Thermal Analysis of Rubbers and Elastomers

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September 6, 2017

Thermal Analysis

What does it measure and what is it used for?

Thermal Analysis is a series of complementary techniques to measure various properties of materials as a function of temperature and time

- **Thermogravimetric Analysis (TGA)**
  - Weight loss, weight gain, compositional and thermal stability of a material. ***[Sorption Analysis]***
  - Provides information to aid in the interpretation of DSC data. Extremely complementary to DSC.
- **Differential Scanning Calorimetry (DSC)**
  - Measures Heat Flow into or out of a sample
  - Modulated DSC – Separates Heat Flow into Heat Capacity, Reversing and Non Reversing Heat Flow
- **Thermomechanical Analysis (TMA)**
  - Determines dimensional changes of a material, coefficient of thermal expansion, glass transition

What Materials?

- Iron and Steel
- Aluminum and other metals (Mg)
- Adhesives and Sealants
- Textiles / Leather
- Rubbers and elastomers
- Thermoplastic Polymers
- Composites
- Thermosets ans Resins
- Coatings and Paints
- Fluids and Lubricants
- Glass
- Other (electronics, fuel cell, gasoline, nano-materials, ceramics, sensors, etc.)

Agenda

1. Thermogravimetric Analysis

Standard and Hi-Res TGA™, TGA-MS, Decomposition and Lifetime Kinetics

2. Differential Scanning Calorimetry

Technique Overview, Conventional vs. Modulated DSC®, Curing Kinetics

Thermogravimetric Analysis (TGA)

Thermogravimetric Analysis (TGA)

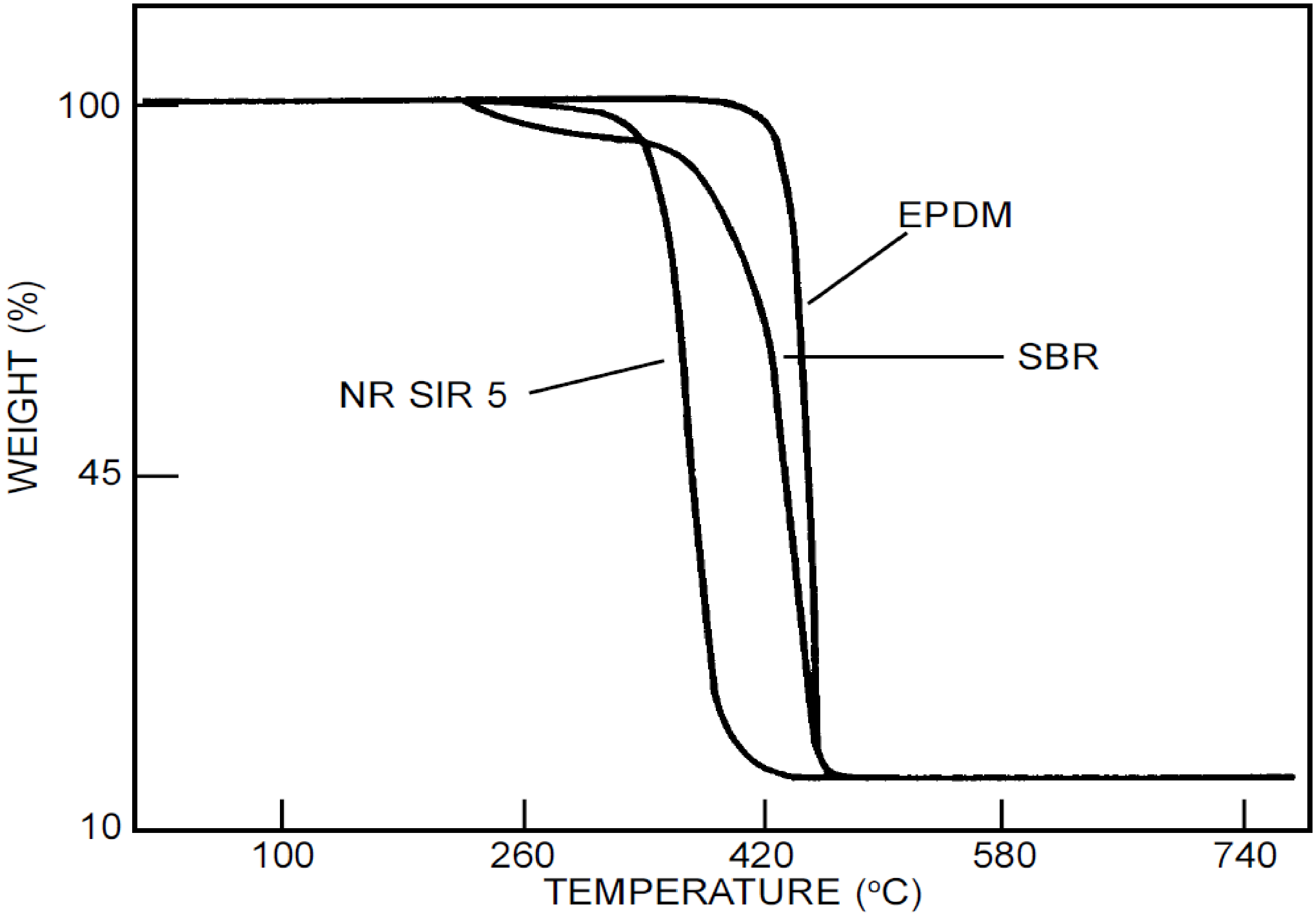
- TGA measures amount and rate of weight change vs. temperature or time in a controlled atmosphere
- Used to determine composition and thermal stability up to 1000°C (Q50 & Q500); 1200°C (Discovery TGA) & 1500°C (SDT)
- Characterizes materials that exhibit weight loss or gain due to decomposition, oxidation, or dehydration

Mechanisms of Weight Change in TGA

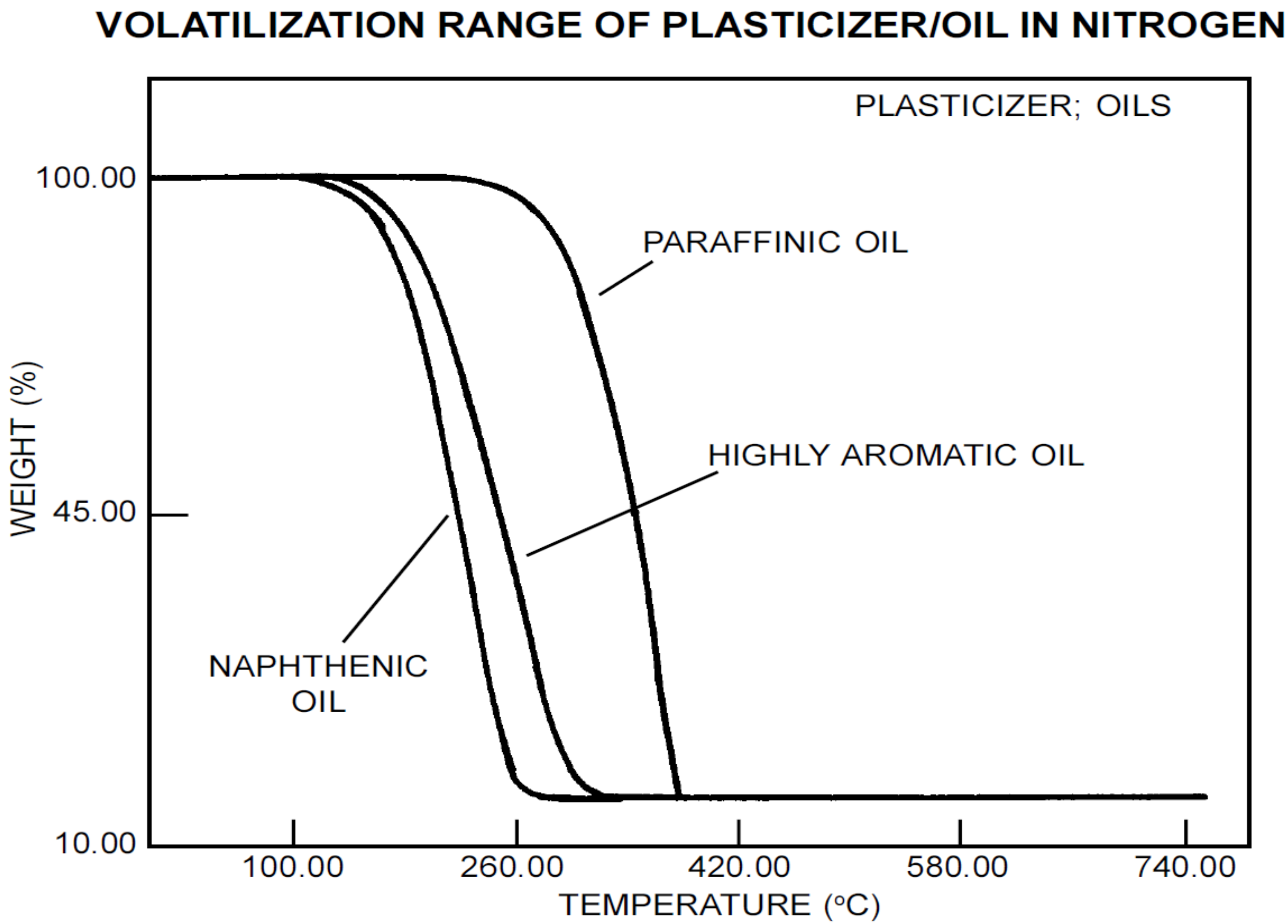
- Weight Loss:
  - Decomposition: The breaking apart of chemical bonds.
  - Evaporation: The loss of volatiles with elevated temperature.
  - Reduction: Interaction of sample to a reducing atmosphere (hydrogen, ammonia, etc).
  - Desorption.
- Weight Gain:
  - Oxidation: Interaction of the sample with an oxidizing atmosphere.
  - Absorption.

