Analyzing & Testing

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Proven Excellence.

New Software for Thermal Simulation of Curing Reactions in Large Volumes

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38APS, Auckland, 20 February 2024

The NETZSCH Group

And its globally acting business units

Erich NETZSCH GmbH & Co. Holding KG

Analyzing & Testing

Thermal analysis instruments and instruments for the determination of thermophysical properties as well as Fire Testing and Rheology

Grinding & Dispersing

Comprehensive machine program for wet and dry grinding as well as mixing, dispersing, homogenizing and classifying

Pumps & Systems

Always the right positive displacement pump for your application

Products and Services for Applications in the Low- and High-Temperature Range from -260°C up to 2800°C

Thermal Analysis

Determination of changes in dimension and mass, phase transitions and enthalpies as functions of the temperature

Thermophysical Properties

Determination of thermal conductivity, specific heat capacity and thermal expansion coefficient

Accelerating Rate Calorimetry

Analysis of degradation and reaction processes with regard to temperature, dissipated heat and pressure curve

Fire Tester

Determination of the fire behavior of products in the automotive, construction, electronics and polymer industries; classification into "European fire classes”

Rheology

Determination of the rheological properties of non-Newtonian liquids and soft solids - from formulation to product use

Agenda

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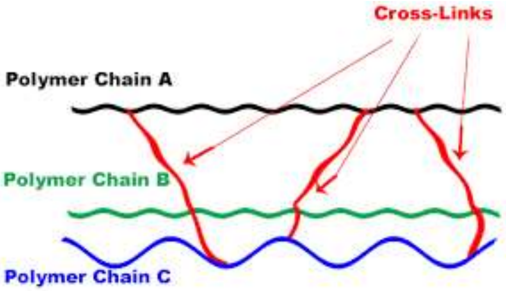
1. Background
2. Thermal Simulation of Large Volumes
3. Input Data for Thermal Simulations
4. Application Example – Epoxy curing
5. Summary

1 Background

Background: The Curing Process

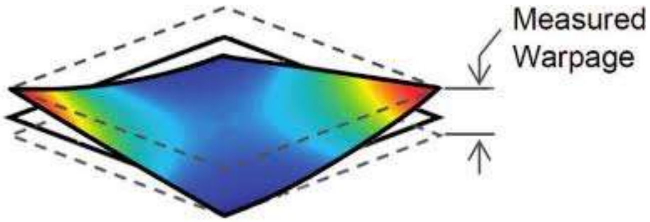
- Curing refers to an **irreversible chemical process** that transforms a material from a **soft, pliable state to a rigid, stable one**.
- This transformation usually involves the **formation of cross-links** between the individual molecules or chains within the material.
- Curing is an **exothermic process** and is typically seen in thermosets (epoxies, polyesters, silicones), elastomers, paints and coatings, adhesives etc.



Source: https://uspackagingandwrapping.com

Background: The Curing Process

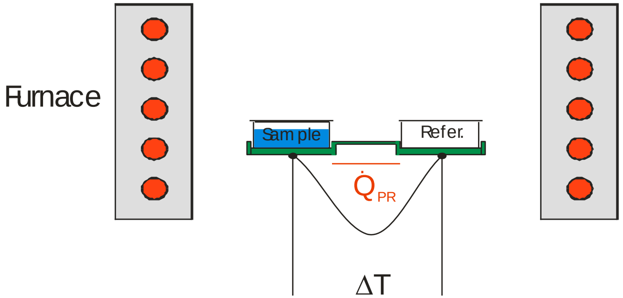
- In product manufacturing the **industrial processes must be designed with utmost care** to reduce scrap production, processing defects and catastrophic failures.
- **Incorrect curing cycles can lead to overheating** and subsequent product defects including:
    - Cracking and warping
    - Bubble voids
    - Optical properties
    - Loss of mechanical properties
- **Technology leaders** in thermoset component manufacturing use **experimental and computational methods to risk minimise** their manufacturing processes



Source: https://journals.sagepub.com/doi/pdf/10.1177/00219983211002247

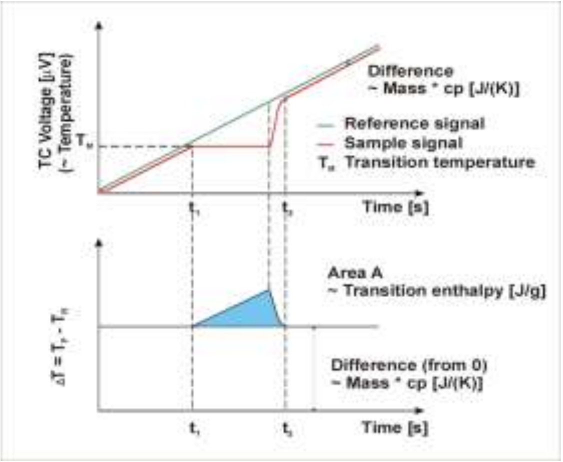
DSC Method
A commonly used technique for checking degree of cure

DSC - Heat Flux Type



DSC = Heat Flow (S) – Heat Flow (R)

NETZSCH DSC 300 *Caliris*® Classic



Step 1 – Check Conversion of CFRP Prepreg (12 hour cycle)

