
96.29°C
98.27°C

100.92°C(H)
101.96°C(H)
102.80°C(H)
105.13°C(H)

Exo Up
Universal V2.7A TA Instruments
<table>
<thead>
<tr>
<th>Heating Rate (°C/min)</th>
<th>Heat Flow @ 80°C</th>
<th>Tg Onset (°C)</th>
<th>Tg Midpoint (°C)</th>
<th>½ Width of Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>-0.84</td>
<td>95.9</td>
<td>100.9</td>
<td>5.0</td>
</tr>
<tr>
<td>5.0</td>
<td>-1.66</td>
<td>96.0</td>
<td>102.0</td>
<td>6.0</td>
</tr>
<tr>
<td>10.0</td>
<td>-3.31</td>
<td>96.3</td>
<td>102.8</td>
<td>6.5</td>
</tr>
<tr>
<td>20.0</td>
<td>-6.62</td>
<td>98.3</td>
<td>105.1</td>
<td>6.8</td>
</tr>
</tbody>
</table>
2. Baseline curvature and drift limit the sensitivity of DSC for detecting weak transitions (Figure 9).

- MDSC eliminates baseline curvature and drift in the Heat Capacity and Reversing signals by using the ratio of two measured signals rather than the absolute heat flow signal as measured by DSC.

\[
C_p = \frac{\text{Amplitude Mod Heat Flow}}{\text{Amplitude Mod Heating Rate}} \times K
\]

Reversing = \(C_p \times \text{Avg Heating Rate}\)

[See Figure 10]
Figure 9

Sample: Tablet Binder, 44% RH
Size: 3.0800 mg
Method: MDSC 1/60 @ 5°C/Min
Comment: HERMETIC PAN WITH PINHOLE, N2 PURGE

Where is the Glass Transition?
Figure 10

Sample: Tablet Binder, 44% RH
Size: 3.0800 mg
Method: MDSC 1/60 @ 5°C/MIN
Comment: HERMETIC PAN WITH PINHOLE, N2 PURGE

**DSC**

File: C:\DATA\DSC\Pharm.001
Operator: THOMAS

- Modulated Heat Flow (mW)
- Reversing
- Total
- Modulated Heating Rate
- Deriv. Modulated Temp (°C/min)

**Temperature (°C)**
- Exo Up

Universal V2.7C TA Instruments
3. Transitions are often difficult to interpret because DSC can only measure the Sum of Heat Flow within the Calorimeter (Figure 11).

- MDSC minimizes this problem by providing not only the Total Heat Flow signal but also the heat capacity and kinetic components of it (Figure 12).
Figure 11

Sample: Xenoy 1102; Quenched to RT
Size: 14,7000 mg
Method: R10
Comment: DSC @ 10

DSC
File: F:\Lent\Neste 008
Operator: App Lab

How Would You Interpret This DSC Experiment?
Figure 12

Sample: Xenoy 1102 Quench to RT from 250°C
Size: 14.790 mg
Method: MDSCNatass2
Comment: MDSC 318/80 @ 2°C/min

DSC

File: F:\LenNatass99.004
Operator: Lab, Standard Ref Pan

Exo Us

Universal V2 TC TA Instruments
4. The DSC measurement of polymer crystallinity is often wrong because it fails to detect the formation of crystalline structure as the sample is heated (Figure 13).

- MDSC minimizes this problem by providing signals that are proportional to the amount of crystal structure forming as the sample is heated (Nonreversing) and the amount of melting occurring (Reversing). The sum of the Reversing and Nonreversing signals is used to calculate crystallinity (Figure 14).

\[
\text{Reversing} + \text{Nonreversing} = \text{Crystallinity} \\
86.4 \text{ J/g} + (-85.2 \text{ J/g}) = 1 \text{ J/g}
\]
Figure 13

Sample: Quench Cooled PET  
Size: 9.7000 mg  
Method: Heat at 10°C/min  
Comment: DSC@ 10°C/min  

What was the crystallinity of this sample prior to heating in this DSC experiment?
Figure 14

Sample: Quenched PET
Size: 13.3700 mg
Method: MDSCNatas4
Comment: MDSC 318/80@2
Natural Limitations of DSC (cont.)