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

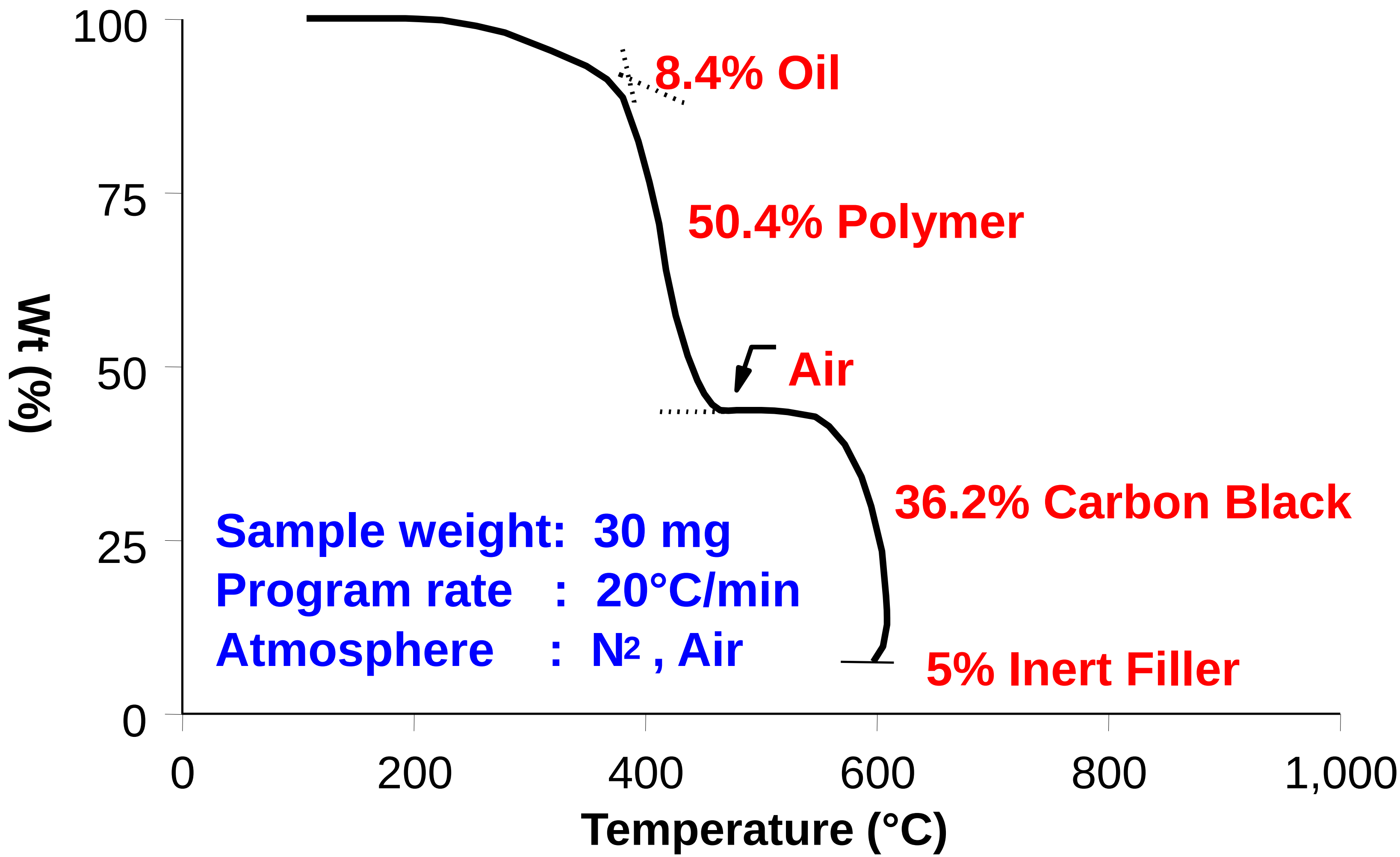
Decomposition of Elastomers in Nitrogen



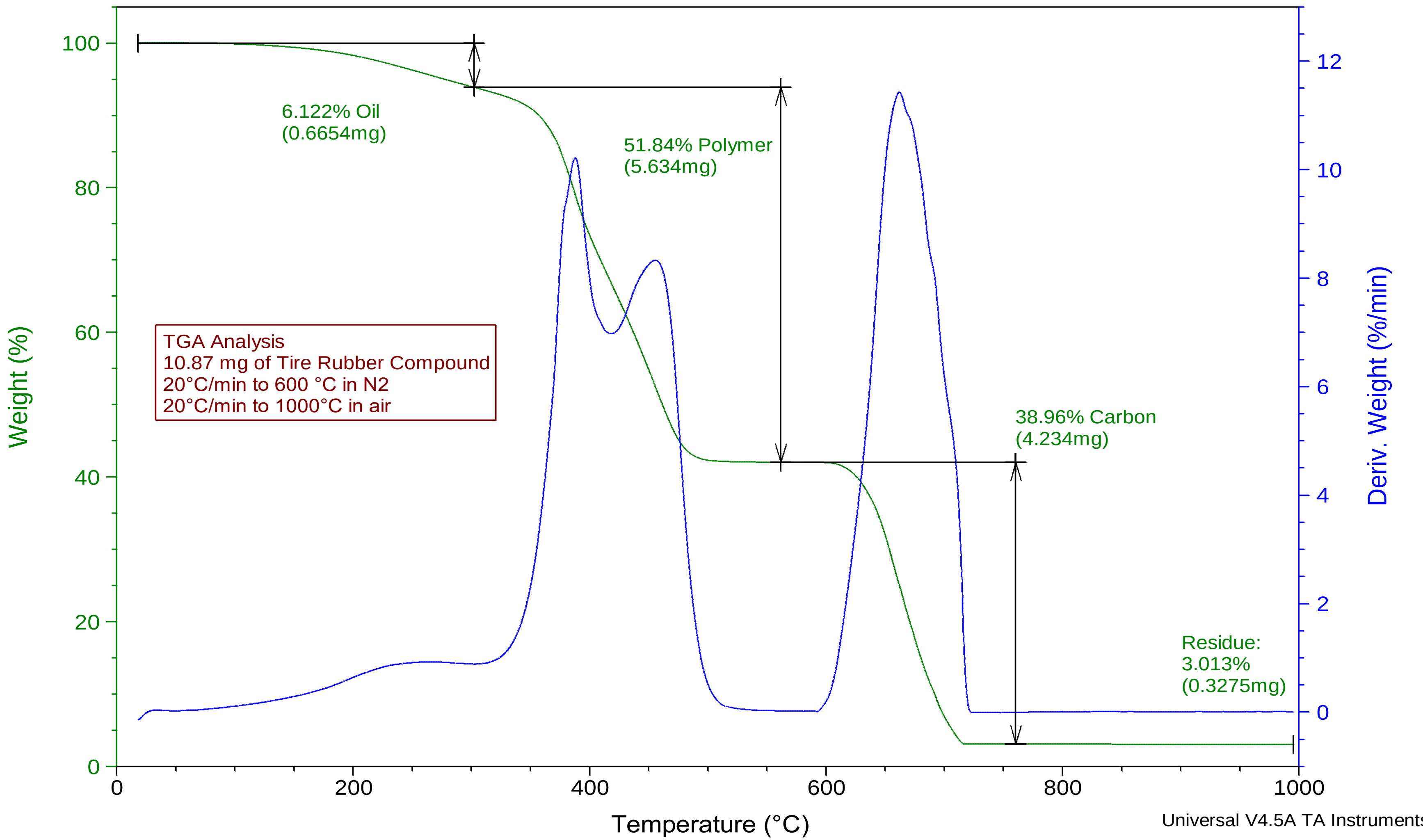
Volatilization of Plasticizers/Oils



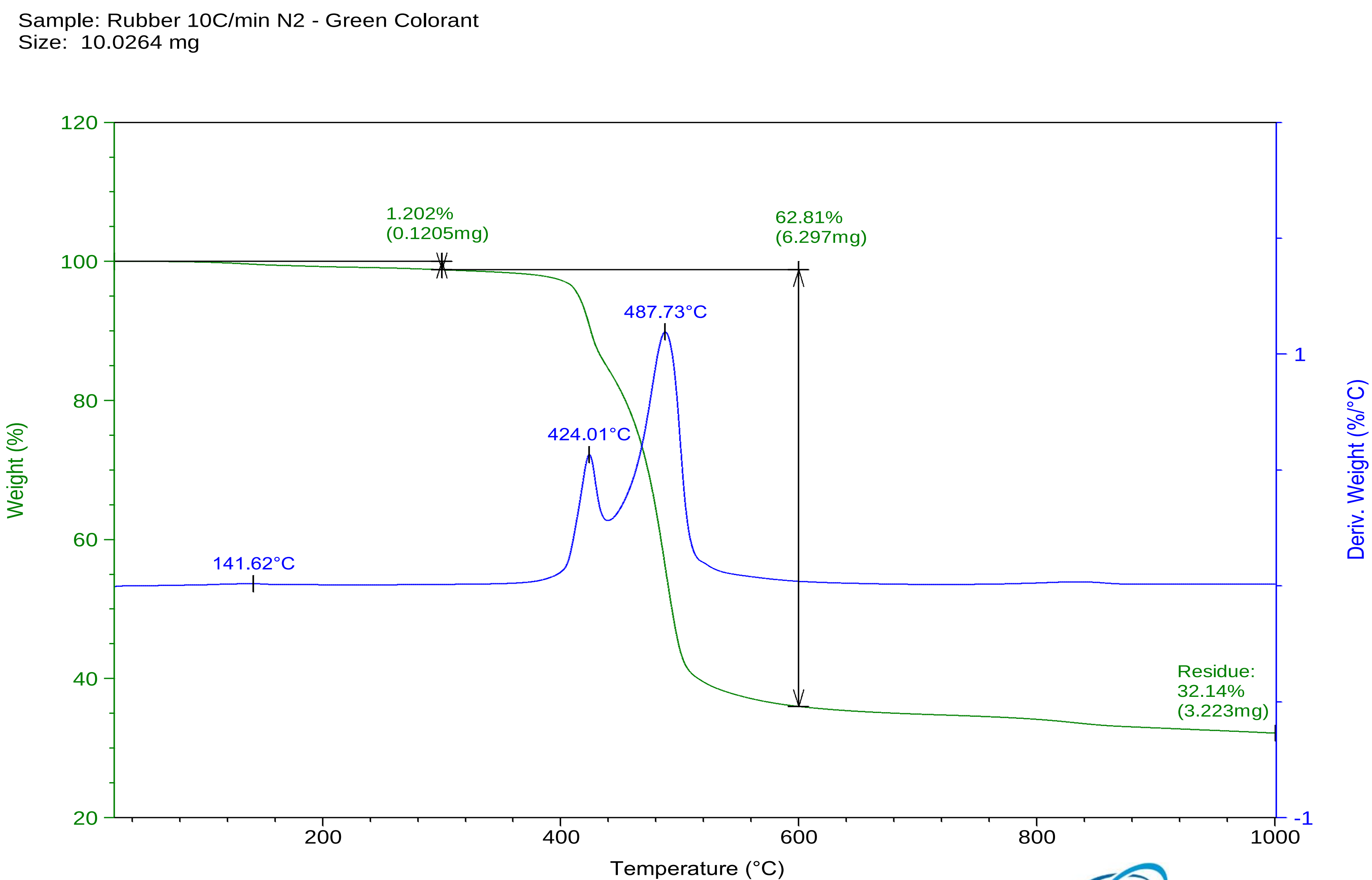
Styrene-Butadiene Rubber Analysis



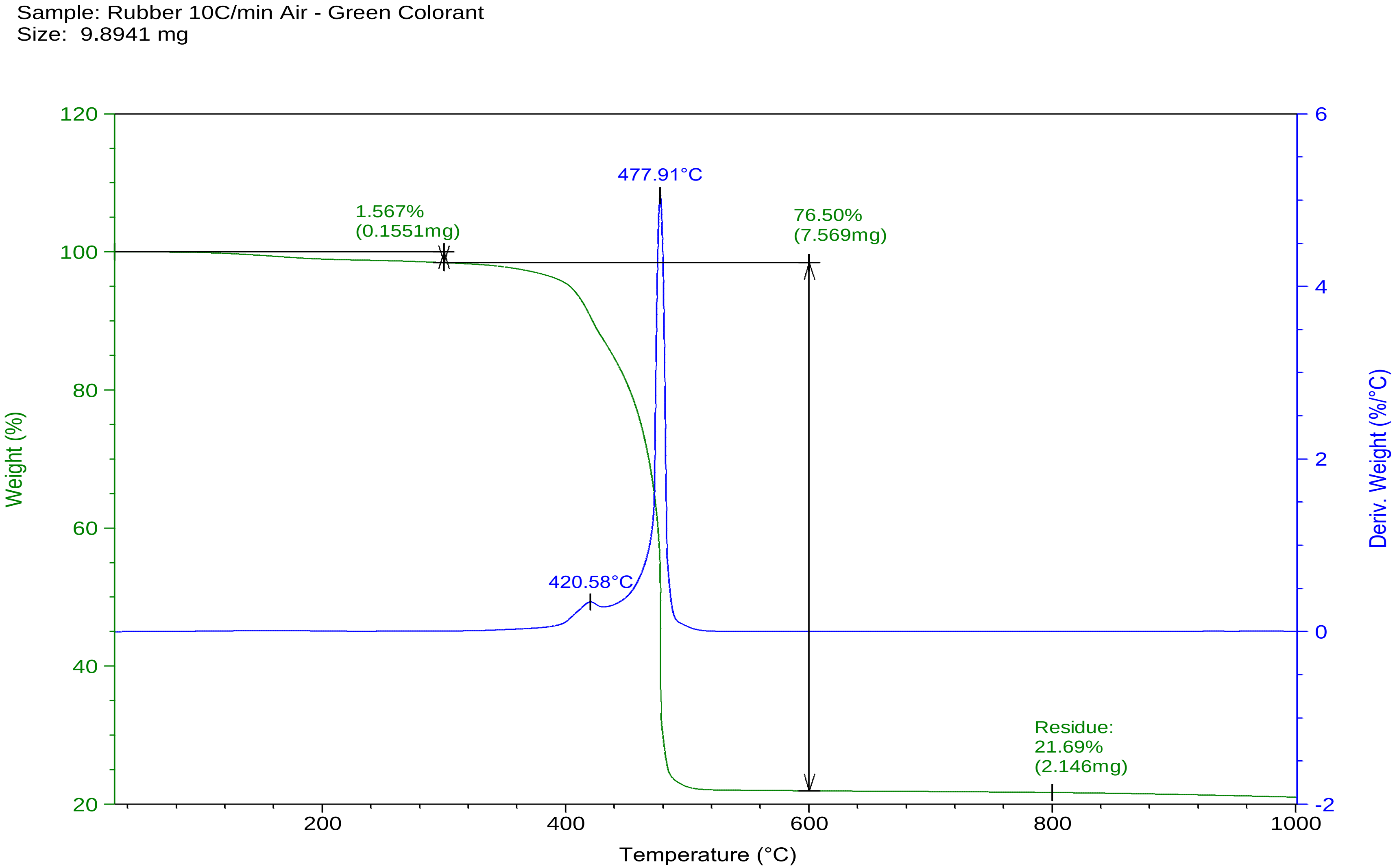
TGA of Tire Rubber



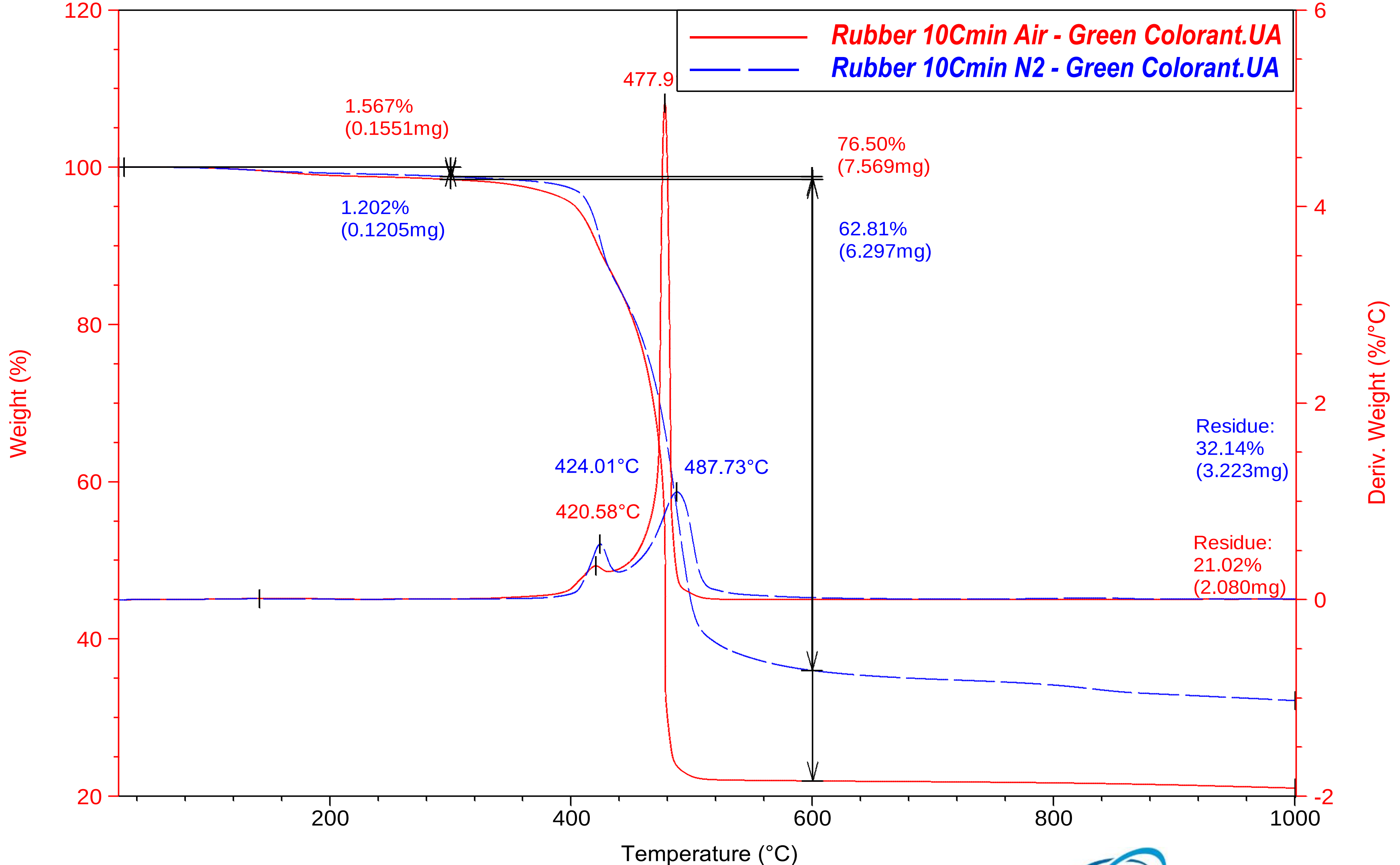
TGA of Rubber in Nitrogen



TGA Rubber in Air

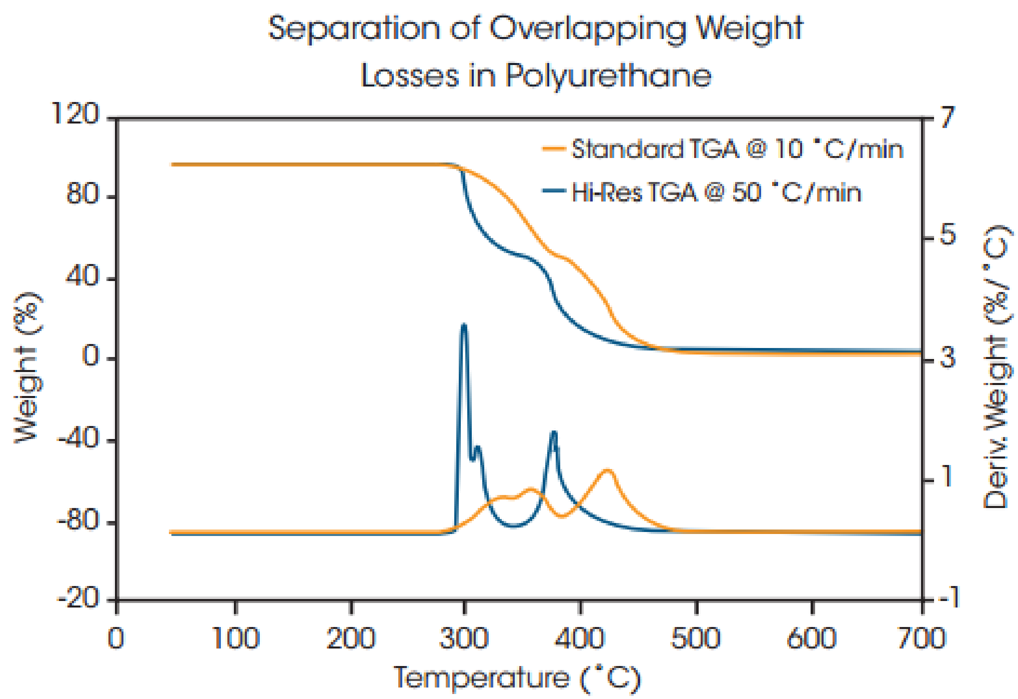


TGA Rubber in Air vs Nitrogen

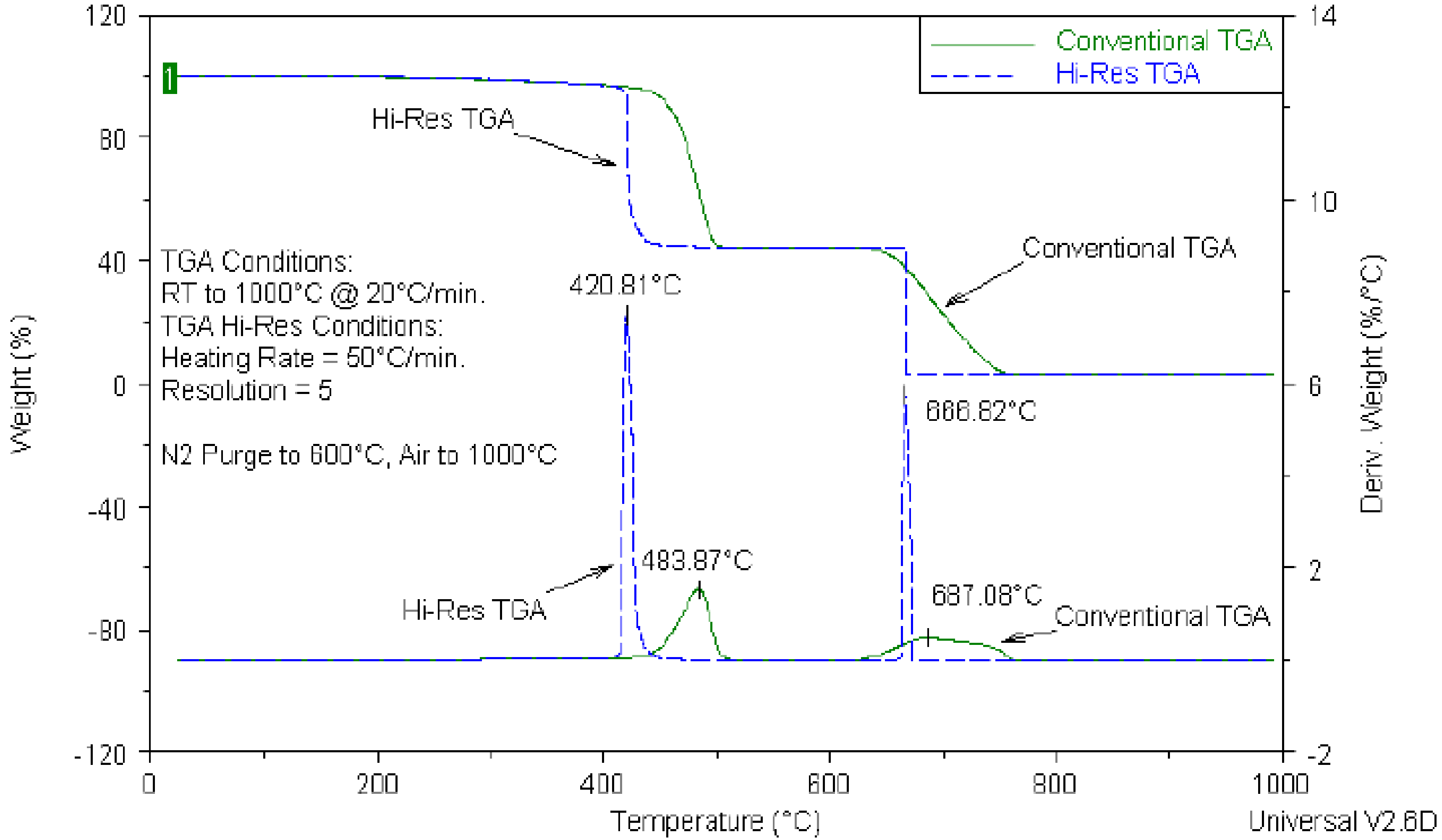


Hi-Res™ TGA

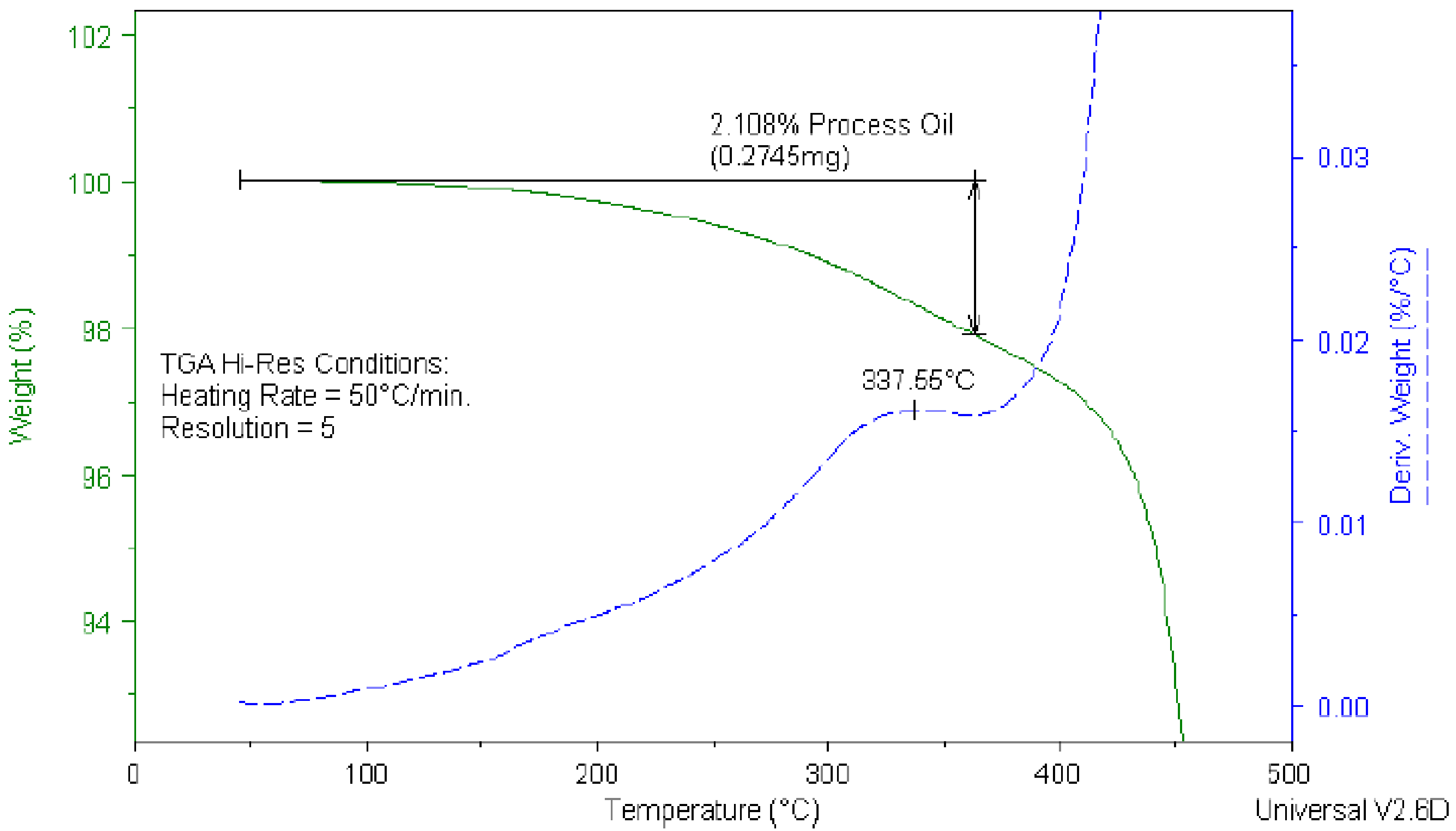
- In a Hi-Res™ TGA experiment the heating rate is controlled by the rate of decomposition.
- Faster heating rates during periods of no weight loss, and slowing down the heating rate during a weight loss – therefore not sacrificing as much time
- Hi-Res™ TGA can give better resolution or faster run times, and sometimes both