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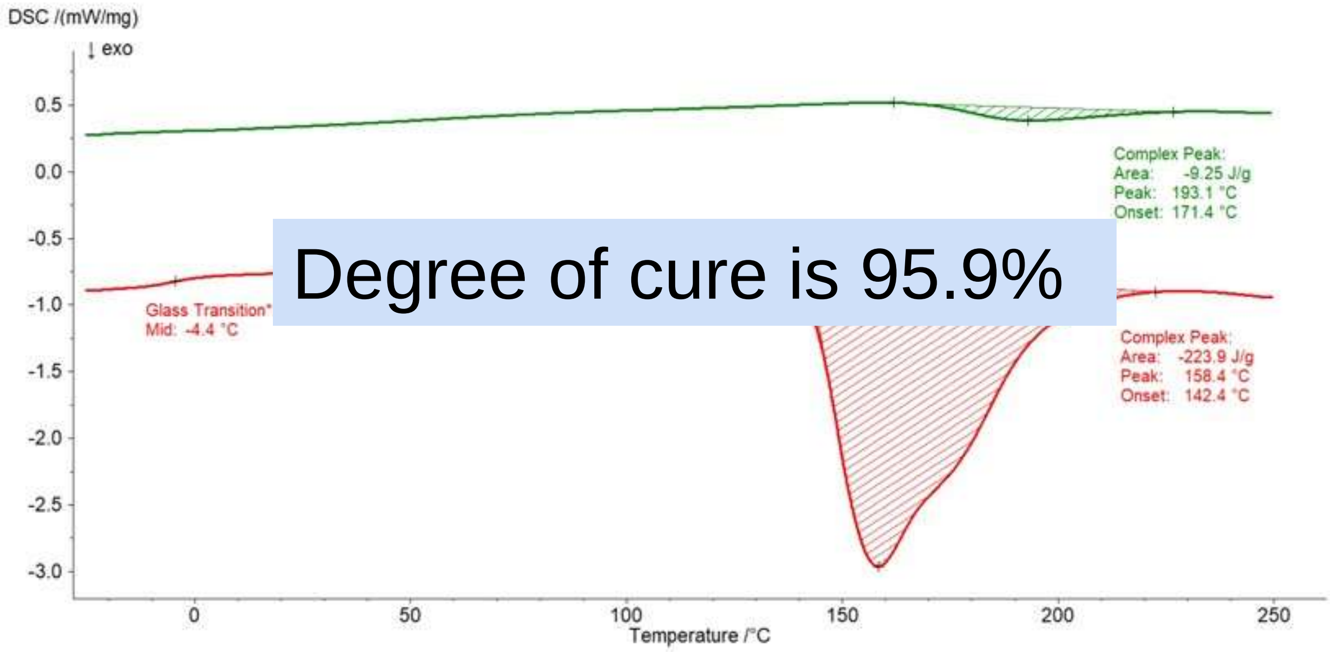

DSC 214 *Polyma*®
Sample: CFRP prepreg
Atmosphere: Nitrogen
Heating Rate: 20K/min

$$\alpha = \frac{H_{tot} - H_{res}}{H_{tot}}$$

α= degree of cure
H_{tot} = total enthalpy of cure
H_{res} = residual cure

A DSC measurement alone is not enough for optimisation of a cure cycle

Background: Kinetic Modelling of Curing Reaction

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1) *"Kinetics"*: the study of chemical processes and reaction rates to understand the influences that affect the reaction mechanisms.

2) Curing is generally a diffusion controlled reaction – after gel point point mobililty of molecules decreases and results in lower reaction rates

3) Mathematical models fit **real measurement data** to further describe and predict the reaction

$$\frac{d\alpha}{dt} = A(\alpha)exp\left(\frac{-E_a(\alpha)}{RT}\right) f(\alpha)$$

conversion rate

reaction model

Arrhenius equation: temperature dependency of the reaction rate

α: conversion

A: pre-exponential factor (likelihood-factor for molecular collisions)

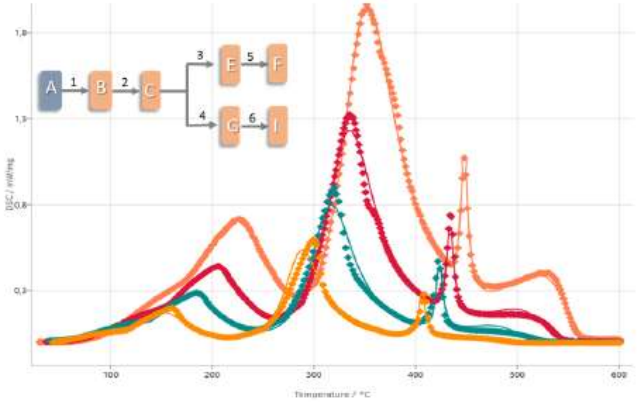
E_a: activation energy

T: temperature

R: ideal gas constant

KINETIC ANALYSIS

I) Multiple Measurements
(DSC, TGA, Rheology...)
↓
ASCII Data
↓
II) NETZSCH *Kinetics Neo* software
↓
Kinetic Analysis
↓
III) Predictions, Optimizations, Simulations
(Rxn Progress, Concentration/s, TTT Diagram)



- **Model-Free Analysis (Single/Multipoint)**
  - ASTM E698 (Arrhenius), E2890, E1641
  - Friedman/Ozawa-Flynn-Wall Analyses/Vyazovkin
  - Numerical Optimization (based on Friedman)
- **Model-Based Analysis**
  - multi-variate non-linear regression (NLR)
  - 21 different reaction types
  - unlimited combinations of reaction steps

Application Example: Optimising the Cure Cycle of a CFRP Bike Wheel

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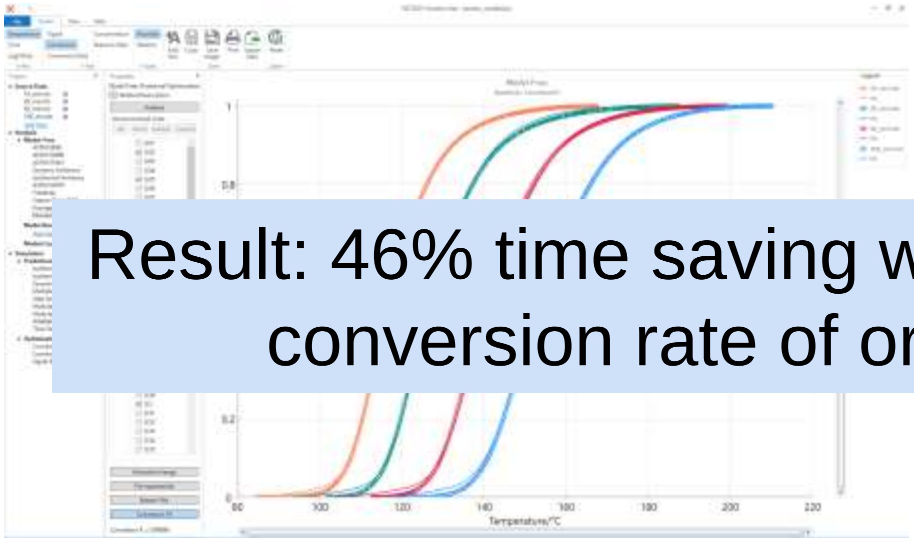
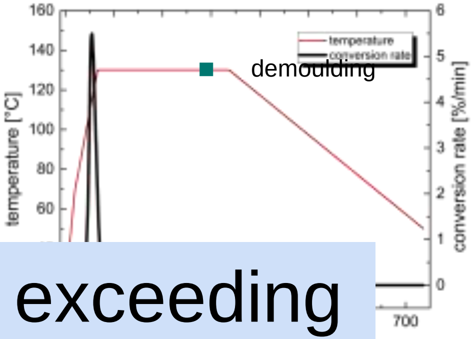
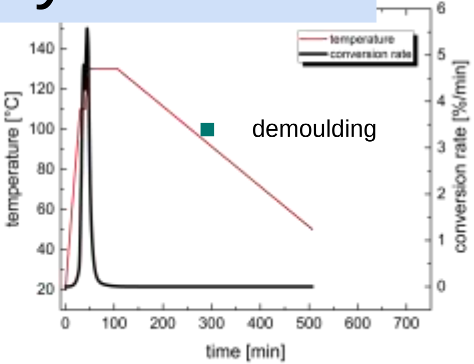


Conventional Cycle



Result: 46% time saving without exceeding conversion rate of original cycle



‘Numerical Optimisation’ Provides Easy One Click Solution – R^2=0.99896

Kinetic Analysis does not consider the temperature gradients in the reacting volume

2 Thermal Simulation of Large Volumes

Why Kinetic Analysis is not enough?

