Analyzing & Testing

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Proven Excellence.

CURING KINETICS:

Measurements, Models, Kinetics analysis and process optimization by Kinetics Neo

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Webinar, February,18 2025

Agenda

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1. Kinetics for thermosets, composites, photopolymers:
   Introduction and Workflow
2. Thermal analysis methods for study of curing process:
   Properties and methods
3. Kinetic models for curing process, dependence on time and temperature
   Kinetic approached, models, autocatalysis, diffusion control
4. Time-Temperature-Transformation diagram, including gelation and vitrification
   Construction and Validation
5. Dependence of curing on additional parameter
   1. UV intensity
   2 Concentrations
6. Simulation of curing process in thick layers depending on thickness and surrounding. Termica Neo software

1 Kinetics for Thermosets, composites, photopolymers

Idea: How to solve the problems

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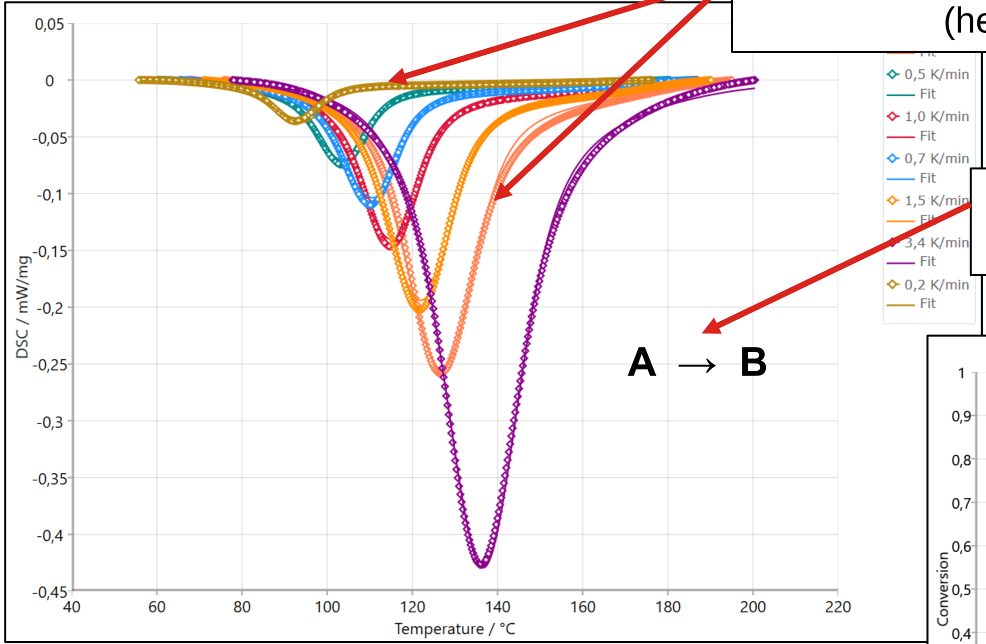
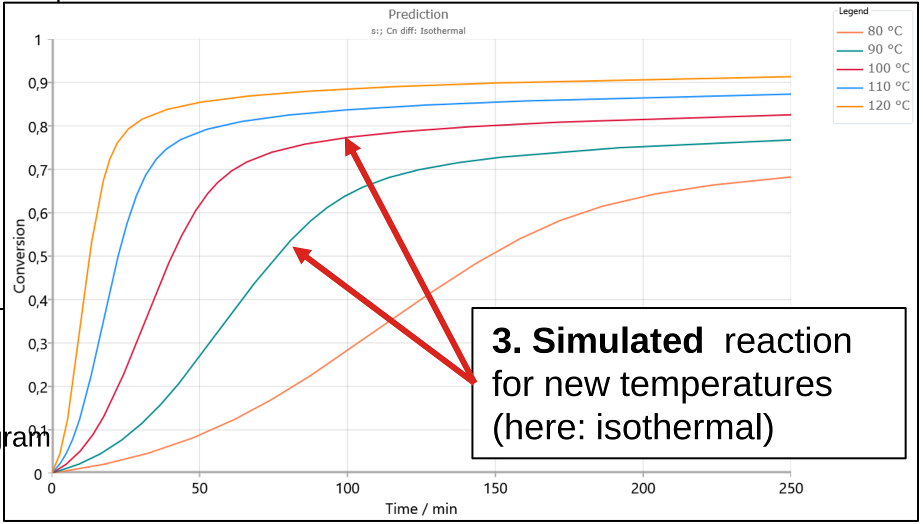
1. Measured data for the process
at different temperature conditions
(here: heating for epoxy resin)