5. DSC cannot measure Heat Capacity under isothermal conditions.

- Since MDSC has two independent heating rates (average and modulated), the average heating rate can be zero (isothermal) while the actual temperature is modulated higher and lower than the average. This permits the measurement of the sample’s heat capacity and an analysis of how structure in the sample is changing as a function of time at that temperature.

[Figures 15 – 17]
Figure 15: MDSC Quasi-Isothermal Heat Capacity of Quench Cooled 40% Sucrose Solution

Temperature (°C)

Complex Cp (Jg/°C)

30 min. isothermal steps after quenching

Temperature

-44.94°C

1.835 J/g/°C

Time (min)
Figure 16: MDSC Quasi-Isothermal Heat Capacity of Quench Cooled and Slow Cooled 40% Sucrose Solution
MDSC Theory
Heat Flow Equation

\[
\frac{dH}{dt} = Cp \frac{dT}{dt} + f(T,t)
\]

\[
\frac{dH}{dt} = \text{Total Heat Flow measured by the calorimeter}
\]

\[
Cp = \text{Specific Heat Capacity}
\]

\[
\frac{dT}{dt} = \text{Underlying Heating Rate}
\]

\[
f(T,t) = \text{kinetic response of sample}
\]
Heat Flow Due to Heat Capacity

Heat Flow (mW)

Temperature (°C)

5°C/min

10°C/min

20°C/min

106.85°C
-2.137mW

106.85°C
-4.018mW

106.85°C
-8.104mW
The magnitude of measured kinetic heat flow is a function of time at a constant temperature.
Standard DSC Measures the Sum of Heat Flow

Heat Flow due to Heat Capacity

Heat Flow due to Kinetic Events
Heat Flow Can Be Separated

Heat Flow due to Kinetic Events

Heat Flow due to Heat Capacity

\[ f(T, t) \]

\[ Cp \frac{dT}{dt} \]
General Theory of MDSC

Heat flow from DSC experiments is composed of two parts but DSC can only measure the sum of the two.

\[
\frac{dH}{dt} = Cp \left( \frac{dT}{dt} \right) + f(T, t)
\]

Total Heat Flow (DSC) = Heat Capacity Component + Kinetic Component

= Heating Rate Dependent + Time Dependent

= MDSC Reversing + MDSC Nonreversing
Distribution of Transitions in MDSC Experiments

Total = Heat Capacity Component + Kinetic Component

= Reversing Heat Flow + Nonreversing Heat Flow

- glass transition
- melting (some)
- enthalpic relaxation
- evaporation
- crystallization
- decomposition
- cure
- melting (some)
# Physical Measurement Technique

## Apply Stimulus → Measure Response

<table>
<thead>
<tr>
<th>Technique</th>
<th>Stimulus</th>
<th>Response</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTIR</td>
<td>IR Radiation</td>
<td>Absorbance Wavelength</td>
</tr>
<tr>
<td>NMR</td>
<td>Magnetic Field</td>
<td>Resonance Frequency</td>
</tr>
<tr>
<td>X-Ray Diffraction</td>
<td>X-Ray Radiation</td>
<td>Angle of Diffraction</td>
</tr>
<tr>
<td>MDSC</td>
<td>Sinusoidal Heating Rate</td>
<td>Amplitude of Heat Flow</td>
</tr>
</tbody>
</table>
MDSC Temperature Profile – Step-Iso

Sample: PET, Quench to RT, 30m ann 130°C
Size: 9.7000 mg
Method: PET-HR mth
Comment: N2 purge

DSC
File: C:\TADAT\DSC\PET-HR.001
Operator: Thomas

---

Period: 80 seconds
Amplitude: 0.319 (Heat-Iso)
Heating Rate: 2°C/min

Measured Temperature
Modulated Heating Rate (Heat-Iso Conditions)