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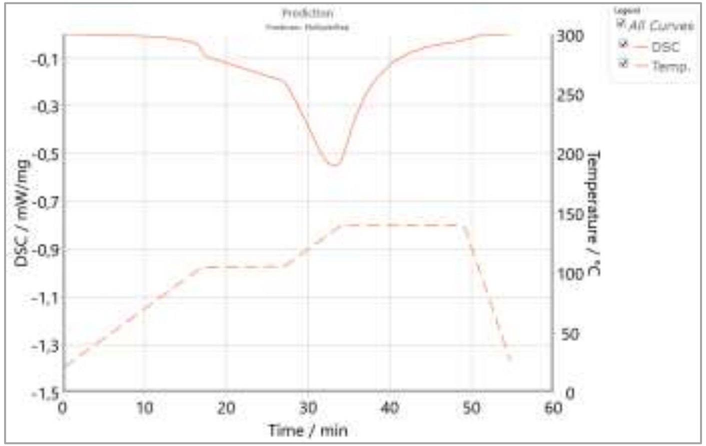
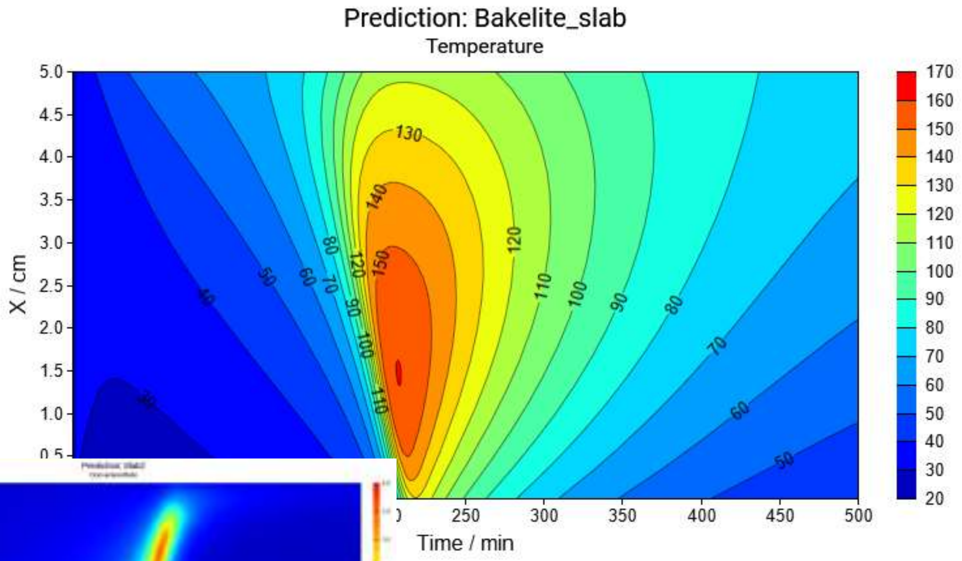
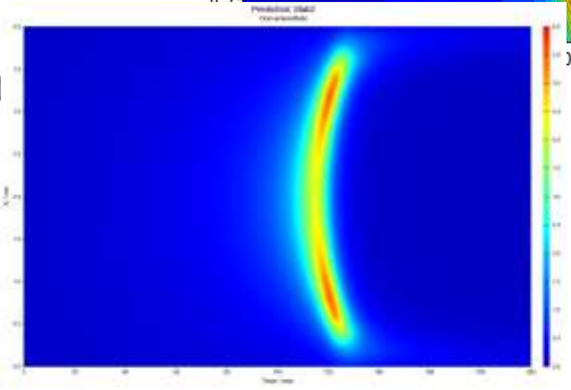
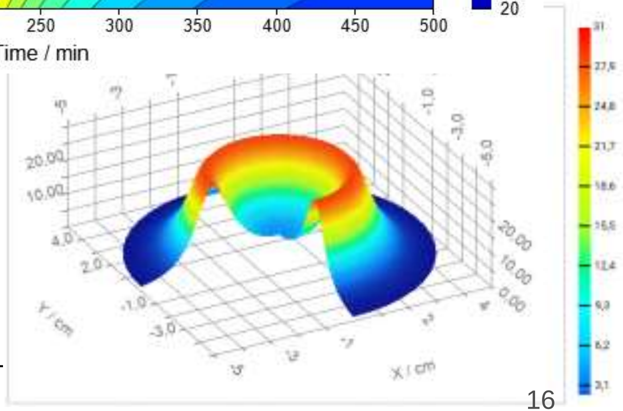




Kinetic Analysis:
Infinitesimally small material volume at defined temperature





Industry needs:
Consideration of large material volumes, including temperature gradients and heat transfer

Why a new software was needed?

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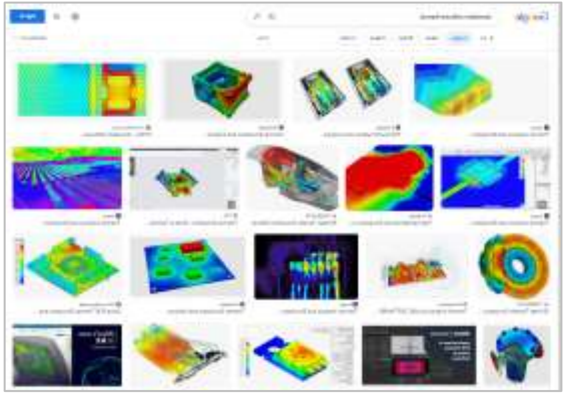
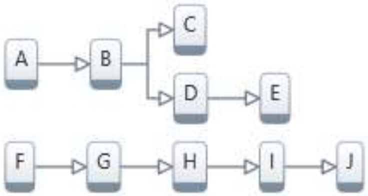