EPDM Rubber by TGA & Hi-Res™ TGA



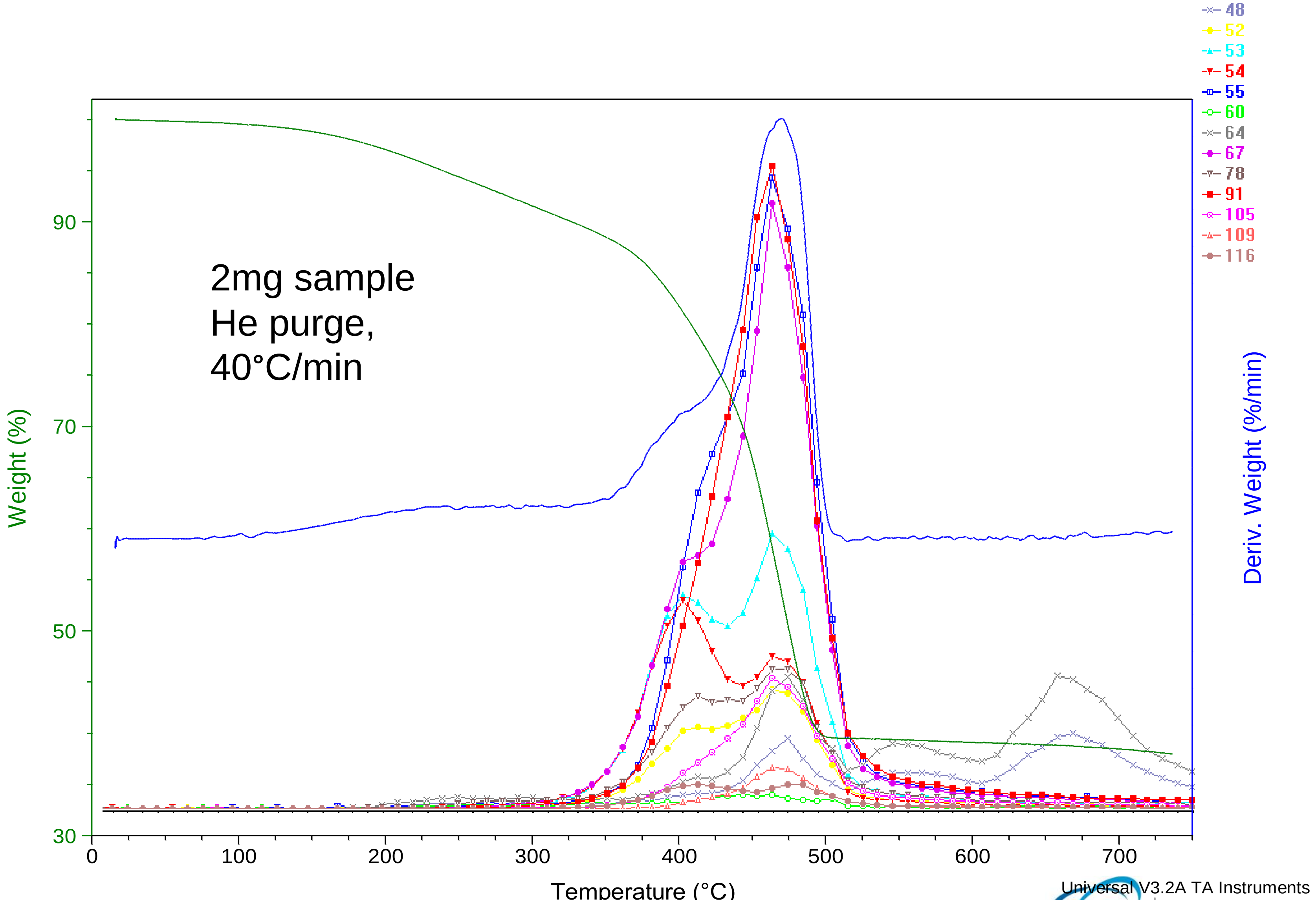
Process Oil in a Rubber Compound by Hi-Res TGA



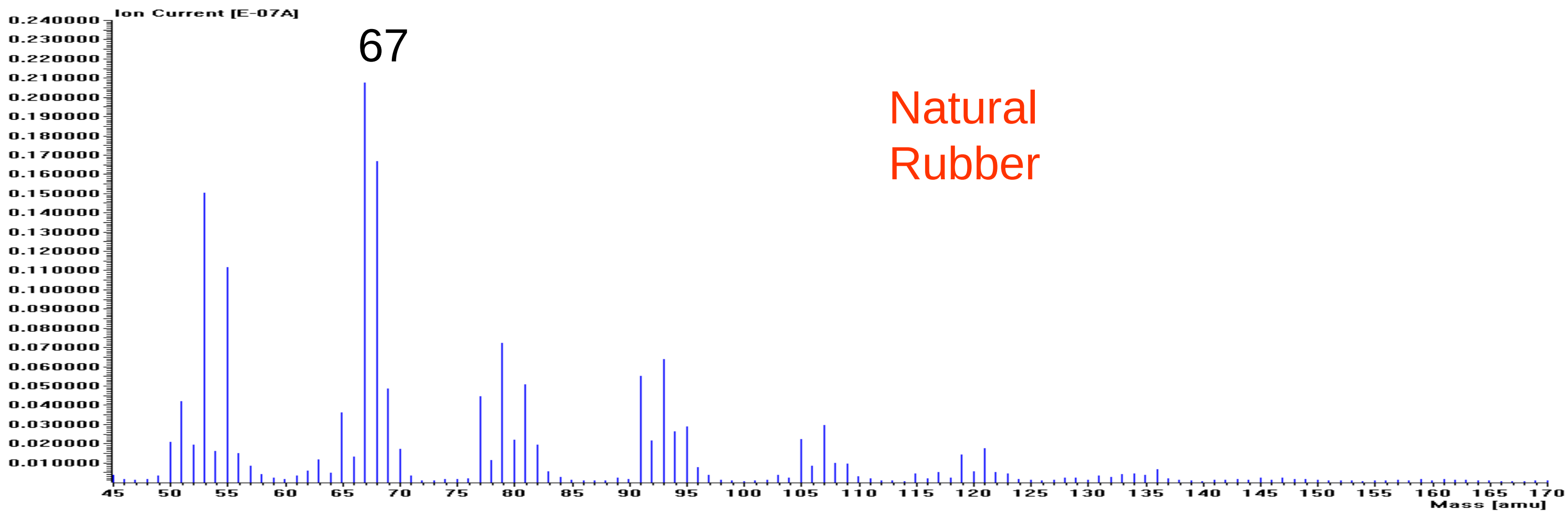
TGA-Evolve Gas Analysis (EGA)

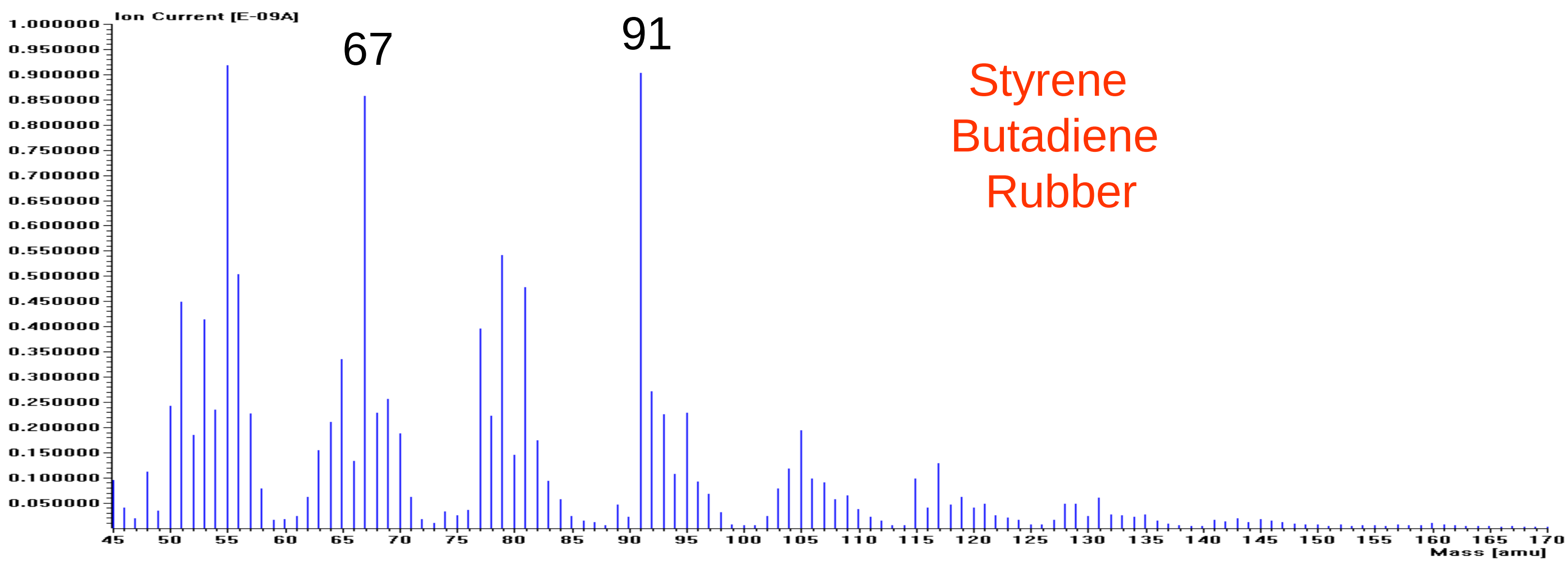
- TGA measures weight changes (quantitative)
- Difficult to separate, identify, and quantify individual degradation products (off-gases)
- Direct coupling to identification techniques (Mass Spec, FTIR) reduces this problem

TGA-MS of Styrene Butadiene Rubber (SBR)

