Welcome

COVALENT METROLOGY

OPTIMIZING MATERIALS WITH THERMOGRAVIMETRIC ANALYSIS (TGA) AND DIFFERENTIAL SCANNING CALORIMETRY (DSC)

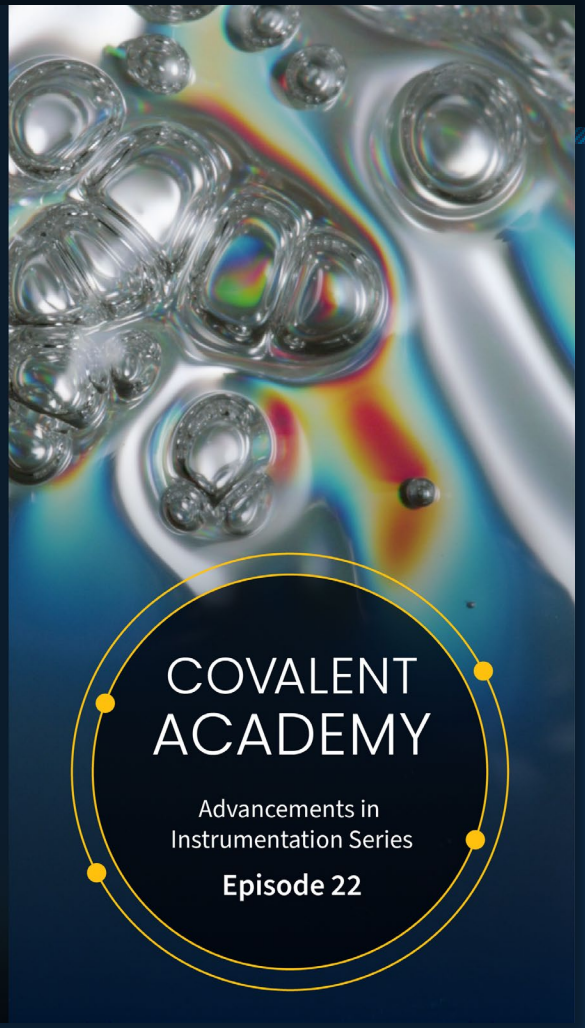
SPEAKER:

Parth N. Vakil, PhD
Applications Scientist,
TA Instruments

May 6, 2021 | 11AM PT

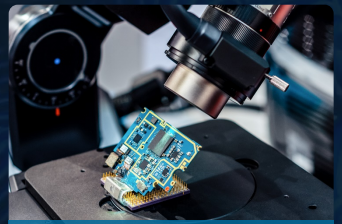
TA Instruments

COVALENT METROLOGY



COVALENT METROLOGY

Silicon Valley-based analytical labs and platform delivering quality data and expert analysis for advanced materials and device innovation



Comprehensive Solutions Stack

40+ cutting-edge instruments, offering 100+ Techniques

Analytical Services

Advanced Modeling

Method Development

Temp. Staffing Solutions

Affordable and Fast

Fast Turnaround Times, No Expedite Fees

Volume Savings

Instant Access to Data and Reports in Secure Portal

Flexible Business Model

Custom Consulting Solutions and Certified Onsite Support

Training and Certification on Instrumentation

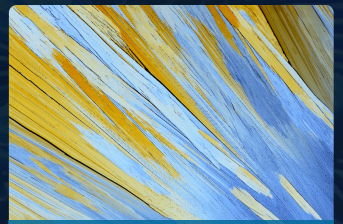
Co-op and Tool-Share Opportunities

Laboratory Audits

Rich Network of Partnerships & Collaborations

Partner to World's Leading Instrument Manufacturers and Labs

Expanding Instrumentation, Lab Connections and Learning



Who We Are, Who We Serve

500 Clients + 40-60 New Clients/ Quarter

40 People, 13 PhDs

Cutting-edge Analytical Capabilities

Lab Locations: Sunnyvale, Santa Clara

Covalent Technical Groups and Organization

COVALENT METROLOGY

PCBA, Semiconductor, and Electronic Device Metrology & Failure Analysis

- DPA / Mechanical Cross-section
- Dye & Pry Test
- Hot Spot Detection
- IR Imaging / Emission Microscopy
- Root-Cause Failure Analysis
- EBIC / OBIC failure analysis

+ many more advanced methods!

Electron / Scanning Probe Imaging & Microscopy

- SEM (+EDS)
- FIB-SEM (+EDS)
- S/TEM (+EDS / +EELS)
- AFM & Advanced AFM Modes
- Scanning Acoustic Microscopy (SAM)

Optical Microscopy & Spectroscopy

- Laser Scanning Confocal
- White Light Interferometry
- Chromatic Aberration
- Digital Optical Microscopy
- Spectral Ellipsometry
- UV-Vis-NIR Spectroscopy

X-Ray Characterization

- X-Ray Diffraction
- X-Ray Reflectometry
- Micron-spot ED-XRF
- WDXRF
- Micro-CT
- 2D X-ray Inspection & X-ray Radiography

Chemical Analysis

- ICP-MS & LA-ICP-MS
- GC-MS
- FTIR
- Raman
- NMR (1D or 2D; solid-state and solution-state)
- EPMA

Nanoparticle Analysis

- Dynamic Light Scattering (DLS)
- Laser Diffraction Particle Size Analysis (PSA)
- Particle Zeta Potential

Material Property Characterization

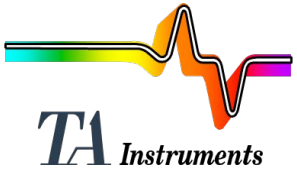
- DSC
- TGA
- DMA & TMA
- Rheometry
- Surface Zeta Potential
- Nanomechanical Analysis
- Tensile-Test
- Taber Test

Surface Analysis

- X-ray Photoelectron Spectroscopy (XPS)
- Ion Scattering Spectroscopy (ISS)
- Ultraviolet Photoelectron Spectroscopy (UPS)
- ToF-SIMS (Static-SIMS)
- Dynamic-SIMS

Who is TA Instruments?

1960's to 1990



1990

1996

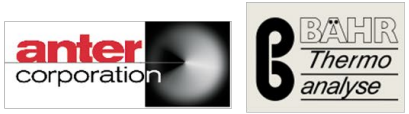
1992

2008

2006

2003

2007



2011

2013

- Global market leader in thermal analysis, thermophysical properties, microcalorimetry and rheology
- Headquarters in Delaware (DE)

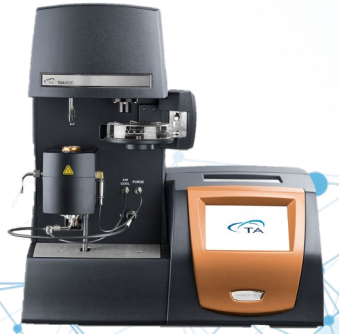
Characterization Solutions Offered by TA Instruments

- Differential Scanning Calorimetry (DSC)
  - Modulated DSC®
- Thermogravimetric Analysis (TGA)
- Dynamic Mechanical Analysis (DMA)
- High Force Mechanical Analysis/ High Force DMA or Load Frames
- Rheology (including Rubber)
- Thermomechanical Analysis (TMA)
- Vapor Sorption Analysis (SA)
- Microcalorimetry (NanoDSC and Isothermal Titration Calorimetry (ITC))
- Flash Diffusivity
- Thermal Conductivity
- Dilatometry

Parth N. Vakil, PhD

Applications Support Engineer II,
TA Instruments

- Applications Engineer / Applications Scientist with TA Instruments
- Engineering bachelor's degree from the University of Toronto (Canada) with a focus in Nano-engineering
- During his undergraduate studies, interned with Sanofi Pasteur's Analytical R&D Unit and participated in summer research positions at the University of Toronto and McGill University
- Materials Chemistry PhD degree from Florida State University in the Strouse Lab
- Work at TA supports the sales teams and current TA customers, assisting them with multiple material analysis instrumentation/methods including DSC, TGA, TMA, SDT (simultaneous DSC and TGA), Sorption Analysis, DMA, and Rheology



Optimizing Polymers and Adhesive Materials with Thermogravimetric Analysis and Differential Scanning Calorimetry

Presenter: Dr. Parth N. Vakil (TA Instruments – Waters LLC)

Date: 6 May 2021

Differential Scanning Calorimetry (DSC)

COVALENT METROLOGY

Differential Scanning Calorimetry

A DSC measures the **difference** in Heat Flow Rate between a **sample** and inert **reference** as a function of time and temperature; typically associated with a phase change in a material.

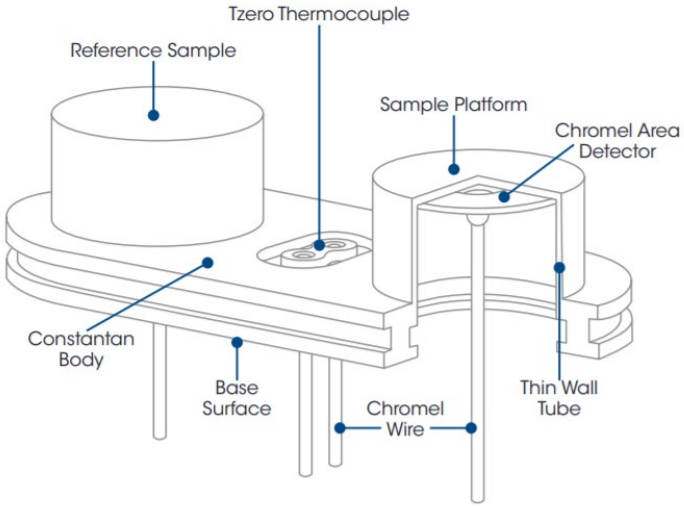
$$\frac{dH}{dt} = Cp\frac{dT}{dt} + f(T, t)$$