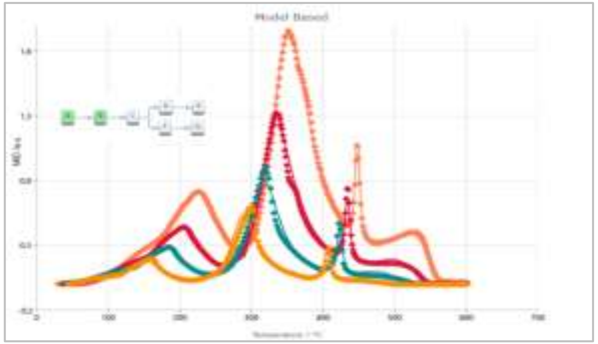
Existing FEM solutions:

1. Existing software works with complex geometry but with simple chemical processes
2. Problems with transfer of kinetic parameters from kinetic software to simulation software
3. Some processes have complex mathematical description and can not be transferred to simulation software

New Thermal Simulation software:



1. Simple geometry, but complex processes
2. Automatic loading of kinetic parameters and equations from NETZSCH Kinetics Neo
3. No limitation for complexity of the chemical system



Our Complete Solution for Simulating Reactions in Large Volumes

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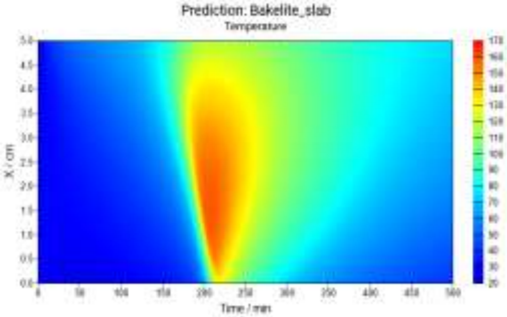
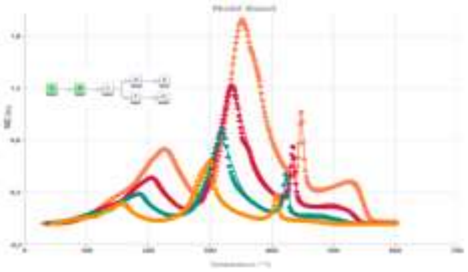
3. Simulation (kg, ton)



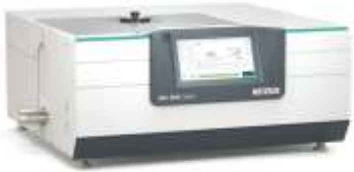
TERMICA NEO

2. Chemical Kinetics (mg)



KINETICS NEO

1. Laboratory measurements (mg)



Laboratory Instrument:
DSC / DIL / Rheometer …

Heat balance for small element with reaction heat as the heat source

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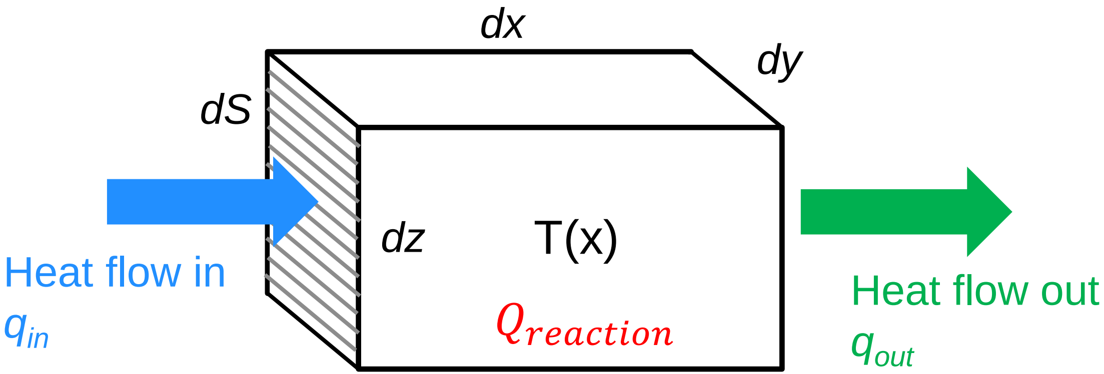

$$Cp \cdot dm \cdot \frac{dT}{dt} = q_{in} - q_{out} + Q_{reaction}$$

$$\frac{\partial T}{\partial t} = a \frac{\partial^2 T}{\partial^2 x} + \Delta T_{ad} \frac{d\alpha}{dt}$$

$$\frac{\partial T}{\partial t} = a \left[\frac{\partial^2 T}{\partial^2 x} + \frac{\partial^2 T}{\partial^2 y} + \frac{\partial^2 T}{\partial^2 z} \right] + \Delta T_{ad} \frac{d\alpha}{dt}$$

$dS = dy\ dz$	Area
$dV = dx\ dy\ dz$	Volume
$dm = \rho\ dV$	Mass
$q_{in} = dS\ \lambda \left. \frac{\partial T}{\partial x} \right\|_{x - \frac{dx}{2}}$	Heat flow *in* at point x-dx/2
$q_{out} = dS\ \lambda \left. \frac{\partial T}{\partial x} \right\|_{x + \frac{dx}{2}}$	Heat flow *out* at point x+dx/2
$Q_{reaction} = \Delta H \cdot dm \cdot \frac{d\alpha}{dt}$	Reaction Heat
$Cp \cdot dm \cdot \frac{dT}{dt}$	Self-heating
$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot \exp\left[\frac{-E}{RT}\right]$	Reaction rate
$q_{in} - q_{out} = dS\ \lambda \frac{\partial^2 T}{\partial^2 x}$	Heat flow difference
$a = \lambda / (Cp \cdot \rho)$	Thermal diffusivity
$\Delta T_{ad} = \Delta H / Cp$	Adiabatic Temperature increase

3 Data for simulations

Kinetic data for analysis with information about Heat Production

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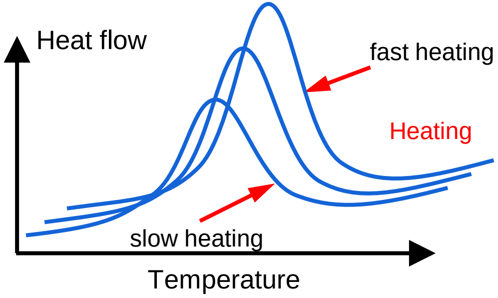
Thermosets, Composites
Curing, Cross-linking

