Agenda - Day 1

8:30 - 9:00 AM	Light Breakfast and Introductions
9:00 - 9:45 AM	Survey of thermal analysis instrumentation from TA, TGA 55xx, DSC 25xx, X3 DSC, TMA, etc.
9:45 - 10:15 AM	Fundamentals of TGA
10:15 - 10:35 AM	Morning Break with Beverages and Snacks
10:35 - 12:00 PM	TGA calibration, experimental setup, Evolved Gas Analysis, and application examples
12:00 - 1:00 PM	Lunch
1:00 - 2:00 PM	Fundamentals of DSC
2:00 - 2:30 PM	DSC Calibration and Experimental Setup
2:30 - 3:30 PM	DSC Application Examples
3:30 - 4:00 PM	TRIOS Software (TGA and DSC) – Analysis, Batch Processing, Reports, and Analysis Automation

Thermal Analysis Toolkit for Materials Characterization

Austin J. Ryan, PhD
Field Application Scientist

TGA

TGA 5500

Discovery SA

Rubotherm

IsoSorp

Discovery HP-TGA

What is Thermogravimetric Analysis (TGA)?

TGA measures weight/mass change and rate of weight change as a function of temperature, time and atmosphere.

Weight Loss:

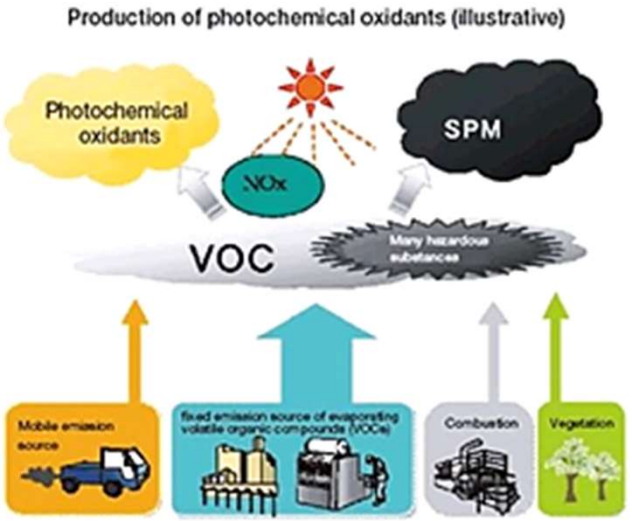
- Decomposition: The breaking apart of chemical bonds.
- Evaporation: The loss of volatiles with elevated temperature.
- Reduction: Interaction of sample to a reducing atmosphere (hydrogen, ammonia, etc.).
- Desorption: Loss of moisture/gas/solvent from surface/pores of material

Weight Gain:

- Oxidation: Interaction of the sample with an oxidizing atmosphere.
- Absorption: Uptake of moisture/gas/solvent onto material / into pore

All of these are kinetic processes (i.e. there is a rate at which they occur)

TGA: Structure-Property-Function Relationship



Measure Mass Change and Stability

- Thermal / Oxidative stability
- Composition information
- Decomposition kinetics / lifetime
- Effects of reactive and corrosive atmospheres
- Moisture and Volatile Content of Materials
- Residue

Caused by

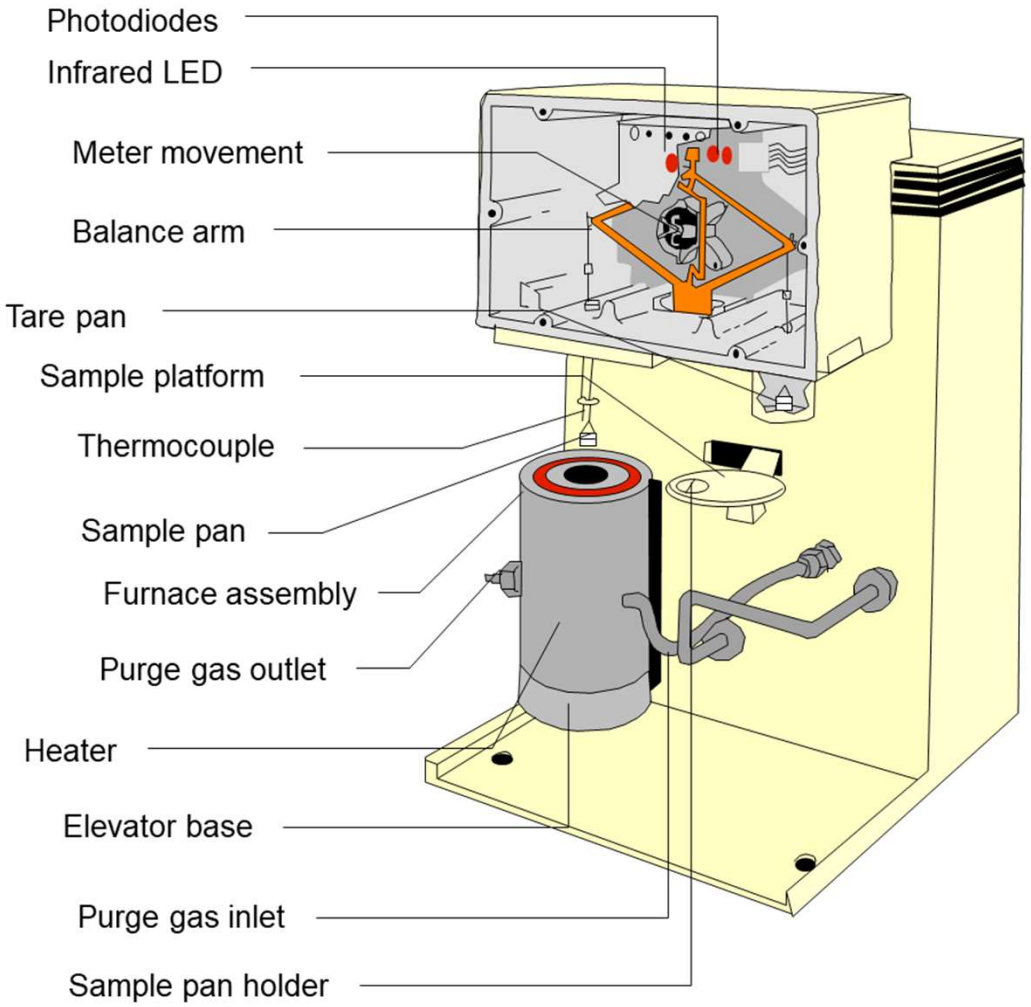
- Formulation
- Molecular Weight & Distribution
- Molecular Structure
- Concentration
- Atmosphere

Understand & Predict

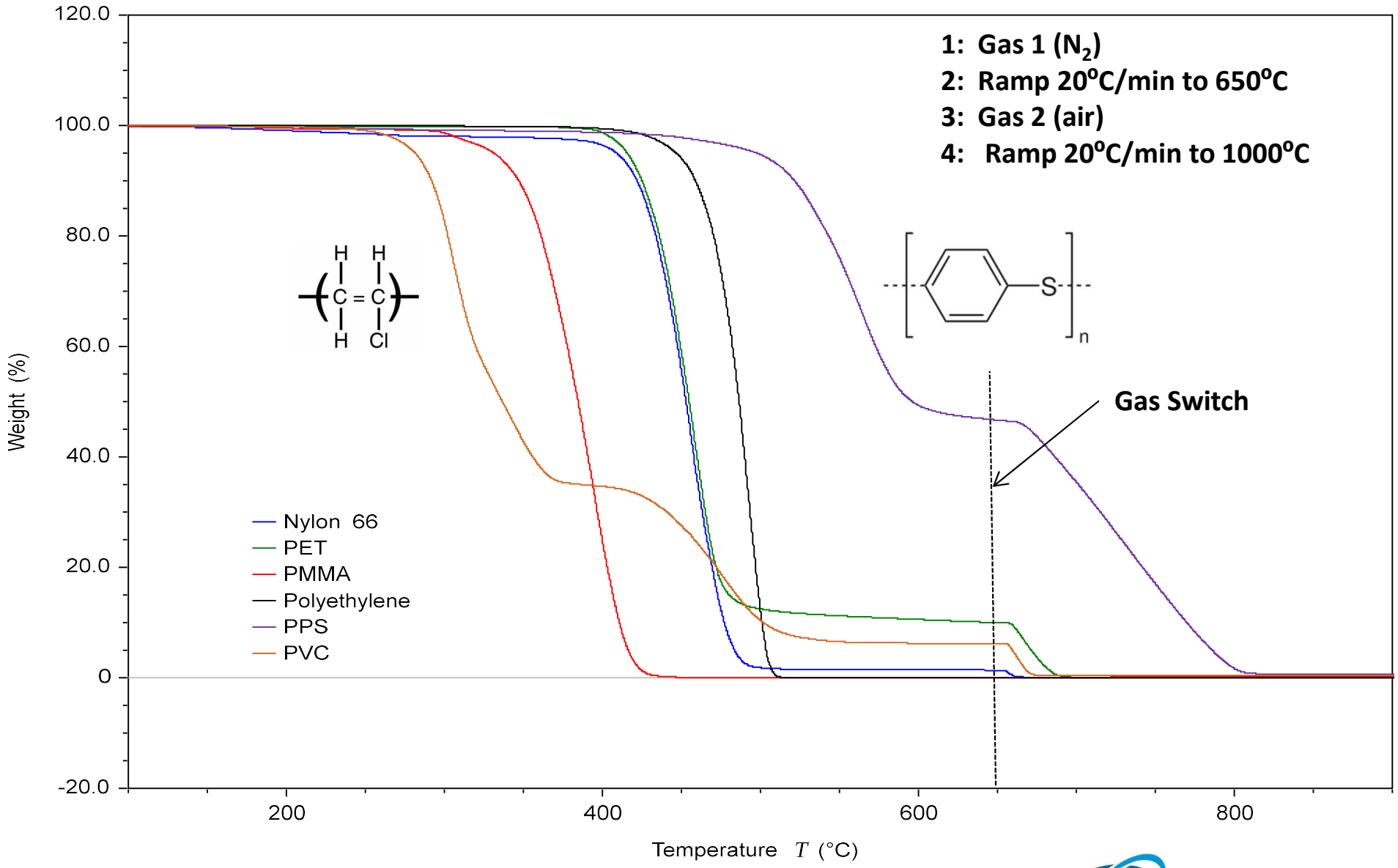
- Processing Limits
- Chemical Nature
- Product Performance
- Volatile Organic Content
- Storage Stability
- Useful Lifetime

TGA - Schematic Diagram

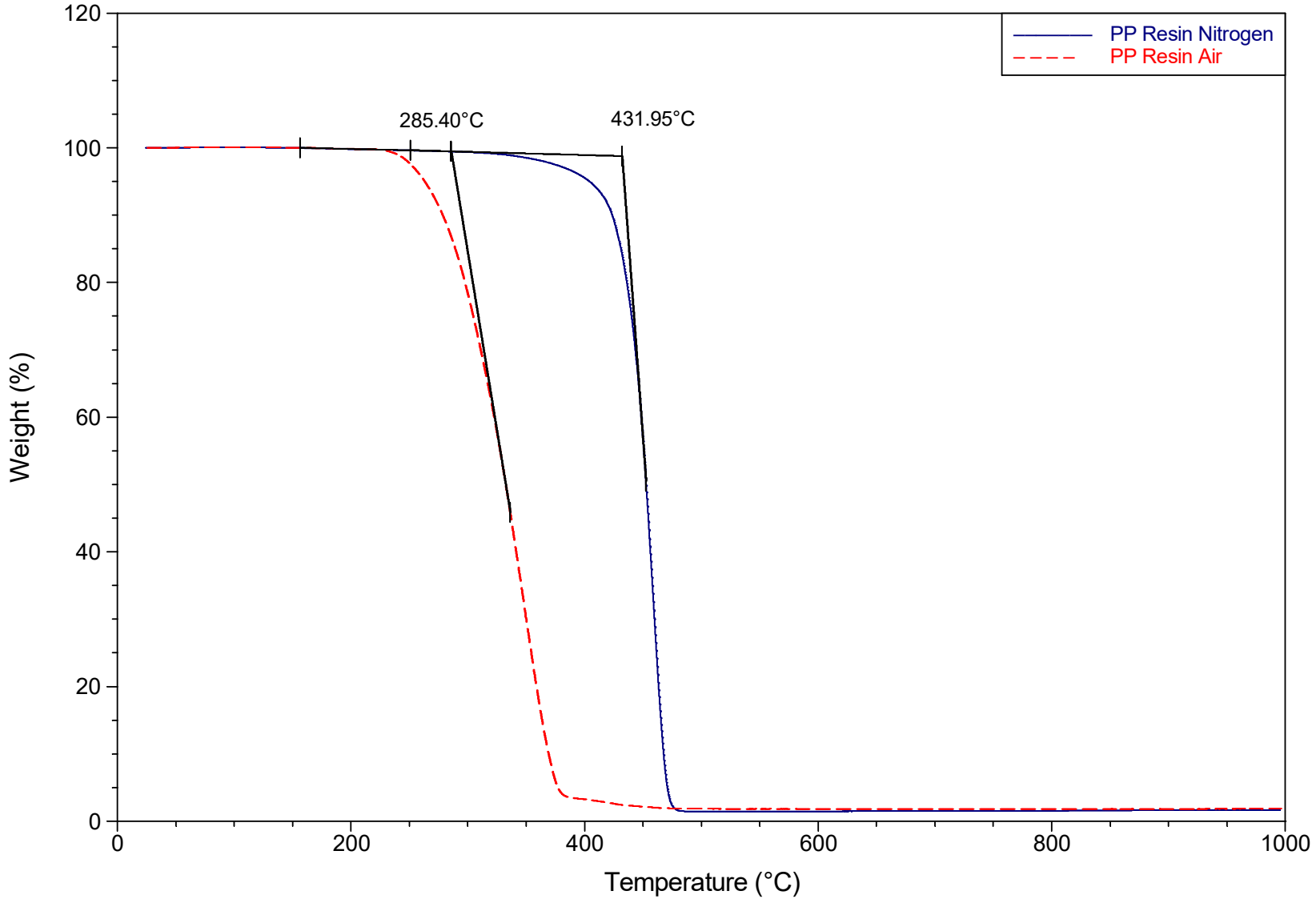
Null-balance (“Regular” TGA / Discovery SA)