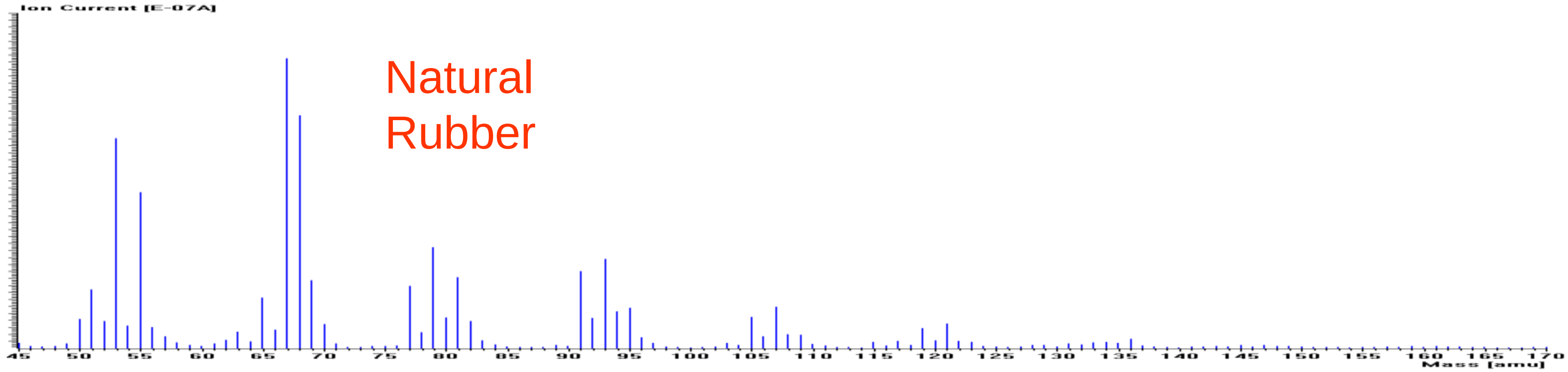


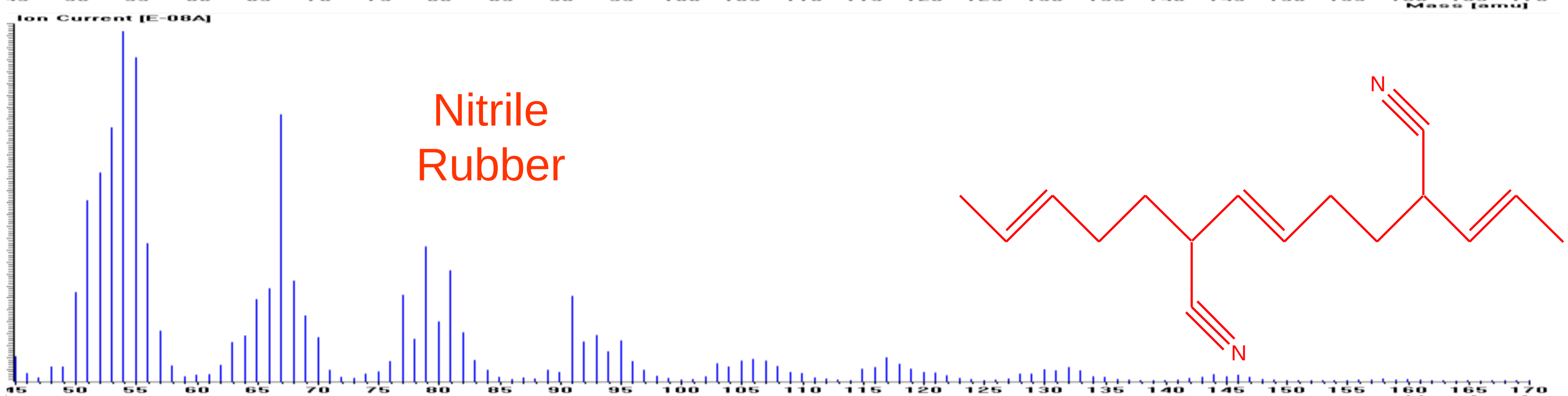
Fingerprint of Natural Rubber vs SBR



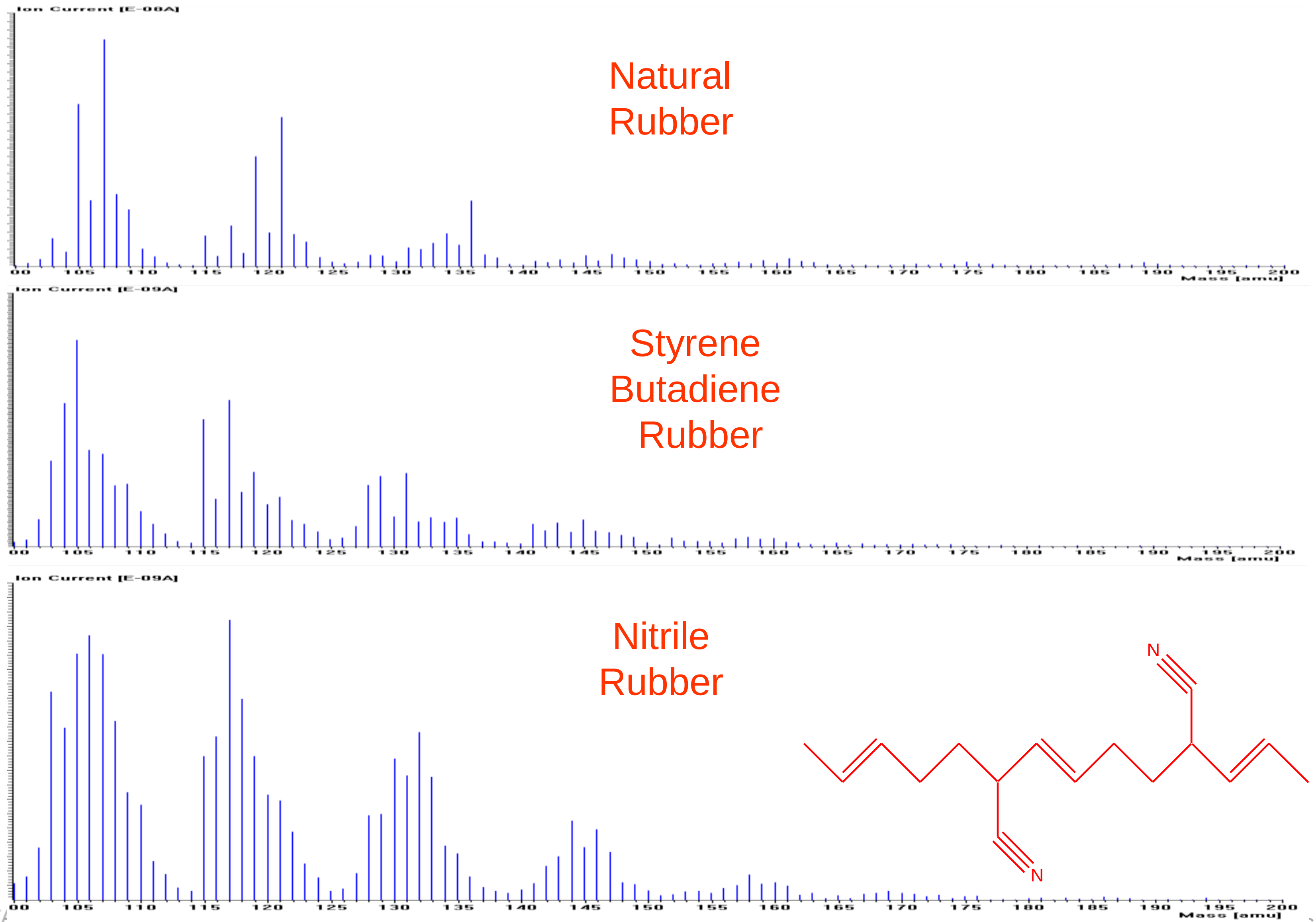


Mass 45 to 170

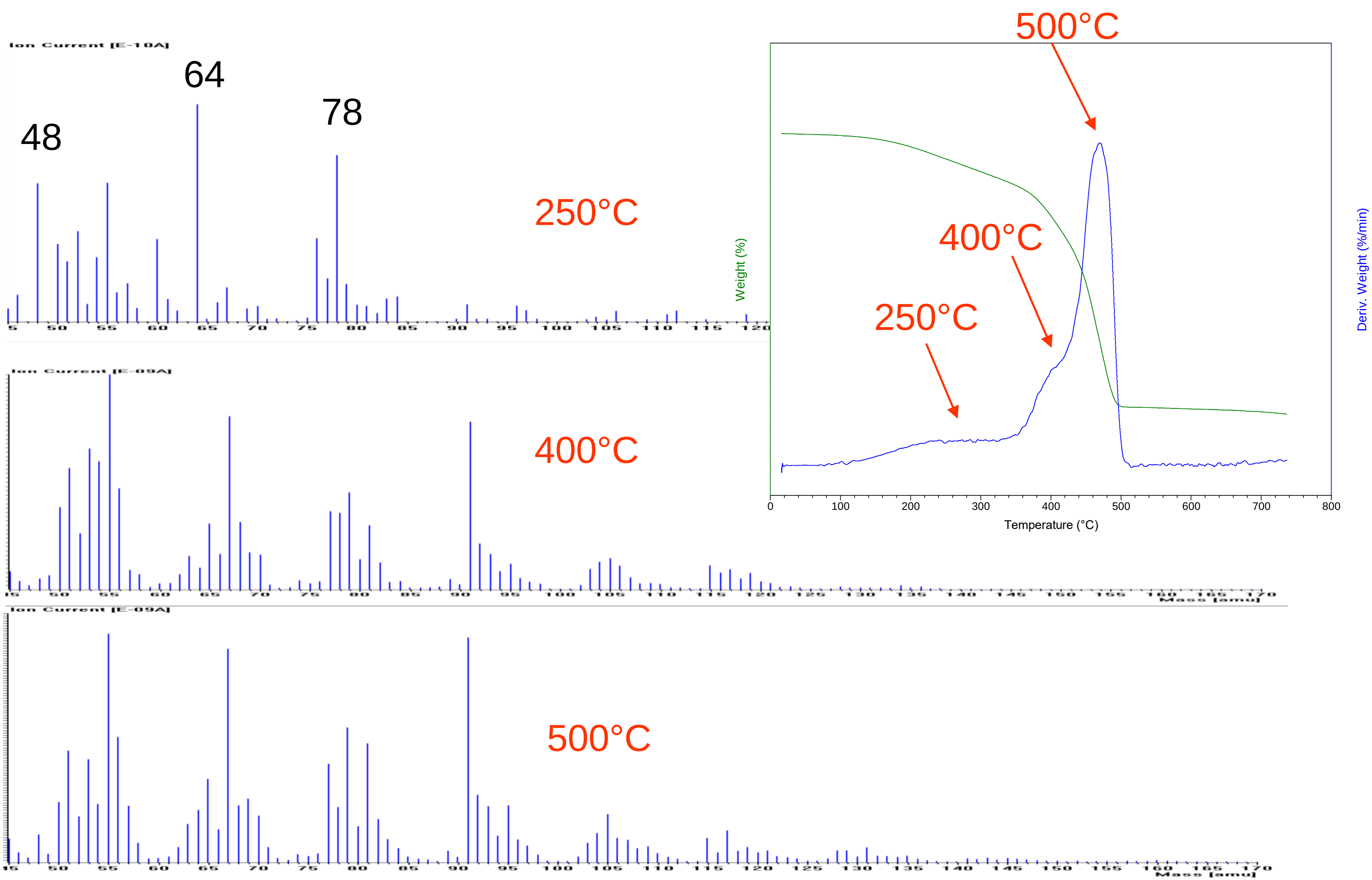




Mass 100 to 200



Styrene Butadiene Rubber



Decomposition and Lifetime Kinetics

Simple Polymer Decomposition

$$\phi = A\exp\left(\frac{-\Delta E}{RT}\right)$$

$$\ln\phi = A - \left(\frac{\Delta E}{RT}\right)$$

where

$\phi = \text{heating rate}\ (°\text{C}/\text{min})$

$\text{A} = \text{pre-exponential}$

$\Delta\text{E} = \text{Activation Energy}\ (\text{kJ}/\text{mol})$

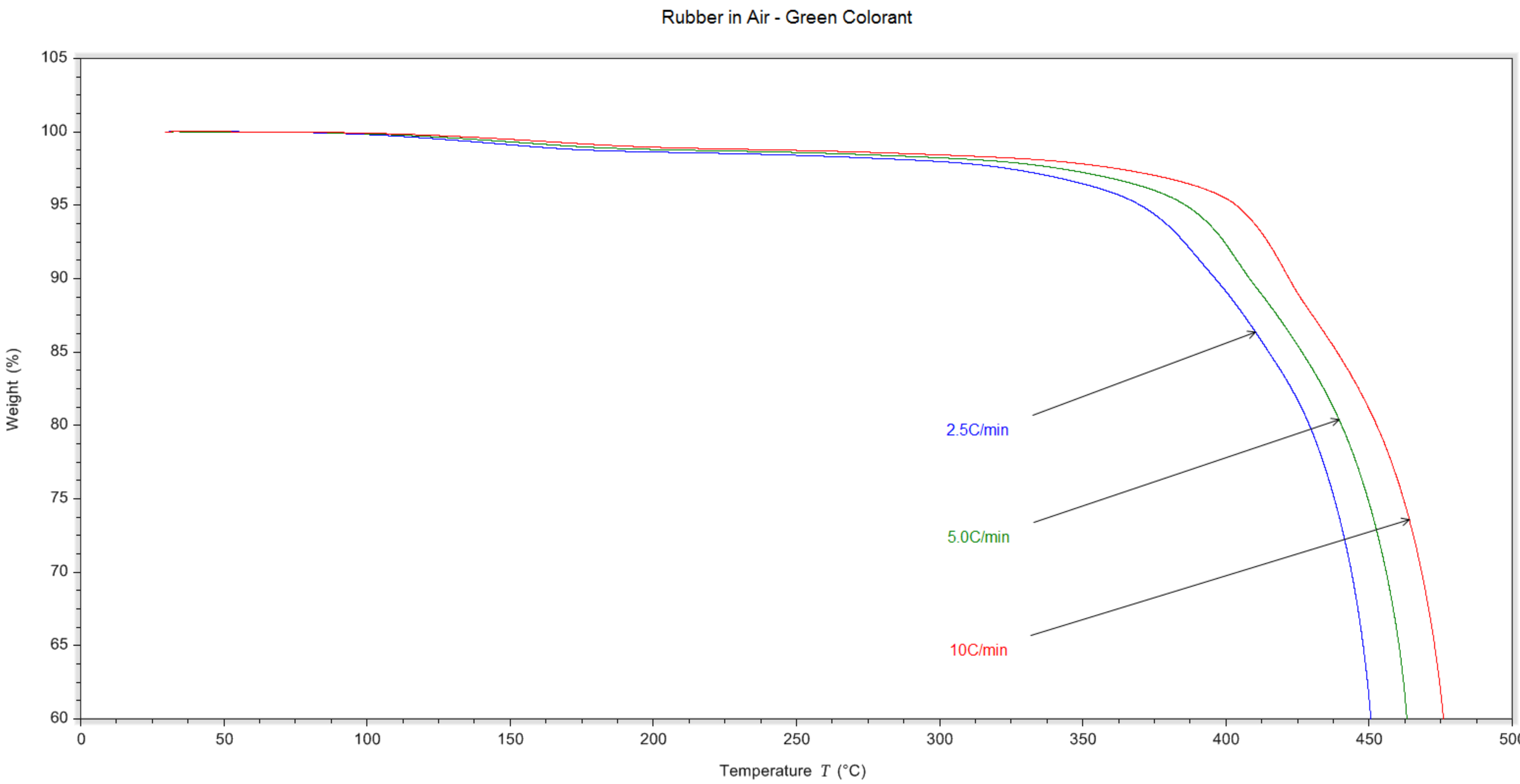
$\text{T} = \text{temperature}\ (\text{K})$

$\text{R} = \text{Universal Gas Constant}$

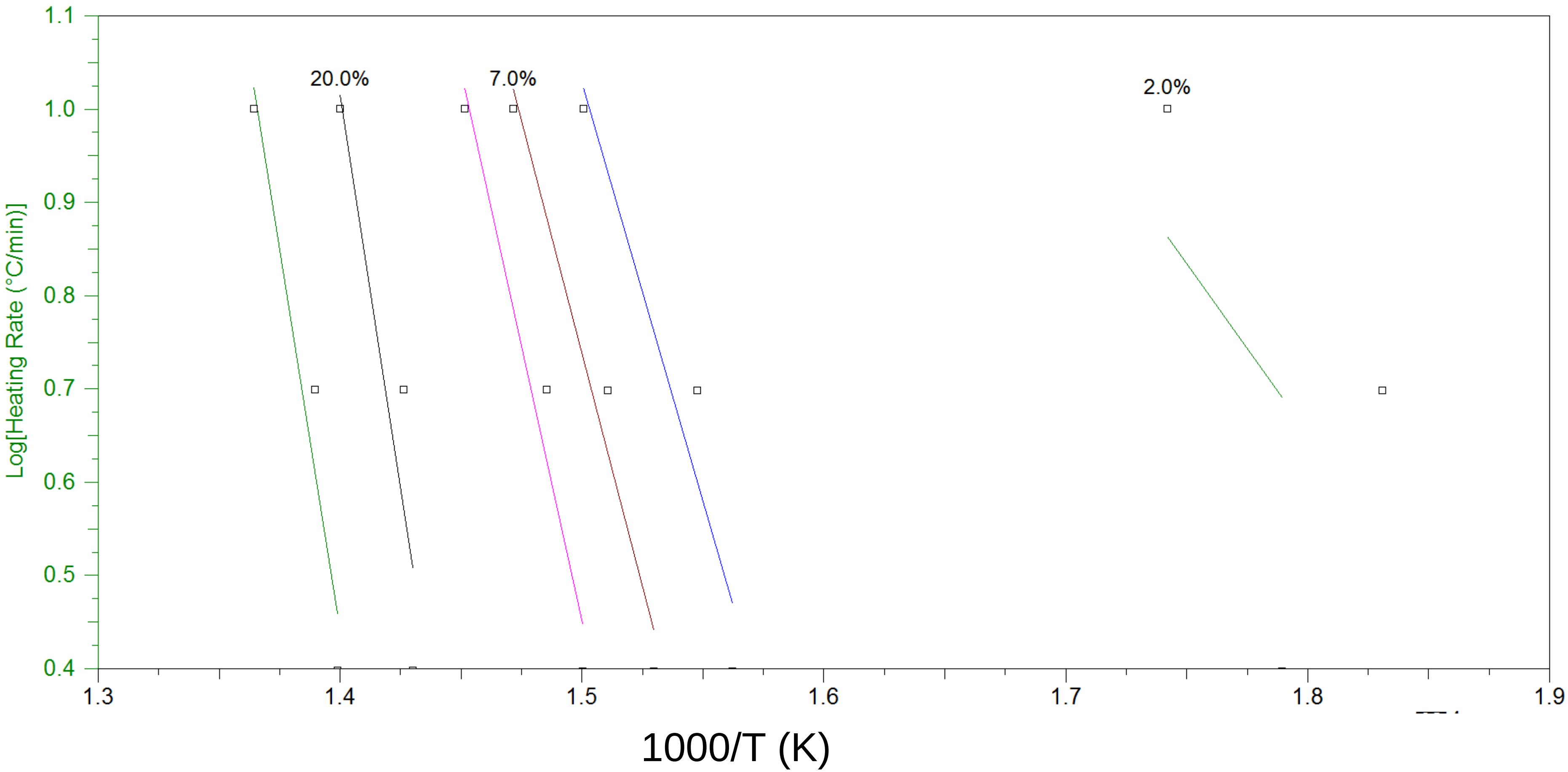
Simple Polymer Decomposition

- Experimental
- Run TGA experiment on polymer at 4 different heating rates. Use the same gas for each – typically nitrogen or air.
- Obtain a temperature at an isoconversional point – for example 2% weight loss for each heating rate
- Plot the ln of the heating rate (ϕ) versus 1/T (temperature units must be in Kelvin)
- Slope of the line is (-ΔE/R). Multiply the slope of the line by –(8.314×10^{-3}) to obtain the activation energy in kJ/mol.

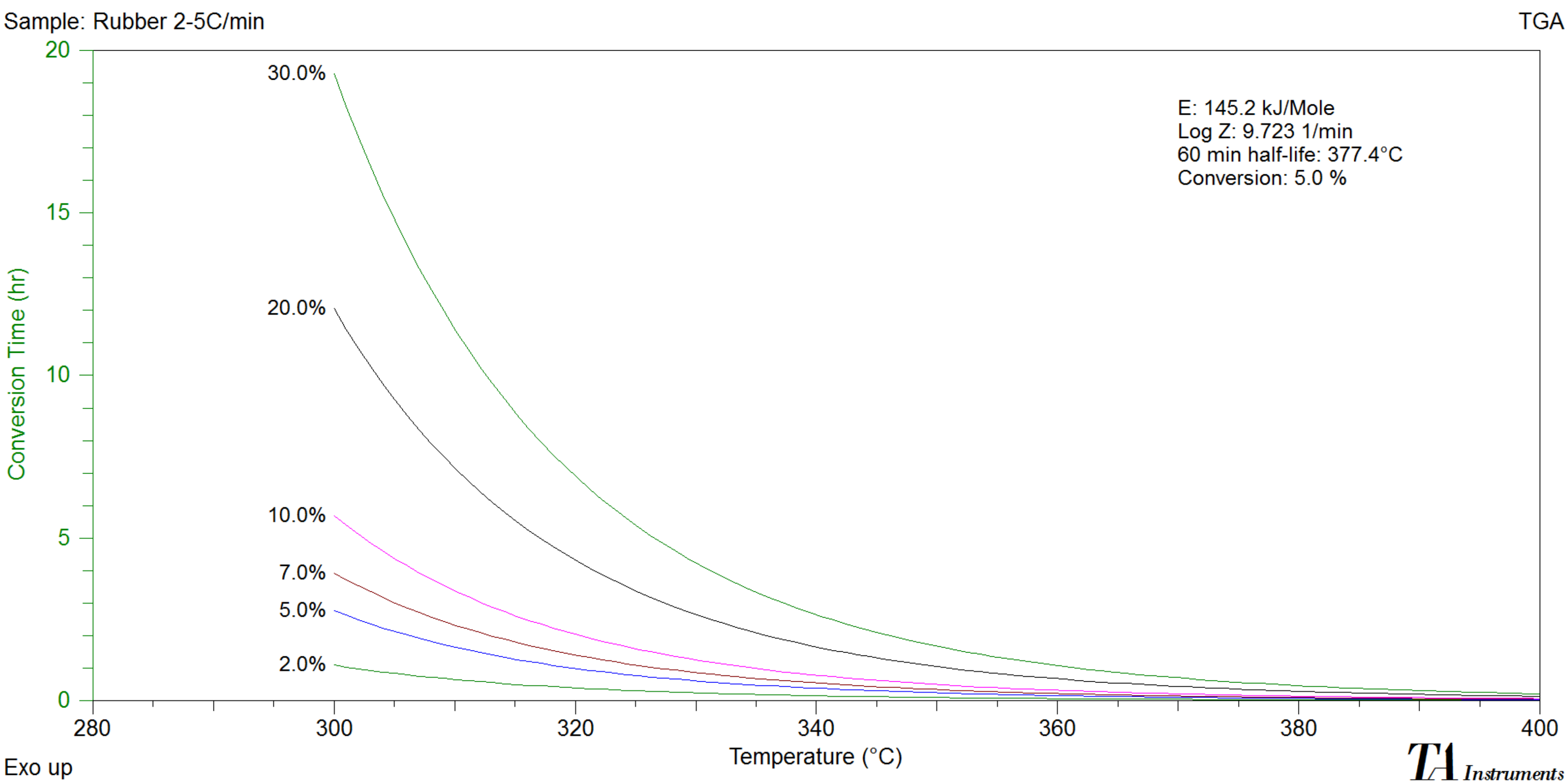
Decomposition Kinetics



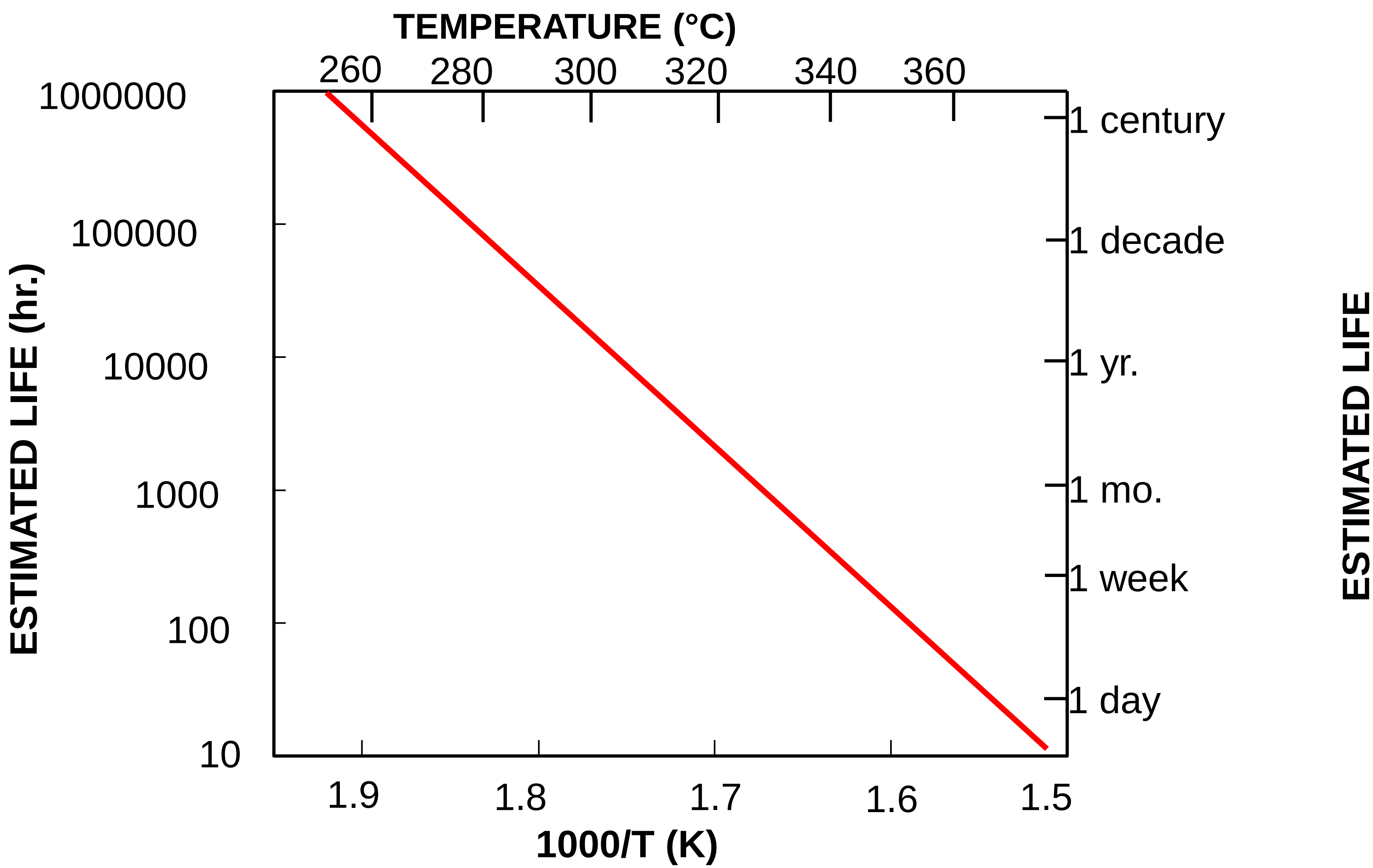
Decomposition Kinetics



TGA Kinetics – Isoconversion Plot



TGA Kinetics - Estimated Lifetime



TA Instruments Application Note TA125

Estimation of Polymer Lifetime by TGA Decomposition Kinetics

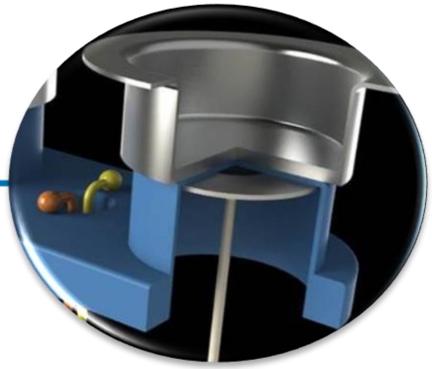
Differential Scanning Calorimetry (DSC) and Modulated DSC® (MDSC) Overview

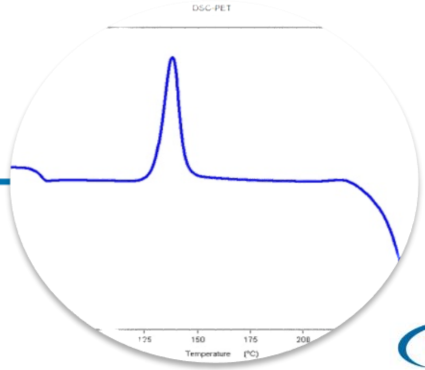
Differential Scanning Calorimetry (DSC)

- Differential Scanning Calorimetry (DSC) is most popular thermal analysis technique
- DSC measures endothermic and exothermic transitions as a function of temperature
  - Endothermic heat flows into a sample
  - Exothermic heat flows out of the sample
- Used to characterize polymers (thermosets, thermoplastics, elastomers)
- Also used with pharmaceuticals, foods/biologicals, organic chemicals and inorganics
- Transitions measured include Tg, melting, crystallization, curing and cure kinetics, onset of oxidation and heat capacity

What is Differential Scanning Calorimetry?