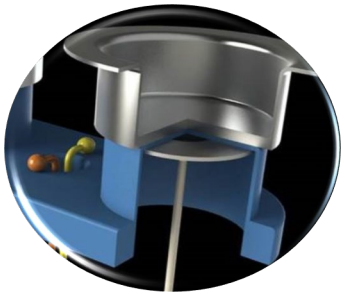
Heat Capacity

- Glass Transition

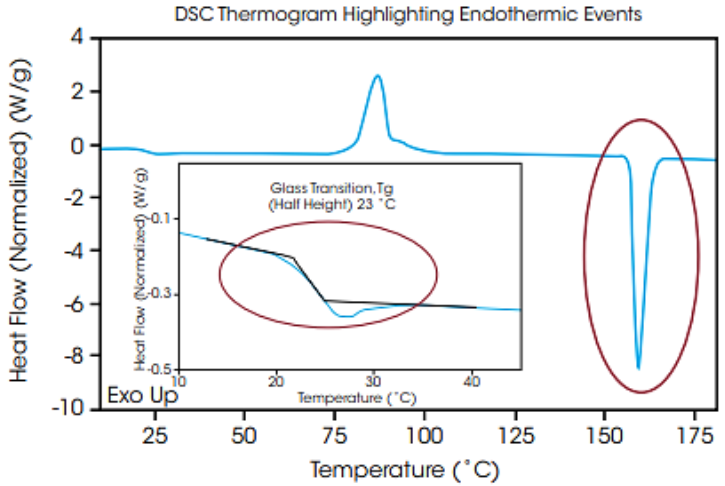
Kinetic

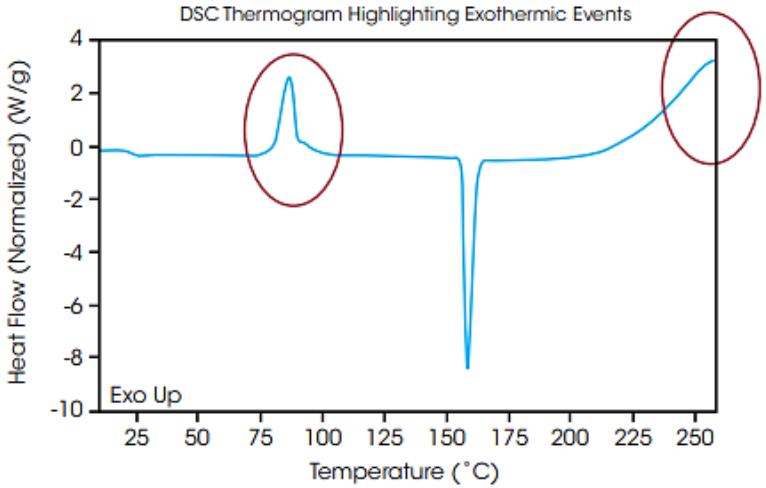
- Crystallization
- Cure reactions
- Volatilization
- Decomposition
- Denaturation





Exchange of Heat Due to Phase Changes





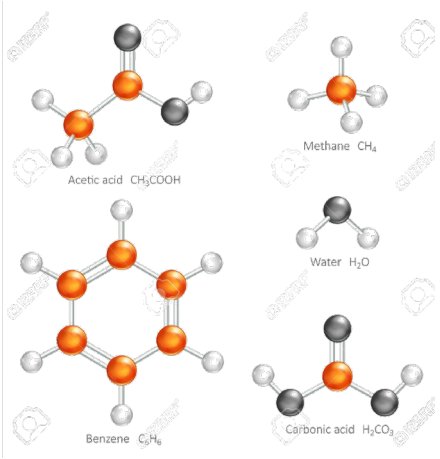
Endothermic Events

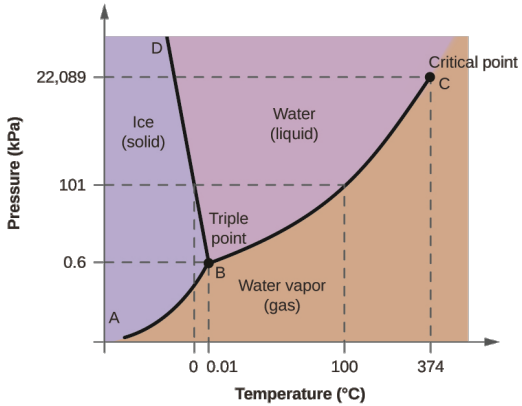
- Glass Transition
- Melting
- Evaporation/Volatilization
- Enthalpic Recovery
- Polymorphic Transitions
- Some Decompositions

Exothermic Events

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

DSC: 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

Instrument Hardware and Gas Selection Considerations

Temperature Range Dependent On The Cooling System

- RCS90: -90°C to 550°C

Purge Gas Selection

- **Nitrogen**
  - inert, inexpensive and readily available
  - flow rate of 50ml/min
- **Helium**
  - a high thermal conductivity gas which improves response time and cooling capabilities
  - the recommended purge gas when using the LN2 accessory at temperatures below -100°C
  - flow rates of 10-25ml/min are typically used; cell constant affected by flow rate
- **Air/Oxygen**
  - used when studying oxidative stability of materials

Sample Press and Pan Selection

- Aluminum: max. temperature of 600°C
- Gold
- Copper
- Graphite, Alumina
- Platinum
- Stainless Steel

Tzero™ Heat Flow Equation

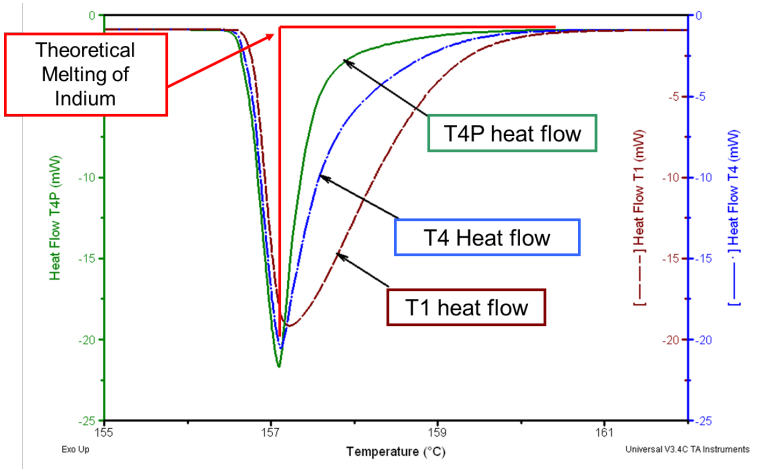
$$q_{T4} = -\frac{\Delta T}{R_r} + \Delta T_0\left(\frac{1}{R_s} - \frac{1}{R_r}\right) + (C_r - C_s)\frac{dT_s}{d\tau} - C_r\frac{d\Delta T}{d\tau}$$