2. Kinetic Model for the chemical reaction
Simulated curves must fit experimental data

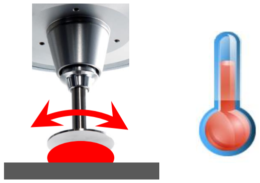


3. Simulated reaction
for new temperatures
(here: isothermal)

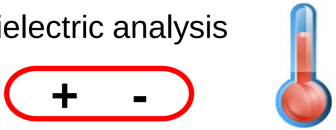
Kinetic analysis helps to

- **Find** and describe the kinetic **mechanism of chemical reaction**
- **Predict** degree of conversion and reaction rate for given temperature program
- **Optimize** industrial processes: decrease production time and costs
  and improve the quality of product

2 Thermal analysis methods for curing process



Dielectric analysis



Material properties, important for curing kinetics

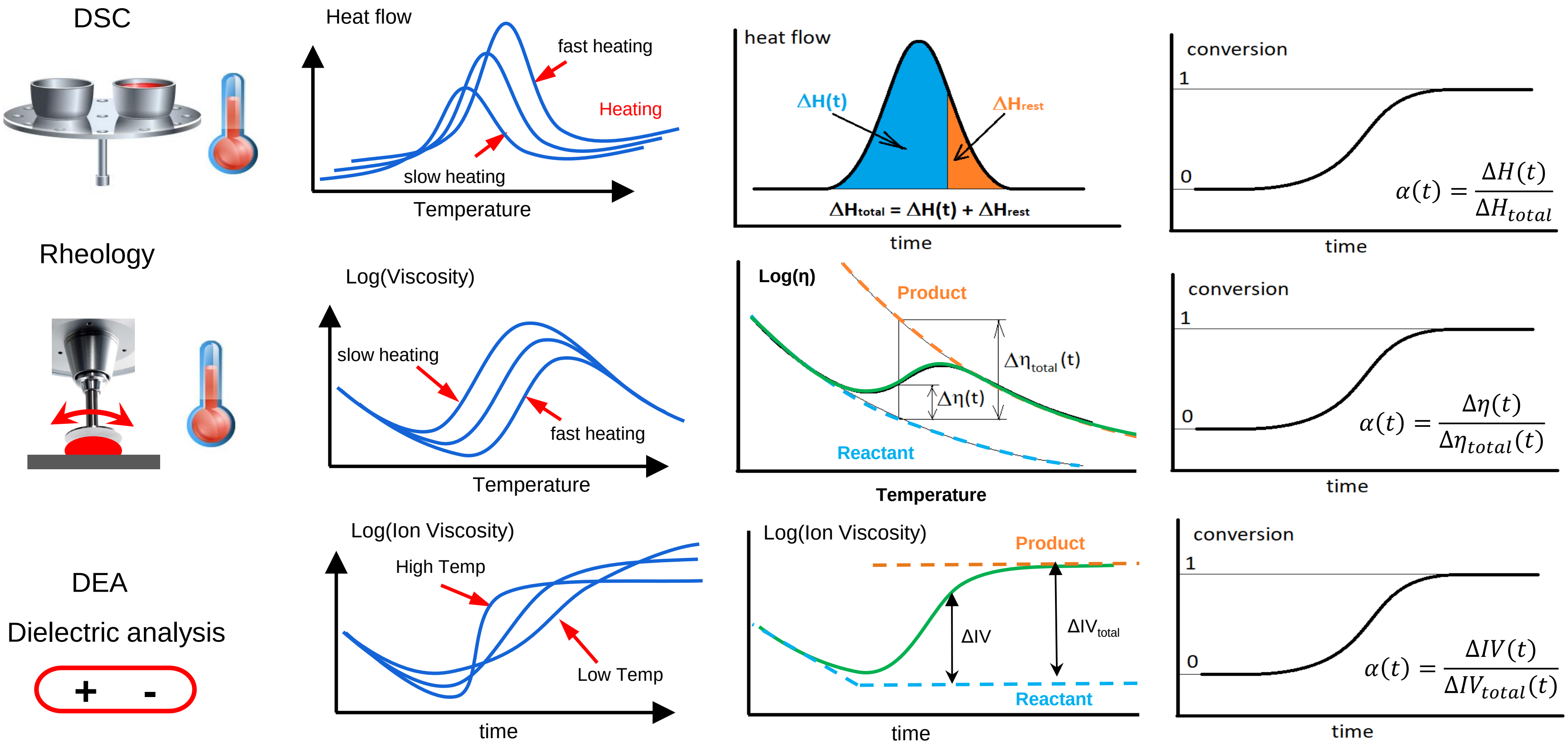
Properties:

- Enthalpy of reaction
- Gel point,
- Glass transition temperature,
- Heat capacity
- Viscosity

Methods:

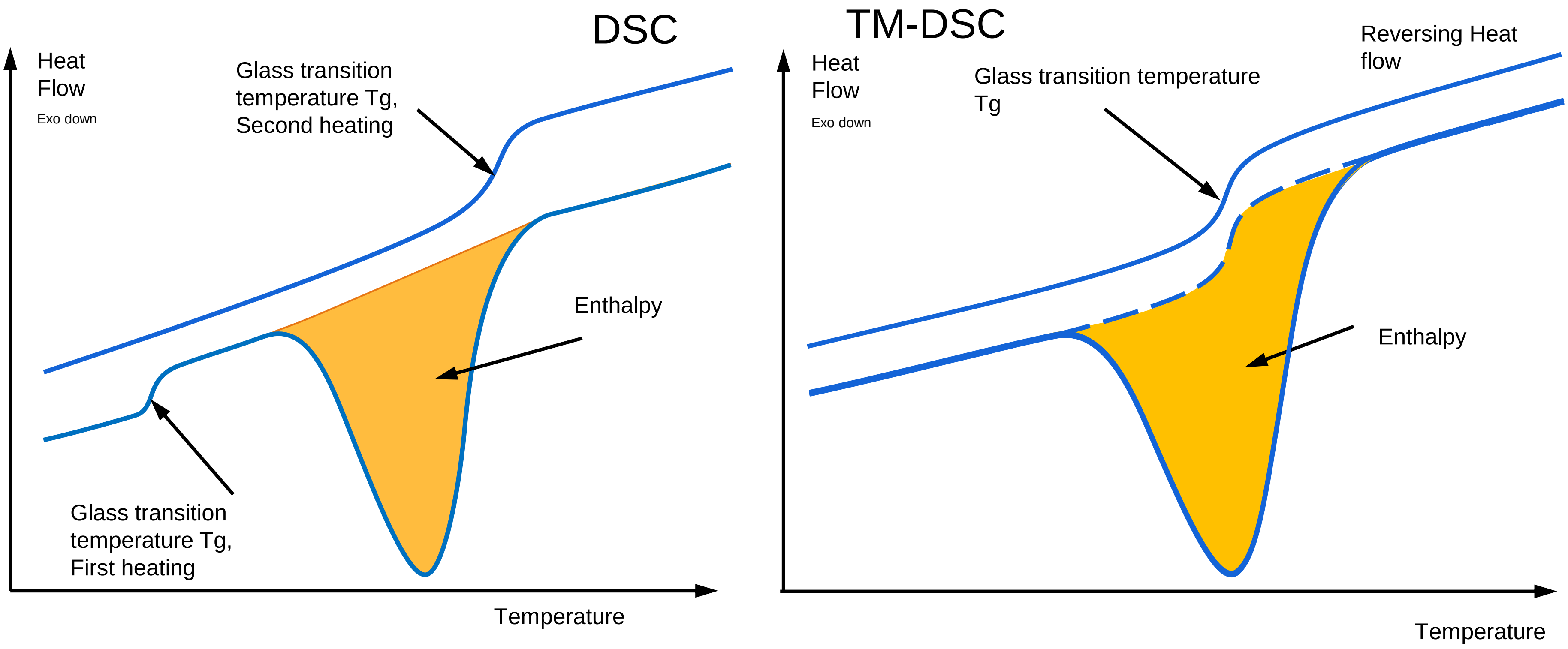
- DSC,
- TM-DSC,
- rheology,
- dielectric analysis