- Calorimetry is a technique for determining the quantity of heat that is either absorbed or released by a substance undergoing a physical or chemical change.
- A DSC measures the difference in Heat Flow Rate between a sample and inert reference as a function of time and temperature.



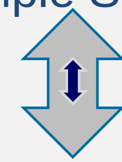


Simple Heat Flux DSC Cell Schematic

Reference Sensor

An empty pan on the reference sensor should react similarly to the pan on the sample sensor, thus canceling out any pan contribution

Sample Sensor



Heat **absorbed** by the sample gives an endothermic response

Heat **released** by the sample gives an exothermic response

DSC Heat Flow

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

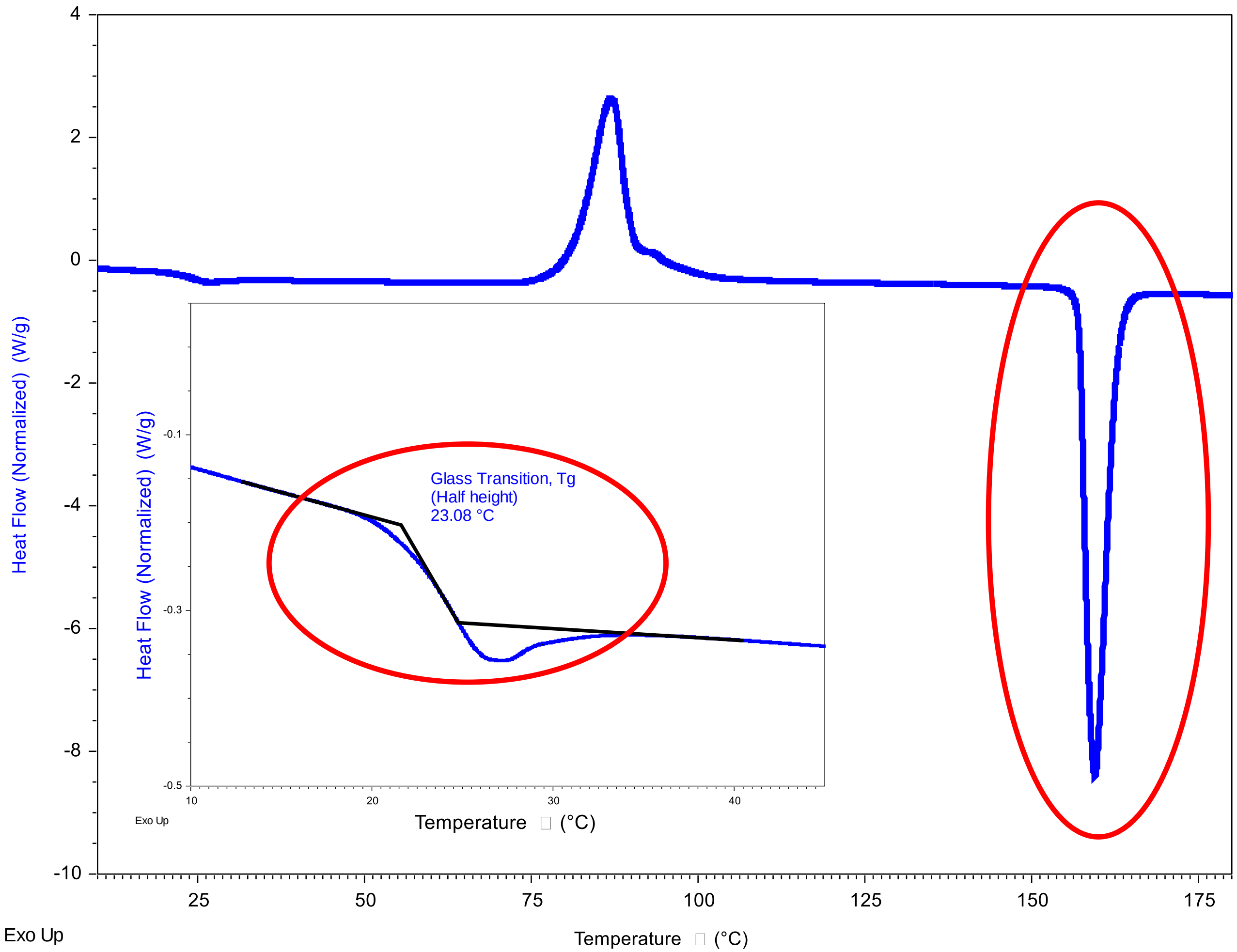
Heat Capacity

- Glass Transition

Kinetic

- Crystallization
- Cure reactions
- Volatilization
- Decomposition
- Denaturation

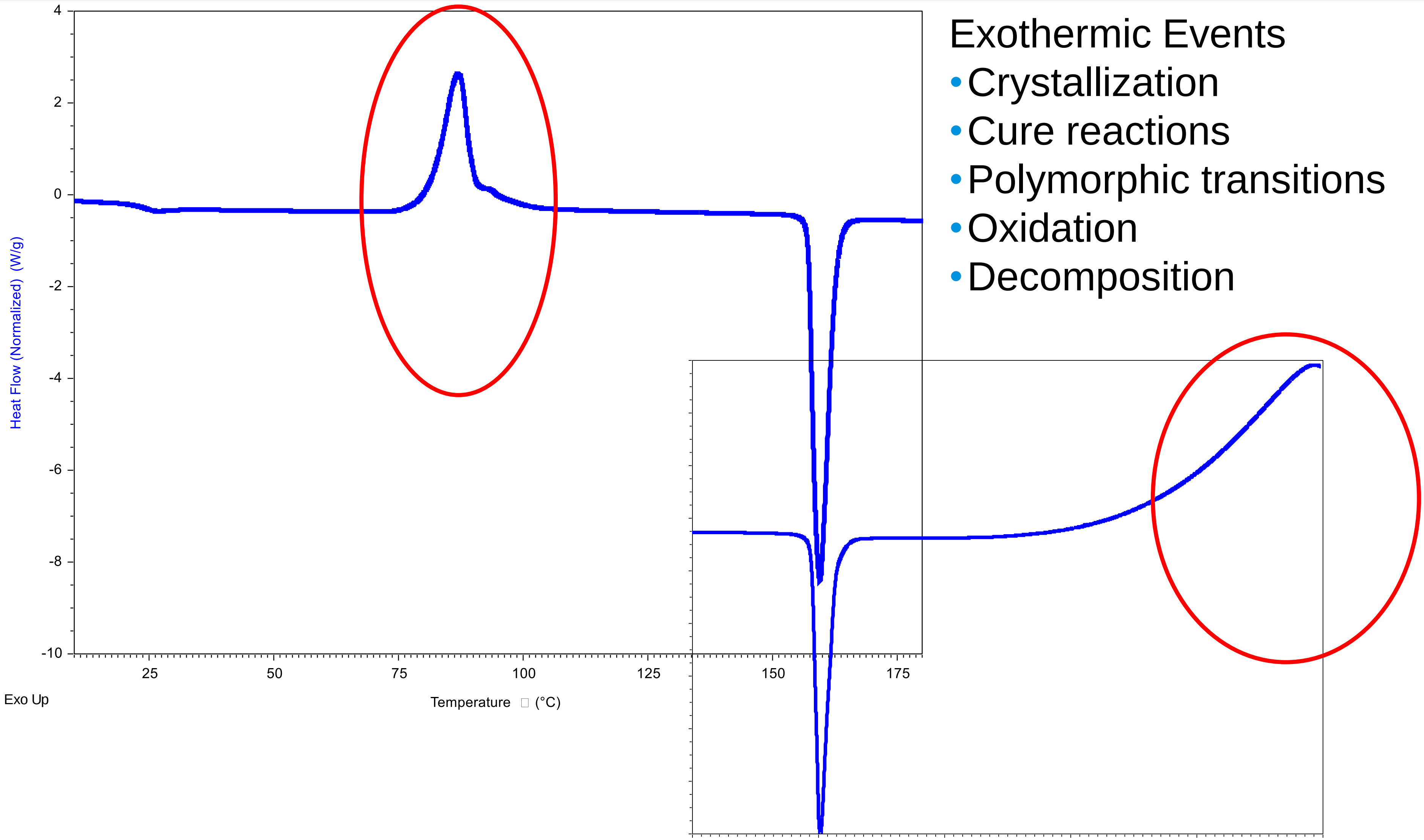
Endothermic Heat Flow
Heat Absorbed by Substance



Endothermic Events

- Glass transition
- Melting
- Evaporation/ volatilization
- Enthalpic recovery
- Polymorphic transitions
- Some decompositions

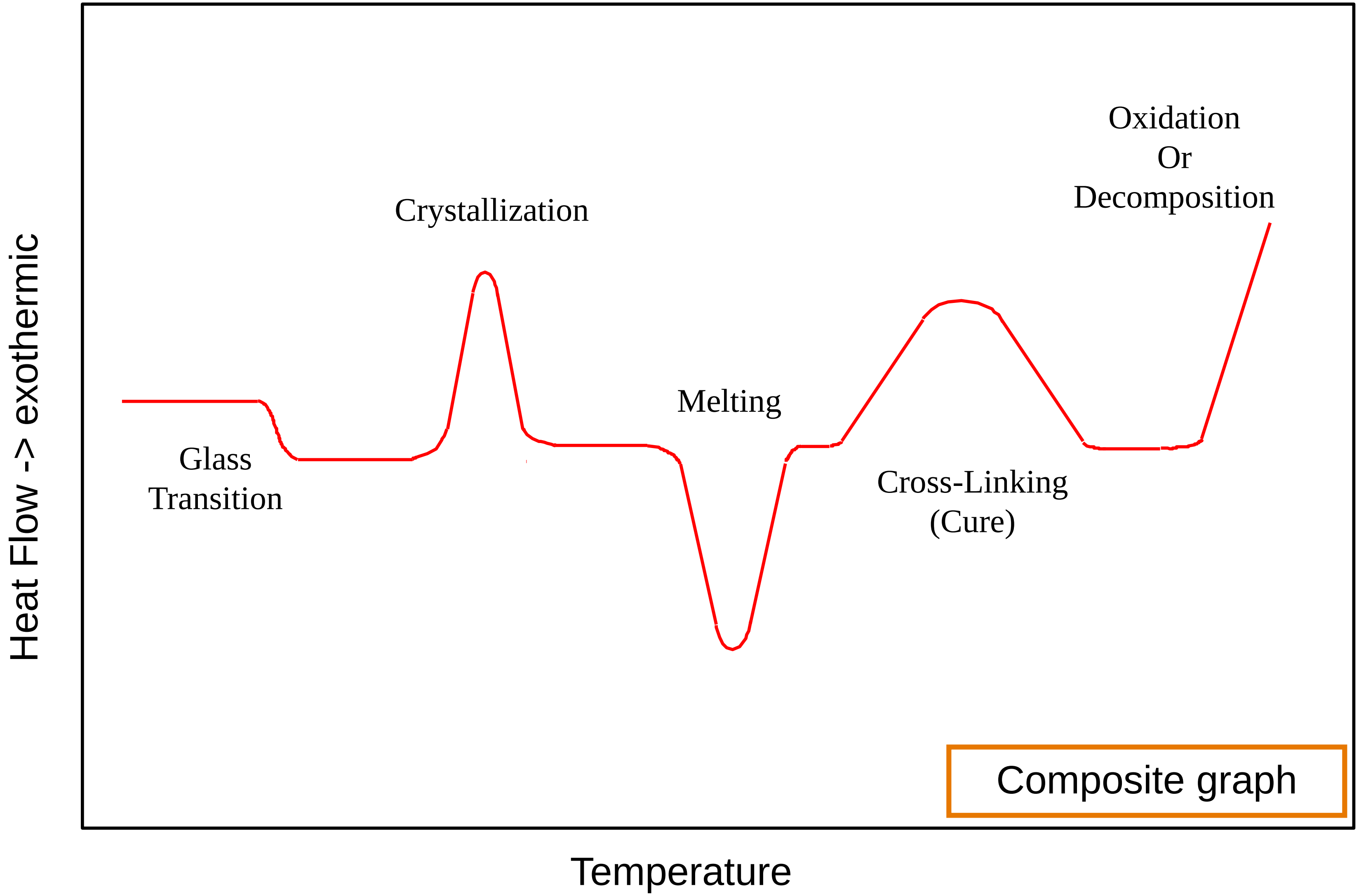
Exothermic Heat Flow
Heat Released by Substance



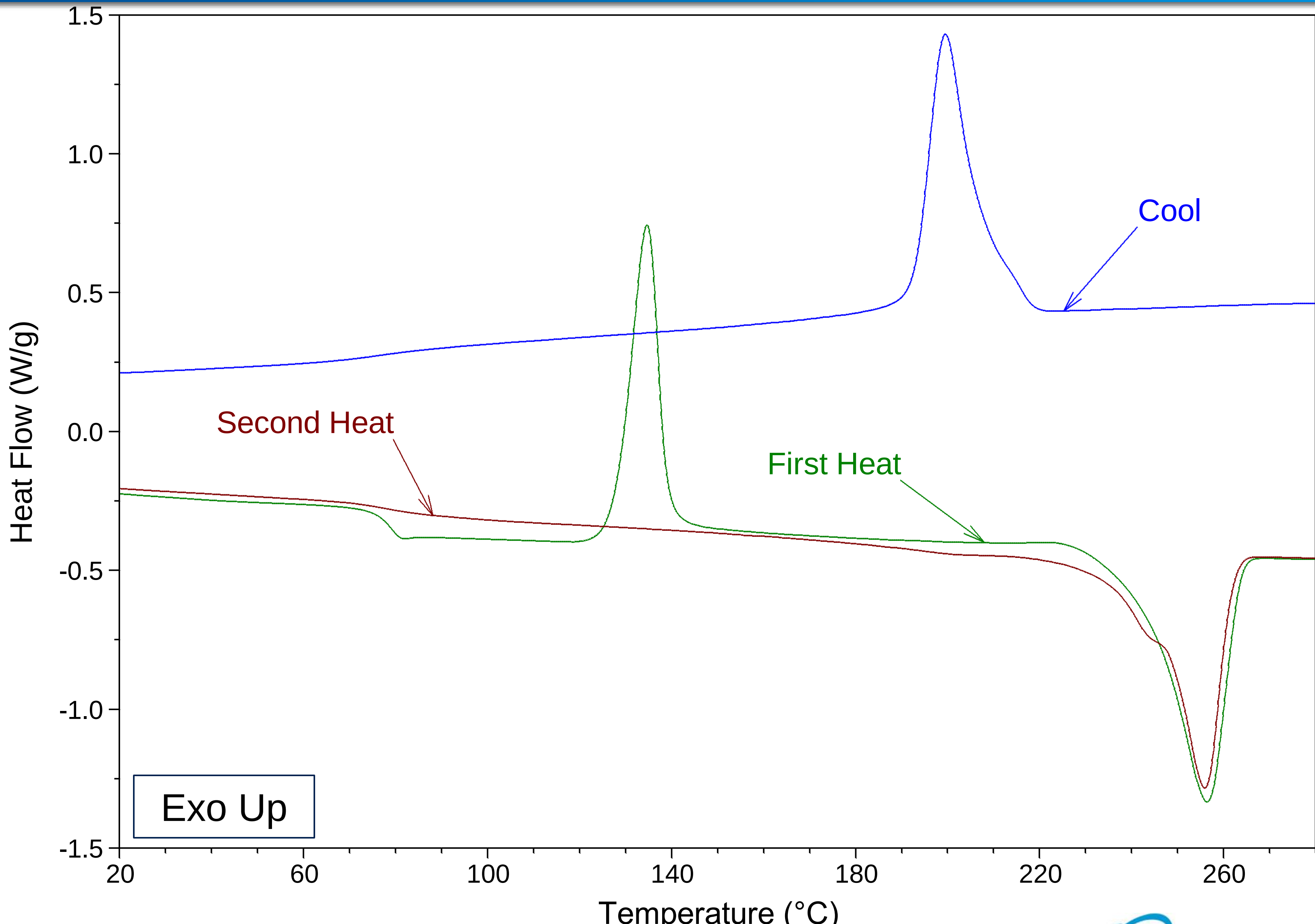
Exothermic Events

- Crystallization
- Cure reactions
- Polymorphic transitions
- Oxidation
- Decomposition