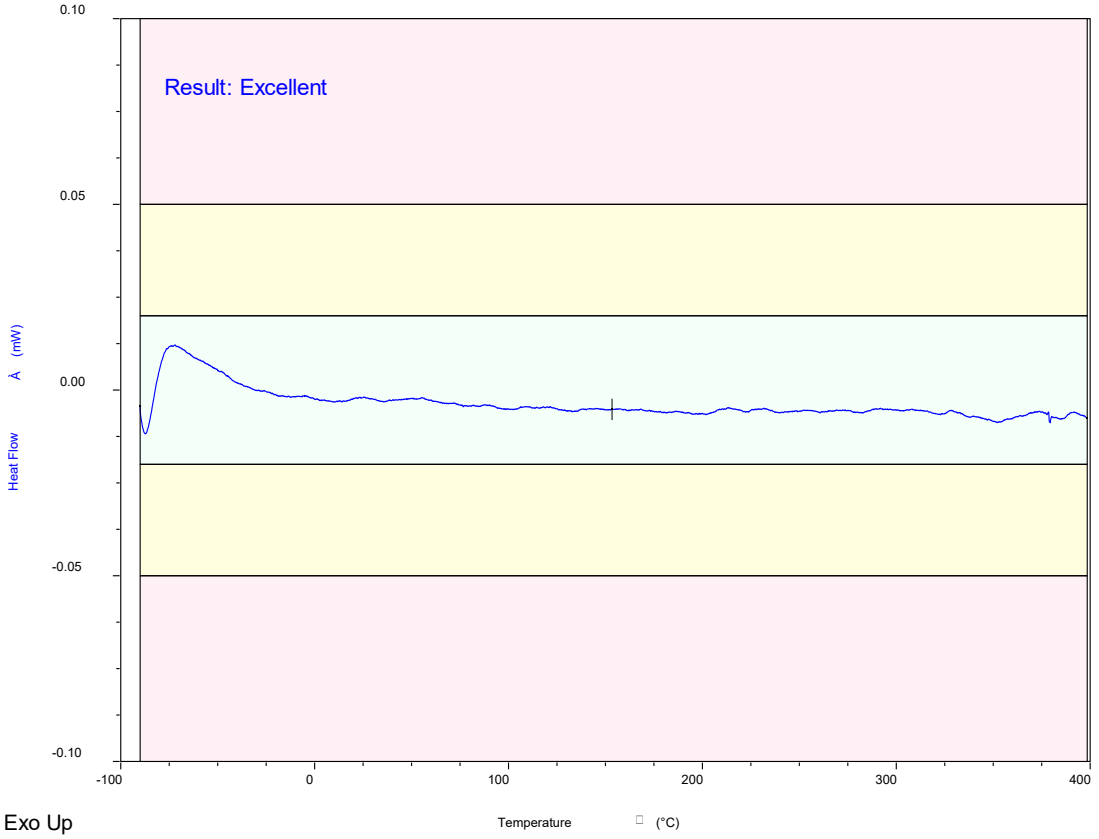
Thermal Resistance Imbalance

Heating Rate Difference

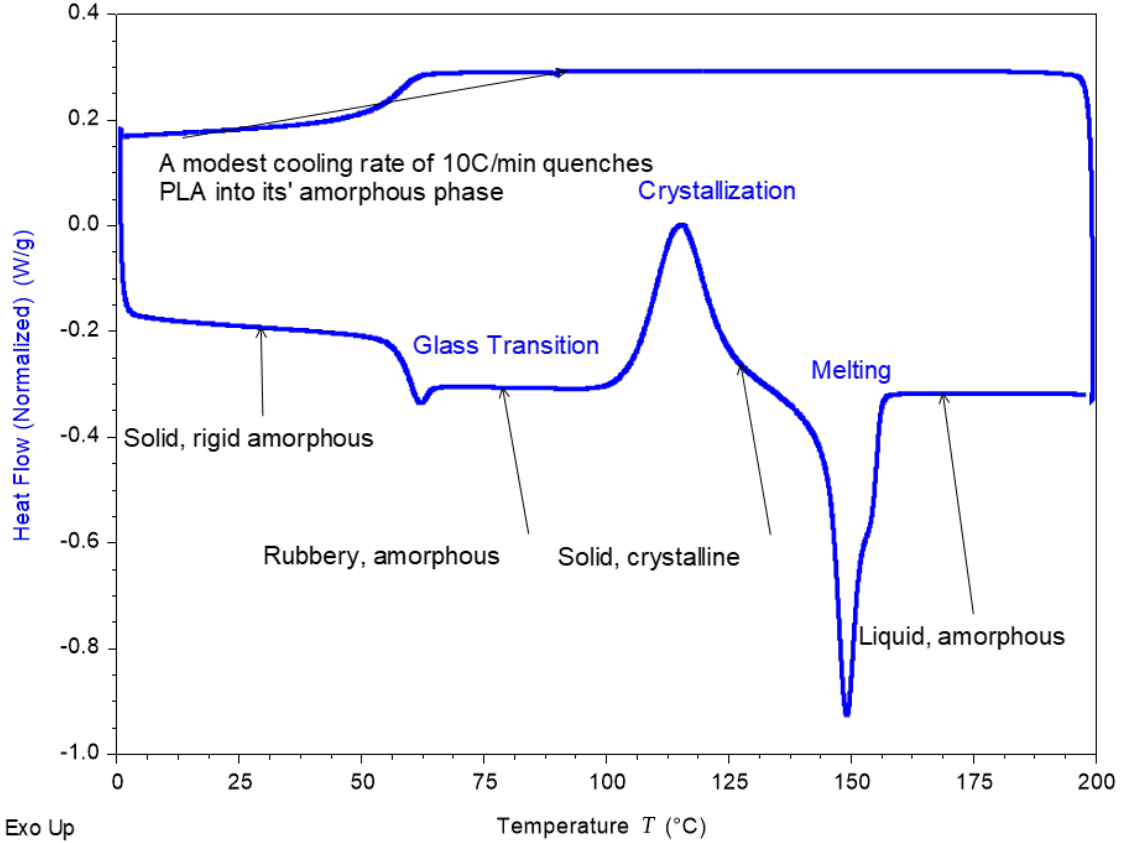
Principal DSC Heat Flow

Heat Capacity Imbalance

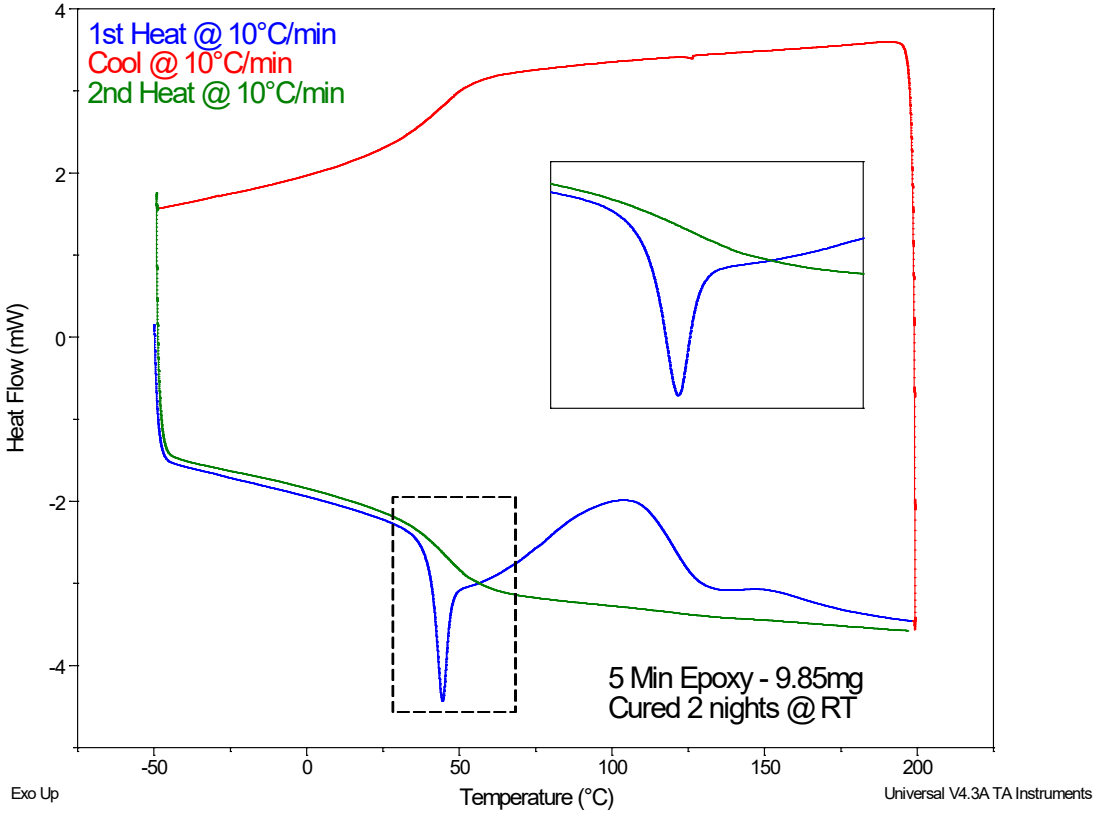




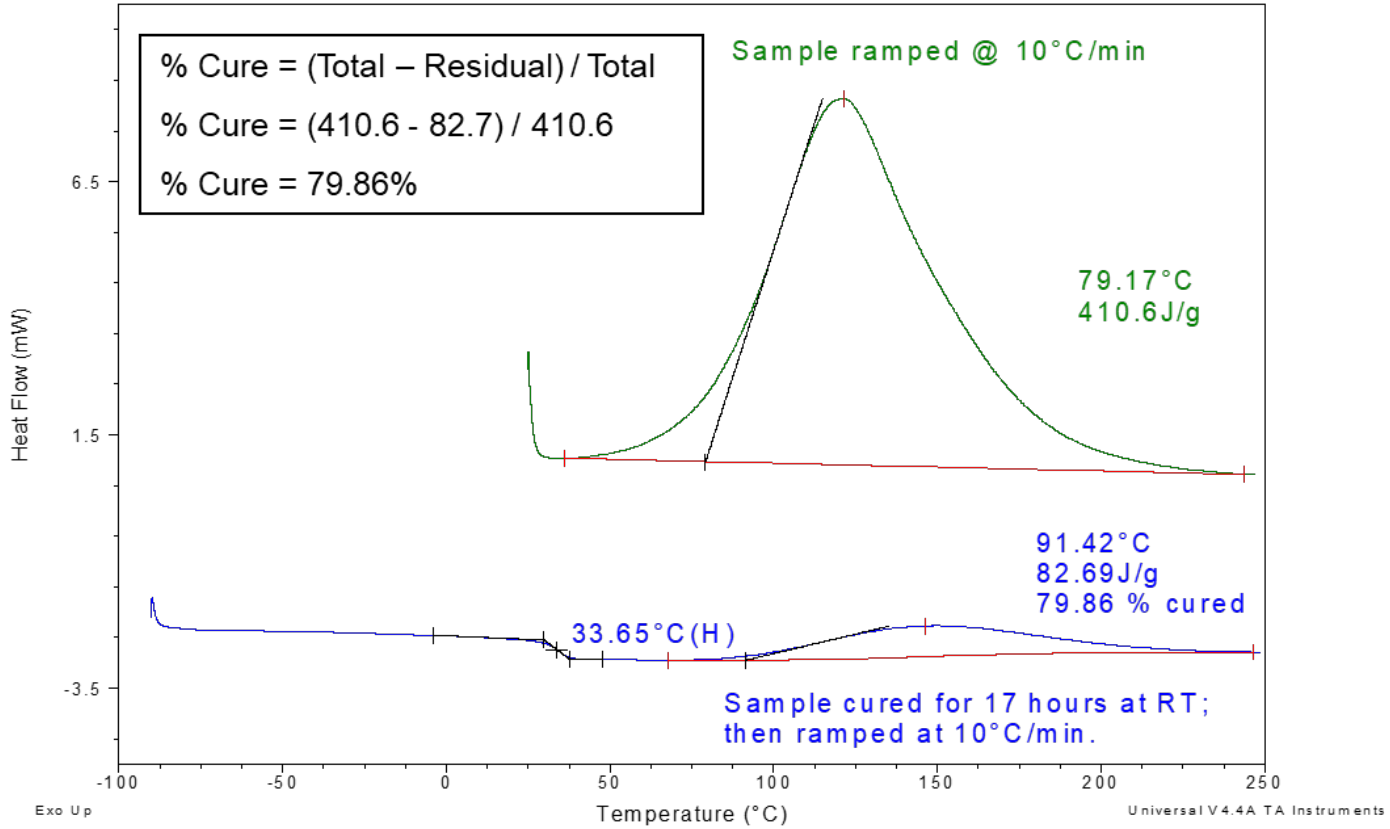
DSC Analysis of Polylactic Acid (PLA)