---

Time (min)
MDSC Temperature Profile – Heat Only

Sample: PET, Quench to RT, 30m ann 130°C
Size: 9.7000 mg
Method: PETvHR.mth
Comment: N2 purge; same as .001 except 3°C/min

DSC
File: C:\DATA\DSC\PETvHR.002
Operator: Thomas

Period: 80 seconds
Amplitude: 0.319 (Heat-Only)
Heating Rate: 3°C/min

Measured Temperature

Modulated Heating Rate (Heat-Only Conditions)

Universal V2 TC TA Instruments
MDSC Temperature Profile - Conventional

Sample: PET, Quench to RT, 30m ann 130C
Size: 97000 mg
Method: PETMHR mth
Comment: N2 purge; same as .001 except 1°C/min

DSC
File: C:\TADATA\DSC\PETMHR.006
Operator: Thomas

Period: 60 seconds
Amplitude: 0.319 (Heat-Cool)
Heating Rate: 1°C/min

Measured Temperature

Modulated Heating Rate (Heat-Cool Conditions)

Universal V2.7C TA Instruments
Raw Signals in MDSC

All Modulated DSC Signals are derived from three measured parameters.

- Time
- Modulated Temperature (Stimulus)
- Modulated Heat Flow (Response)
NOTE: ALL TRANSITIONS OF INTEREST ARE CONTAINED IN MDSC RAW DATA SIGNALS.
MDSC Signals: Total Heat Flow

The average value of the modulated heat flow signal. This signal is qualitatively and quantitatively equivalent to the heat flow signal from conventional DSC at the same average heating rate.

**Definition:** The sum of all thermal events in the sample

**Calculation:** Fourier Transformation analysis of the modulated heat flow signal is used to continuously calculate its average value.
Total Heat Flow: Average of Modulated Heat Flow Signal
MDSC Signals: Heat Capacity

\[ \text{Cp} = \frac{A_{\text{MHF}}}{A_{\text{MHR}}} \times K \]

Where:
- \( A_{\text{MHF}} \) = Amplitude of Modulated Heat Flow
- \( A_{\text{MHR}} \) = Amplitude of Modulated Heating Rate
- \( K \) = Heat Capacity Calibration Factor

Definition: The amount of heat required to raise the temperature of a material 1°C.

Calculation: The basis for making the heat capacity measurement in MDSC can be explained from a series of conventional DSC experiments at different heating rates.
Conventional DSC Cp Measurement

\[ \text{Cp} = K \times \frac{\text{HF}_S - \text{HF}_{MT}}{\text{Heat Rate} \times \text{wt}} \]

Where:
- \( K \) = Calibration constant
- \( \text{HF}_S \) = Differential heat flow with sample
- \( \text{HF}_{MT} \) = Differential heat flow with empty pans
- \( \text{wt} \) = weight of sample

\[ \text{HF}_S \quad \text{HF}_{MT} \quad 0 \quad \text{HF} \downarrow \text{endo} \quad \text{Temp.} \]
Alternative DSC Cp Measurement

\[ \text{Cp} = K \times \frac{\text{HF}_{\text{HR2}} - \text{HF}_{\text{HR1}}}{(\text{HR2} - \text{HR1}) \text{ wt}} \]

Where:
- \( K \) = Calibration constant
- \( \text{HF}_{\text{HR1}} \) = Differential heat flow of sample at \( \text{HR}_1 \)
- \( \text{HF}_{\text{HR2}} \) = Differential heat flow of sample at \( \text{HR}_2 \)
- \( \text{HR}_2 \) = Heating rate 2
- \( \text{HR}_1 \) = Heating rate 1
- \( \text{wt} \) = weight of sample

[Diagram showing temperature (Temp.) and heat flow (HF) with endo indicated]
Heat Capacity from MDSC Raw Signals

![Graph showing heat capacity, modulated heat flow, and modulated heating rate vs. temperature.](graph.png)

- **Deriv. Modulated Temp (°C/min)**
- **Temperature (°C)**
- **Modulated Heat Flow (W/g)**
- **Complex Cp (J/g/°C)**

- **Heat Capacity**
- **Modulated Heat Flow**
- **Modulated Heating Rate**
MDSC Signals - Reversing Heat Flow  
(Heat Capacity Component)

Reversing Heat Flow is the heat capacity component of the total heat flow. It is calculated by converting the measured heat capacity into a heat flow signal using the classical heat flow equation as a theoretical basis.