Main data for kinetic analysis of curing systems: heat flow, shear viscosity, ion viscosity

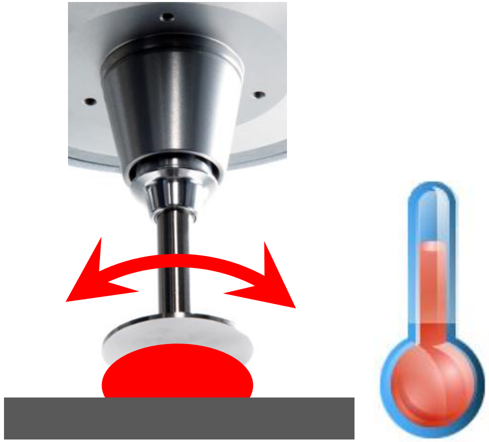


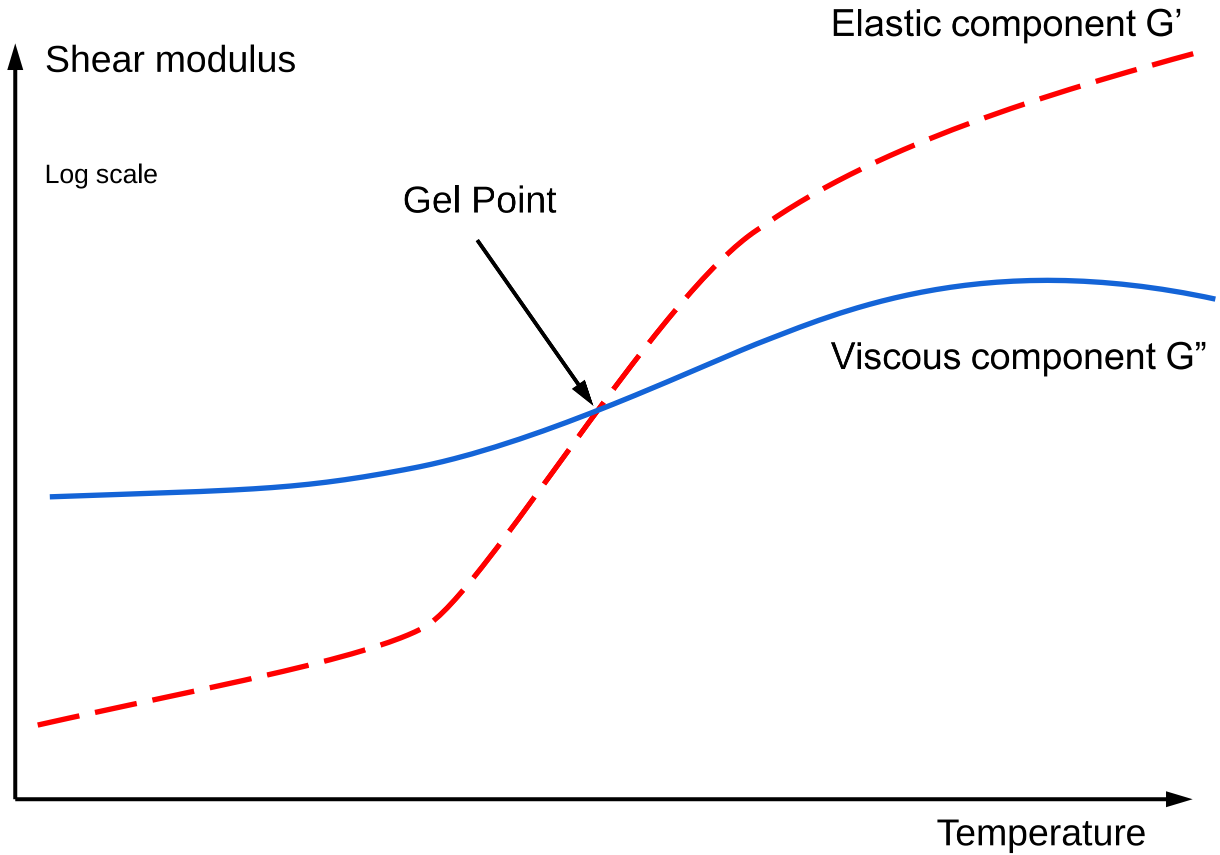
Temperature conditions: heating with different heating rates or isothermal at different temperatures