Typical DSC Transitions



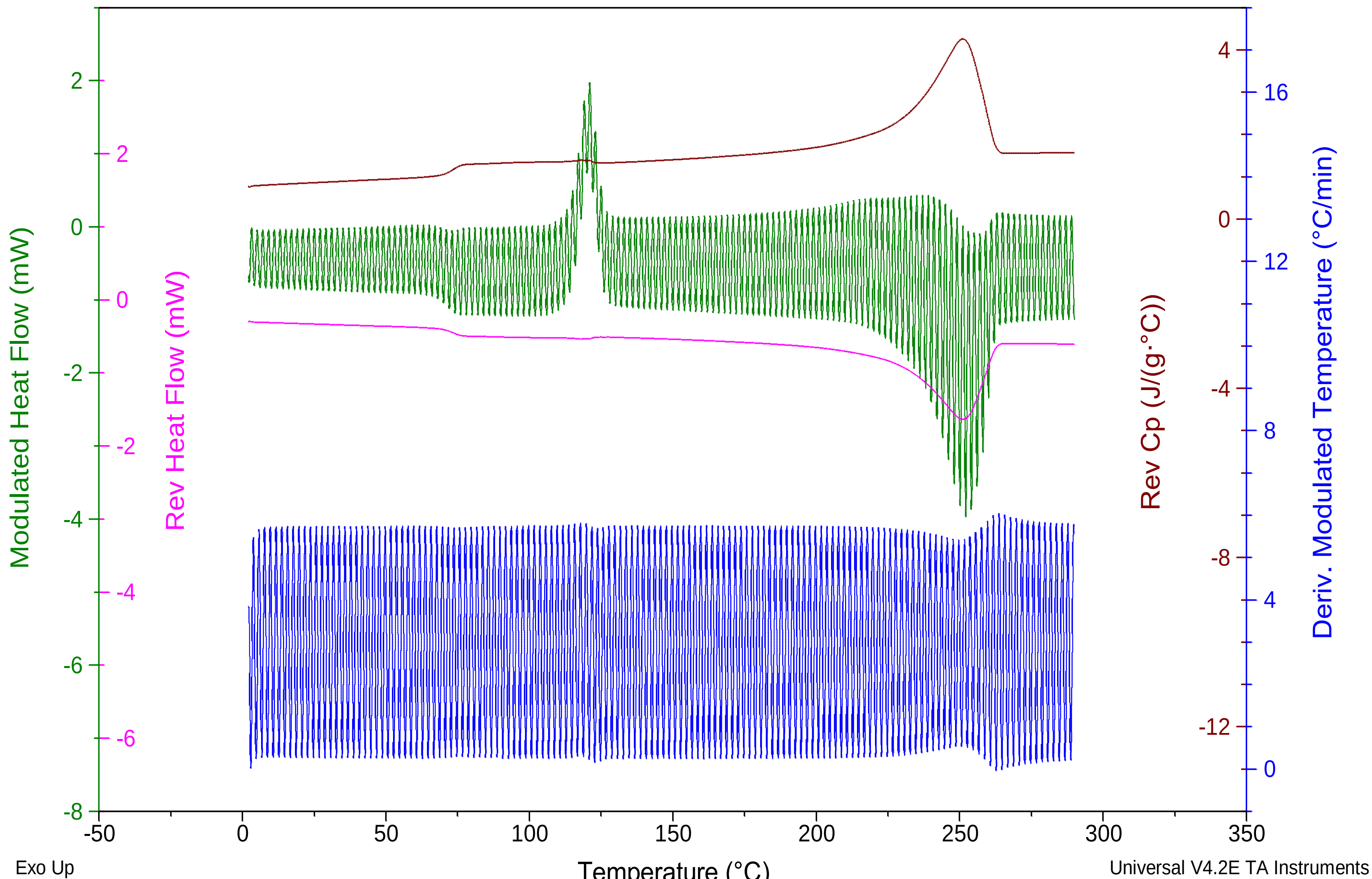
Polyethylene Terephthalate (PET)



What Does MDSC® Measure?

- MDSC separates the Total heat flow of DSC into two parts based on the heat flow that does and does not respond to a changing heating rate
- MDSC applies a changing heating rate on top of a linear heating rate in order measure the heat flow that responds to the changing heating rate
- In general, only heat capacity and melting respond to the changing heating rate
- The Reversing and Non-reversing signals of MDSC should never be interpreted as the measurement of reversible and nonreversible properties