Reversing Heat Flow = \(-C_p \times \text{Avg. Heat Rate}\)

**Basis for Calculation**

\[
\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)
\]

Where:

- \(\frac{dH}{dt}\) = total heat flow
- \(C_p\) = measured heat capacity
- \(\frac{dT}{dt}\) = average heating rate
- \(C_p \frac{dT}{dt}\) = heat capacity component (Reversing)
- \(f(T, t)\) = heat flow from kinetic process (Nonreversing)
Reversing Heat Flow from MDSC Raw Signals

![Graph showing heat capacity and reversing heat flow against temperature.]
Quench Cooled PET: Total vs. Reversing Heat Flow
Nonreversing Heat Flow is the kinetic component of the total heat flow. It is calculated by subtracting the heat capacity component from the total heat flow using the classical heat flow equation as a theoretical basis.

\[ \text{Nonreversing} = \text{Total} - \text{Reversing} \]

**Basis for Calculation**

\[ \frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t) \]

\[ \frac{dH}{dt} = \text{total heat flow} \]

\[ C_p \frac{dT}{dt} = \text{heat capacity component (reversing)} \]

\[ f(T, t) = \text{kinetic component (nonreversing)} \]
Quench-Cooled PET: Deconvoluted Signals

![Graph showing heat flow and temperature relationship for Quench-Cooled PET with deconvoluted signals, including NONREVERSING, TOTAL, and REVVERSING categories.](image-url)
Calibration
Calibration for MDSC

There are three calibration steps necessary to produce accurate and precise MDSC results.

• Baseline Calibration
• Heat Flow Calibration (Cell Constant)
  – Melting temperature provides temperature calibration
• Heat Capacity Calibration
Cell Constant Effect on Modulated Heat Flow

Heat Flow (W/g)

\[ E = 0.5 \]
\[ E = 1.0 \]
\[ E = 1.6 \]

Temperature (°C)
The heat capacity calibration constant, $K$, is a multiplying factor which provides for the quantitative measurement of heat capacity by MDSC.

\[
\frac{A^{MHF}}{A^{MHR}} \times K = Cp
\]
The heat capacity calibration constant, $K$, is calculated as the ratio of the theoretical heat capacity of a standard material, to the measured heat capacity of the material.
Calibration - Conclusions

- Nitrogen provides for the greatest stability of the heat flow & heat capacity measurements.

- $K$ is stable to changes in conditions above a 50-second period.

- Periods below 50 seconds may be used.
  - Use thin samples to minimize gradients.
  - Calibrate at the same conditions for the best accuracy.
Analyzing Glass Transitions by MDSC
What is the Glass Transition?

"... reversible change in an amorphous material or in amorphous regions of a partially crystalline material, from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle one."

ASTM E 1142
Why is the Tg Important?

Why important?

Region of dramatic & rapid property changes

Thus critical to: 
- Processing
- Storage
- Use
Some Properties Affected at Tg

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Response on heating through Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Volume</td>
<td>Increases</td>
</tr>
<tr>
<td>Modulus</td>
<td>Decreases</td>
</tr>
<tr>
<td>Coefficient of thermal expansion</td>
<td>Increases</td>
</tr>
<tr>
<td>Specific Heat</td>
<td>Increases</td>
</tr>
<tr>
<td>Enthalpy</td>
<td>Increases</td>
</tr>
<tr>
<td>Entropy</td>
<td>Increases</td>
</tr>
</tbody>
</table>
Measuring Width of Tg

- Make sure there are at least 4-6 cycles across the step change in the total heat flow.
Choosing the Period/Heating Rate Combination

If the transition is 12°C wide, and you wish to use a 60 second period.