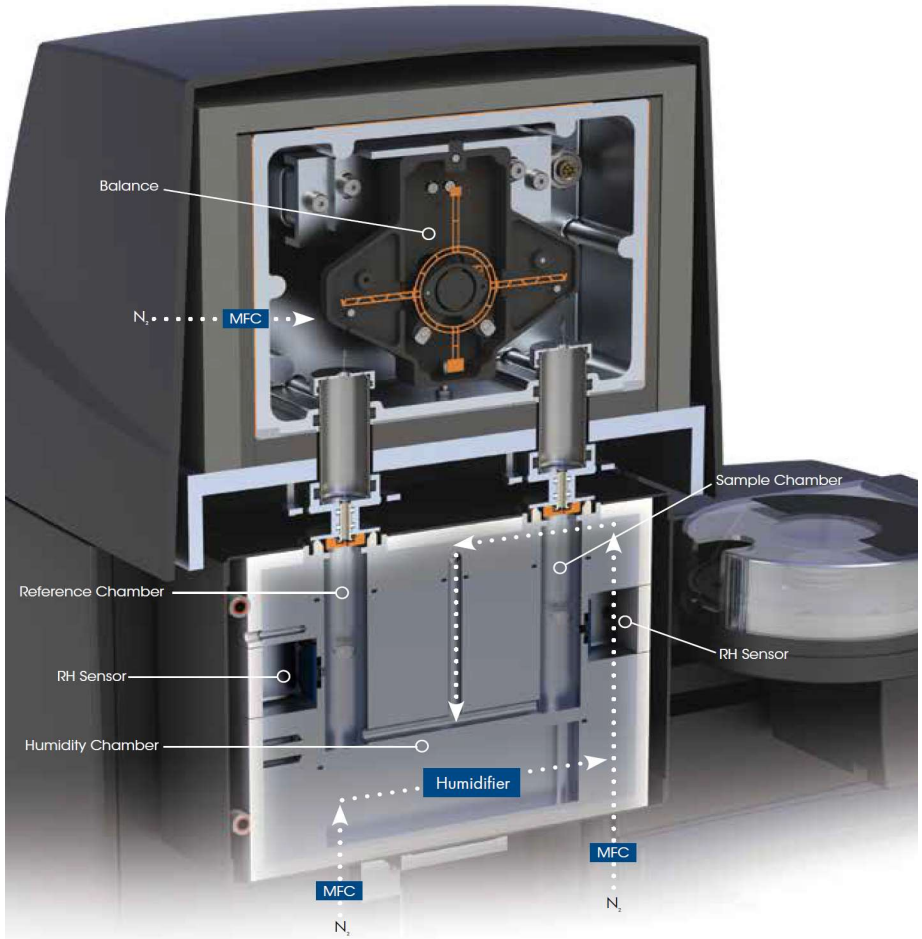
Thermal Stability of Polymers



Oxidative Stability (Polypropylene)



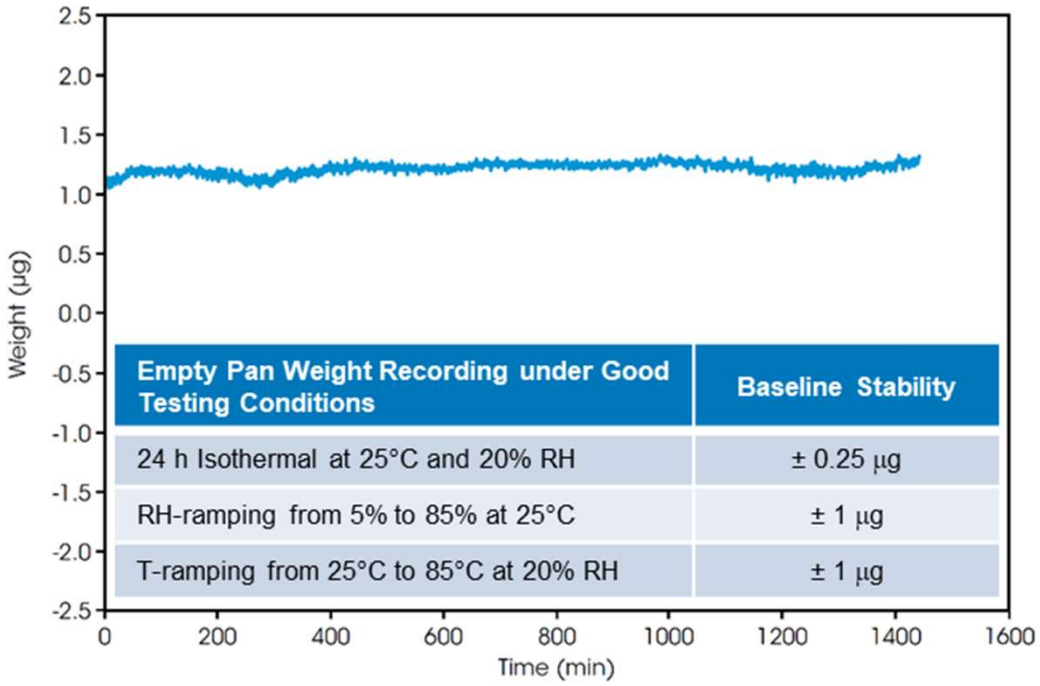
Discovery SA (successor to Q5000SA)



Applications

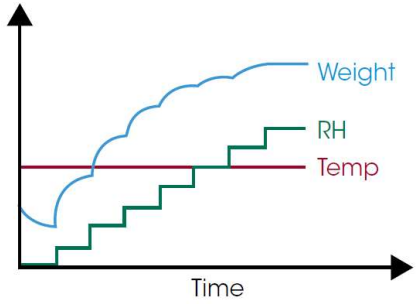
Analyzing the interaction of a sample material with humidity to assess **wetting, drying, hygroscopicity, hydrothermal stability, hydrate formation, humidity induced phase changes**

for the following industries, materials or workflows: **pharmaceuticals, polymers, food, electronics, inorganic materials, adsorbents, catalysts, building materials**



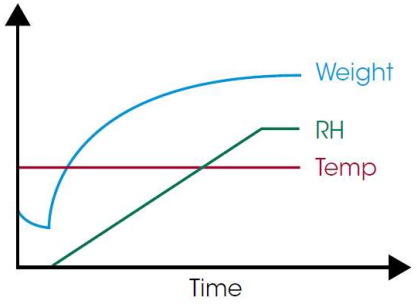
Empty Pan Weight Recording under Good Testing Conditions	Baseline Stability
24 h Isothermal at 25°C and 20% RH	± 0.25 µg
RH-ramping from 5% to 85% at 25°C	± 1 µg
T-ramping from 25°C to 85°C at 20% RH	± 1 µg

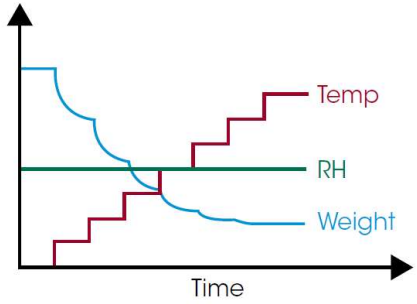
DISCOVERY SA



Isothermal experiment with stepped humidity

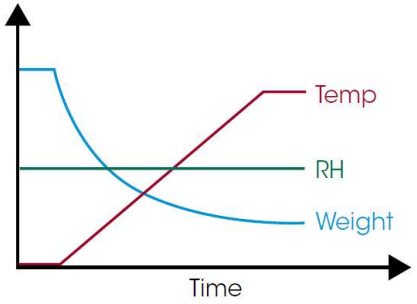
Isothermal experiment with ramped humidity





Iso-humidity experiment with stepped temperature

Iso-humidity experiment with ramped temperature



Accuracy for Best Sorption Data

A symmetric microbalance and advanced humidity chamber design deliver industry-leading stable baselines and weighing resolution. The SA provides accurate data for sorption analysis on small material quantities and/or on hydrophobic samples.

Productivity & Reliability

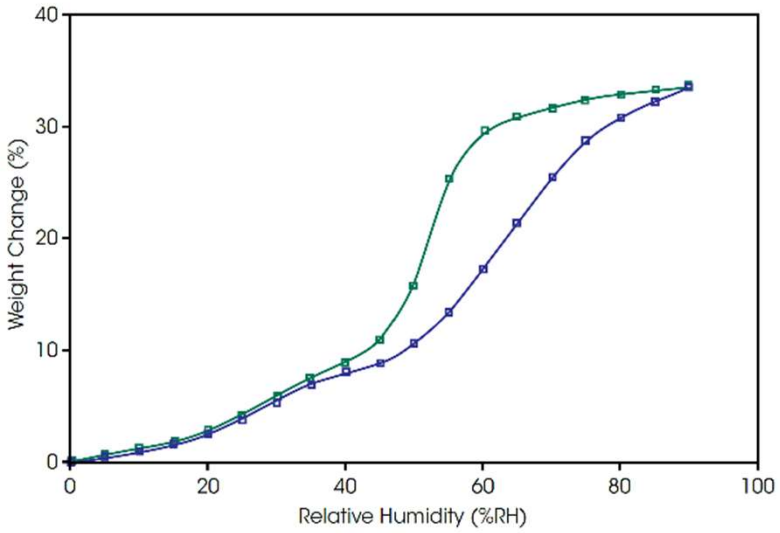
Autosampler and humidifier autofill pump allow for programming experimental queues of up to 10 or 25 samples. Even at high humidity and temperature or long lasting measurements, 24/7 productivity and absolute reliability are provided without user interaction.

Ease of use & Compliance

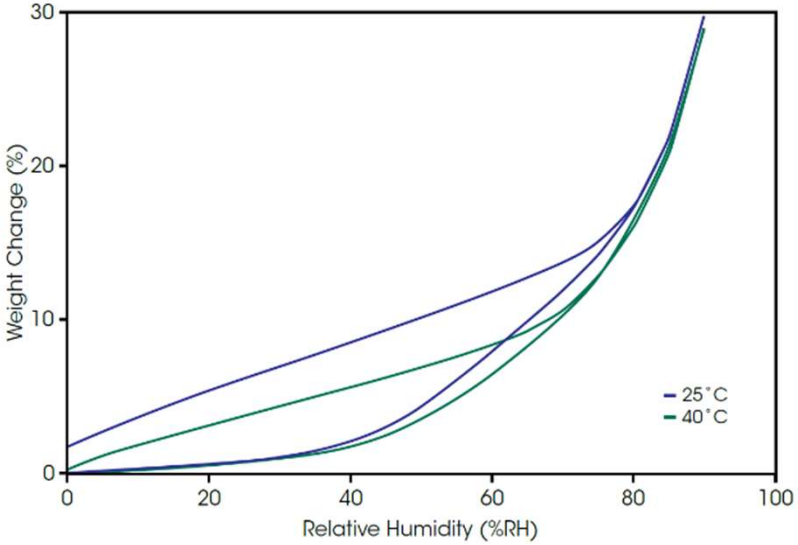
The App-style touchscreen and 21 CFR Part 11 compliant TIROS software provide a unique user experience throughout the complete workflow from instrument control, method setup, and experiment to data evaluation.

Discovery SA

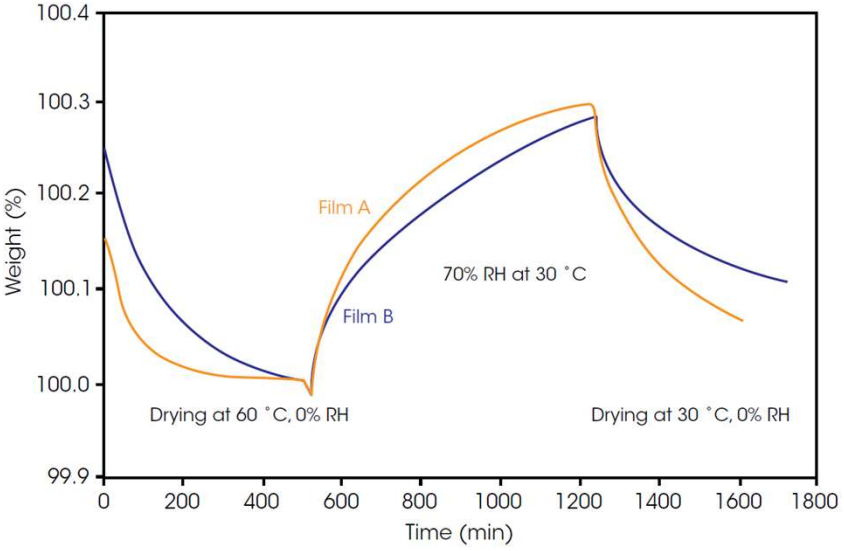
Water ad- and desorption on activated carbon



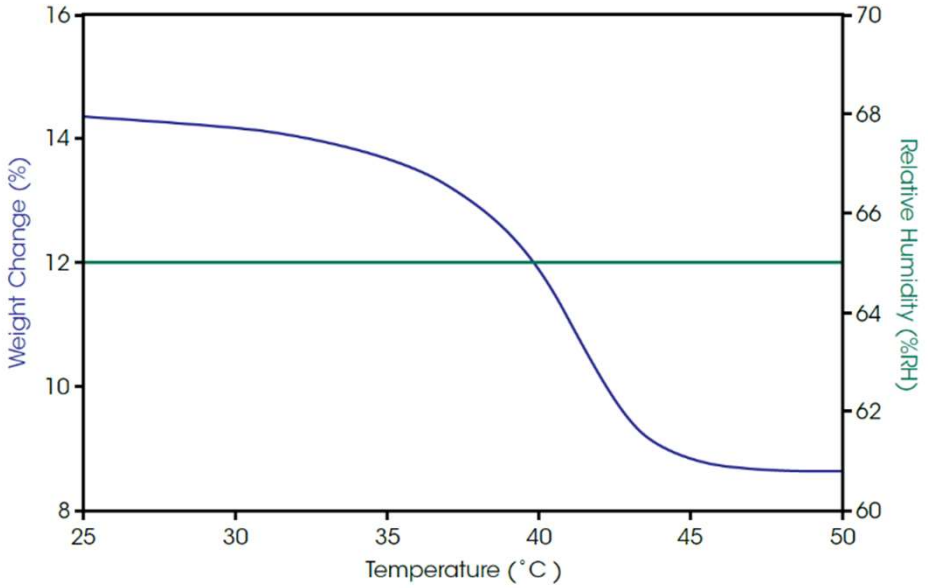
Water ab- and desorption on cornflakes



Kinetics of water vapor sorption on two polymeric packaging films during T and RH cycling