Epoxy Cured 48 Hours: Heat Cool Heat



Calculation of % Cure: An Epoxy



MDSC® Theory: Heat Flow Signals

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

Total Heat Flow

- All Transitions

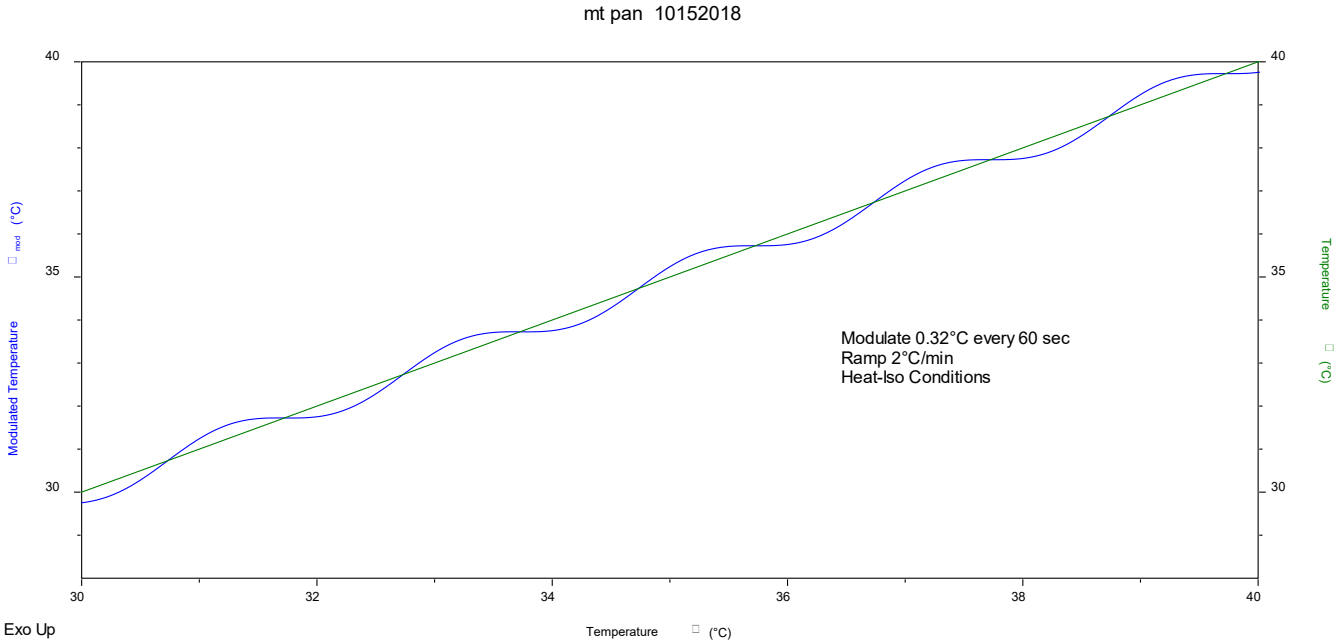
Reversing Heat Flow

- Heat Capacity
- Glass Transition
- Melting

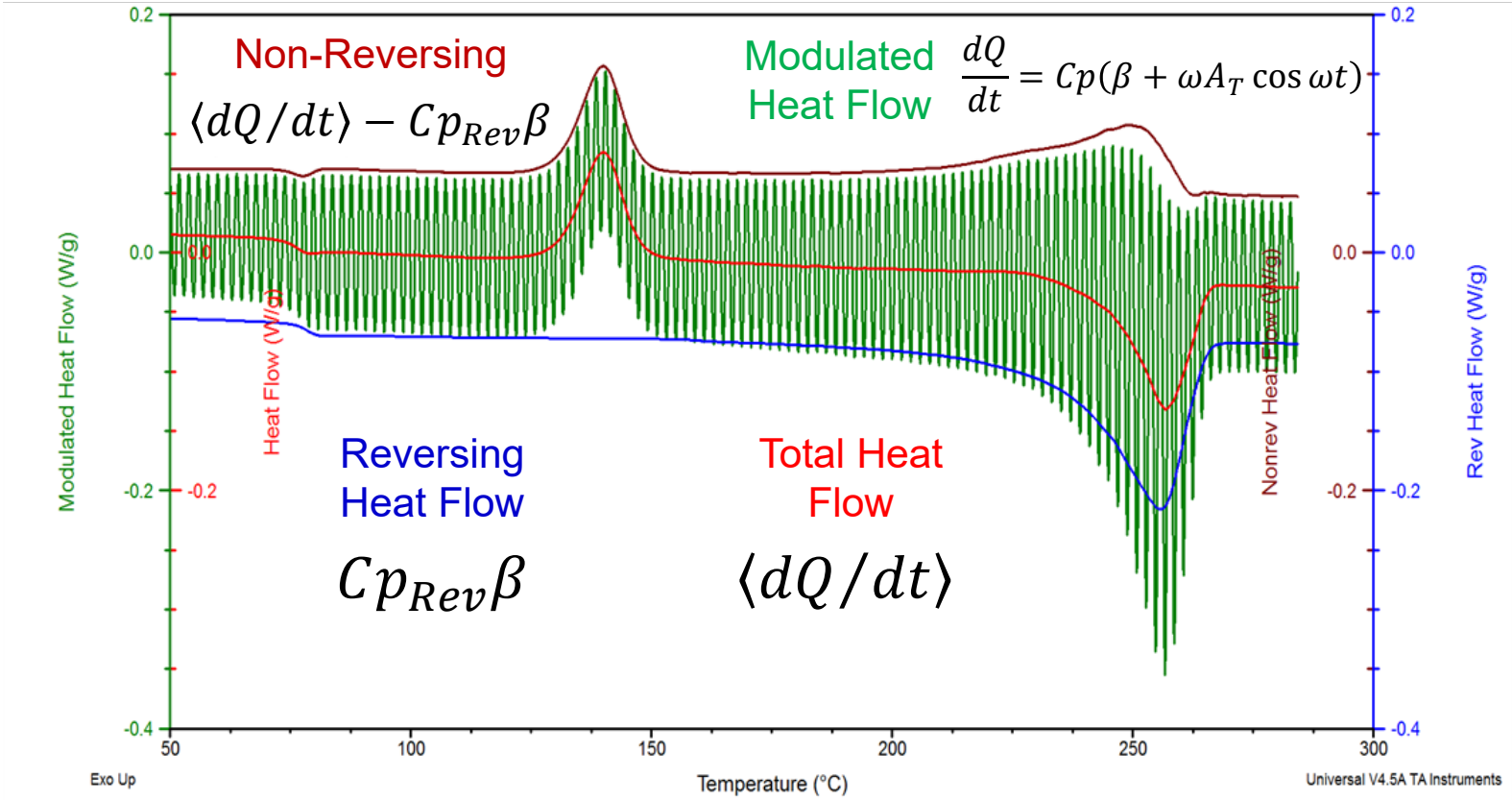
Non-Reversing Heat Flow

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

Average & Modulated Temperature



MDSC® Theory: Calculated MDSC® Heat Flow Signals

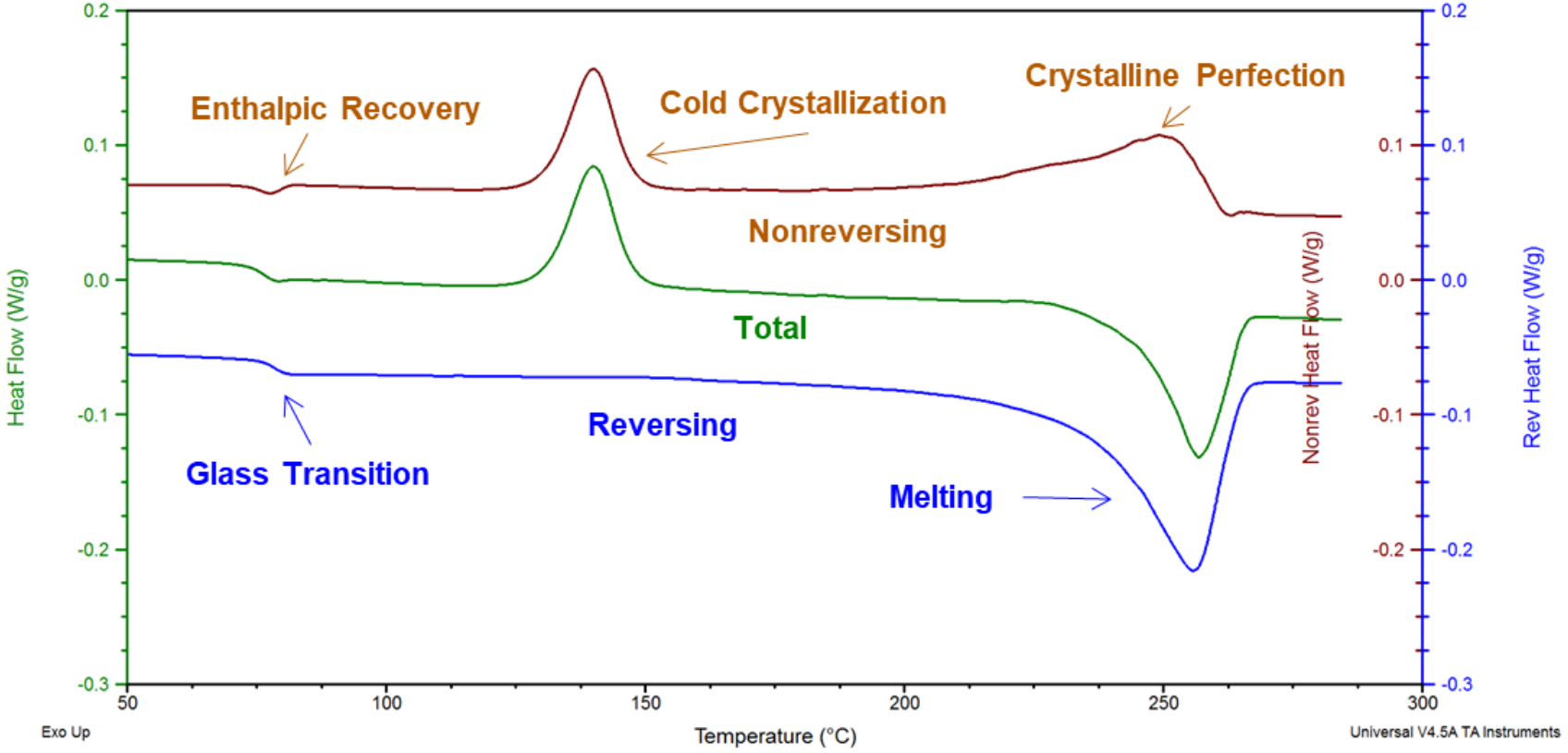


When & Why to Use MDSC?

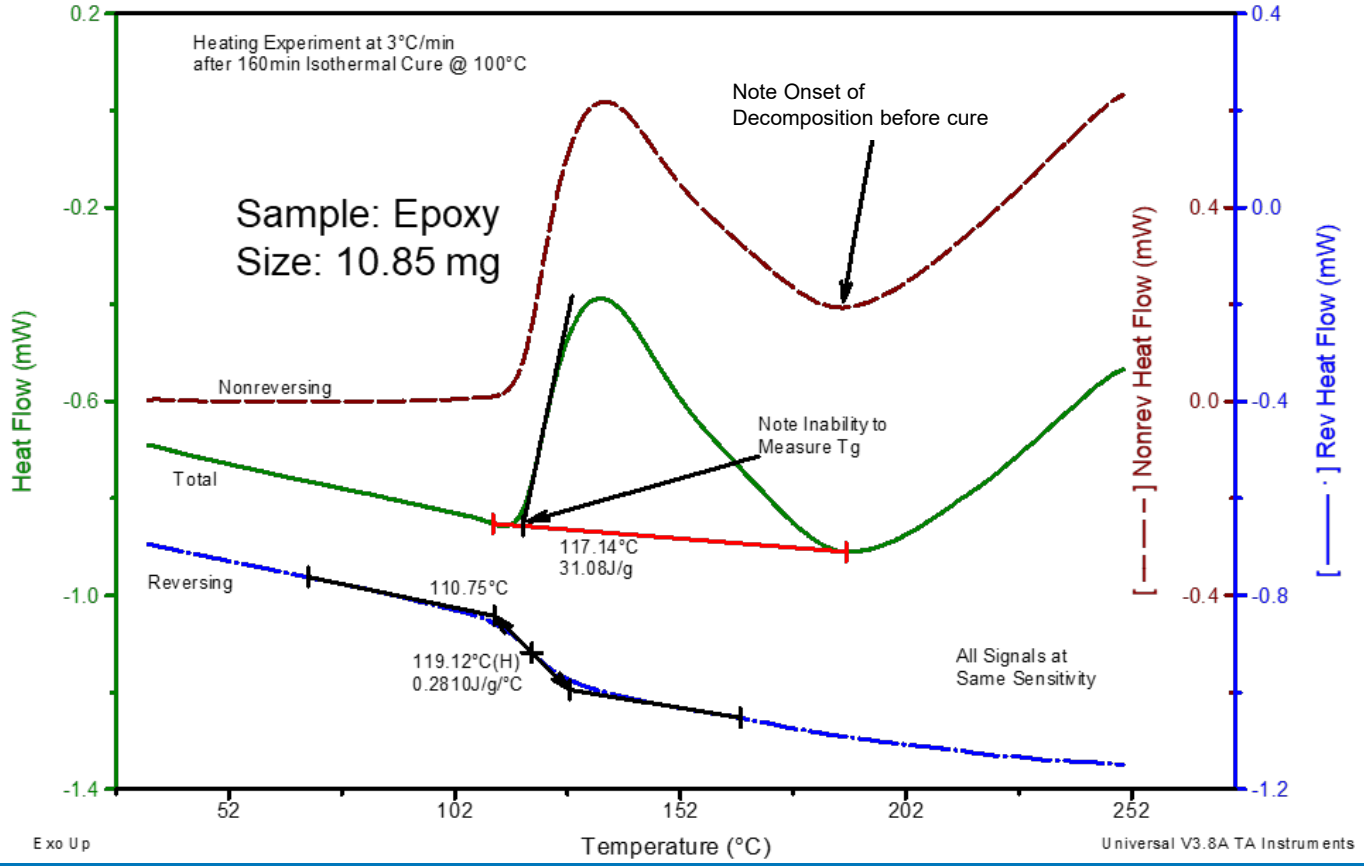
- Run a conventional DSC experiment @ 10°C/min first
  - It may provide all of the information you need.