Differential scanning calorimetry (DSC): enthalpy and glass transition



Rheology: Gel Point Determination over shear modulus





3 Kinetic models for curing process, dependence on time and temperature

Arrhenius equation. Activation energy. Kinetic triplet

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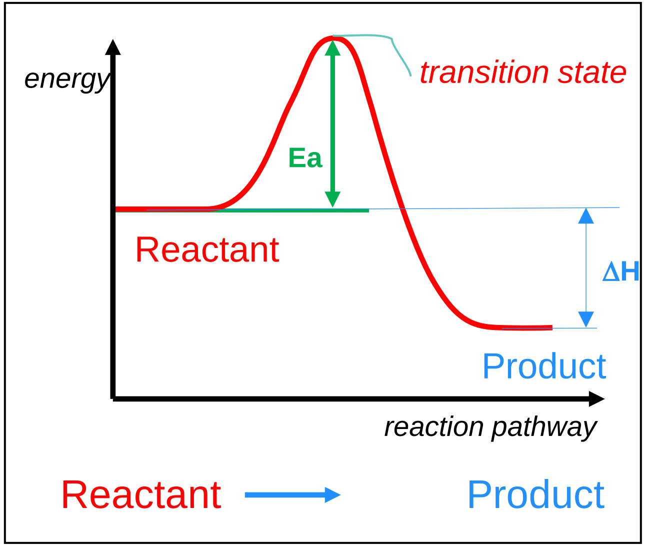


Arrhenius equation (1889) for reaction rate:

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

Conversion α: degree of conversion, changing from 0 to 1

Pre-exponent A: collision frequency [1/s]

Activation energy Ea [kJ/mol]

$f(\alpha)$ Reaction type (nth order, autocatalysis, nucleation …)

Model free approach:

1. Only **one** kinetic equation
2. Ea and A **depend on α**

Model based approach:

1. **Each step has own** kinetic equation
2. Ea and A are independent from **α**

R: gas constant 8.31 [J/(mol K)] T: absolute temperature [K] T[K]=T[°C]+273.15

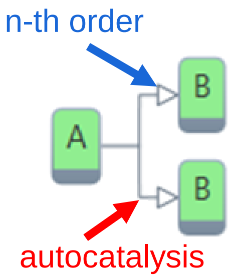
Kinetic Modelling for Curing

Chemical process is **generally** described by Arrhenius equation:

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

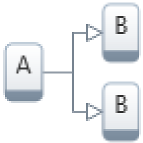
Curing can be described by the equation **Kamal-Sourour** for autocatalytic reaction:

$$\frac{d\alpha}{dt} = \underbrace{A \cdot (1-\alpha)^n \cdot \exp\left(\frac{-E_{a1}}{RT}\right)}_{\text{n-th order}} + \underbrace{A \cdot K \cdot (1-\alpha)^n \cdot \alpha^m \cdot \exp\left(\frac{-E_{a2}}{RT}\right)}_{\text{autocatalysis}}$$



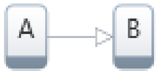
Cmn – reaction of the n^{th} order with autocatalysis of m^{th} order by product

$$\frac{d\alpha}{dt} = A \cdot (1-\alpha)^n \cdot \exp\left(\frac{-E_{a1}}{RT}\right)(1 + K \cdot \alpha^m)$$



Bna – autocatalytical reacton of Prout-Tompkins

$$\frac{d\alpha}{dt} = A \cdot (1-\alpha)^n \cdot \exp\left(\frac{-E_{a1}}{RT}\right) \cdot \alpha^m$$



This **equation** with its parameters A, E_{a1}, n, E_{a2} , K, m, is the **kinetic model**.