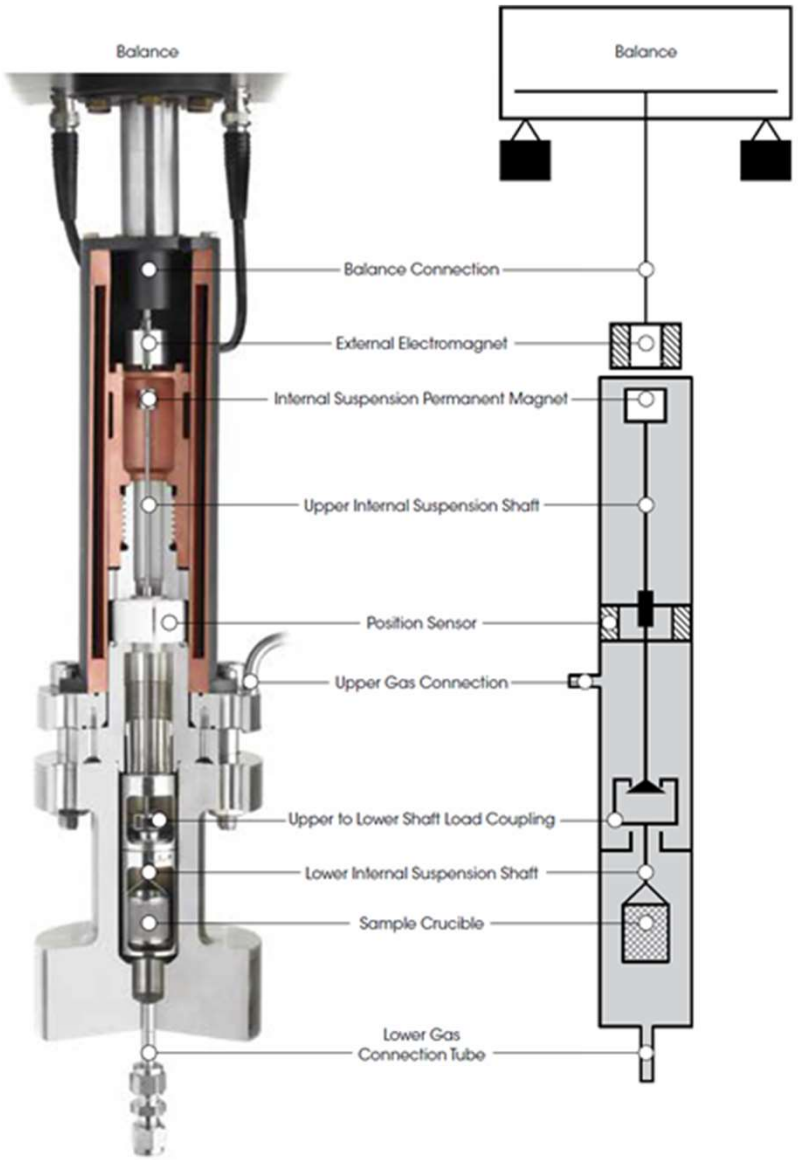


Water vapor sorption on sodium naproxen
Isohume plot at 65% RH

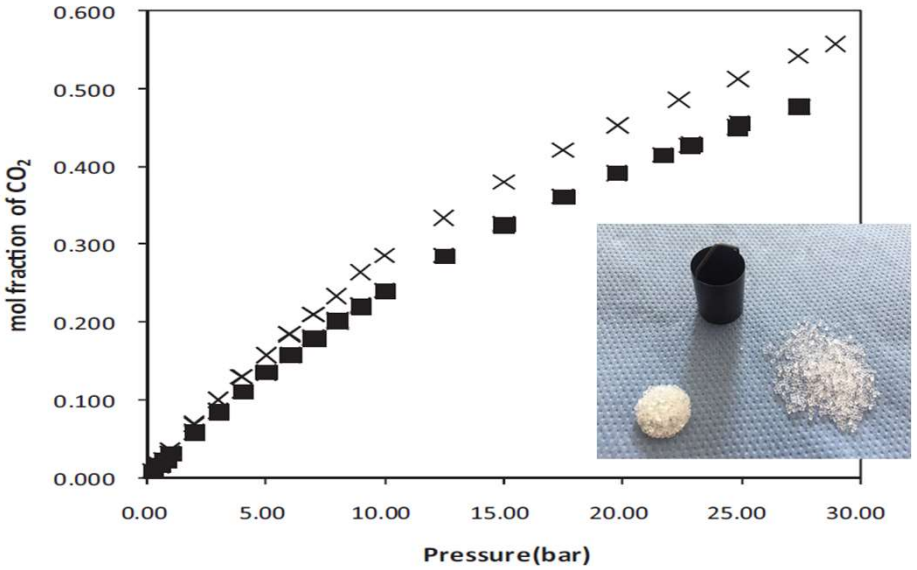


High Pressure Thermogravimetric Analysis

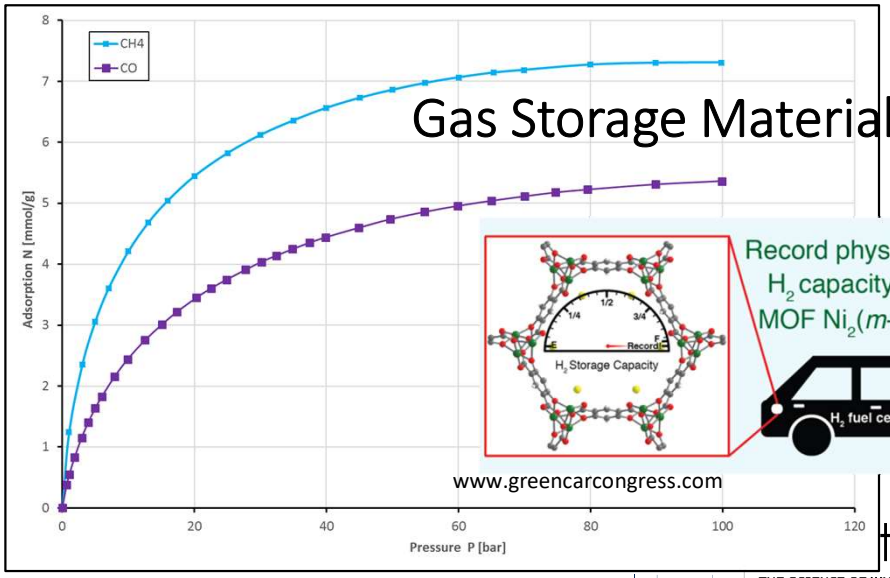
Magnetically Suspended Balance (MSB) – Rubotherm, Discovery HP-TGA, IsoSorp



Gas Solubility Measurement



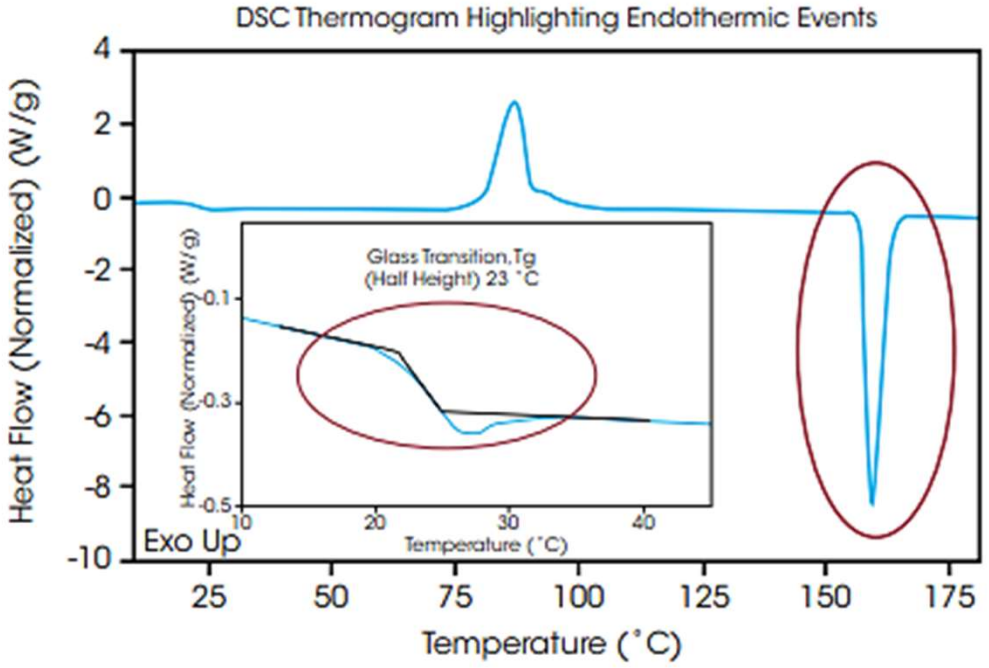
High-P Adsorption Isotherms



DSC

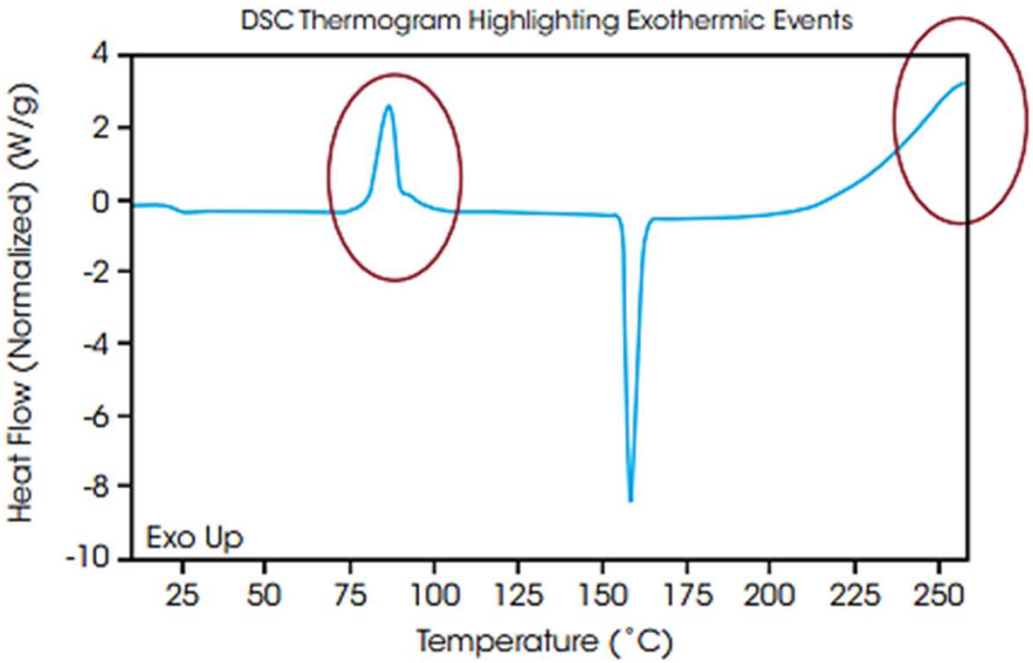
TA | TAINSTRUMENTS.COM

Exchange of Heat Due to Phase Changes



Endothermic Events

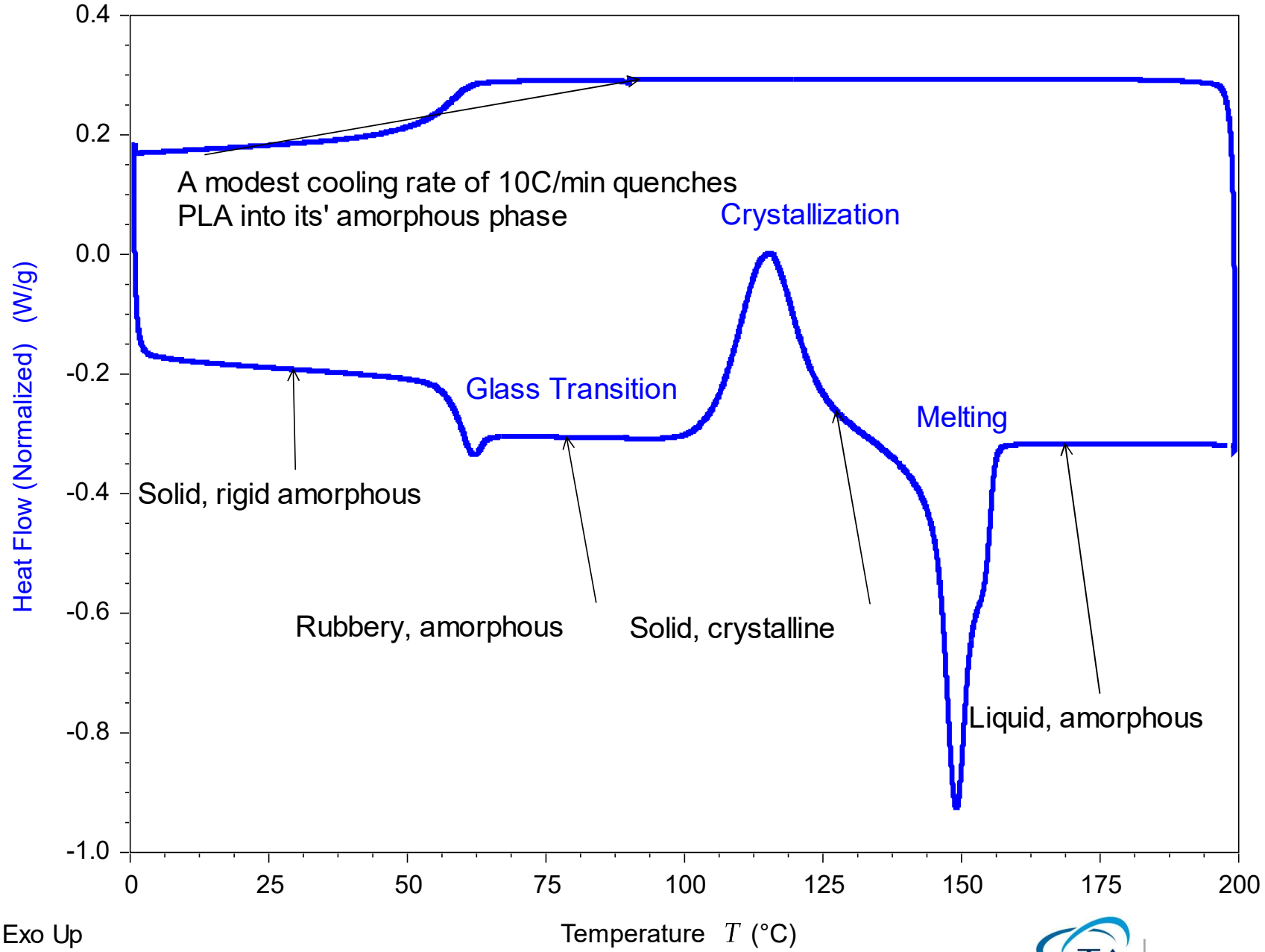
- Glass Transition
- Melting
- Evaporation/Volatilization
- Enthalpic Recovery
- Polymorphic Transitions
- Some Decompositions



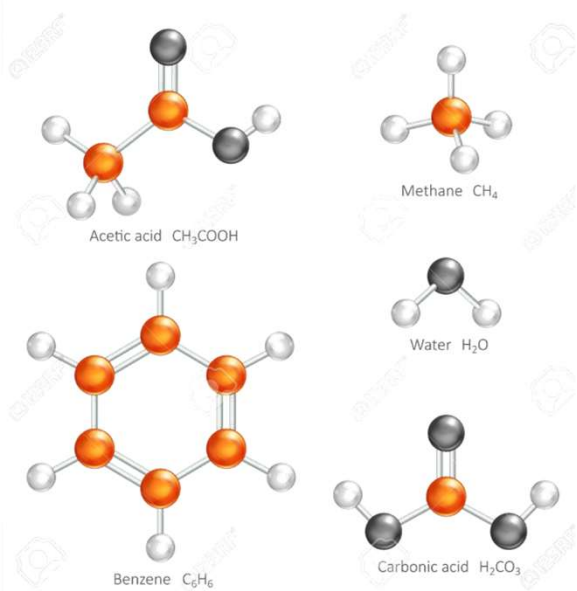
Exothermic Events

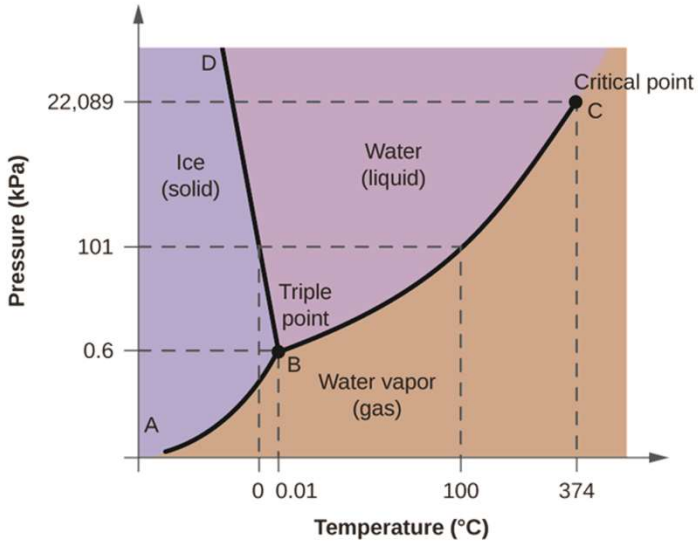
- Crystallization
- Cure Reactions
- Polymorphic Transitions
- Oxidation
- Decomposition
- Freezing