DSC

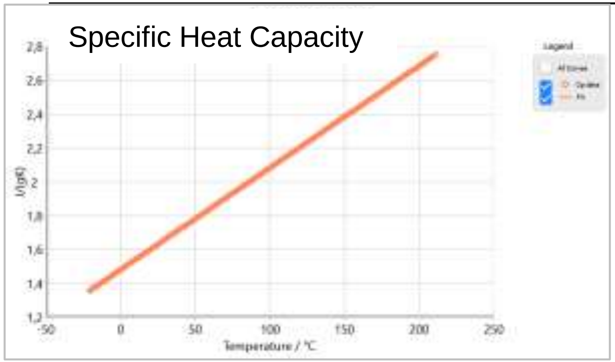


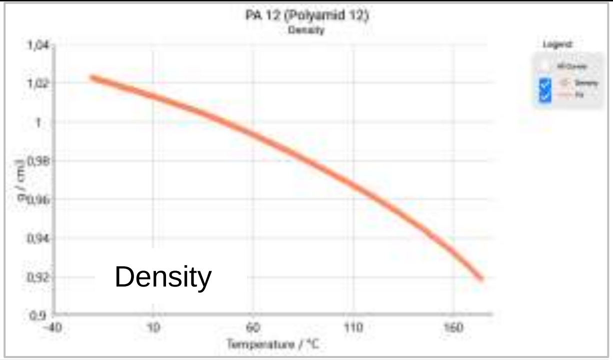
Features:

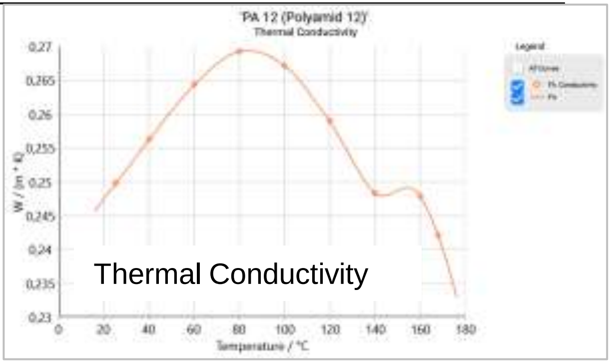
- Temperature range: -170°C ... 600°C
- Heating/cooling rates: 0.001K/min ... 500 K/min
- Automatic sample changer: 20 samples (optional)

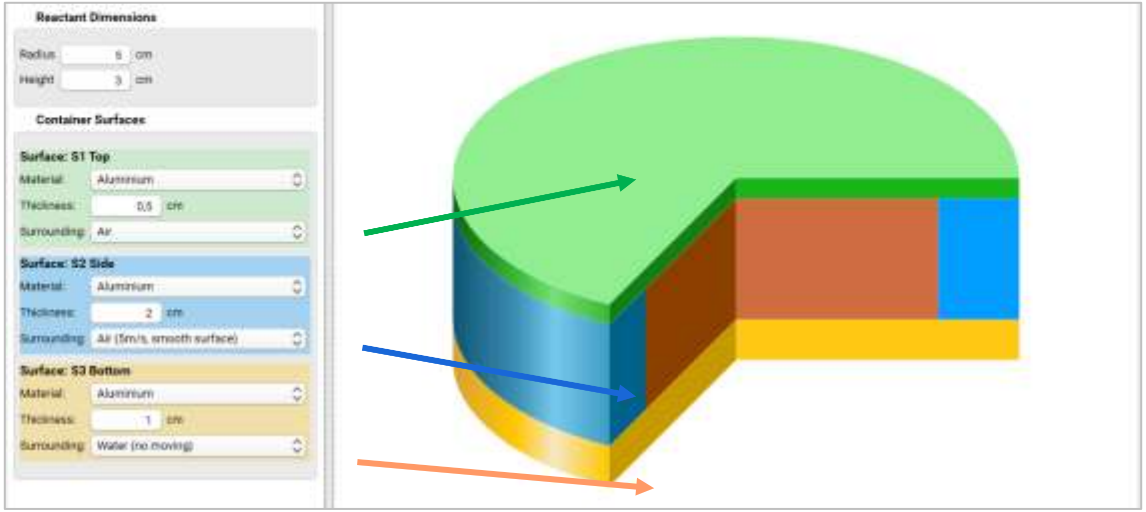
Additional instruments: Other calorimetric instruments