Reversing Heat Flow and Heat Capacity



MDSC Heat Flow Signals

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

Total Heat Flow

- All Transitions

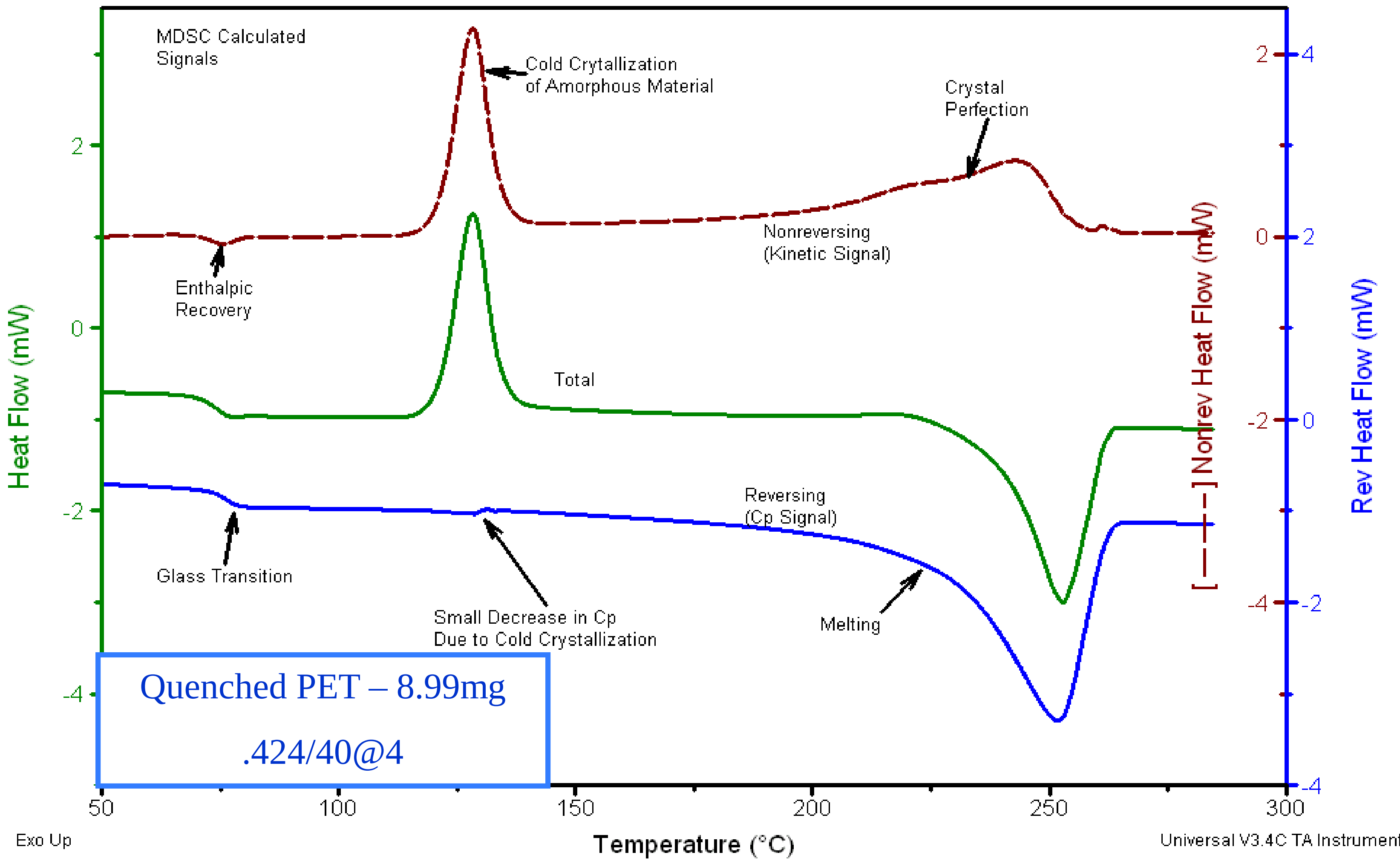
Reversing Heat Flow

- Heat Capacity
- Glass Transition
- Most Melting

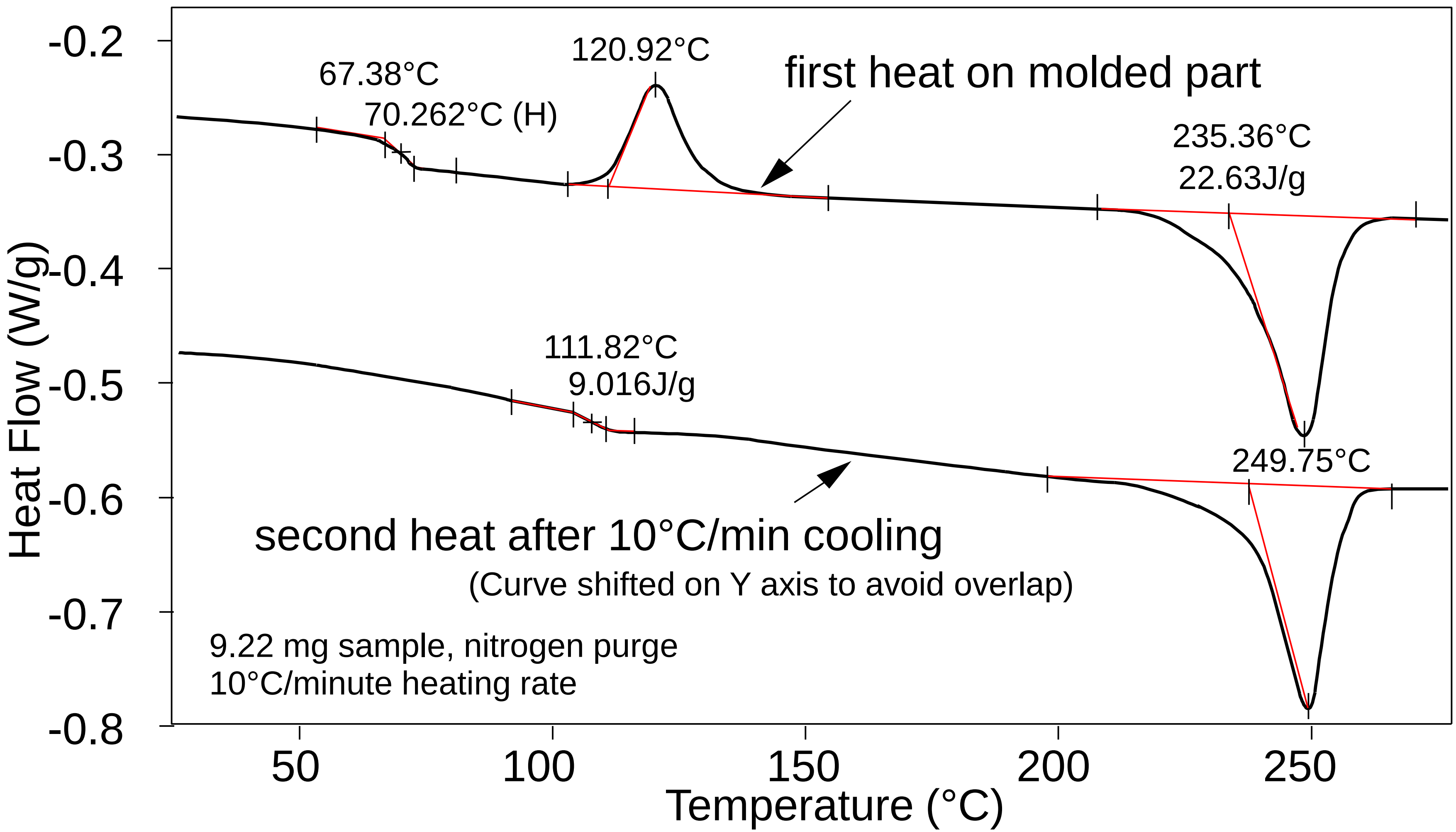
Non-Reversing Heat Flow

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

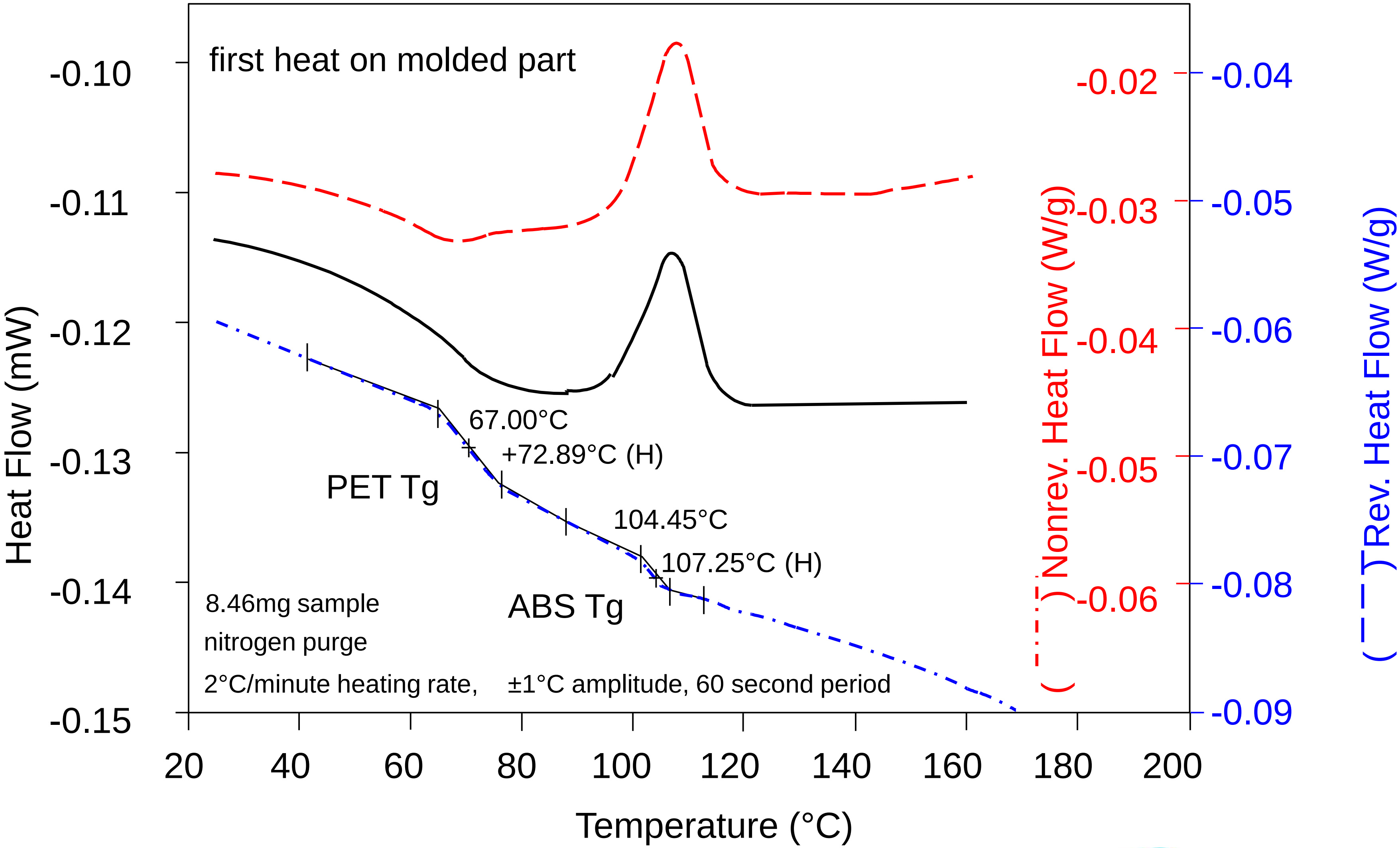
Calculated MDSC Heat Flow Signals



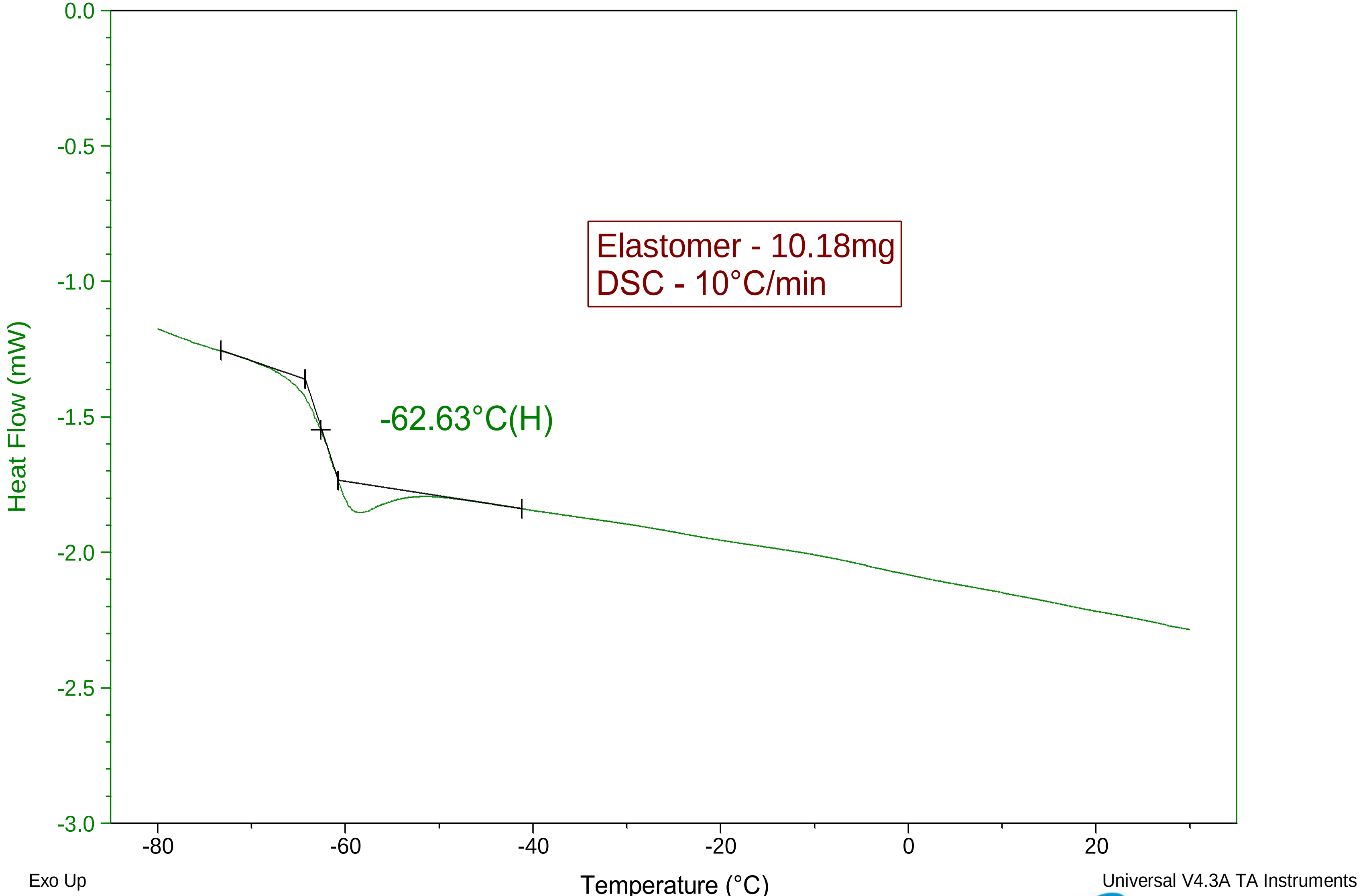
PET/ABS Blend - Conventional DSC



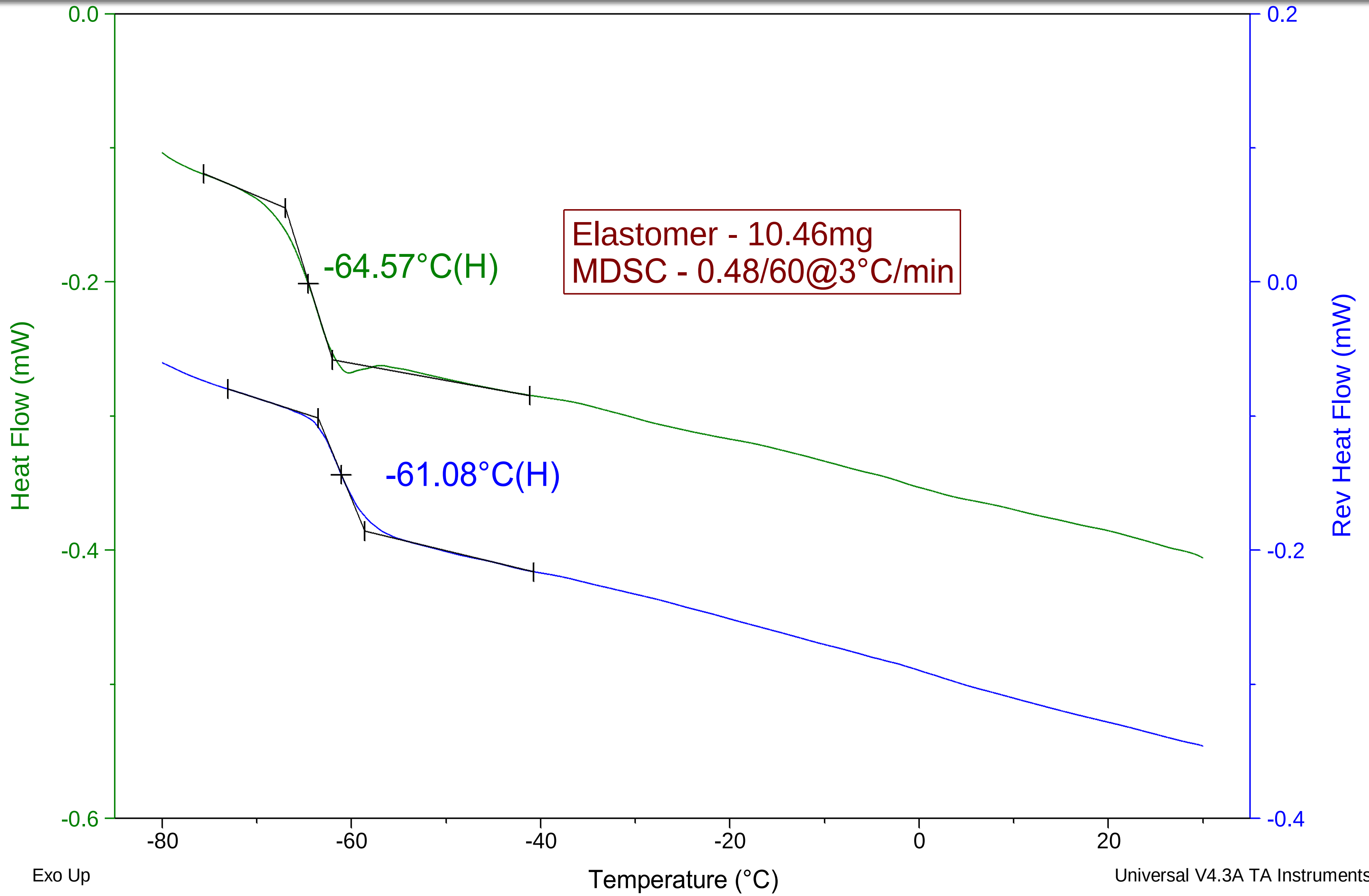
PET/ABS Blend - MDSC



Elastomer Tg by DSC



Elastomer Tg by DSC & MDSC



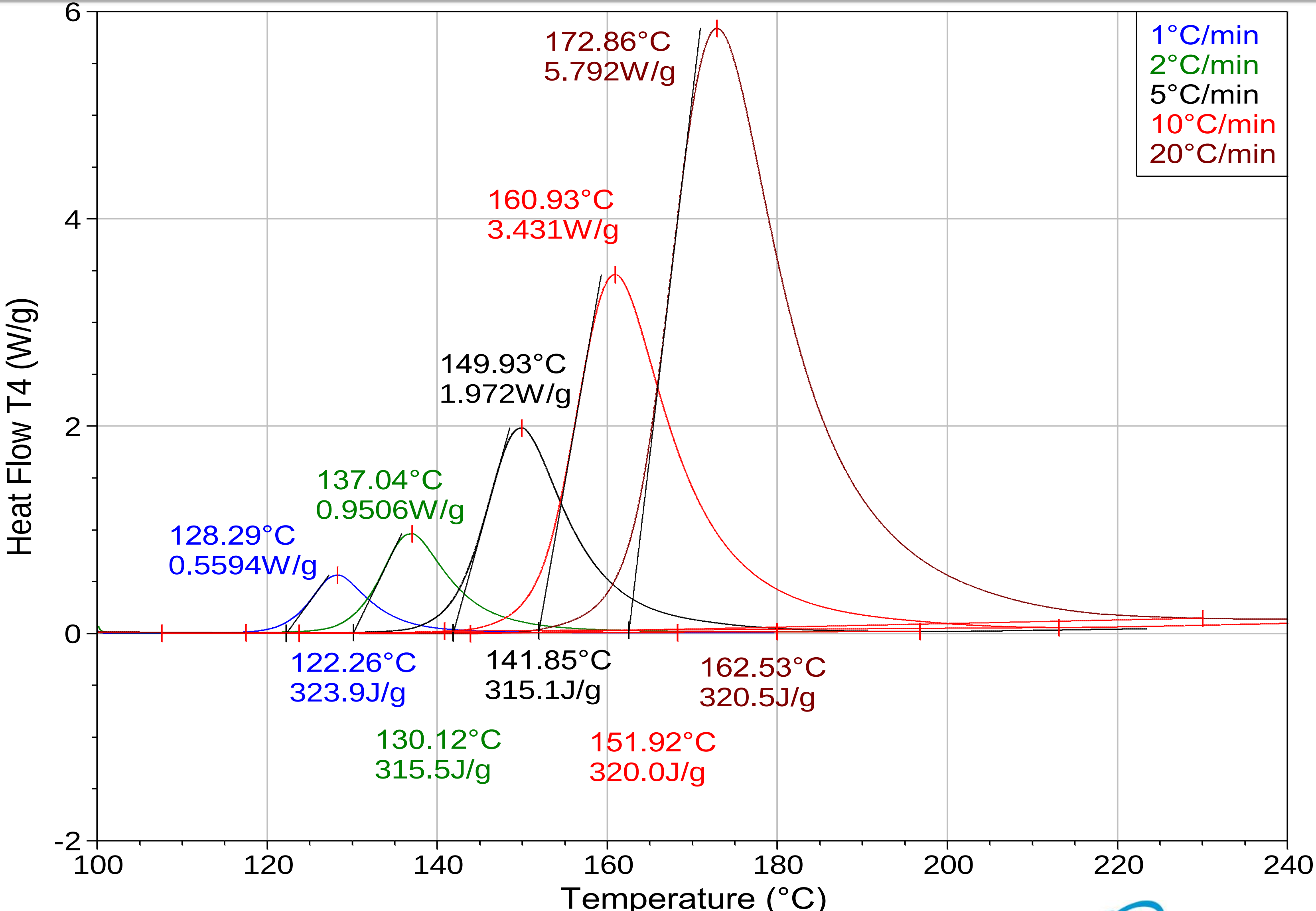
Curing Kinetics

Typical properties of crosslinking reactions

- Crosslinking reactions are generally exothermic. As the chemical reaction takes place, it is almost always accompanied by a release of heat.
- The reactions can be easily monitored using a DSC.
  - **Heat of reaction**
  - **Residual cure**
  - **Glass transition**
  - **Heat capacity**
- Crosslinking reactions are generally accompanied by a sharp change in the material's mechanical properties.
- Increase in modulus that may be accompanied by shrinkage.
- The reactions can thus be monitored using a Thermo-mechanical Analyzer (TMA)/Dynamic Mechanical Analyzer (DMA)/Rheometer.
  - **Viscosity**
  - **Modulus**
  - **Glass transition**
  - **Dimension change (shrinkage)**

These techniques give useful information about the impact of the polymerization conditions on the end product's thermo-mechanical properties.

Curing reactions are kinetic in nature



Use of Kinetic Modeling for Characterization of Curing Reactions

- Predict how long a reaction takes to go to completion
- Optimize polymerization, curing
- Quantify parameters that characterize time-temperature-dependent process behavior under conditions that may not always be experimentally feasible.

Fundamental equation for kinetics

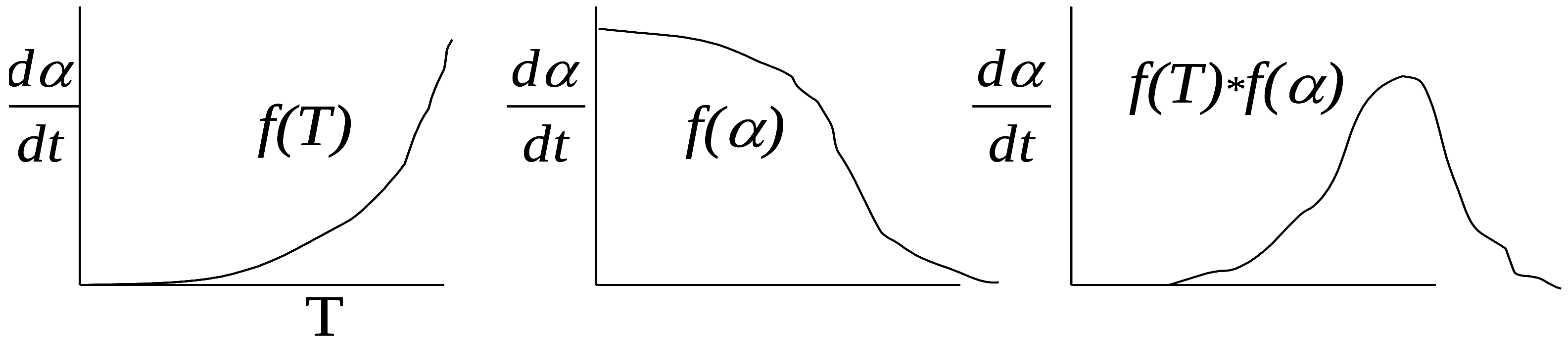
$$\frac{d\alpha}{dt} = f(T) \bullet f(\alpha)$$

α = fraction reacted or converted

$\frac{d\alpha}{dt}$ = reaction rate

$f(T)$ = a function of Temp.

$f(\alpha)$ = a function of α



Our Goal: Use DSC to solve for these functions

Fundamental equation for kinetics: the temperature factor

- Fundamental equation for kinetics

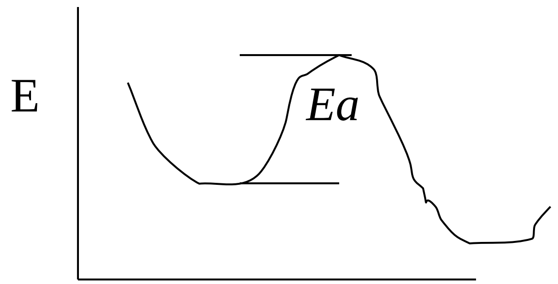
$$\frac{d\alpha}{dt} = \boxed{f(T)} \bullet f(\alpha)$$

- Arrhenius temperature dependence

$$f(T) = Ze^{-Ea/RT}$$

Where Ea is activation energy
Z is the "frequency factor"
R is the gas constant
T in kelvin

- Derived from dilute gas or solution, refined for solids
- Physical significance: Molecules colliding with sufficient kinetic energy to overcome Ea cause a reaction
- Pre-exponential factor, Z, "frequency factor" accounts for steric effects



Selection of appropriate model – the “α” factor

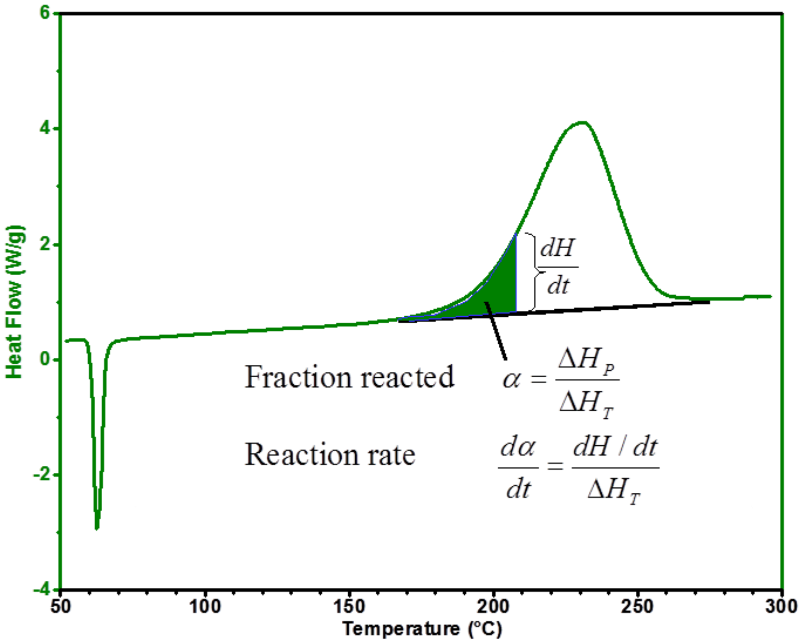
- Fundamental equation

$$\frac{d\alpha}{dt} = f(T) \bullet \boxed{f(\alpha)}$$

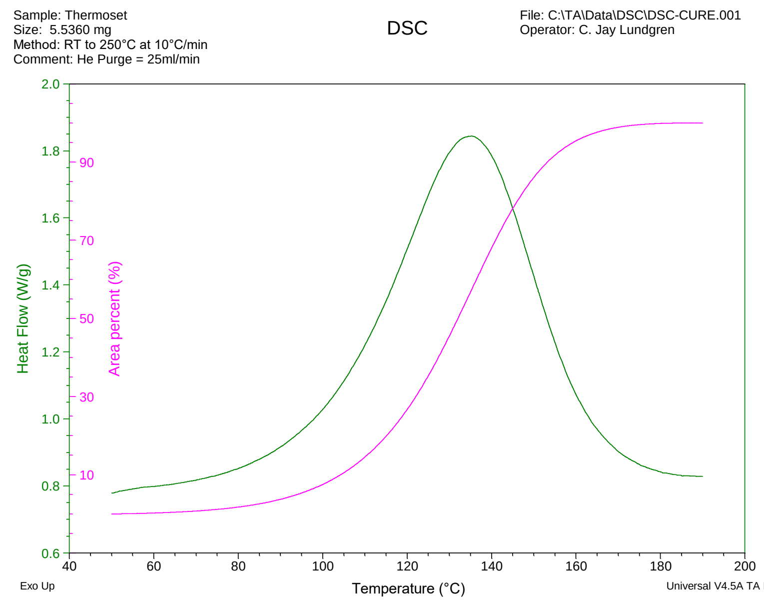
- Many models, three simple ones
  - n^{th} order reaction: $f(\alpha) = (1-\alpha)^n$ n is reaction order
  - Modelling technique:
    - n = 1: ASTM E698[1]/Ozawa, Wall and Flynn method[2]
    - n ≠ 1: ASTM E2041[3]/Borchardt and Daniels method[4]
  - Autocatalyzed reaction: $f(\alpha) = \alpha^m (1-\alpha)^n$ n and m are reaction orders
  - Modeling technique:
    - ASTM E2070[5]/Sestak and Berggren method (Isothermal kinetics)[6]

[1]ASTM E698, ASTM Annual Book of Standards 2005 volume 14.02
[2]Ozawa, T.J. J. Thermal Analysis, 1970, v2, p301
[3]ASTM E2041, ASTM Annual Book of Standards 2005 volume 14.02
[4]Borchardt, H.J., and Daniels, F.J., Am. Chem. Soc. 1956, v79, pg 41
[5]ASTM E2070, ASTM Annual Book of Standards 2005 volume 14.02
[6]Sestak, J., and Berggren, G., Thermochim. Acta, 1971, vol 3, pg 1

Obtaining kinetics information from a DSC experiment



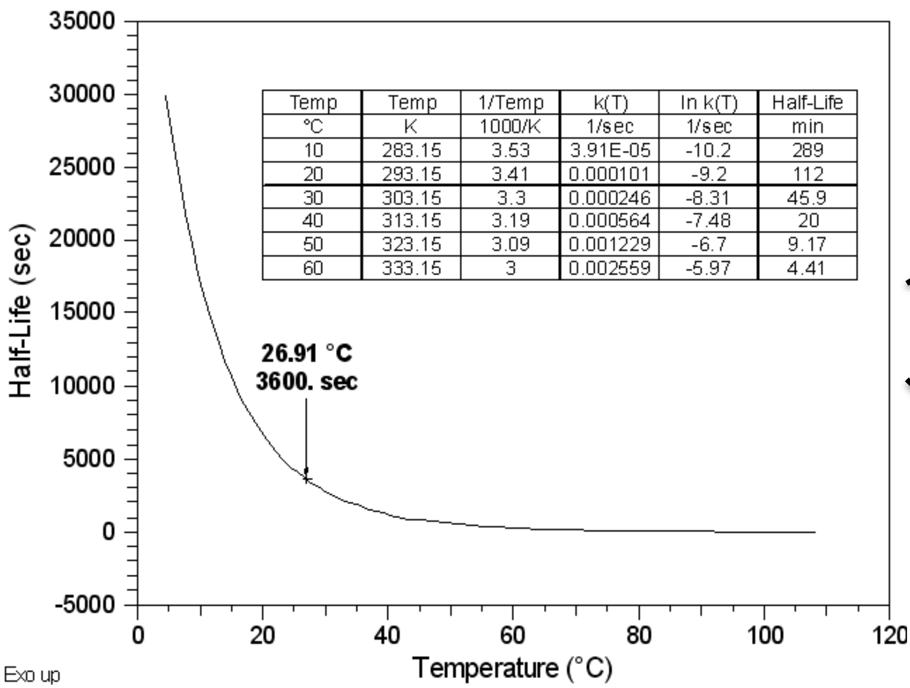
DSC gives us α and $d\alpha/dt$ vs time and temperature