DSC Analysis of Polylactic Acid (PLA)



DSC: STRUCTURE-PROPERTY-FUNCTION RELATIONSHIP





Measure Heat Flow

- Transition Temperatures
- Specific Heat Capacity
- Heats of Reactions and Transitions (Enthalpy)
- Endothermic and Exothermic Events

Caused by

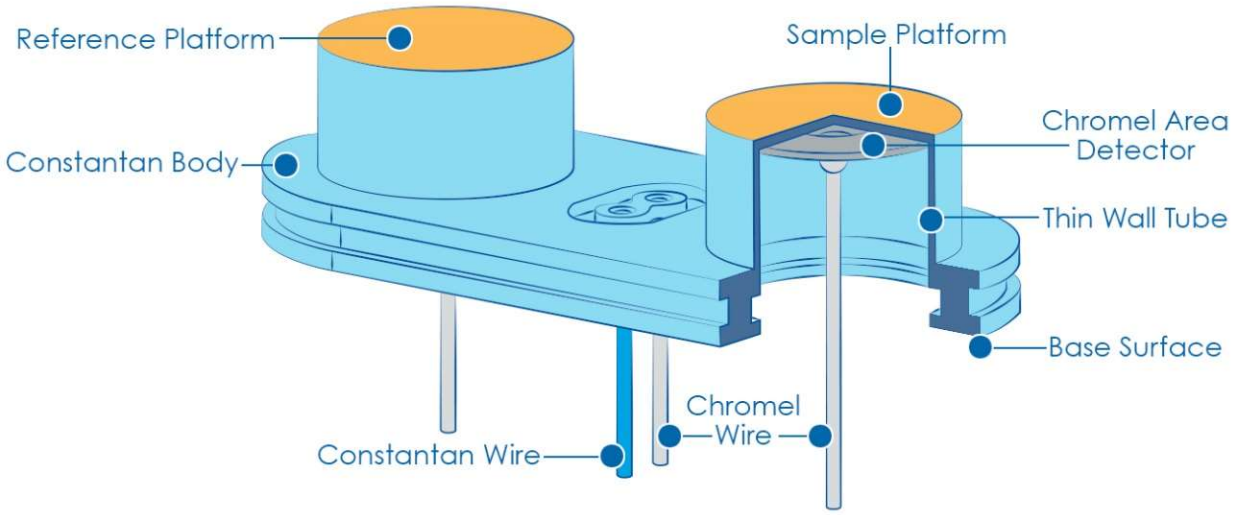
- Formulation
- Molecular Weight & Distribution
- Molecular Structure
- Presence of Crosslinks

Understand & Predict

- Phase diagrams
- Cure reaction profiles
- Formulation Impacts on Performance
- Stability and Compatibility

Measurement of Temperature

- What temperature is being measured and displayed by the DSC?
  - Sample Sensor Temperature
    - Used by most DSCs
    - Measured at the sample platform with a thermocouple, thermopile or PRT
- The actual temperature of the sample is never measured by DSC
  - There is no thermocouple in direct contact with the sample



Tzero™ Heat Flow Equation

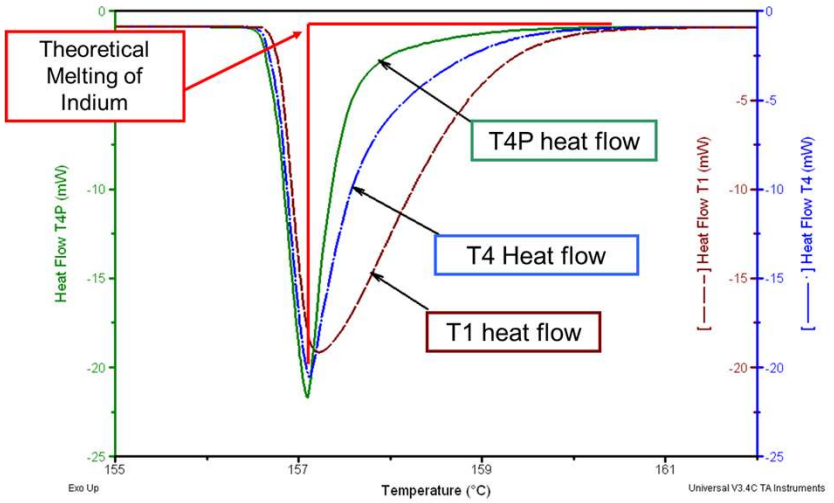
Thermal Resistance Imbalance

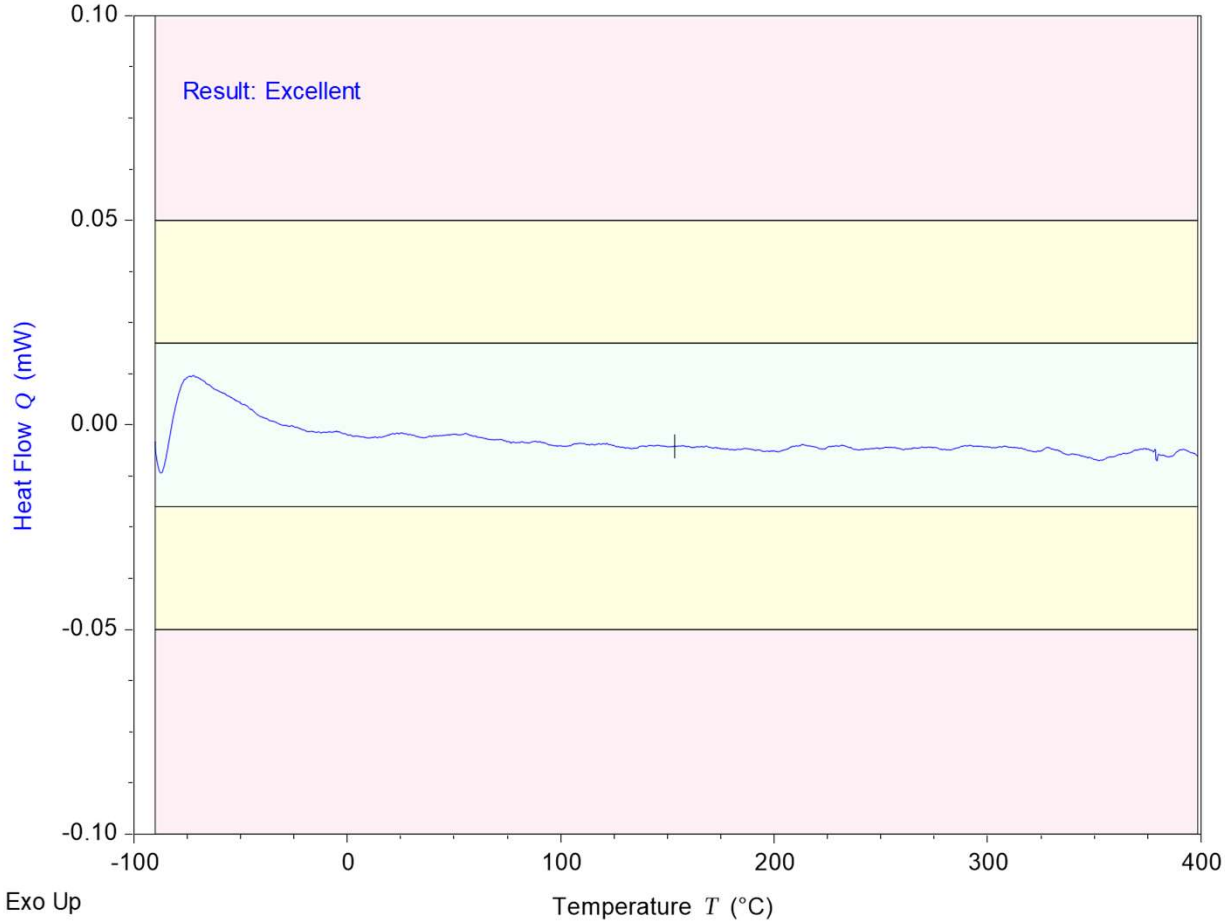
Heating Rate Difference

$$q_{T4} = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{d\tau} - C_r\frac{d\Delta T}{d\tau}$$