Physical data for simulation: reacting media and containers







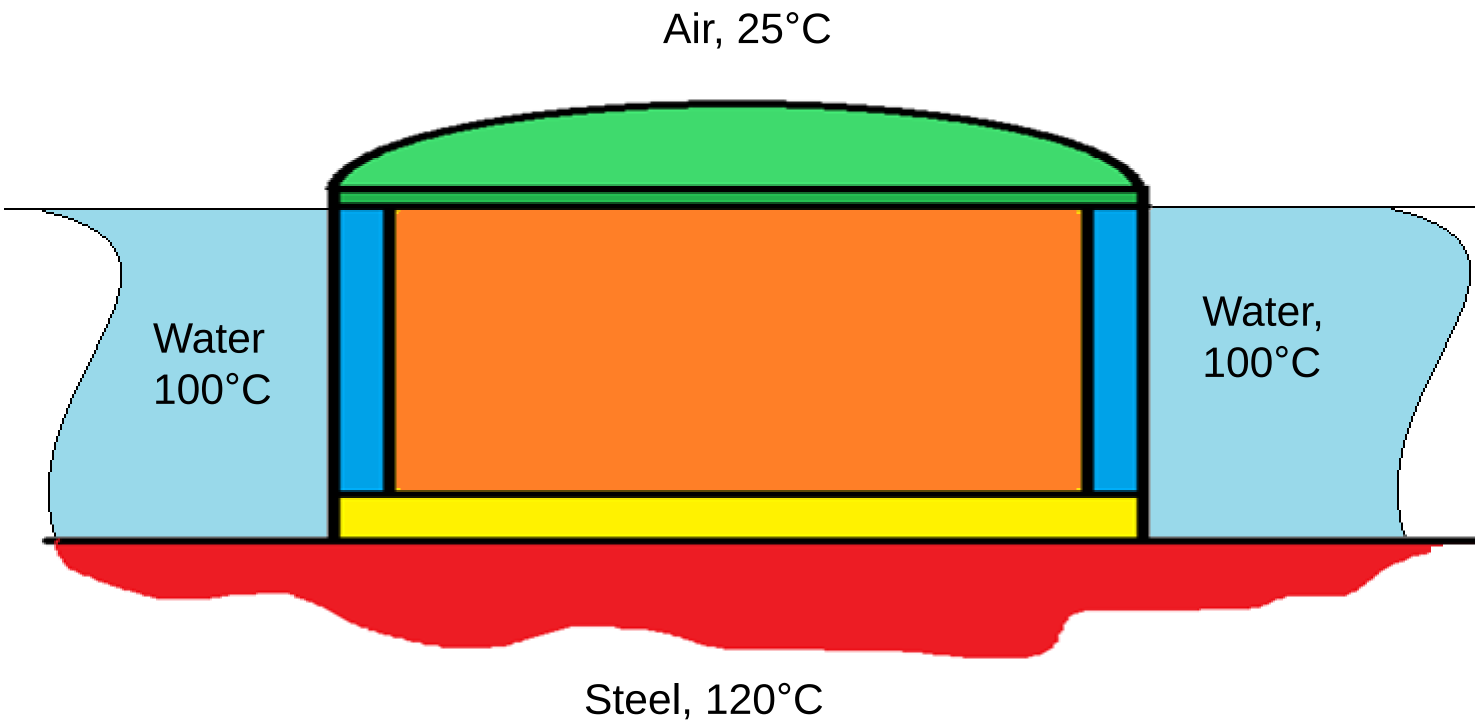


<u>Surface properties:</u>
Heat transfer coefficient and emissivity

All physical properties are temperature-dependent

<u>Material library</u>
contains mostly used materials like polymers, metals, alloys

Define Surrounding Materials and Temperature Profiles



4 Application Example: Epoxy curing

Is the curing reaction finished after 2 hours?

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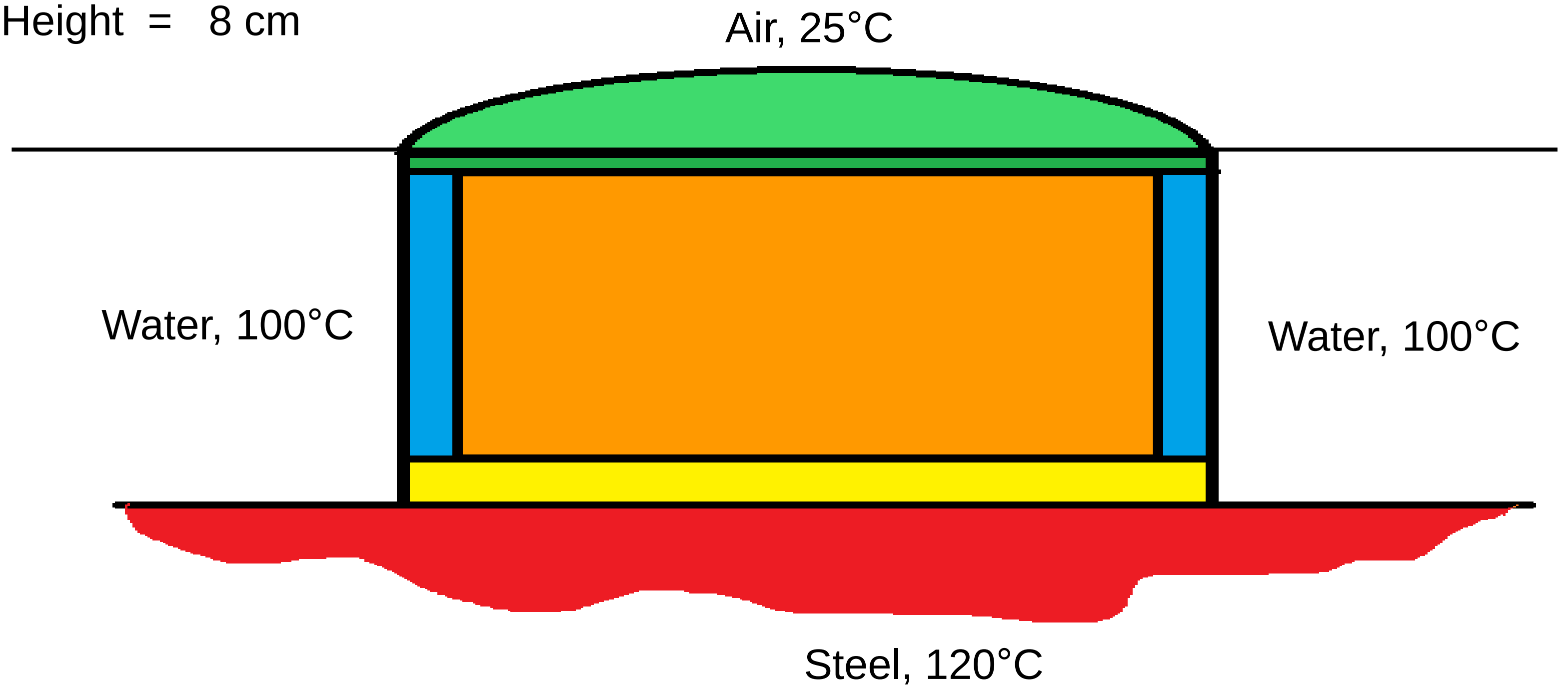
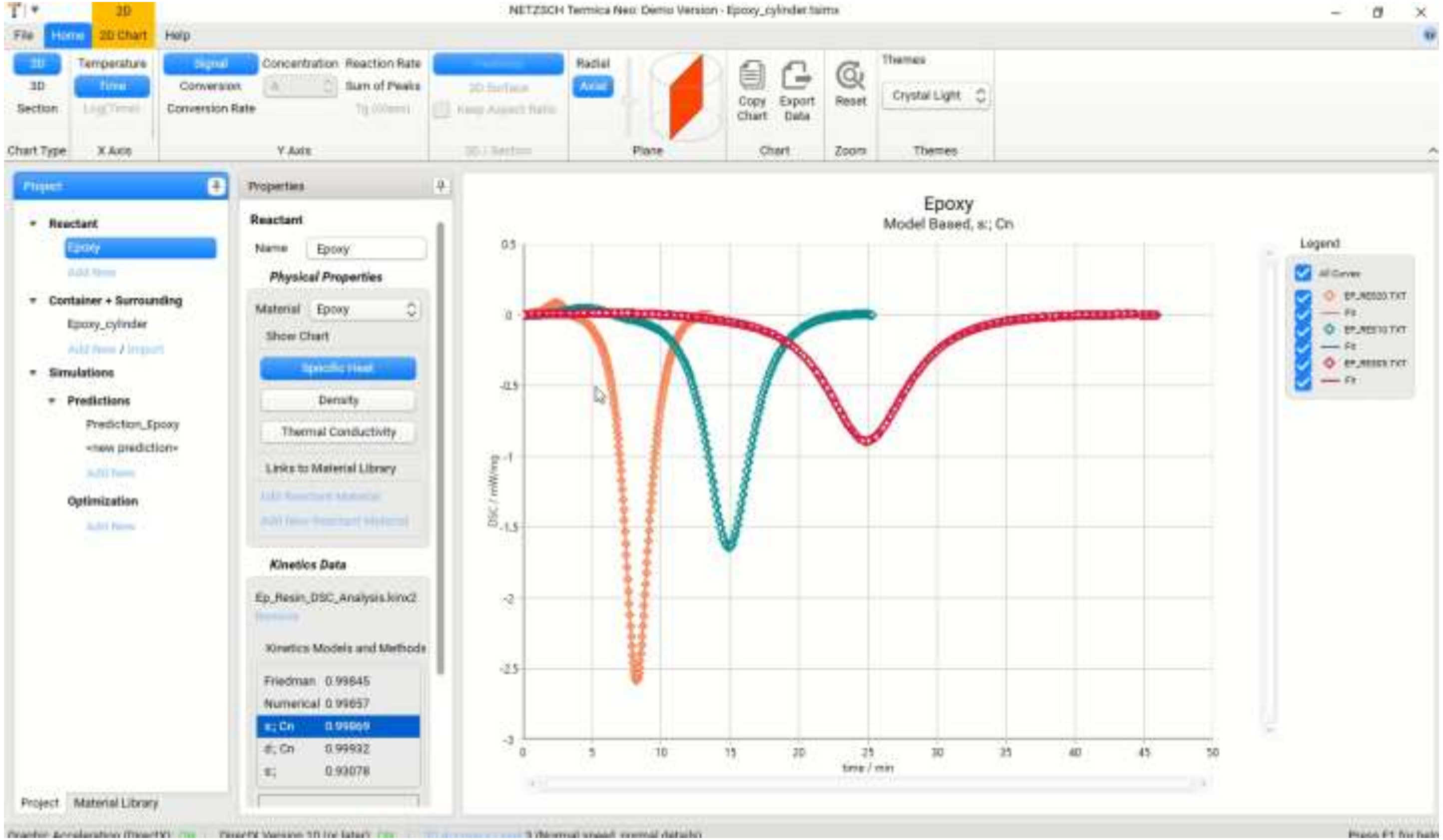
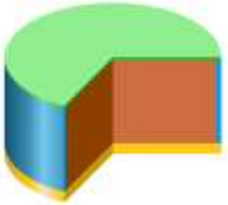
Radius = 10 cm
Height = 8 cm