- Reasons to run MDSC:
  1. Identify heat capacity and kinetic transitions
  2. Separate overlapping thermal transitions
  3. Detect weak glass transitions
  4. Most accurate determination of polymer crystallinity
  5. Accurate measurement of heat capacity in a single experiment
  6. Gain insight into structural change
  7. And many others…

Interpreting MDSC® results



Advantage of MDSC® for Post Cure Scan



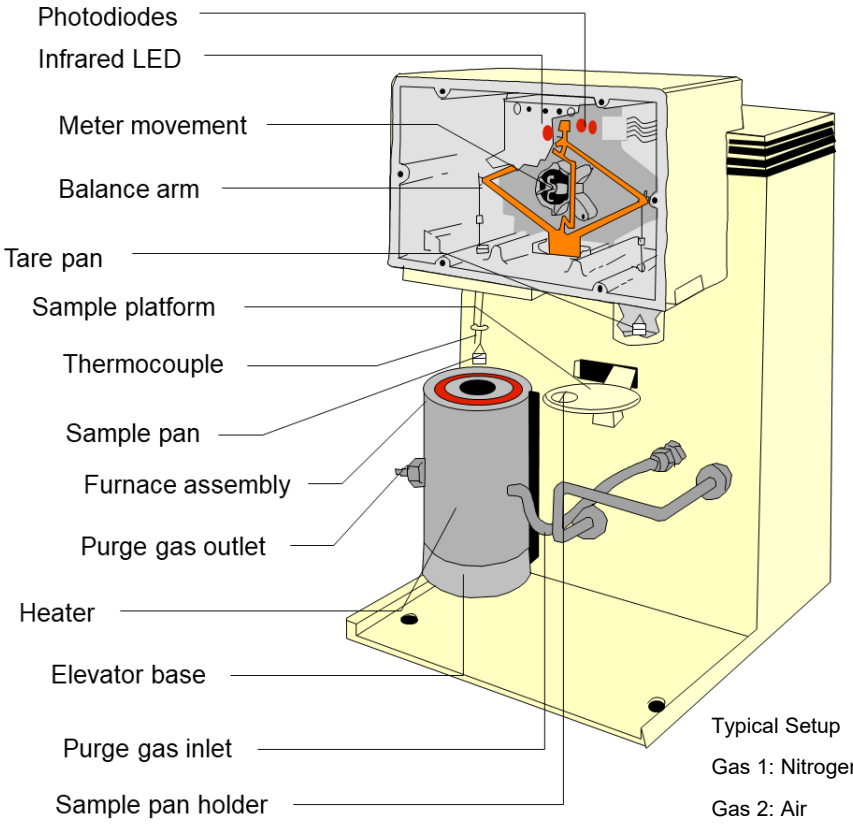
Thermogravimetry Analysis (TGA)

COVALENT METROLOGY

What is Thermogravimetric Analysis (TGA)?

- TGA measures weight / mass change (loss or gain) and the rate of weight change as a function of temperature, time and atmosphere.

Discovery Series TGA 5500 (IR furnace)

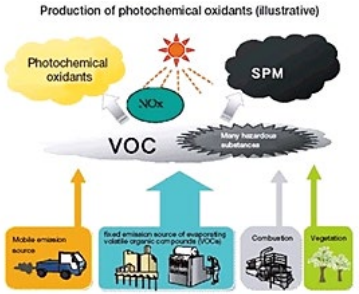


Typical Setup

Gas 1: Nitrogen

Gas 2: Air

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

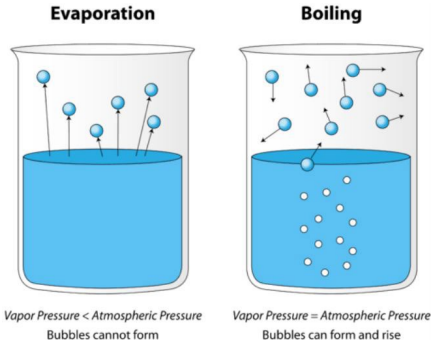
- Formulation
- Molecular Weight & Distribution
- Molecular Structure
- Concentration
- Atmosphere

Understand & Predict

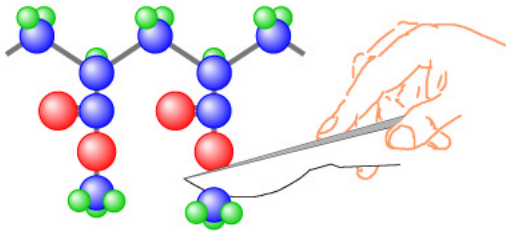
- Processing Limits
- Chemical Nature
- Product Performance
- Volatile Organic Content
- Storage Stability
- Useful Lifetime

Weight Change: Mechanisms

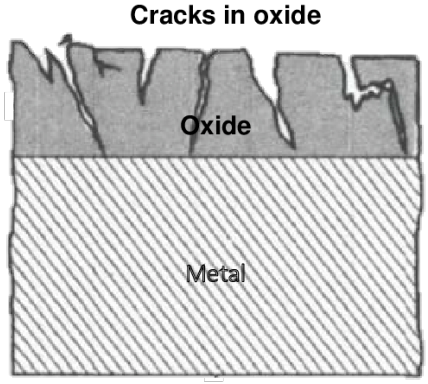
- Upon heating, all materials will eventually at some temperature lose mass. It is also possible, though less common, to gain mass on heating. Mechanisms of weight change on heating include:



Loss of Adsorbed or Absorbed Water or Solvent



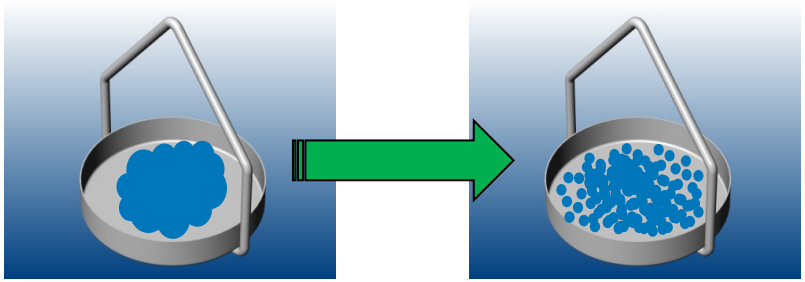
Bond Breaking = Decomposition

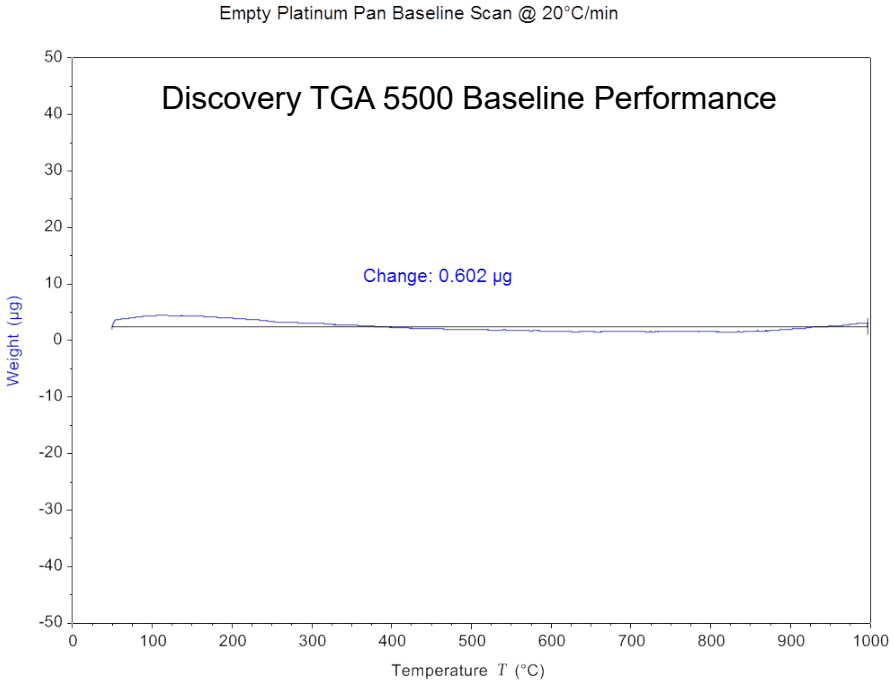


Oxidation/Corrosion/ Surface Reactions

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

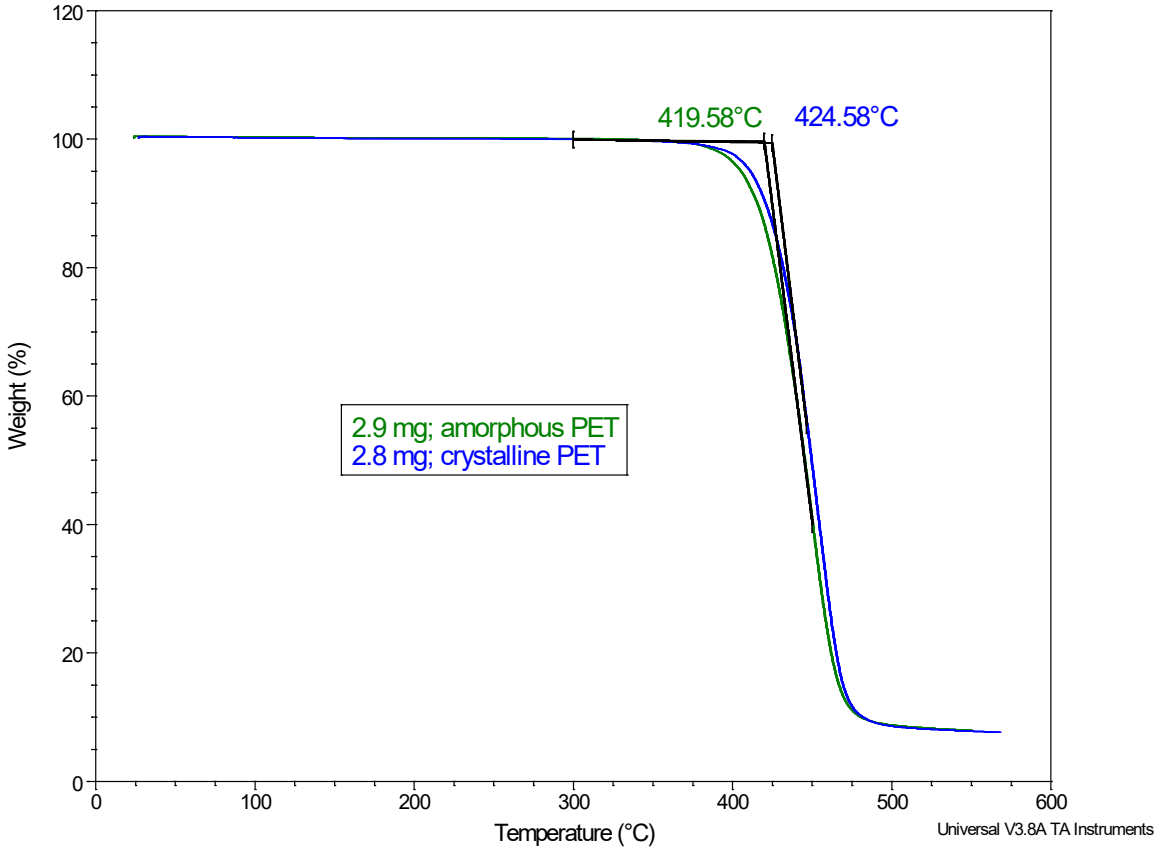
TGA: Sample Preparation



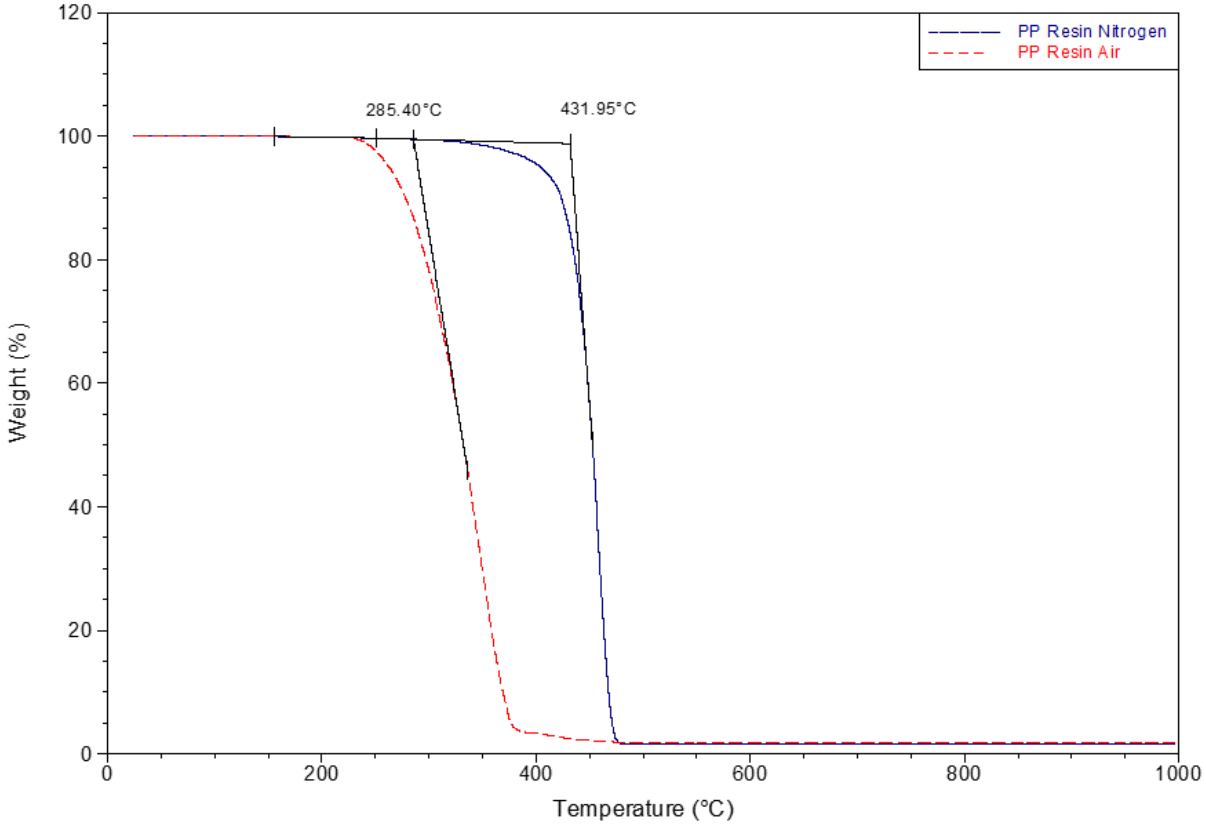


- Pan type
  - Platinum pan
  - Ceramic Pan
- Sample mass
  - 10-20mg for most applications
  - 50-100mg for measuring volatiles or residues
- If a TGA has a baseline drift of +/- 10ug then this is 0.1% of a 10mg sample

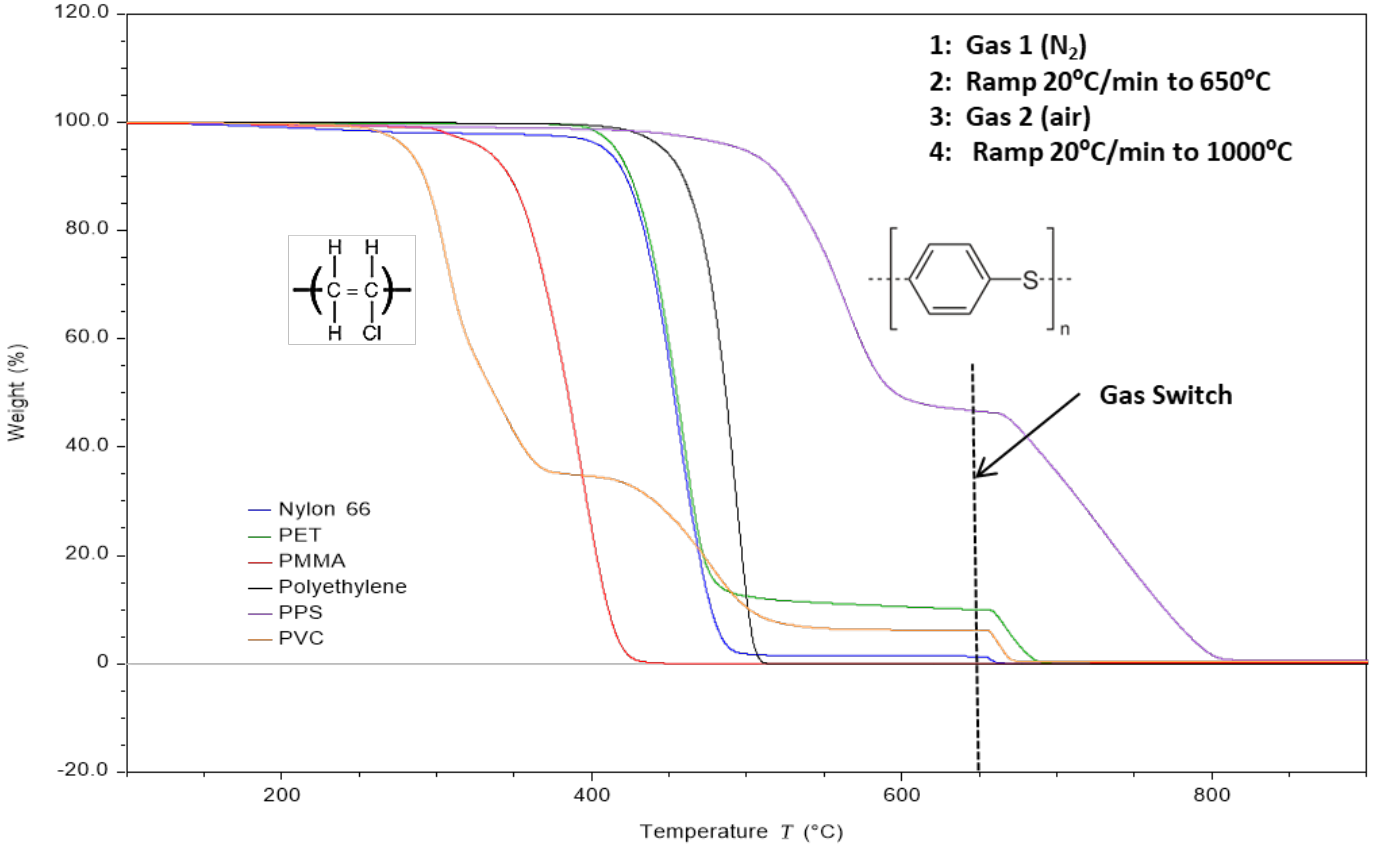
Sample Morphology Effects – PET



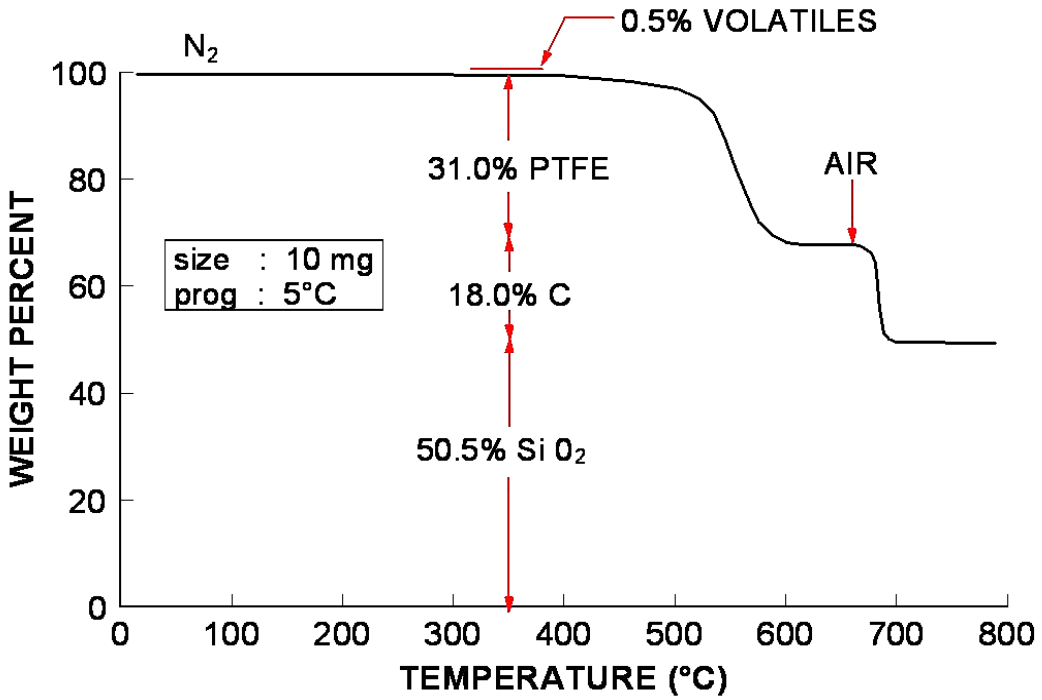
Oxidative Stability (Polypropylene)