Principal DSC Heat Flow

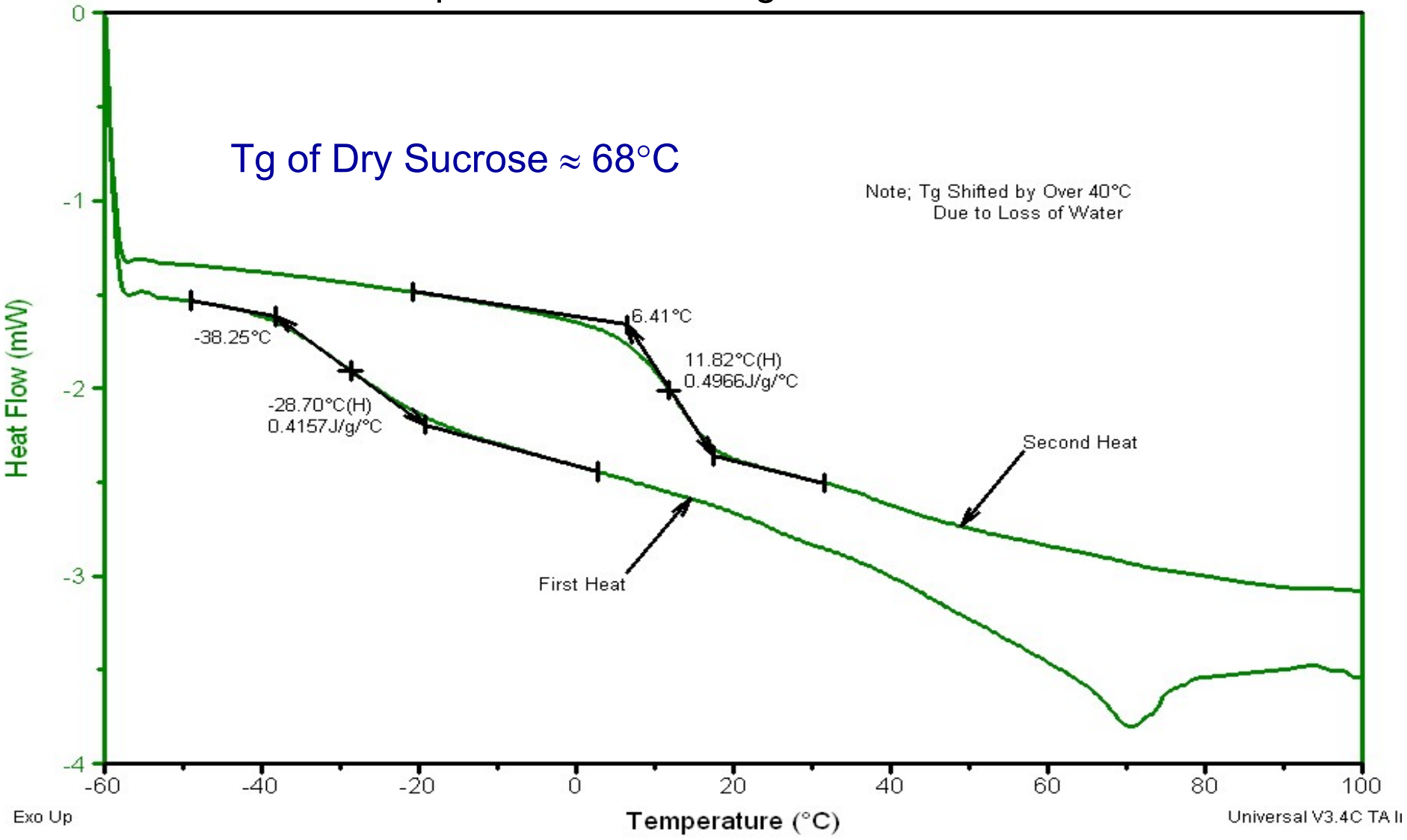
Heat Capacity Imbalance



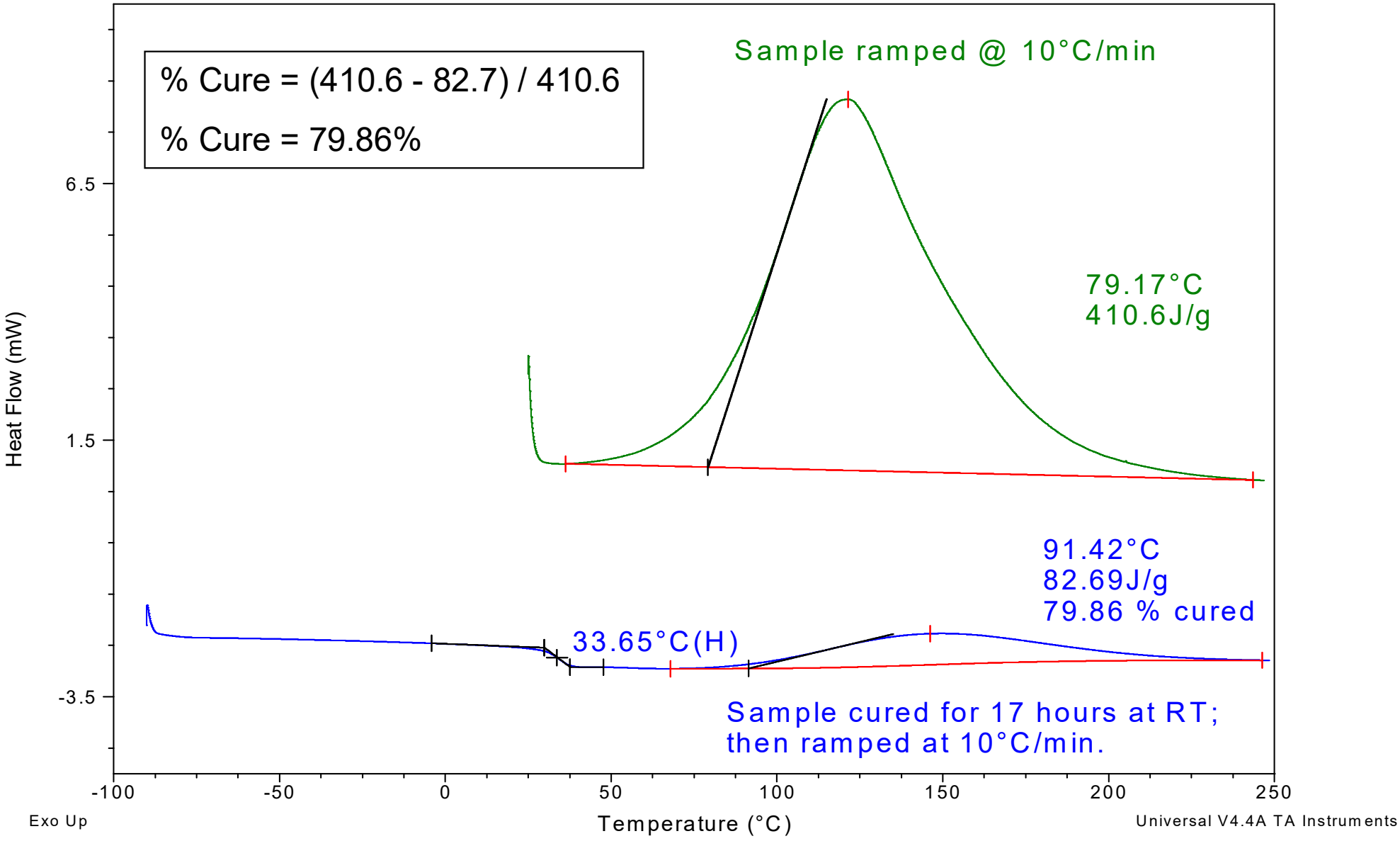


Absorbed Moisture Acts as a Plasticizer to Lower the Tg of Sucrose

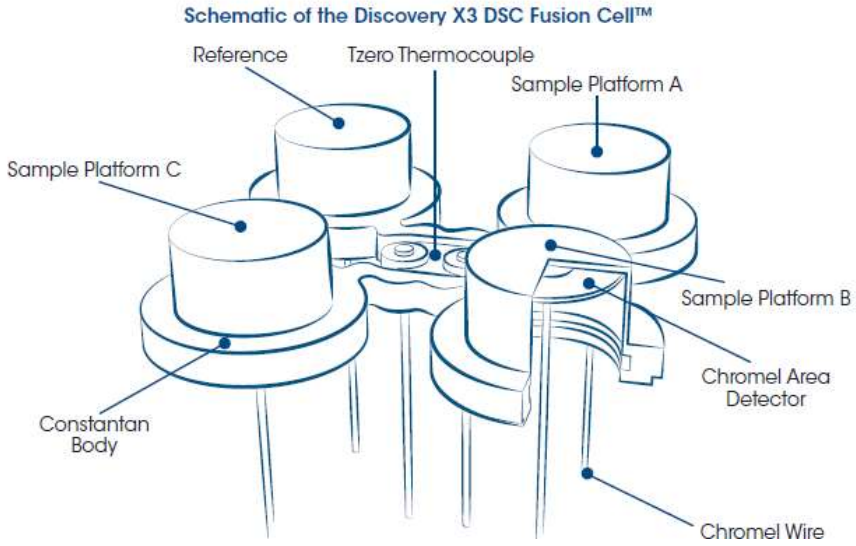
Implications for storage conditions

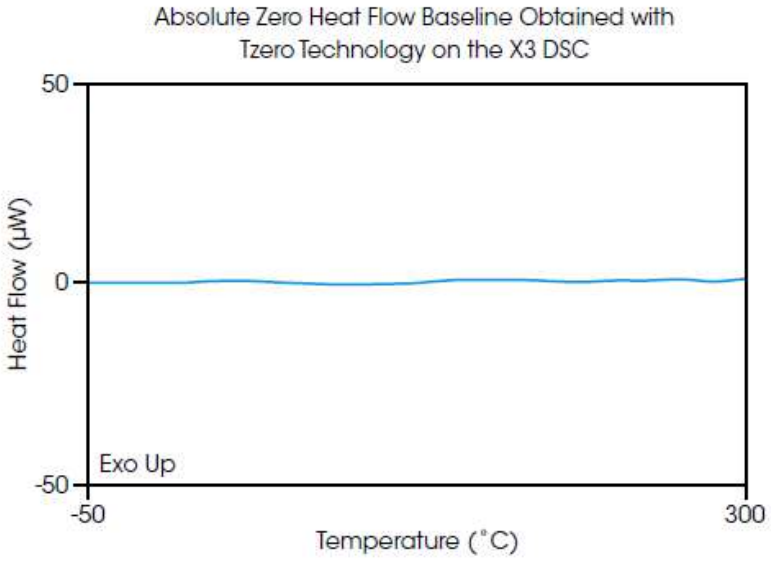


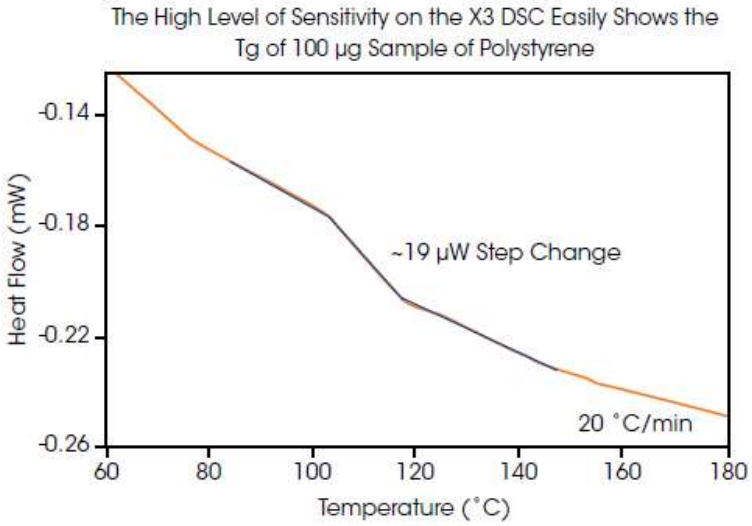
Calculation of % Cure: An Epoxy



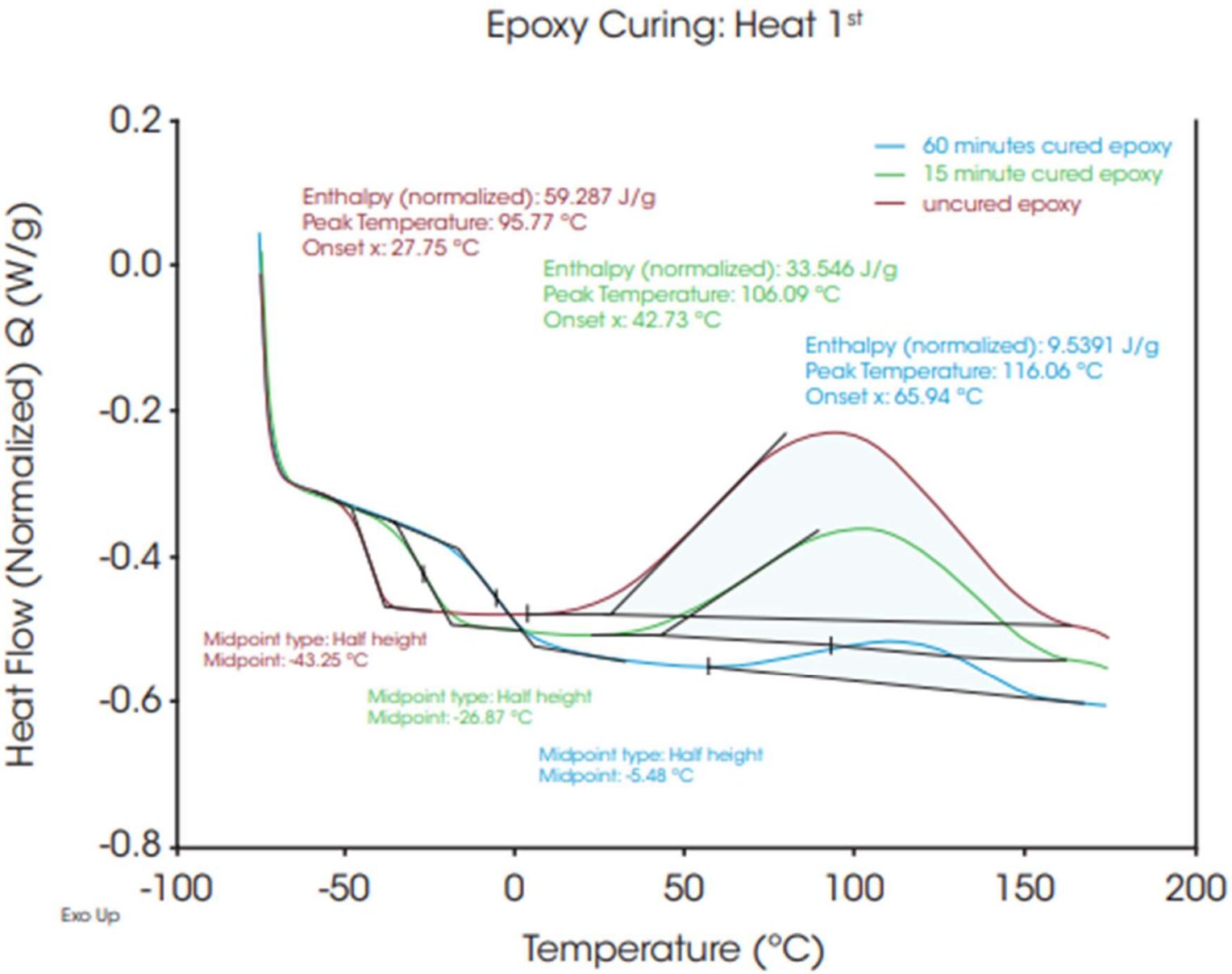
X3 DSC (NEW!)


Schematic of the Discovery X3 DSC Fusion Cell™
Reference
Tzero Thermocouple
Sample Platform A
Sample Platform C
Sample Platform B
Chromel Area Detector
Constantan Body
Chromel Wire

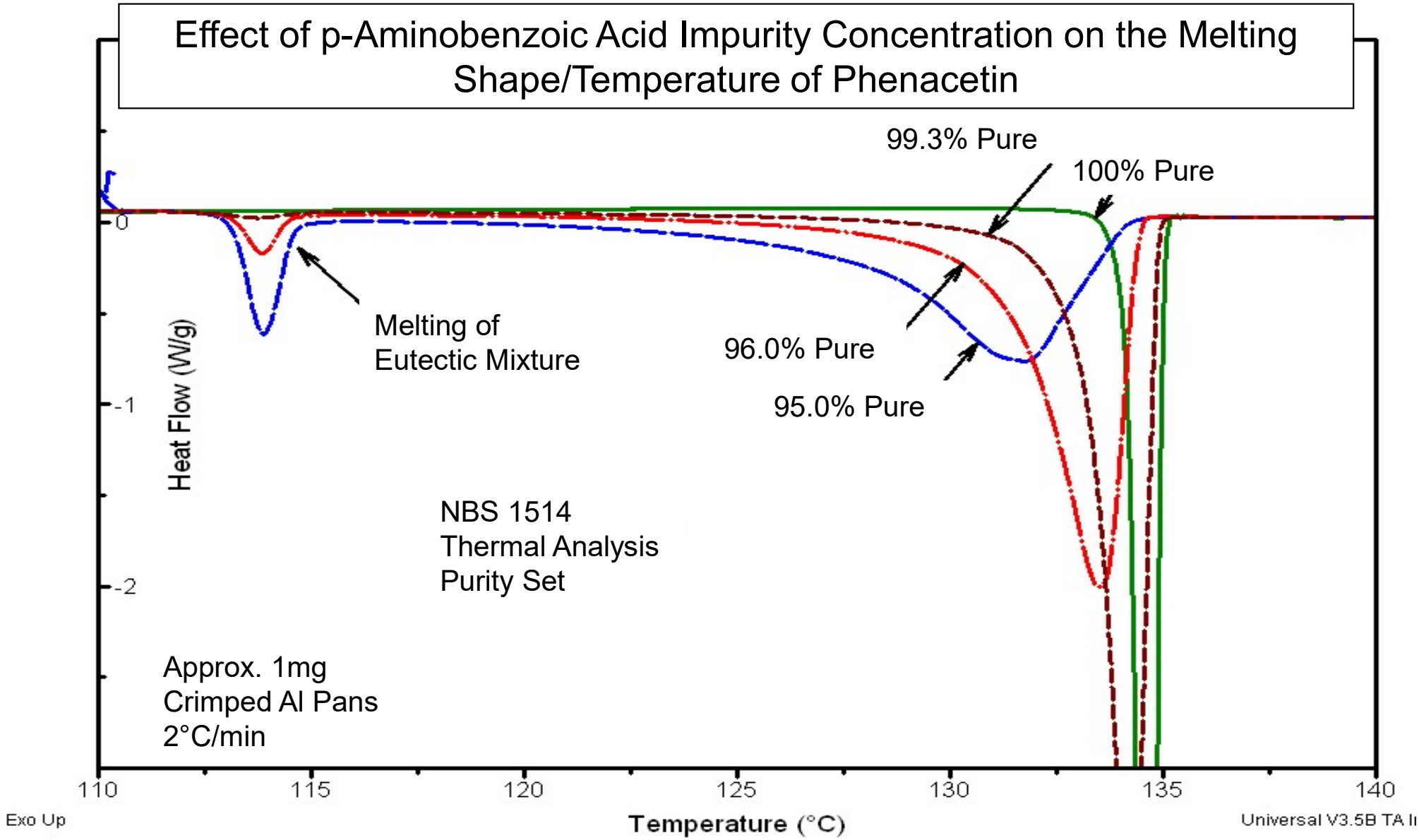

Absolute Zero Heat Flow Baseline Obtained with Tzero Technology on the X3 DSC
50
0
-50
Heat Flow (µW)
Exo Up
-50
300
Temperature (°C)


The High Level of Sensitivity on the X3 DSC Easily Shows the Tg of 100 µg Sample of Polystyrene
-0.14
-0.18
-0.22
-0.26
Heat Flow (mW)
~19 µW Step Change
20 °C/min
60
80
100
120
140
160
180
Temperature (°C)