\[
\frac{12^\circ C}{6 \text{ cycles}} \times \frac{1 \text{ cycle}}{60 \text{ sec}} \times \frac{60 \text{ sec}}{\text{ min}} = \frac{2^\circ C}{\text{ min}}
\]

If the transition is 3°C wide, and you wish to use a 40 second period.

\[
\frac{3^\circ C}{6 \text{ cycles}} \times \frac{1 \text{ cycle}}{40 \text{ sec}} \times \frac{60 \text{ sec}}{\text{ min}} = \frac{0.75^\circ C}{\text{ min}}
\]
Measuring the Width of Enthalpy Recovery
Physical Aging of PET

Amplitude: ±0.3°C
Period: 40 sec
Scan Rate: 2°C/min

Pan type: Standard Al
Spray-Dried Lactose

Evaporation of Water

(nc°)

Heat Flow (W/g)

Exo

Heat Flow (W/g)

Rev

[ ] Nonrev

Heat Flow (W/g)

Heat Flow (W/g)

Temperature (°C)

40 60 80 100 120 140

Lactose Tg

Exo

Rev

Heat Flow (W/g)

-0.14

-0.12

-0.10

-0.08

-0.06

-0.04

-0.02

0.00

0.02

0.04

0.06

0.08

0.10

0.12

0.14

113.18° C

116.09° C

118.67° C

-0.08

-0.06

-0.04

-0.02

0.00

0.02

0.04

0.06

0.08

0.10

0.12

0.14

-0.15

-0.13

-0.11

-0.09

-0.07

-0.05

-0.03

-0.01

0.00

0.02

0.04

0.06

0.08

0.10

0.12

0.14

Exo

Rev

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Standard DSC of Sucrose/Water (40% w/w)

- Heat after quench
- Heat after cool @ 10°C/min

Conventional DSC
Heating rate: 10°C/min
Pan type: Hermetic

**lower curve shifted to facilitate comparison**

Temperature (°C)

Heat Flow (W/g)
Special Operating Conditions
Modulated DSC provides the unique ability to measure heat capacity under quasi-isothermal conditions, i.e., isothermal with the exception of the small temperature modulation.

Stepwise quasi-isothermal MDSC provides for the ultimate in resolution in that the underlying heating rate is essentially zero. In addition, time-dependent effects in the measured $C_p$ can be eliminated, allowing for the measurement of the true, temperature-dependent heat capacity across a transition.
Hysteresis (Time-dependence) at the Tg

3 Heating & Cooling Experiments @ 1°C
Quasi-Isothermal Measurement

ISOTHERMAL Cp @ 1°C ISO STEPS
(40 min each starting @ 120°C)
Constructing the Quasi-Isothermal Measurement

1) Equilibrate @ 100°C
2) Data Storage OFF
3) Modulate ±0.5°C every 80 seconds
4) Isothermal for 10 minutes
5) Data Storage ON
6) Isothermal for 5 minutes
7) Data Storage OFF
8) Increment (-)1°C
9) Repeat Segment 4 30 times
   or
9) Repeat Segment 4 until 130°C
Quasi-Isothermal as a Function of Temperature (stepping down)

ISOTHERMAL Cp @ 1°C ISO STEPS  
(starting @ 120°C)
Quasi-Isothermal (stepping up)

**ISOTHERMAL Cp @ 1°C ISO STEPS**

(40 min each starting @ 88°C)
Quasi-Isothermal as a Function of Temperature (stepping up)

**ISOTHERMAL Cp @ 1°C ISO STEPS**
(starting @ 88°C)
Comparison of Heating, Cooling & Quasi-Isothermal Measurements

Comparison of Heating and Cooling Runs @ 1°C/min with Isothermal Measurements

Complex Cp (J/g/°C) vs. Time (min)