Thermal Stability of Polymers



Composite Analysis

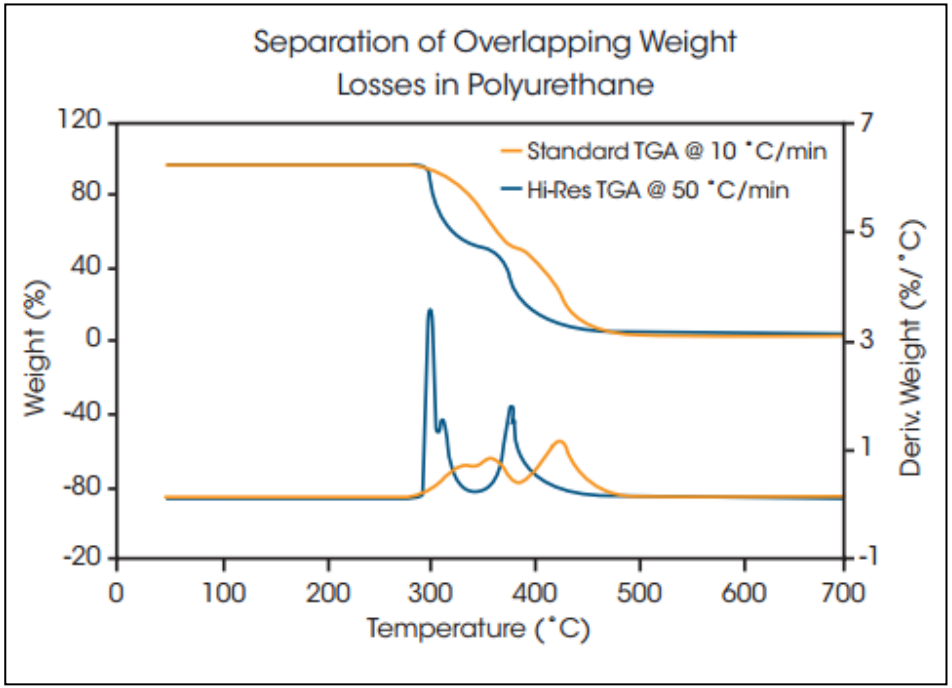


Hi-Res™ TGA

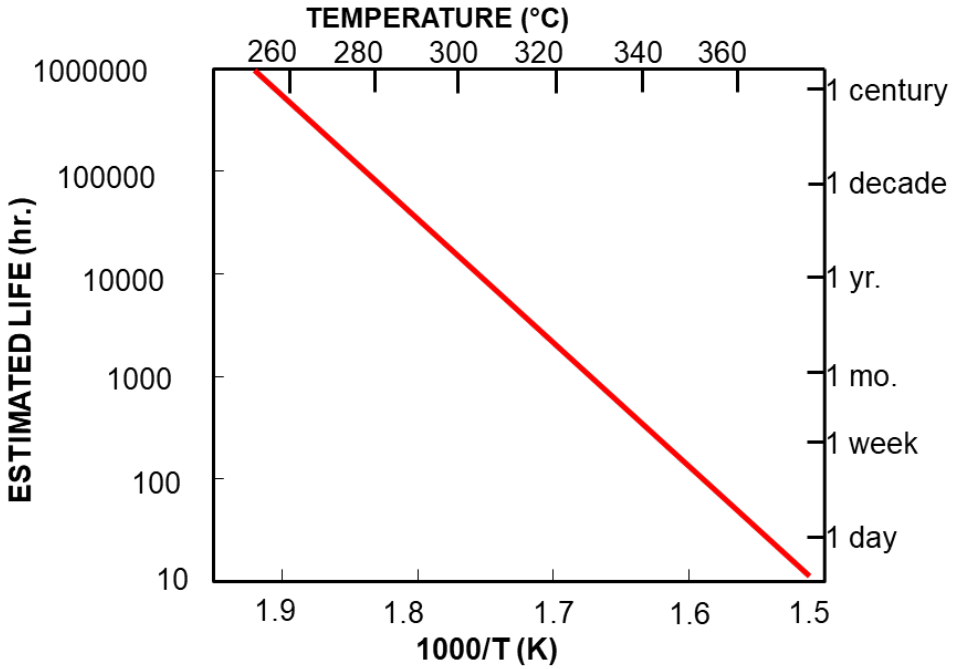
- In a Hi-Res™ TGA experiment the heating rate is controlled by the rate of decomposition.

- Faster heating rates during periods of no weight loss, and slowing down the heating rate during a weight loss – therefore not sacrificing as much time

- Hi-Res™ TGA can give better resolution or faster run times, and sometimes both



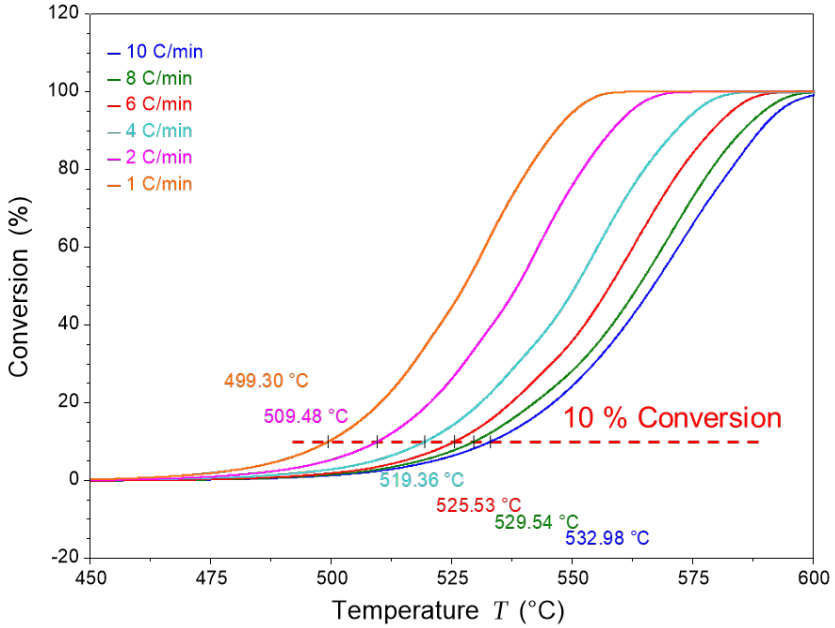
TGA Kinetics - Estimated Lifetime

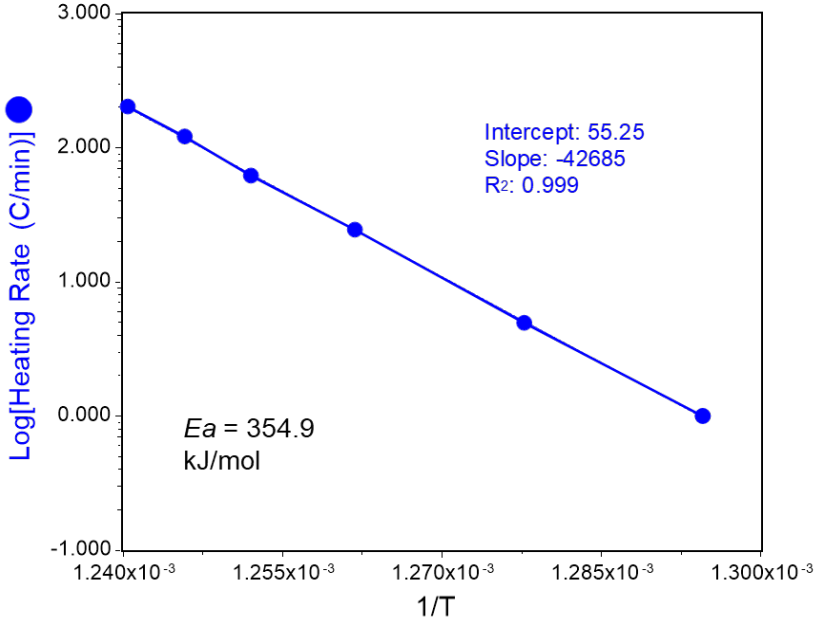


$$\ln t_f = \frac{E}{RT_f} + \ln\left[\frac{E}{\beta R} \cdot P(X_f)\right]$$

TA Instruments Application Note TA125
Estimation of Polymer Lifetime by TGA Decomposition Kinetics

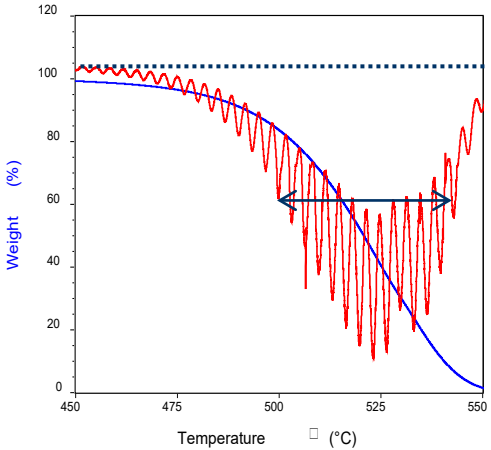
PTFE Decomposition by ASTM E1641

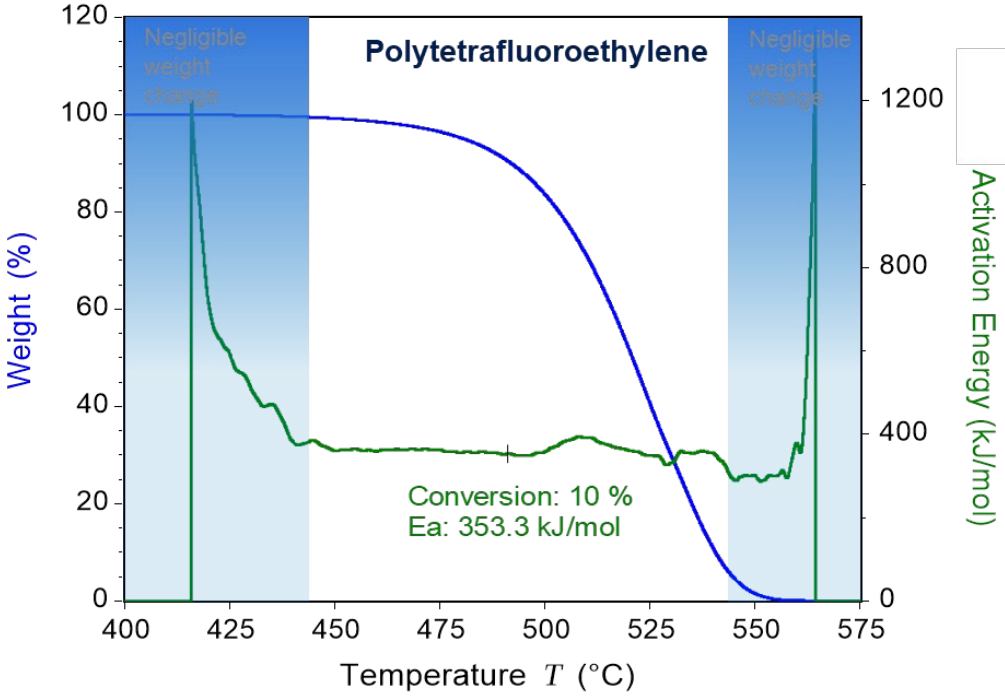




MTGA™ – Typical Values

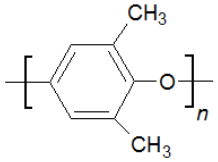
- Modulation period – 200 seconds
- Amplitude – 4-5°C.
- Heating rate – 1 to 2 °C/min.
- Plot derivative of weight loss and calculate the width at half height of the derivative weight loss peak.
  - Need at least 5 modulation cycles across this region.