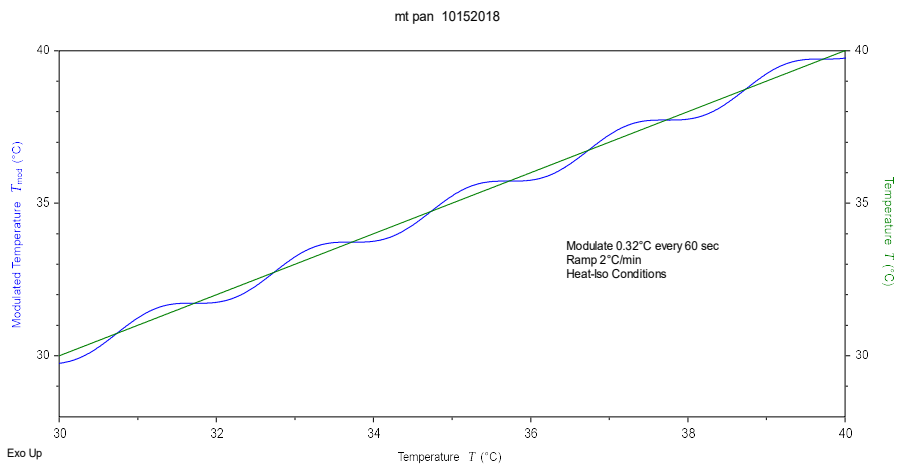
Curing of Thermoset Epoxy using X3 DSC



Effect of Impurities on Melting



Modulated DSC



$$\frac{dQ}{dt} = Cp\,\frac{dT}{dt} + f(T,\ t)$$

Total Heat Flow

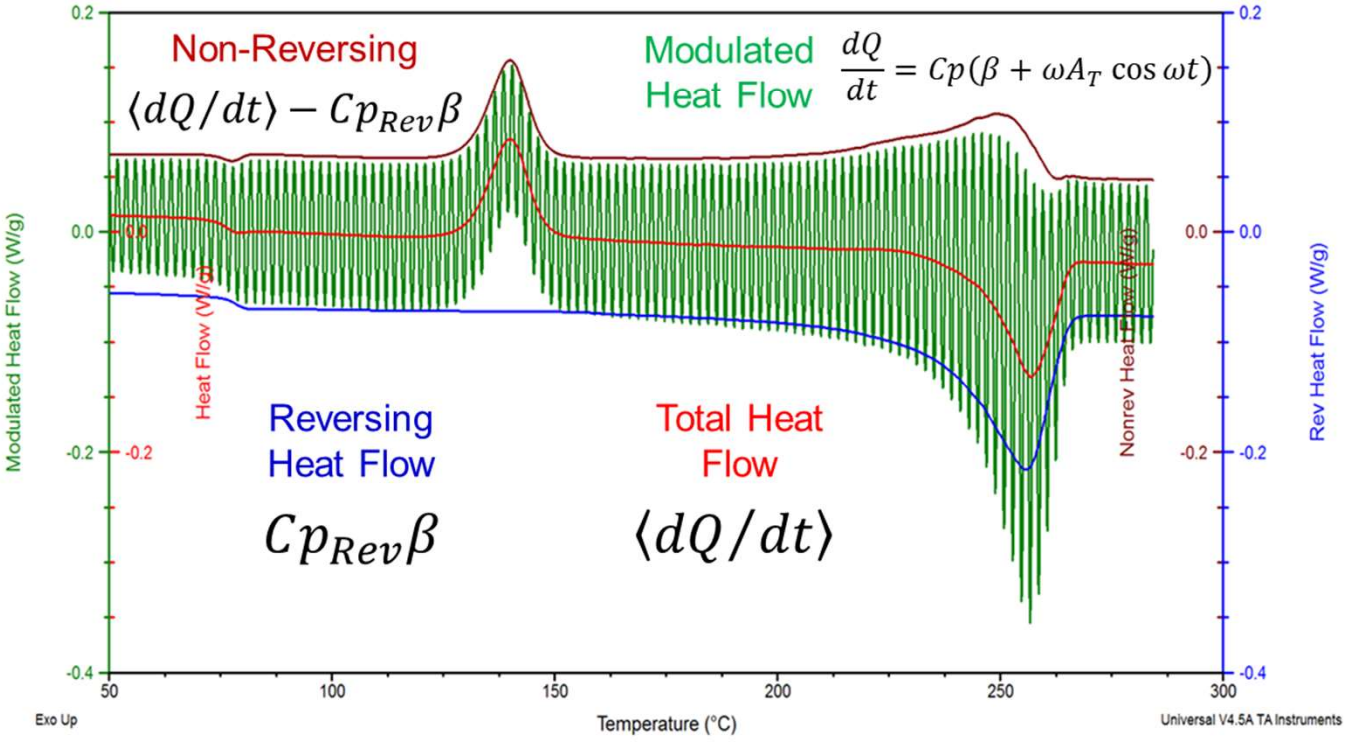
- All Transitions

Reversing Heat Flow

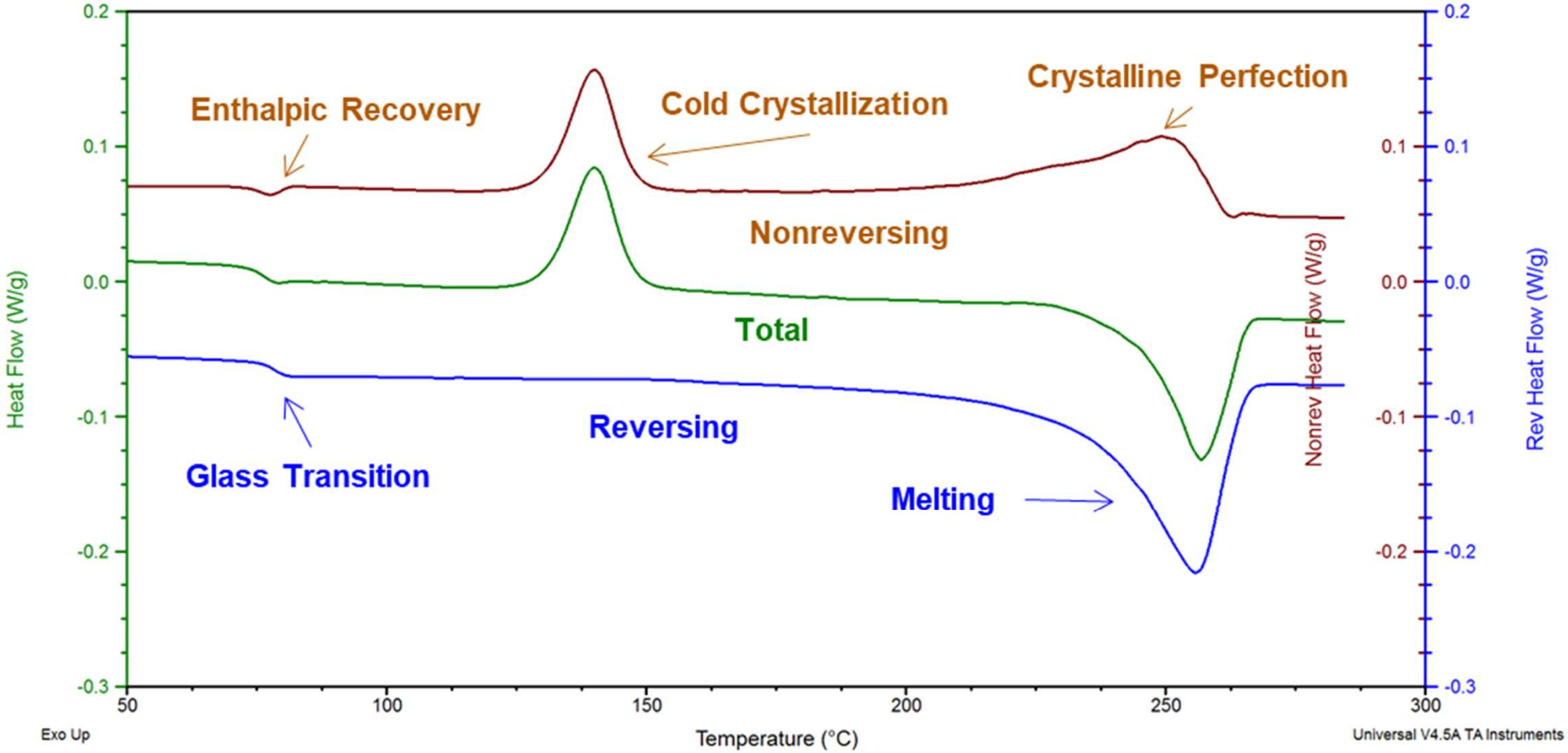
- Heat Capacity
- Glass Transition
- Melting

Non-Reversing Heat Flow

- Enthalpic Recovery
- Evaporation
- Crystallization
- Thermoset Cure
- Denaturation
- Decomposition
- Some Melting
- Chemical Reactions