Running integral option provides α as a direct function of time/temperature

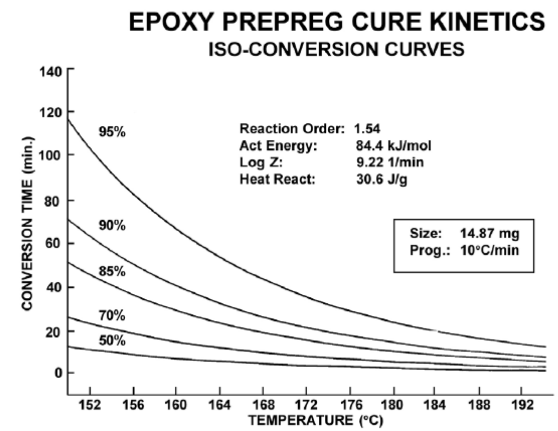
Kinetic analyses can provide valuable information

Half-life of the reaction: Use as litmus test for validity of kinetic model

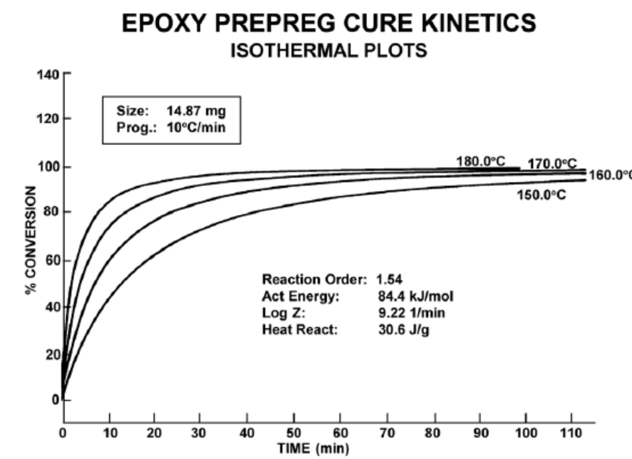


Temp	Temp	1/Temp	k(T)	ln k(T)	Half-Life
°C	K	1000/K	1/sec	1/sec	min
10	283.15	3.53	3.91E-05	-10.2	289
20	293.15	3.41	0.000101	-9.2	112
30	303.15	3.3	0.000246	-8.31	45.9
40	313.15	3.19	0.000564	-7.48	20
50	323.15	3.09	0.001229	-6.7	9.17
60	333.15	3	0.002559	-5.97	4.41

If verifies

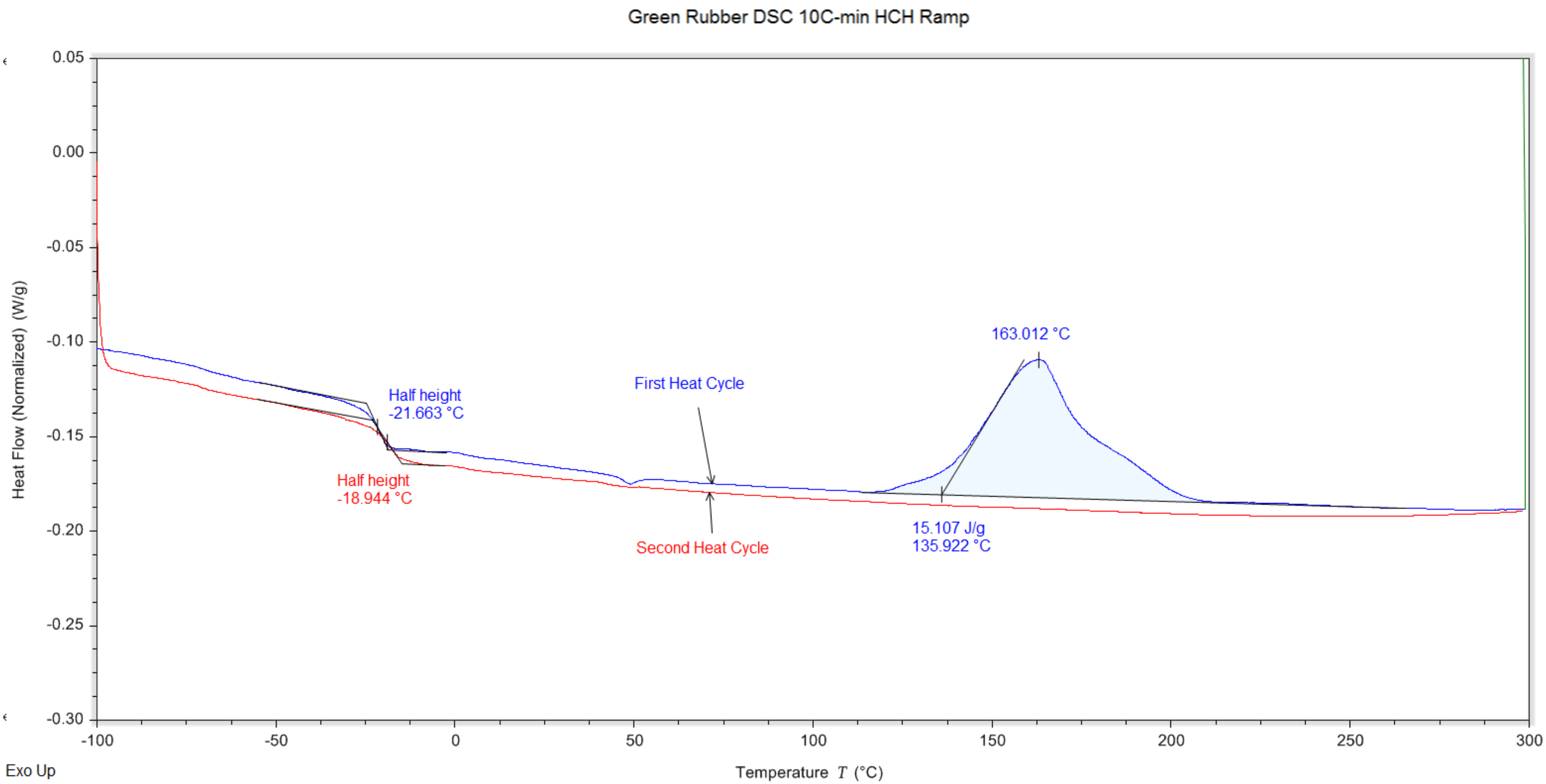


If verifies



Predict the cure temperature for one hour half life and carry out the iso cure in the DSC. Cool the sample after 1 hour and rerun. Was the residual reaction ½ the total heat of reaction?

Case Study: DSC of Green Colorant Rubber

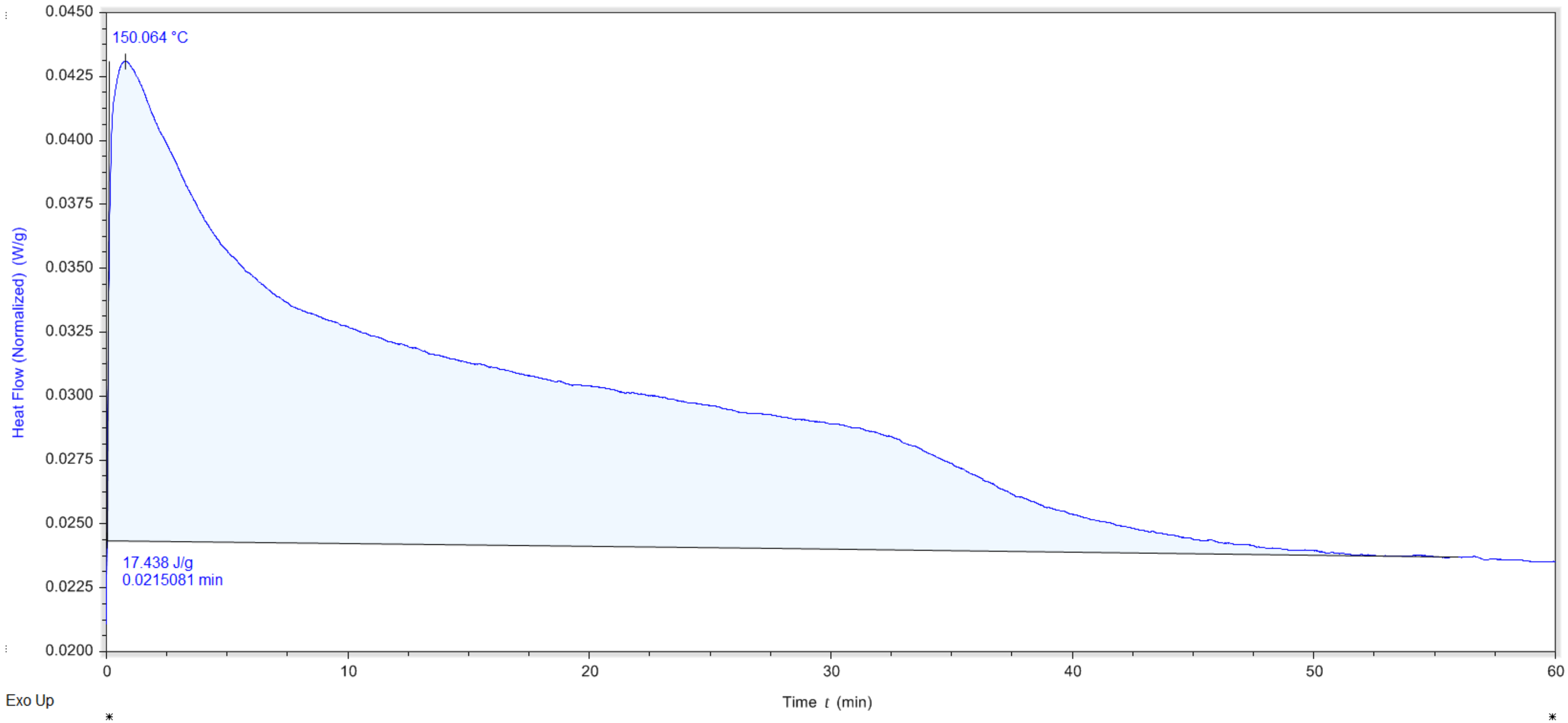


Case Study: Isothermal DSC Curing

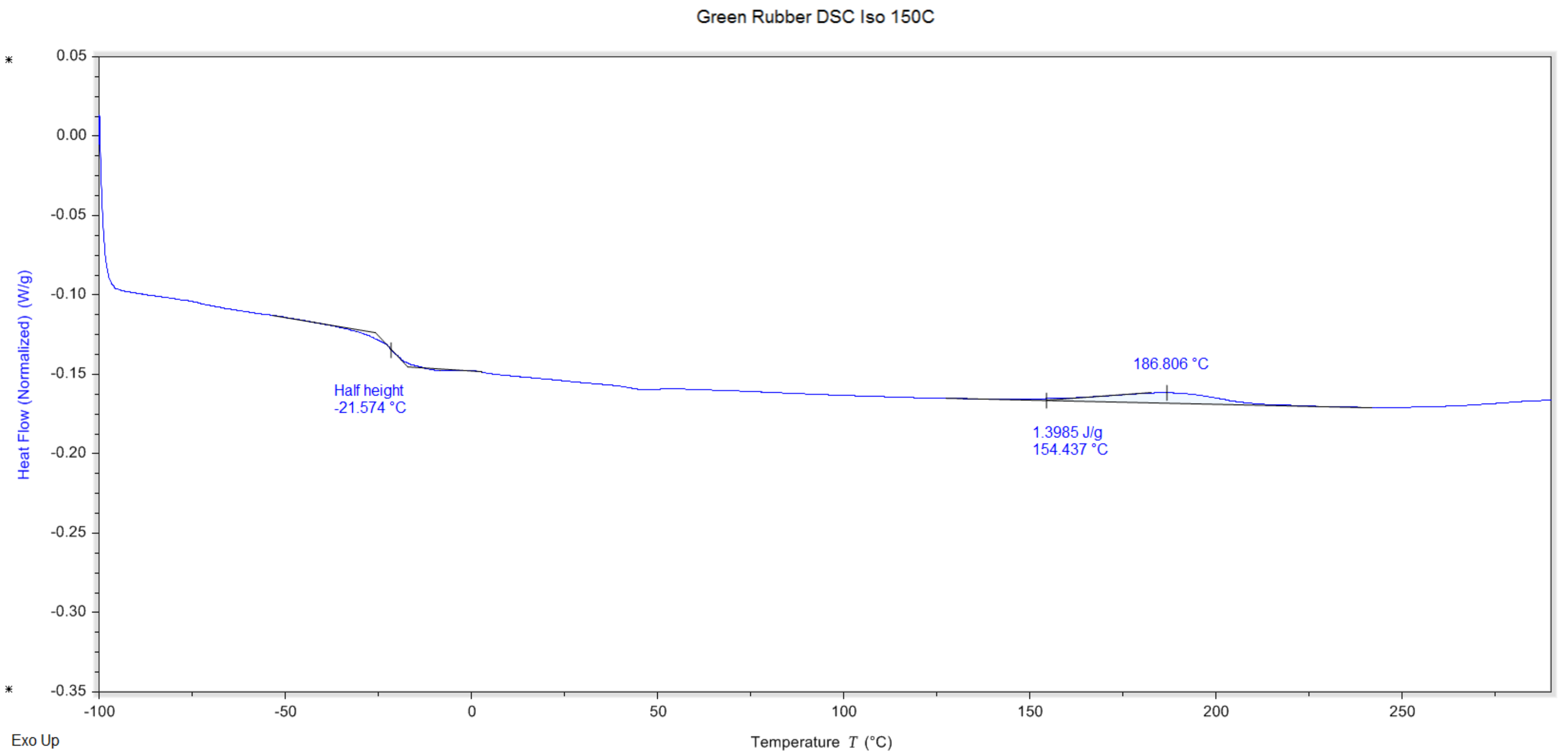
Method:

1. Equilibrate to 150 °C (160, 170, or 180 °C)
2. Mark end of cycle
3. Isothermal for 30 minutes
4. Mark end of cycle
5. Equilibrate to -100°C
6. Ramp 10°C/min to 300°C

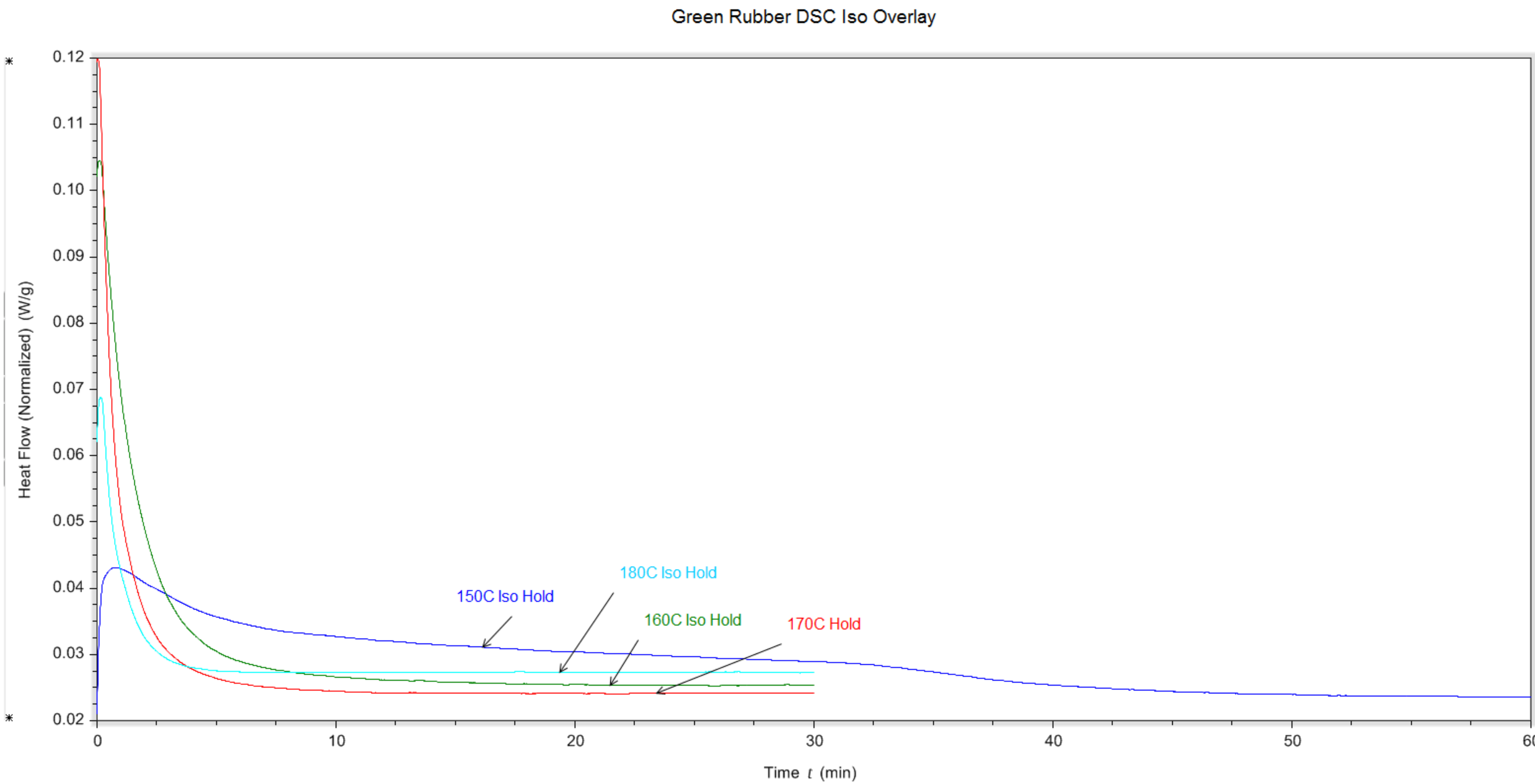
Case Study: DSC Isothermal at 150 °C



Case Study: Green Colorant Rubber Sample Ramp After Iso Hold at 150C



Case Study: DSC Isothermal Treatments



Case Study: Summary

- Differential scanning calorimetry can be used to simulate plant processing of thermosetting materials with limitations
- Common limitations are:
  - Too high a curing temperature to get good DSC data
  - Too low small or no curing exotherm
    - Examples: low level peroxide crosslinkers, vulcanization, highly cured specimens
- DSC can be used both to thermally condition the thermoset and then determine the extent of cure
- DSC kinetic model can be highly predictive
- Ongoing cutting edge academic studies

Section Summary

- Thermal analysis – both TGA and DSC – are widely used in the rubber industry
    - Material characterization (QC, R&D, etc.)
    - Process optimization through cure kinetics
    - Stability (thermal, oxidative)

- TA Instruments is a premier supplies of thermal analytical, rheological, thermal physical and other instrumentation to all technology based industries

Any questions?

Thank You

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