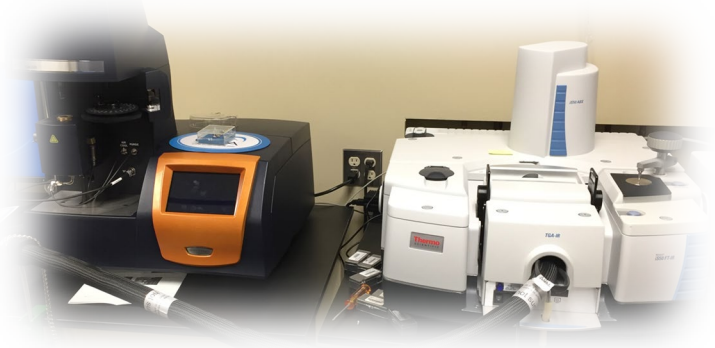


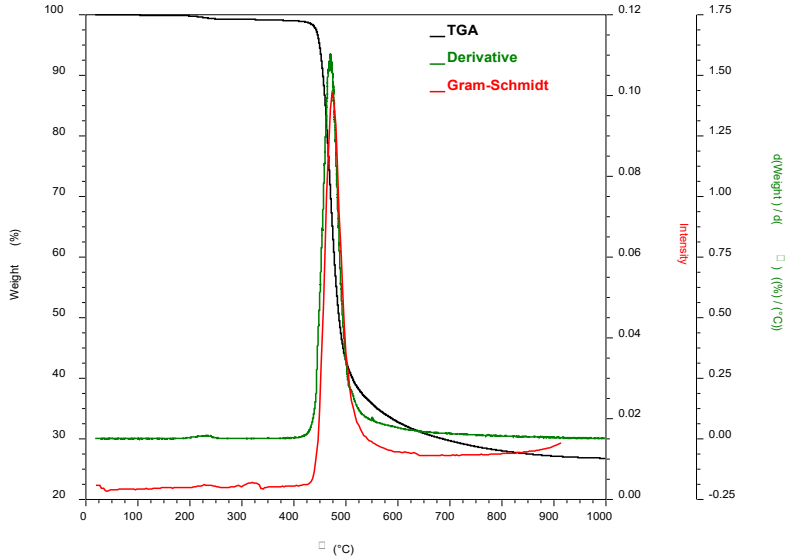
TGA – FTIR for Evolved Gas Analysis

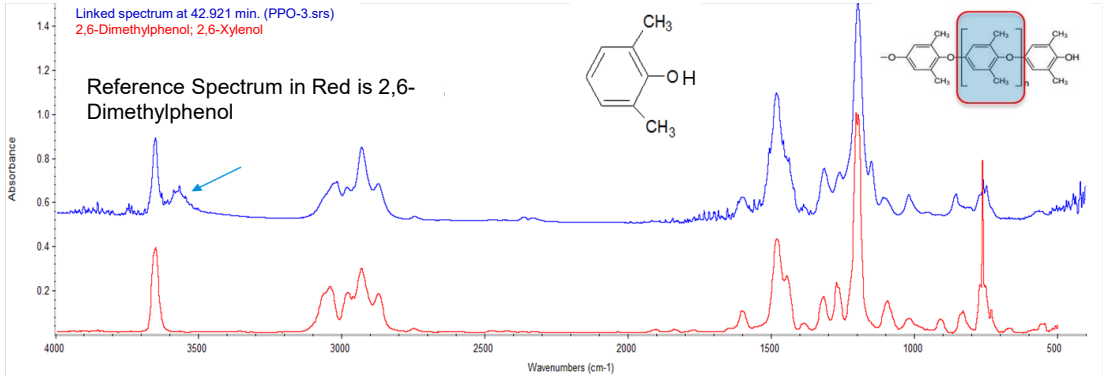
Polyphenylene Oxide



Engineering polymer
-Heat resistant
-Good tensile properties







Thank You

Waters™ | TA Instruments

The World Leader in Thermal Analysis, Rheology, and Microcalorimetry

Coming Up…

COVALENT METROLOGY

Stay Tuned! The next webinar event will explore

Nanoindentation with the new STeP 6 Platform

Details coming soon at www.covalentmetrology.com
And on LinkedIn: www.linkedin.com/company/covalentmetrology

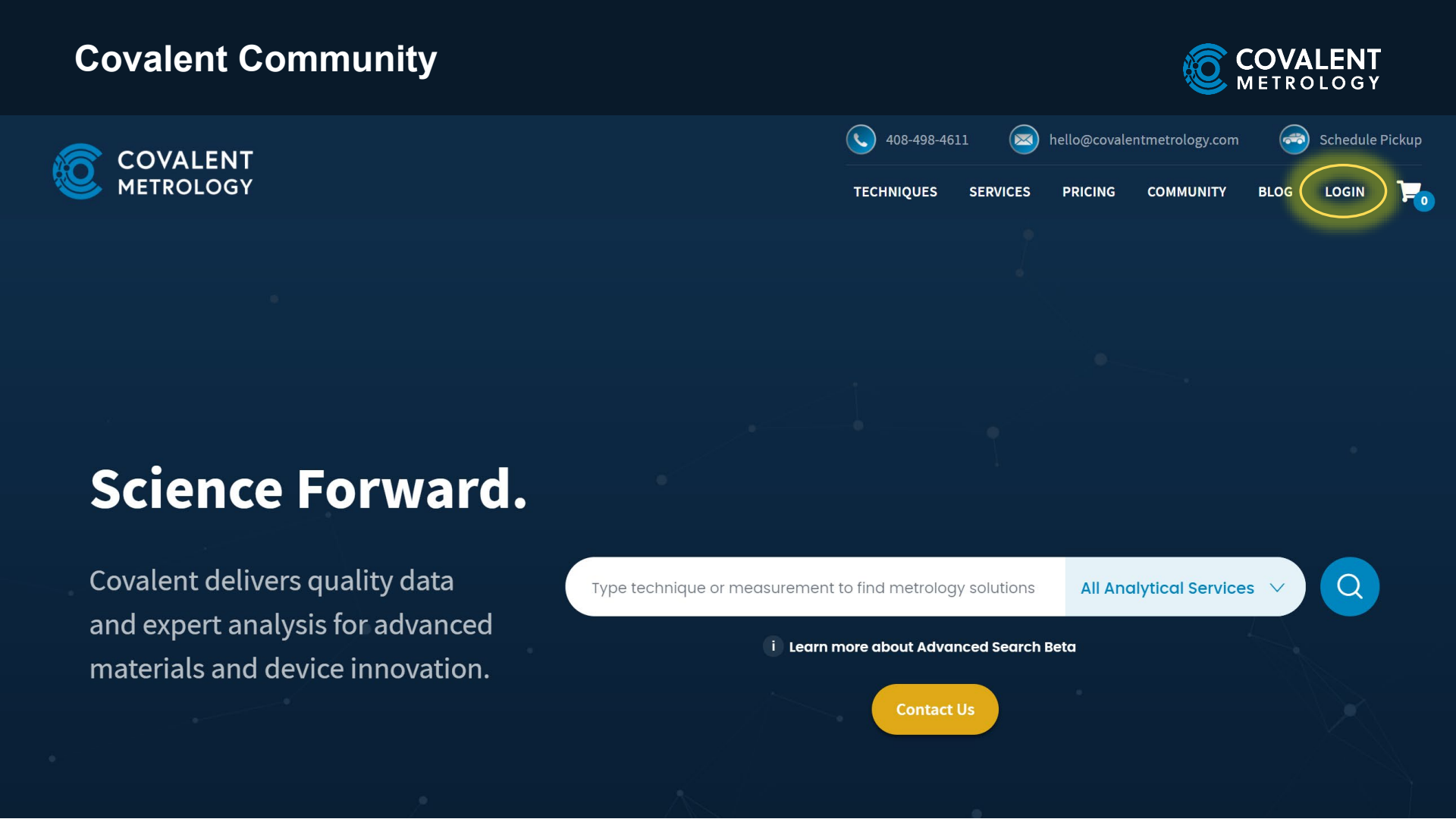
Want to learn more about Covalent's
Thermal Characterization services?

Talk with a Covalent Expert!

Schedule your appointment now with Calendly

- link is in the chat -

Covalent Community



Covalent Community

COVALENT METROLOGY

COVALENT METROLOGY

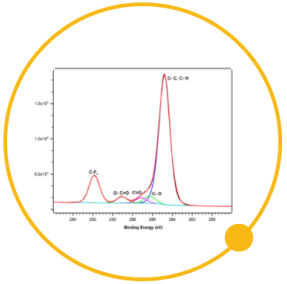
Search Technique or Measurement...

408-498-4611 hello@covalentmetrology.com Schedule Pickup

TECHNIQUES SERVICES PRICING COMMUNITY BLOG LOGIN 0

Access Covalent Portals

Customer Access to Data & Community Content



The DATA PORTAL is used by Customers and Lab Partners for uploading and downloading data. It requires two-factor authentication and advanced password protection. Data Portal users have complete access through their home page on the portal to all Community content, and do not require a separate Community account.

LOGIN TO DATA PORTAL

Community Content Access for All Other Users

The COVALENT COMMUNITY PORTAL requires password entry. It contains webinar and other metrology and characterization-related content that we believe would be useful and educational for the materials science innovation community. It does not provide access to any customer data and should only be used by individuals that are not Covalent customers or lab partners.

LOGIN TO COMMUNITY PORTAL

COVALENT METROLOGY

Q & A Session

Thank you