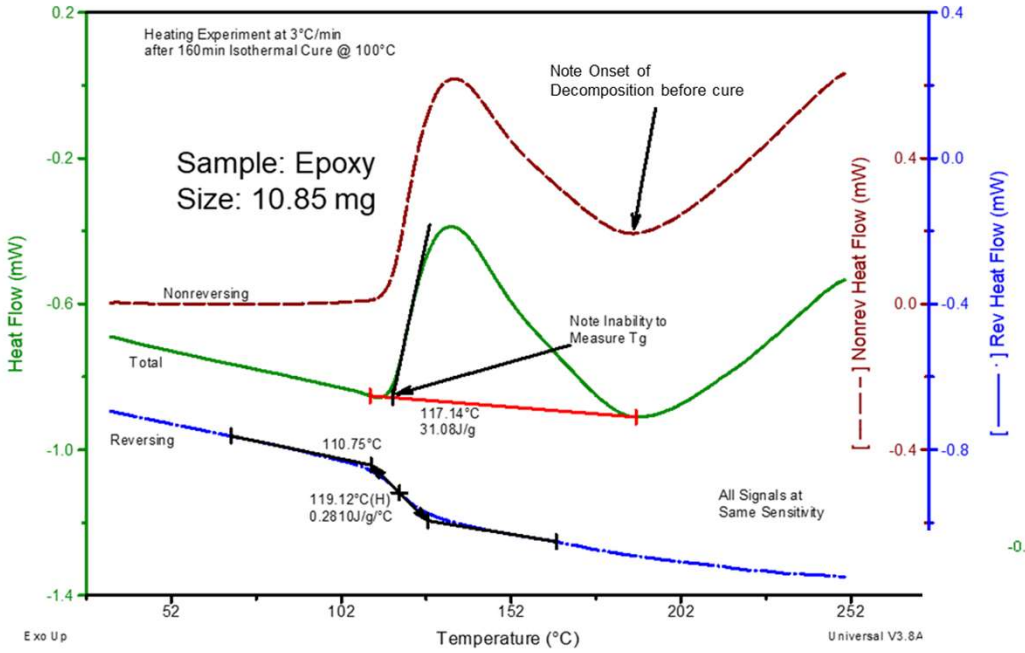


Interpreting MDSC® results

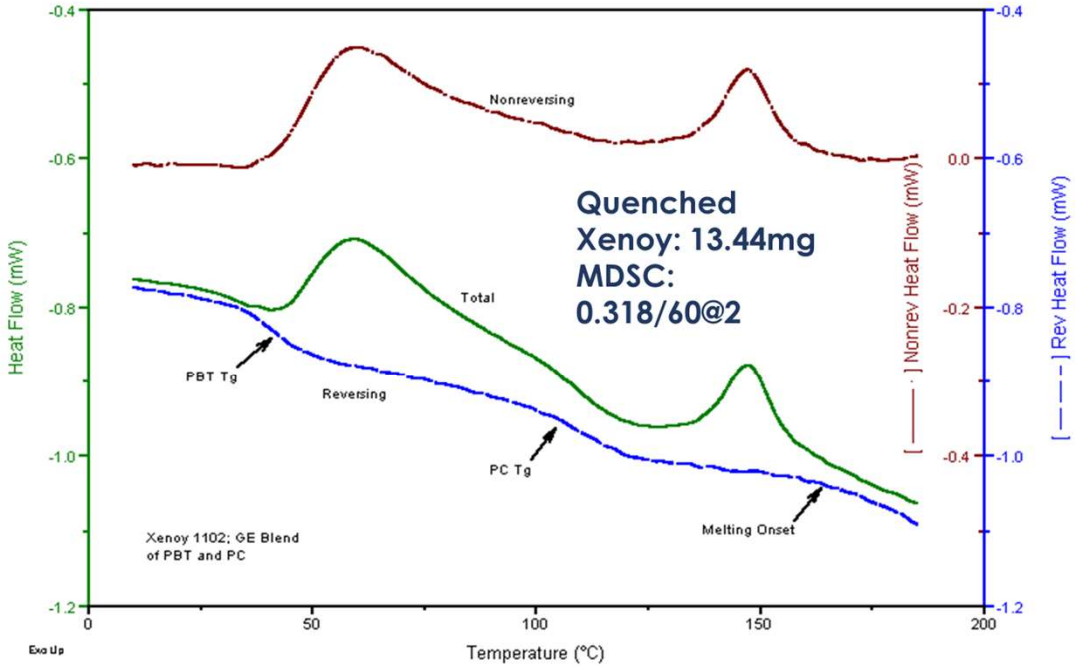


MDSC®

Tg on 1st heat of cure



Getting Tg's of a polymer blend

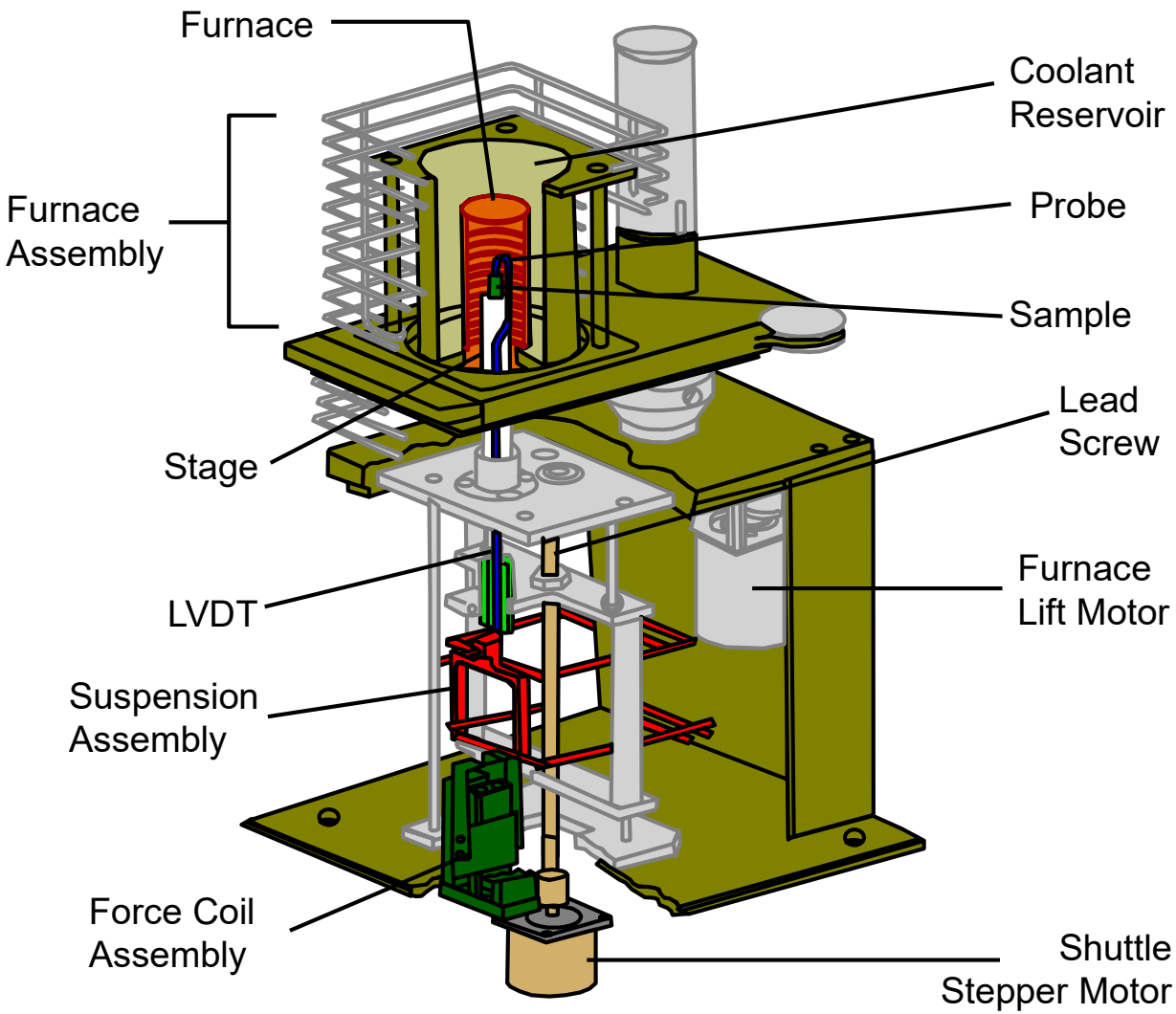


TMA

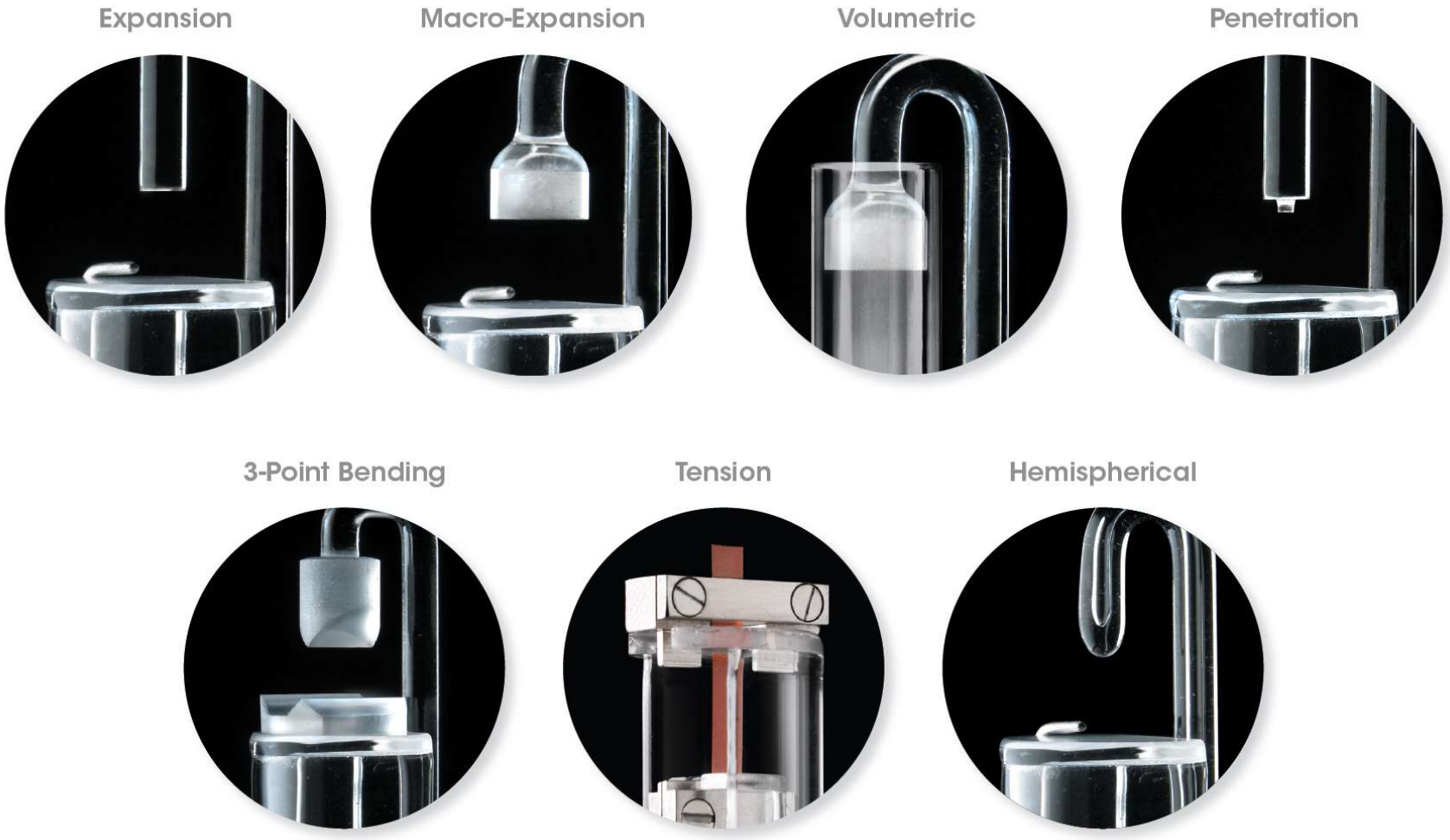
TMA: The Technique

- Thermo-mechanical Analysis measures changes in the dimensions of a sample as a function of time, temperature and force in a controlled atmosphere.
- TMA can measure Coefficient of Thermal Expansion (CTE), along with transitions such as the glass transition (Tg).
- Advance TMA allows for viscoelastic measurements.

TMA Schematic

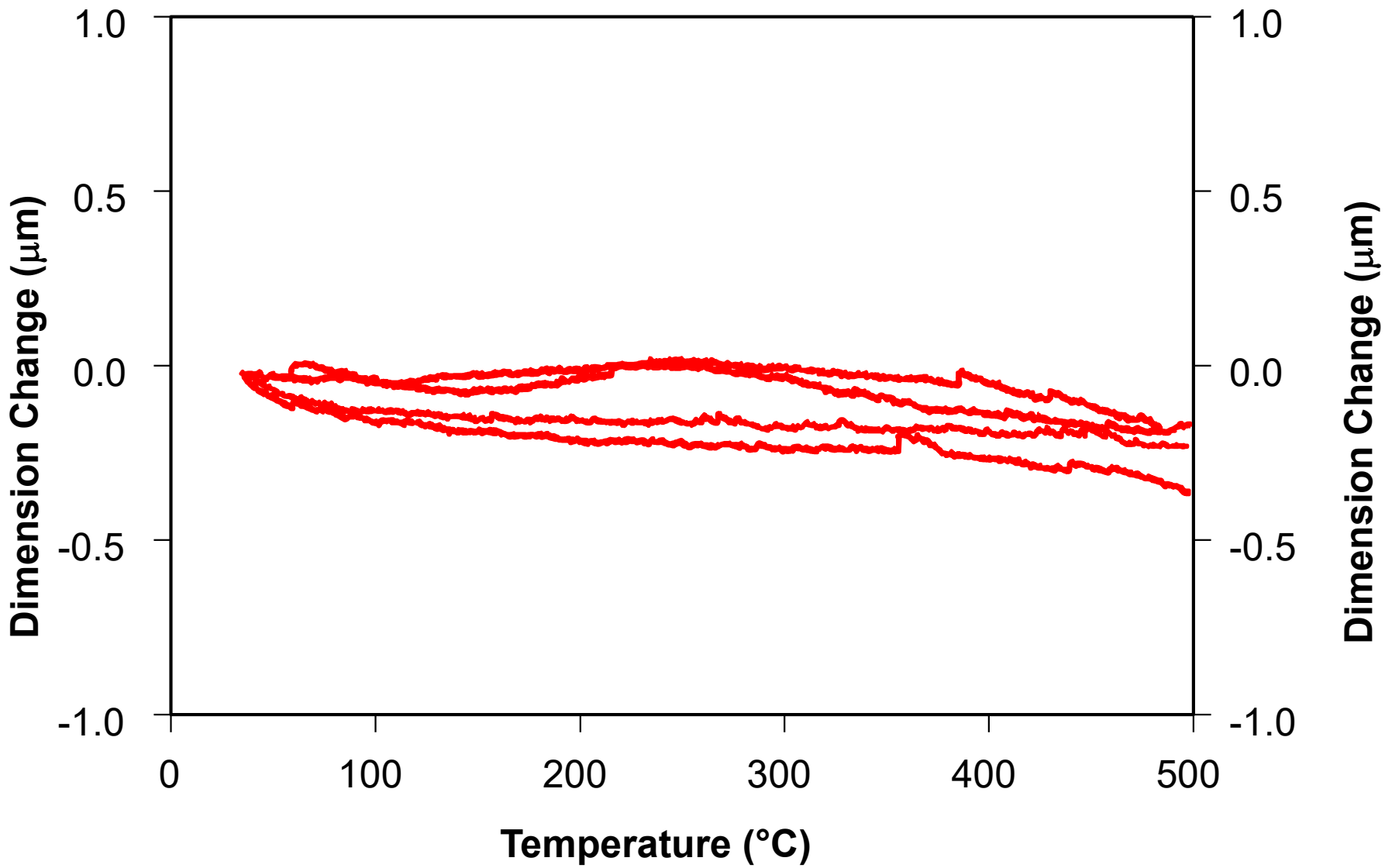


Sample Stage, Probes and Fixtures



The sample stage and probes are made of quartz and are optimized for an operational range of -150 °C to 1000 °C. Quartz is an ideal material because of its rigidity, inertness to corrosion, and very low thermal expansivity.

Baseline Performance



TMA: Structure – Function – Properties Relationship

Measure Dimensional Change Properties

- Change in Length
- Coefficient of Thermal Expansion (CTE)
- Softening Point
- Transition Temperatures
- Stress/Strain

Caused by:

- Formulation
- Molecular structure
- Degree of crystallinity or crosslinking
- Aging

Understand & Predict

- Compatibility
- Deflection Temperature Under Load
- Product Performance/Failure
- Structure Formation

Definition of Coefficient of Thermal Expansion (α)

- Differential or point definition

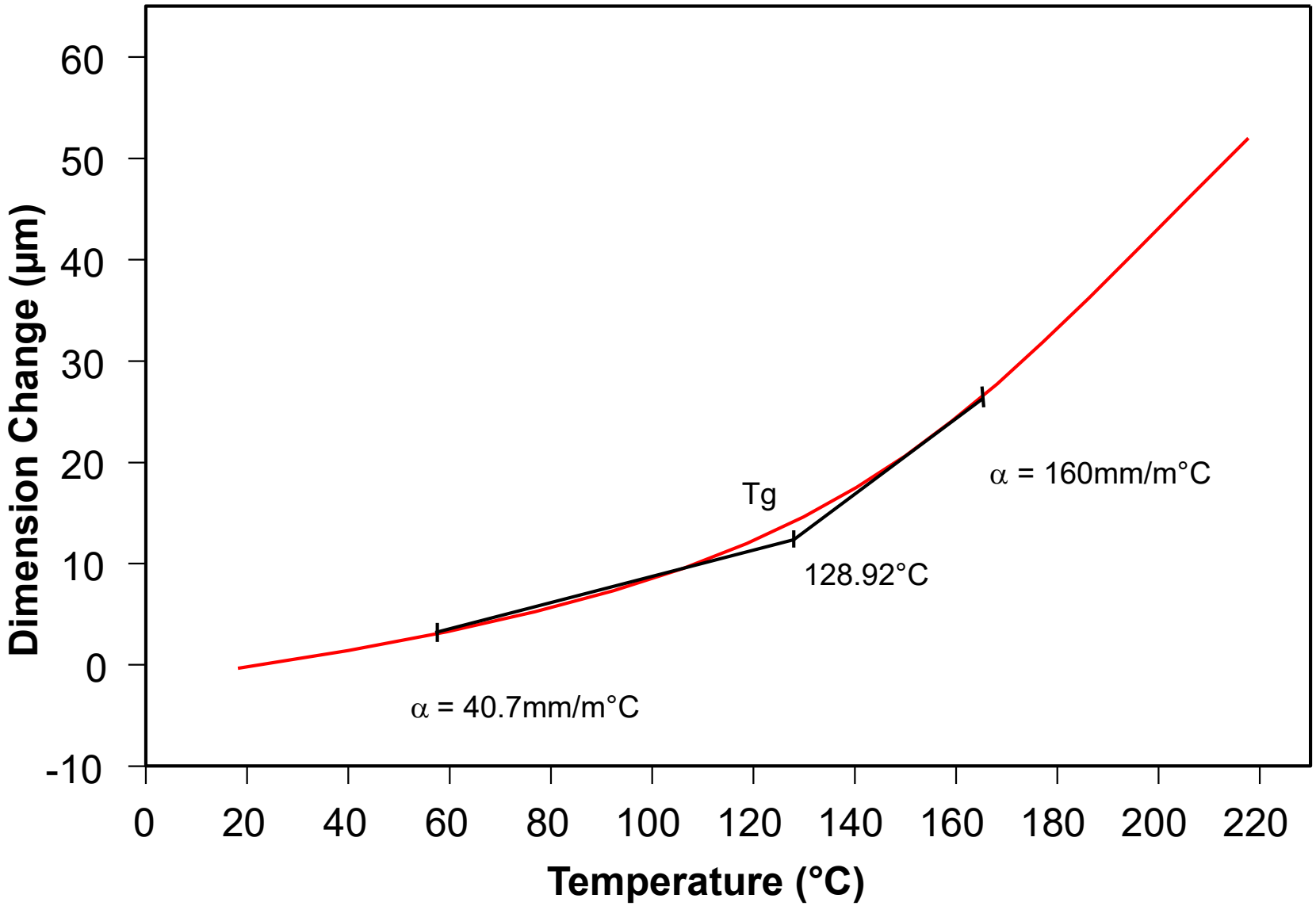
$$\alpha = \frac{1}{L_o}\frac{dL}{dT}$$

- Slope definition

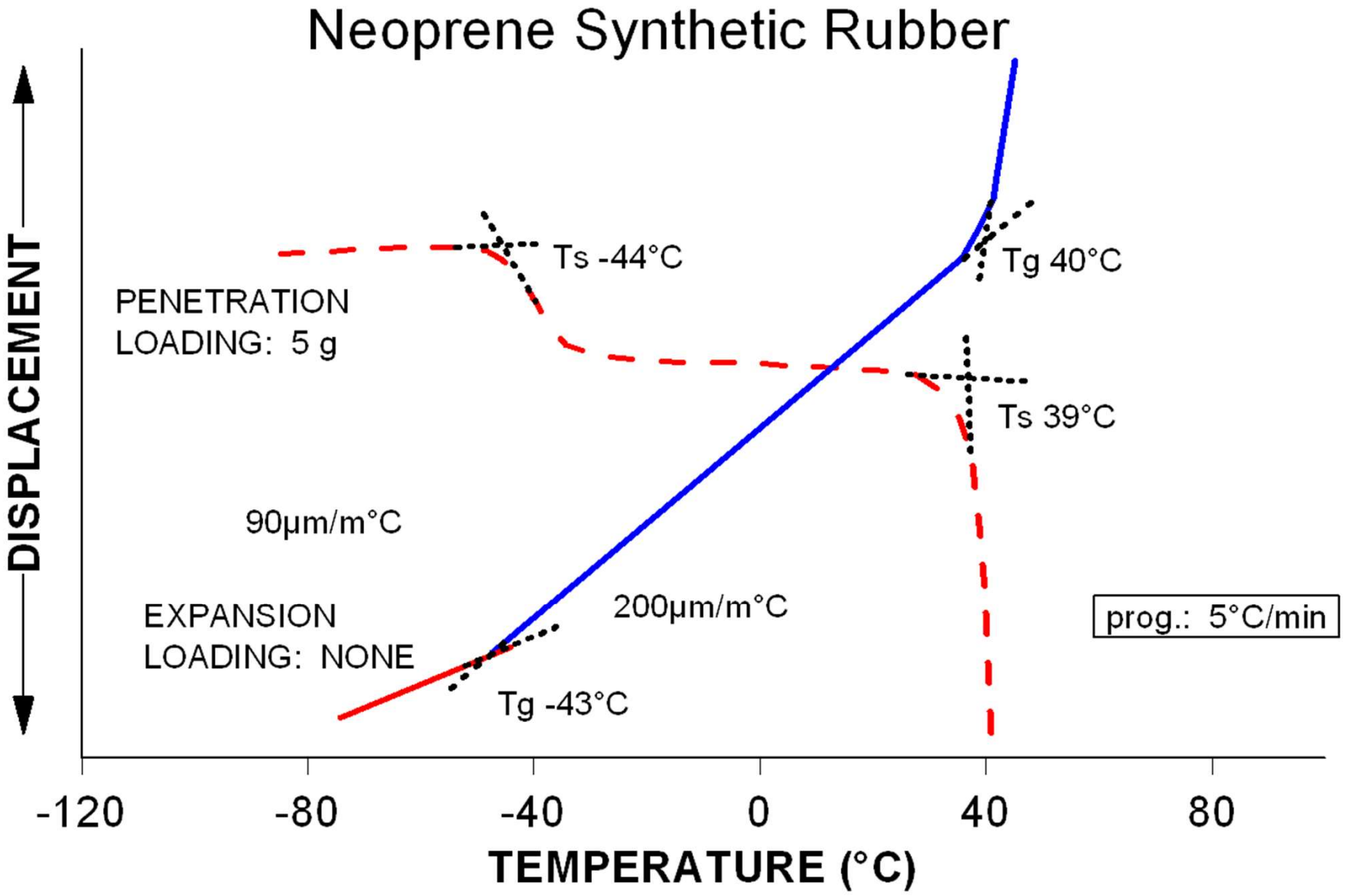
$$\alpha = \frac{1}{L_o}\frac{\Delta L}{\Delta T}$$

- Where Lo is the sample's initial length.