- COOLING
- HEATING
Aged Sample

- REVERSING
- TOTAL
- NONREVERSING
- SAMPLE AGED SEVERAL YEARS

Temperature (°C) vs. Heat Flow (mW) graph showing:
- Temperature range: 25°C to 55°C
- Heat Flow range: -0.8 mW to 0.2 mW
Characterization of Polymer Melting and Crystallization by MDSC®
1. What is being measured during melting?
   Total Heat Flow; like DSC, the Total signal from MDSC®
   is the average value of all heat flows and is qualitatively
   and quantitatively equivalent to DSC heat flow at the
   same average heating rate the Total signal is unaffected
   by the choice of MDSC® experimental conditions

   Reversing Heat Flow or Heat Capacity Component; this
   signal is calculated from the amplitude of the modulated
   heat flow which has at least two components in the
   melting region, heat capacity and latent heat of fusion
   [Figures 1 and 2]
In the melting region, there are two processes which require energy: heat capacity & heat of fusion.
Crystalline PET Melt

Figure 2

The peaks crossing below the superimposed line represent the heat of fusion of the material.

Note: Complete absence of any exothermic activity prior to or during melting.

Sample cooled @ 0.1°C/min from 280°C prior to heating.
Quantification of Signals

Nonreversing Heat Flow; there is no independent measurement of this signal. It is calculated by subtracting the Reversing signal from the Total signal. This is important in the melting region because the Total signal is quantitative and independent of modulated conditions, therefore any error (plus or minus) in the Reversing signal will also occur in the Nonreversing signal but opposite in Sign.

\[
\text{Total} = Cp \frac{dT}{dt} + f(T, t)
\]

\[
\text{Total} = \text{Reversing} + \text{Nonreversing}
\]

Nonreversing = Total – Reversing

Since the Total signal is quantitative and the Nonreversing signal is simply the difference between the Total and Reversing signals, the sum of the Reversing and Nonreversing signals (Initial Crystallinity) must also be quantitative.
Selecting Optimum Experimental Conditions for Analysis of the Melting Transition
Selecting Experimental Conditions

Modulation Period

- The period must be slow enough for the sample to follow the temperature modulation.
- DSC 2900 Series: 60-second periods for samples up to 15mg.
- Q Series: 30-second periods for samples up to 15mg.

Heating Rate

- In order to properly separate the Total heat flow into its components, it is necessary to have a minimum of 4-5 cycles over the critical region of the Transition. For melting, this region is at half-height of the melting peak [Figures 6 - 7].
Choosing the Underlying Heating Rate

Figure 6

- Calculate the width of the transition

![Graph showing heat flow vs. temperature with points at 236.96°C, 45.22 J/g, 12.72°C, and 260.61°C.](image-url)
Choose Heating Rate / Period such that there are 4-6 cycles across the width of the transition (see previous page).
Selecting Experimental Conditions (cont.)

Modulation Amplitude

• The modulation amplitude is the most important parameter from the viewpoint of interpreting the data with confidence.

• There is absolutely no need to guess which amplitude to use. It should always be selected from the table in the manual [Figure 8].

• Why specific amplitudes should be used for characterization of the melting transition:

  1. The recommended amplitudes result in the heating rate going from 0°C/min to a value that is double the average heating rate. These “Heat-Iso” Amplitudes result in no cooling of the sample during temperature modulation [Figure 9].

  Note: This is a psychological reason since the results are essentially the same with and without cooling.
## Heat-Iso Amplitude

**Figure 8**

<table>
<thead>
<tr>
<th>Period (sec)</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>0.1</strong></td>
<td>0.011</td>
<td>0.013</td>
<td>0.016</td>
<td>0.019</td>
<td>0.021</td>
<td>0.024</td>
<td>0.027</td>
</tr>
<tr>
<td><strong>0.2</strong></td>
<td>0.021</td>
<td>0.027</td>
<td>0.032</td>
<td>0.037</td>
<td>0.042</td>
<td>0.048</td>
<td>0.053</td>
</tr>
<tr>
<td><strong>0.5</strong></td>
<td>0.053</td>
<td>0.066</td>
<td>0.080</td>
<td>0.093</td>
<td>0.106</td>
<td>0.119</td>
<td>0.133</td>
</tr>
<tr>
<td><strong>1.0</strong></td>
<td>0.106</td>
<td>0.133</td>
<td><strong>0.159</strong></td>
<td>0.186</td>
<td>0.212</td>
<td>0.239</td>
<td>0.265</td>
</tr>
<tr>
<td><strong>2.0</strong></td>
<td>0.212</td>
<td>0.265</td>
<td>0.318</td>
<td>0.371</td>
<td>0.424</td>
<td>0.477</td>
<td>0.531</td>
</tr>
<tr>
<td><strong>5.0</strong></td>
<td>0.531</td>
<td>0.663</td>
<td>0.796</td>
<td>0.928</td>
<td>1.061</td>
<td>1.194</td>
<td>1.326</td>
</tr>
</tbody>
</table>