Autocatalytic model for mono-functional epoxy (phenyl glycidyl ether with aniline)

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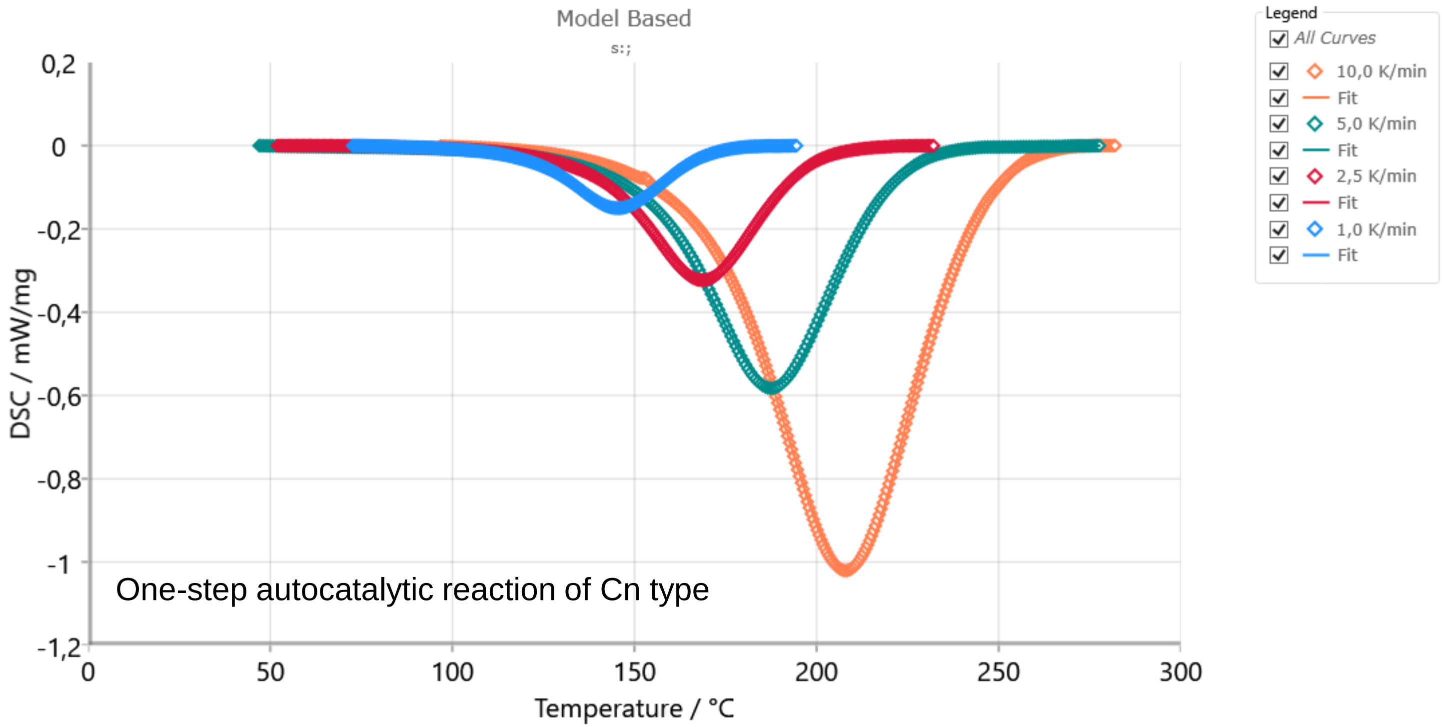
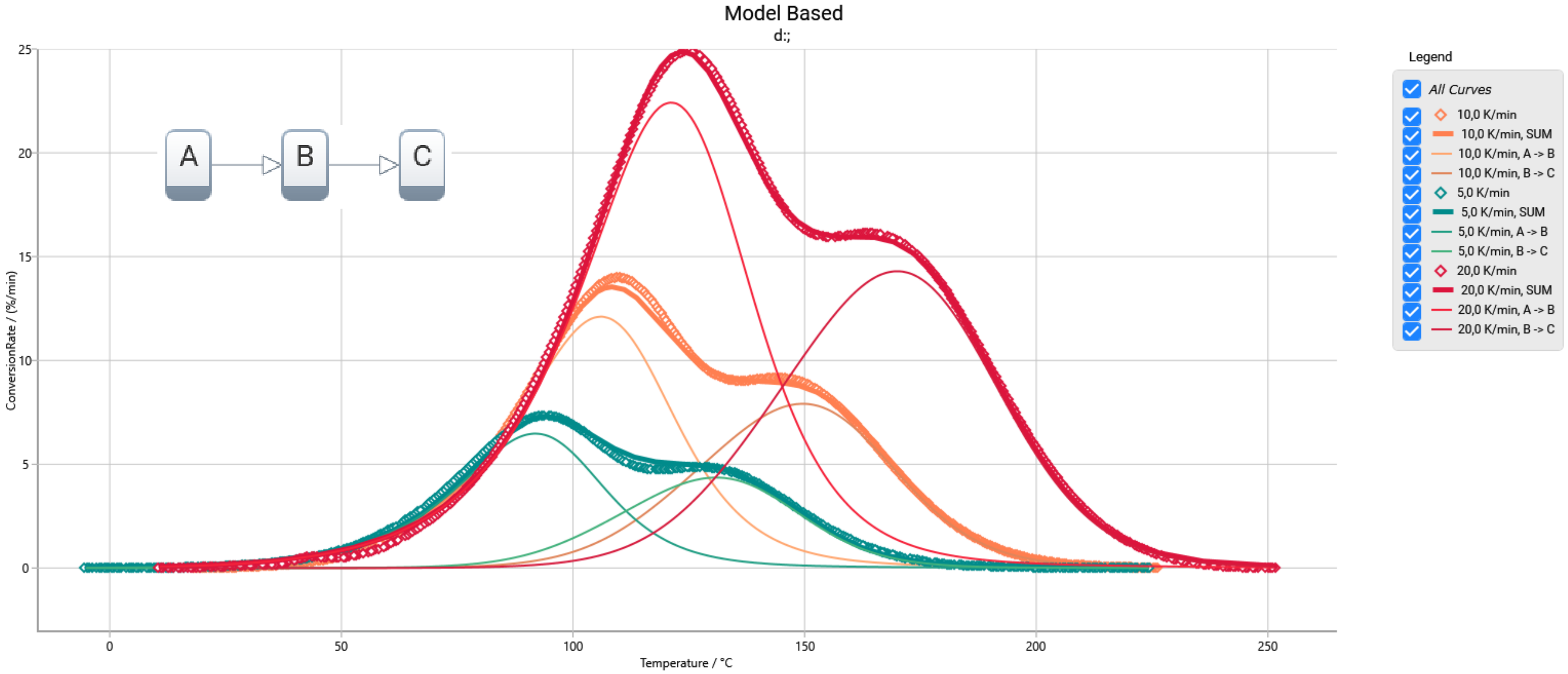