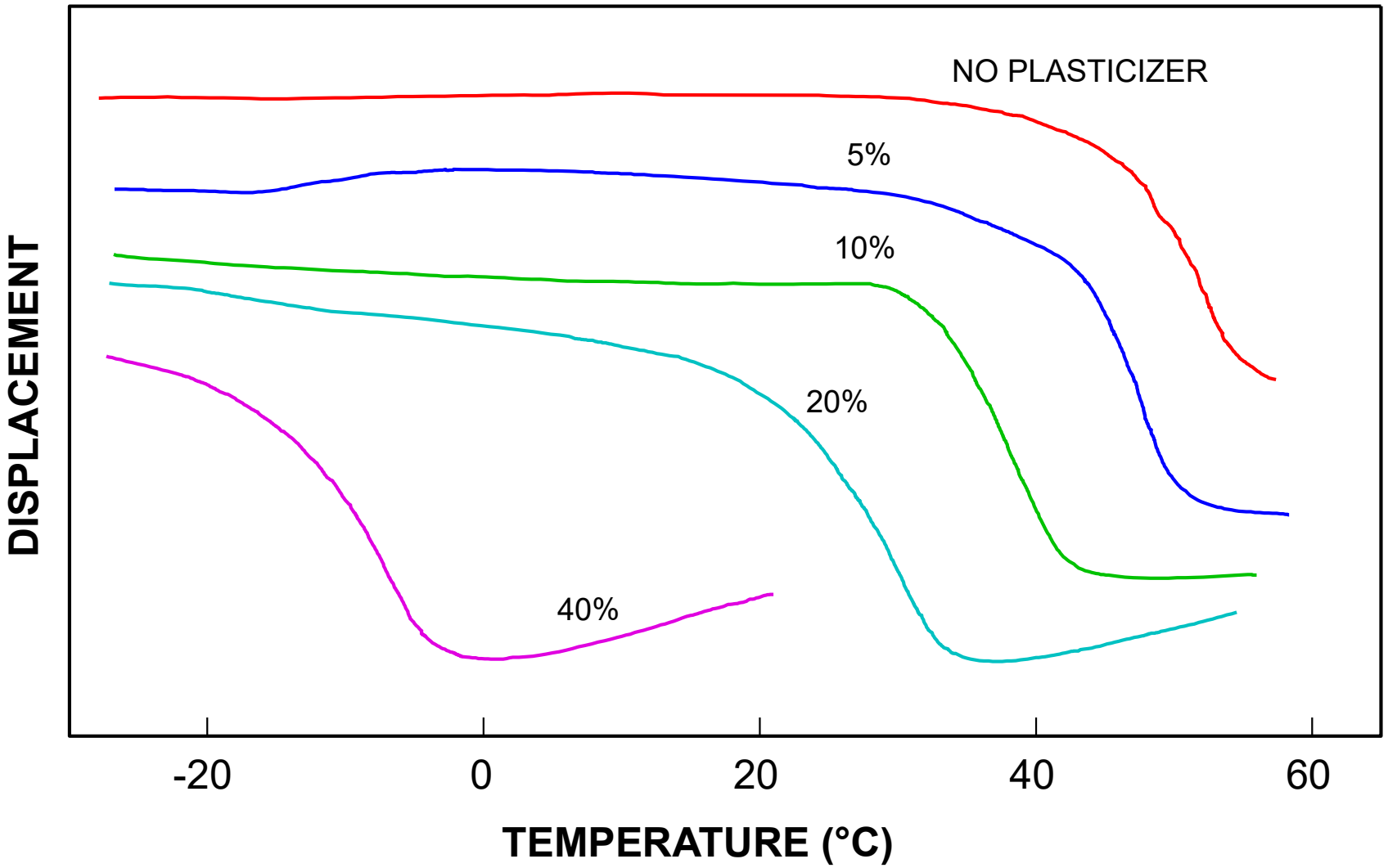
Expansion of PCB Laminate Sample – Expansion Probe



Glass Transitions and Softening Points

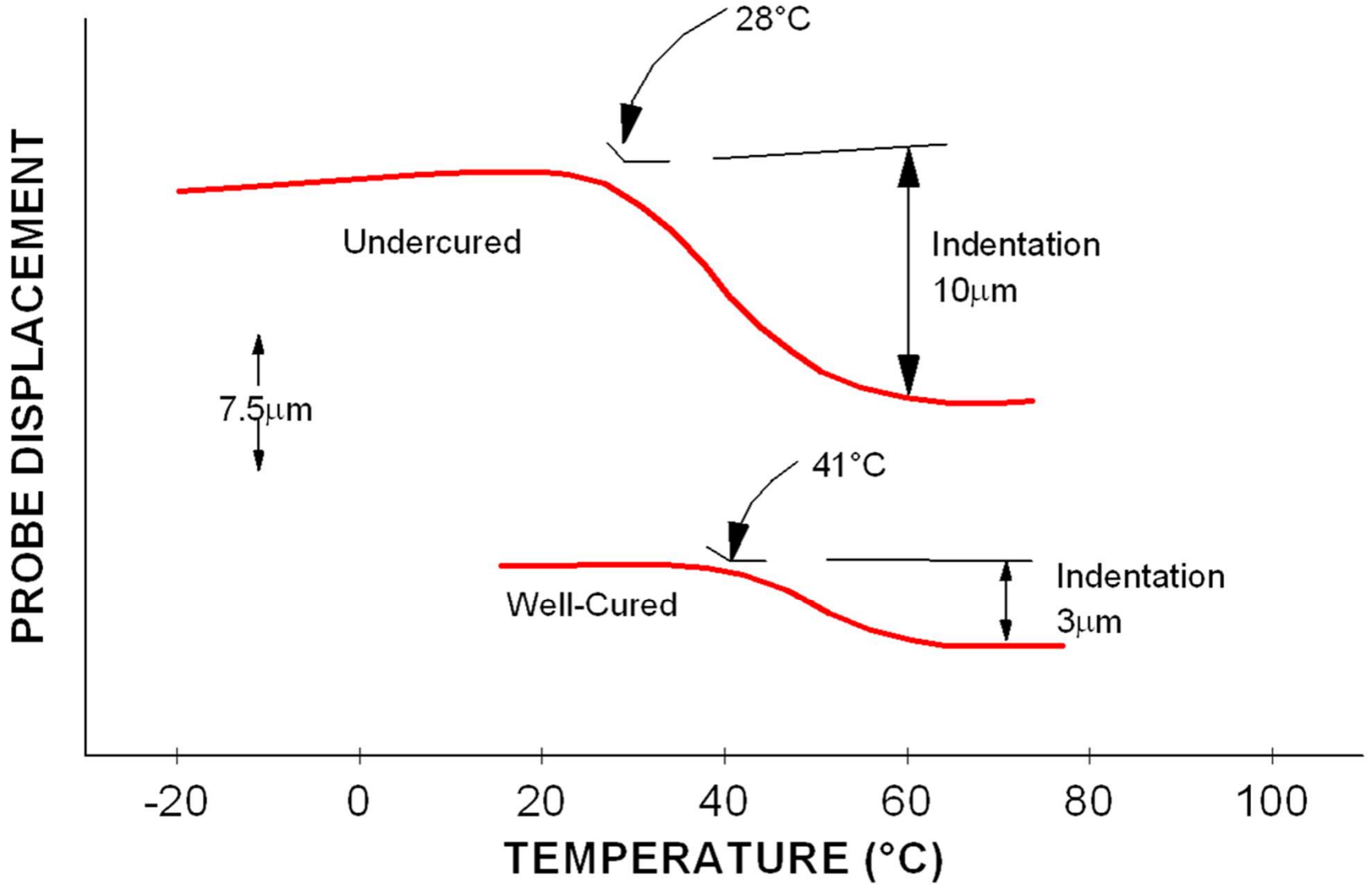


Plasticizer Effects on Polyvinylbutynal



Pollinger and Messing, Materials Science Research, 19
(Advanced Materials Characterization 2), (1985), pp 359-370

Softening of Acrylic Coating



Schoff & Kamarchik in Materials Characterization by Thermomechanical Analysis, ASTM STP, 1136, Riga and Neag Eds., ASTM, Phila., (1991), pp138-149

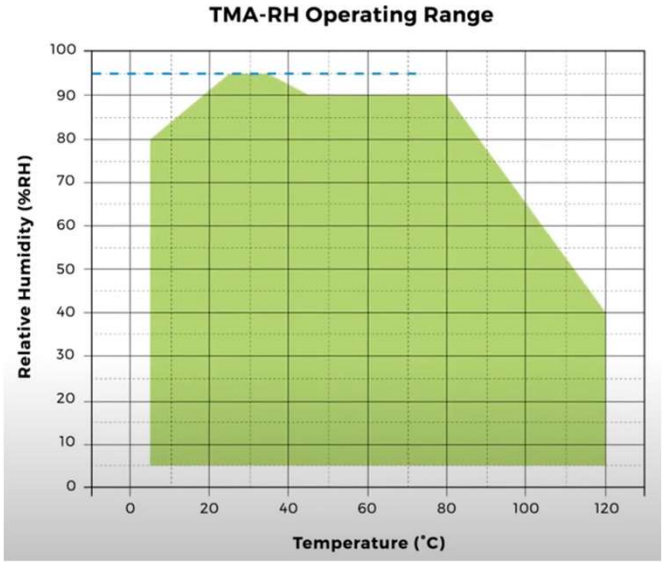
TMA 450 RH: System Components

The TMA 450 RH includes the following:

1. A fully engineered and integrated sample chamber specifically designed to provide the most precise temperature and humidity-controlled environment on the market.
2. The TMA RH Accessory that contains the gas humidifier and controls the flow of humidified gas to the sample chamber.
3. A heated vapor transfer line connecting the TMA RH Accessory to the sample chamber. The transfer line is maintained above the vapor dew point for transfer of the vapor without condensation.

Discovery TMA 450 RH: Features and Specifications

- Broadest range of RH and Temperature of any instrument on the market
- Extensive selection of low-expansion quartz fixtures providing industry leading baseline flatness for superior dimension change measurements
- Non-contact, friction-free motor delivers forces from 0.001N to 2N enabling measurements on the widest range of samples
- Advanced modes for dynamic, creep, stress relaxation, or isostrain experiments

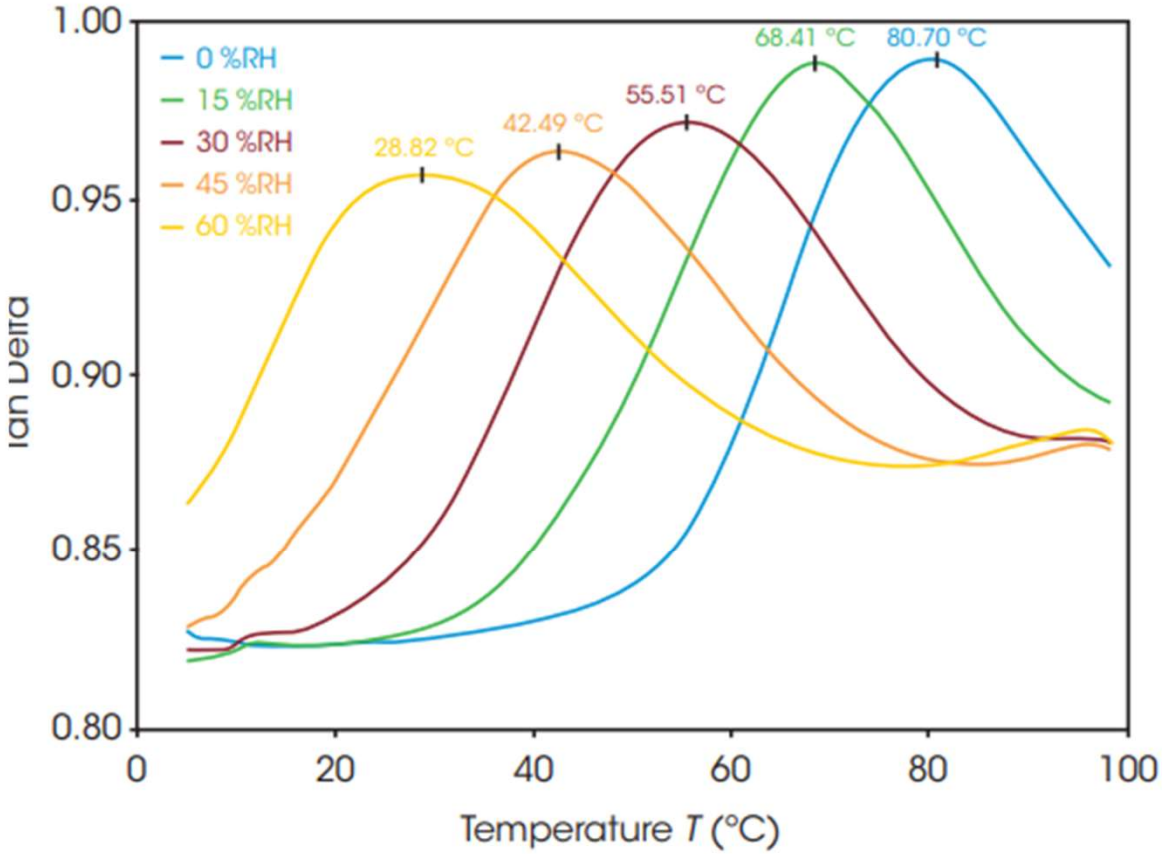


Temperature Range	5 – 120°C
Temperature Precision	±0.1°C
Heating/Cooling Rate	0.1 – 1°C/min
Humidity Range	5 – 95 % (see chart)
Humidity Accuracy	5 – 90% ±3% >90 – 95% ±5%
Humidity Ramp Rate	0.1 – 2 %RH/min
Maximum Sample Size	26 mm
Measurement Precision	±0.1%
Sensitivity	15 nm
Force Range	0.001 – 2 N

TRIOS

One Touch Away™

Effects of RH on Tg of Nylon



Thank You

The World Leader in Thermal Analysis,
Rheology, and Microcalorimetry