Simulation Setup in Termica Neo Software

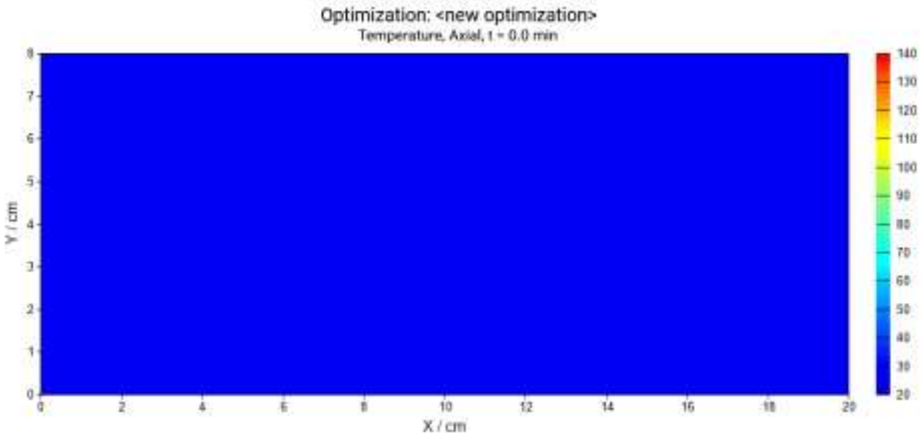


Simulation Results for Cylinder
(2D Heatmap and Conversion Plot)

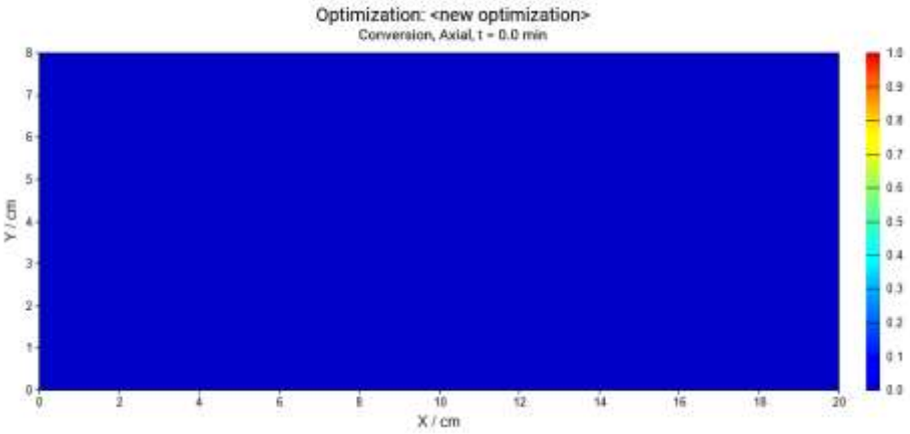


Vertical Section

Temperature vs Time



Conversion vs Time



Output from Termica Neo

Simulation Results for Cylinder
(3D Heatmap and 2D Conversion Plot)