This table is additive, i.e. the heat only amplitude for a period of 40 sec and heating rate of 2.5°C/min. is the sum of the values for 2.0°C/min and 0.5°C/min:

Amplitude (40s, 2.5°C/min) = 0.212 + 0.053 = ±0.265°C
The "heat-iso" amplitude means that the modulated heating rate never becomes negative. In other words, the sample is always heated - never cooled.
Selecting Experimental Conditions (cont.)

**Heat-Iso Amplitudes** (cont.)

Since the top of the raw Modulated Heat Flow (MHF) signal is the heat flow at lowest heating rate, or 0°C/min with the recommended amplitude, its shape should be identical to the calculated Nonreversing signal except in the center of the melting region.

\[
\frac{dH}{dt} = C_p \frac{dT}{dt} + f(T, t)
\]

\[
\frac{dH}{dt} = f(T, t) \text{ when } \frac{dT}{dt} = 0
\]
Sample: XenoY1102 Quench to RT from 250°C
Size: 14.7900 mg
Method: MDSC Natas2
Comment: MDSC .318/60 @ 2°C/min

DSC

File: C:\TA\Data\DSC\Natas99.004
Operator: Lab Standard Ref Pan
Run Date: 15-Feb-99 17:19

Modulated Heat Flow Resulting from Heating Rate Range of 0-4°C/min

Expanded View of the Top of the Modulated Heat Flow Signal (Top @ 0°C/min Heat Rate)
Special Operating Conditions

Lissajous Figures
Special Operating Conditions: Lissajous Plots

The ability to perform a Modulated DSC measurement also provides for an additional utility: Lissajous plots.

The Lissajous plot is useful in that it can provide diagnostic information concerning the stability of the MDSC measurement. In addition, Lissajous analysis can lend more information into the study of phase-equilibria before and during phase transitions such as the Tg or melting of materials.
Lissajous Figure: Any of an infinite variety of curves formed by combining two mutually perpendicular simple harmonic motions.
If the system is under control, the ellipse should retrace.
Interpreting the Lissajous Figure

- Width ~ Heat Dissipation
- Slope = Cp

Deriv. Modulated Temp (°C/min)

Modulated Heat Flow (W/g)
Glass Transition

Graph: A graph showing the relationship between temperature (°C) and modulated heat flow (W/g). The x-axis represents temperature in °C, ranging from 65 to 95. The y-axis represents modulated heat flow (W/g), ranging from -0.3 to 0.3. The graph displays a pattern of oscillations, indicating a glass transition phenomenon.
Glass Transition (cont.)

Below Tg

Above Tg
Special Operating Conditions

Thermal Conductivity
Thermal conductivity is a measurement of the rate at which heat energy can be transferred through a material. It is an important factor in materials engineering and design.

Thermal conductivity and heat capacity are related properties. Since MDSC has the ability to directly measure heat capacity, it can be used to measure thermal conductivity through a series of calibrations and heat capacity measurements.
Conclusions

Once understood and properly used, Modulated DSC provides significant advantages over traditional DSC for characterization of semicrystalline materials. These advantages include the ability to:

1. Interpret complex, overlapping transitions.
2. Better determine the true melting onset temperature.
3. Detect changes in the sample as it is heated which affect both the qualitative and quantitative interpretation of results.
4. More accurately measure the “Initial Crystallinity” which is closer to the real crystallinity of the sample prior to the DSC experiment.