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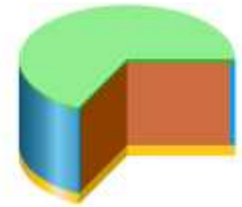
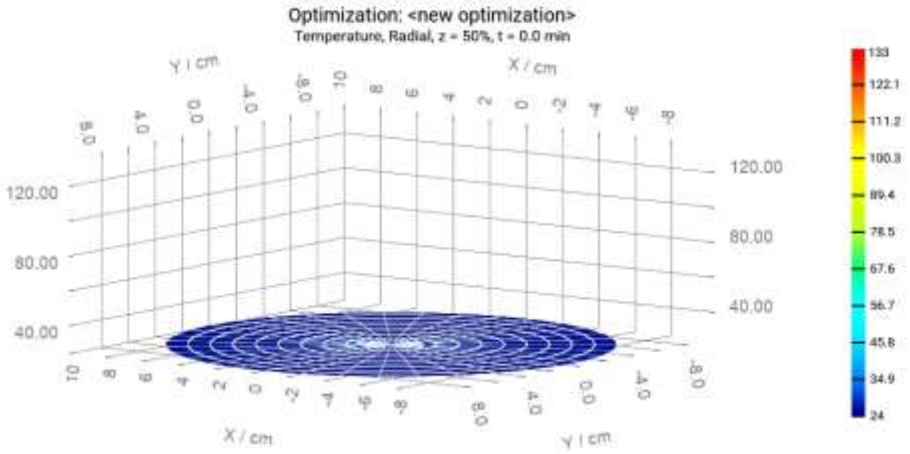
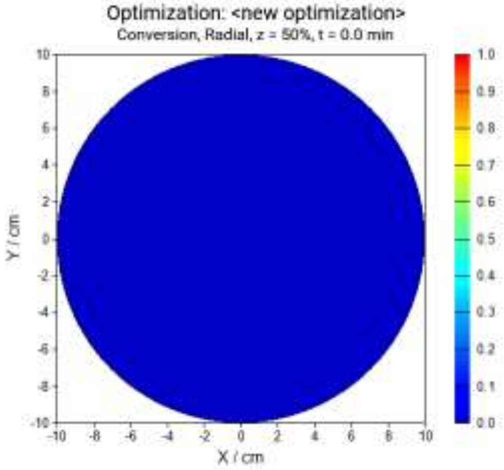


Horizontal Section
(z=50%)

Temperature vs Time



Conversion vs Time



Output from Termica Neo

Conversion vs time at any point of the reacting volume

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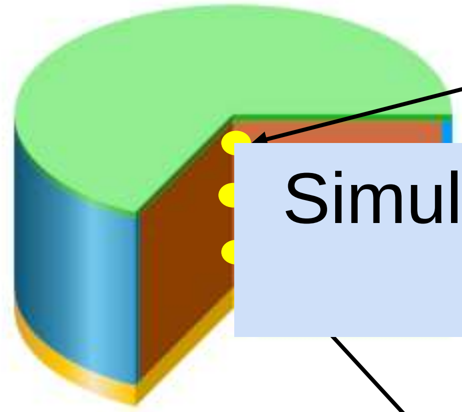
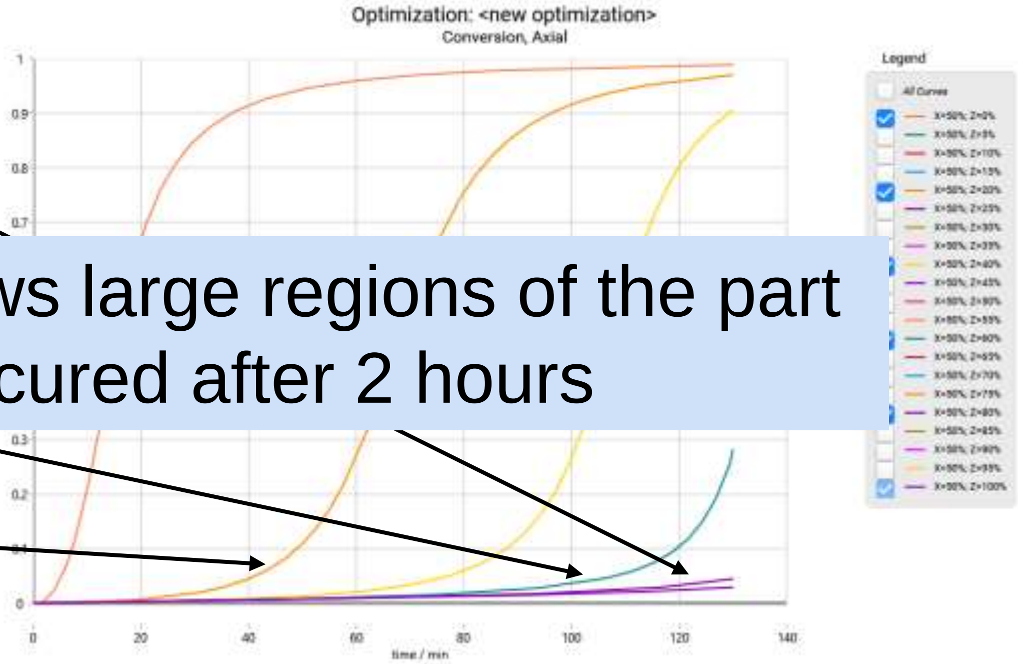
Horizontal position: R=0



Z=80%

Z=20%



Simulation shows large regions of the part are not cured after 2 hours

Possible to show: Temperature, conversion, conversion rate vs time

Applicability of Termica Neo to Large Volumes

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- ✓ Curing, crystallisation, denaturation (DSC, Rheometry)
  eg. polymers, paints, adhesive, inks, resins, food
- ✓ Firing processes (DIL)
  eg. tiles, bricks, porcelainware, powder metallurgy
- ✓ Decomposition processes (TGA)
  eg. debindering, pyrolysis
- ✓ Chemical Industry (ARC, HFC)
  eg. storage of high energetic materials (eg. SADT)

- ➢ Availability of Termica Neo
  - ➢ Standalone software package (free 30 day trial available)
  - ➢ Consulting service (complete solution including optimisation)

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Thank you for your attention!

Andrew Gillen

Head of ANZ Region
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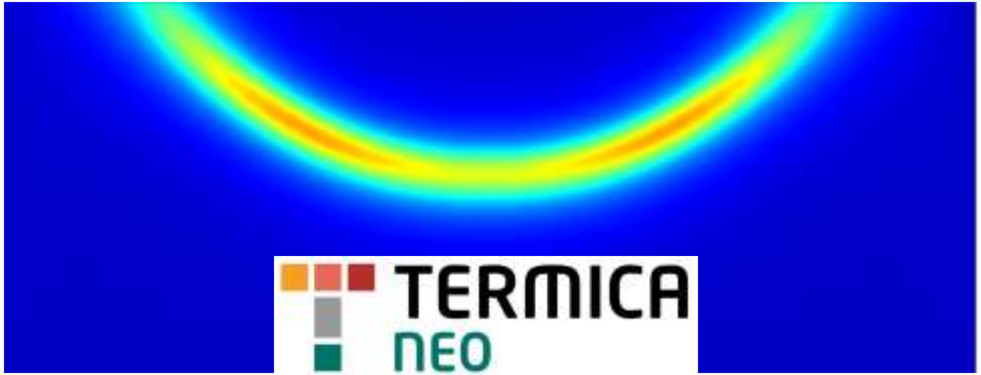

learn more at: **termica.netzsch.com**