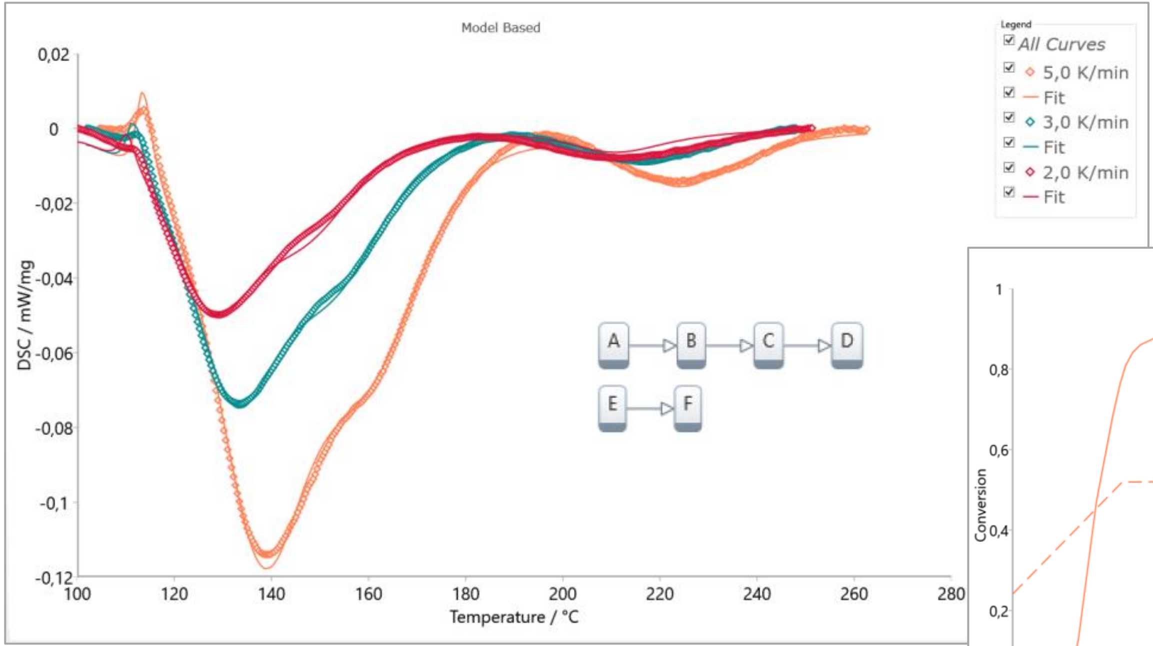
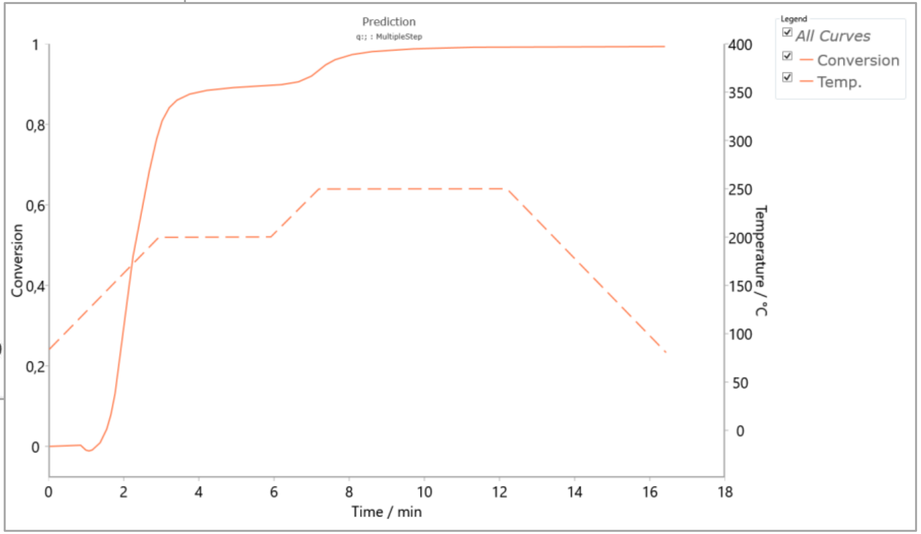


2-step Epoxy curing with two consecutive steps



DSC Measurement of a Phenol Formaldehyd Resin





DSC 214 *Polyma*
Sample: PF resin
Crucible: high-pressure
Sample mass: 20.24 mg
Temperature program: RT… 280°C, 5 K/min

Shear viscosity for Epoxy system (Rheology)

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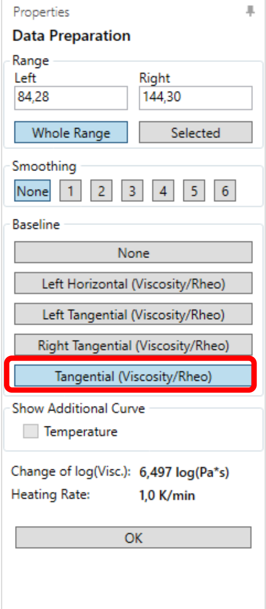
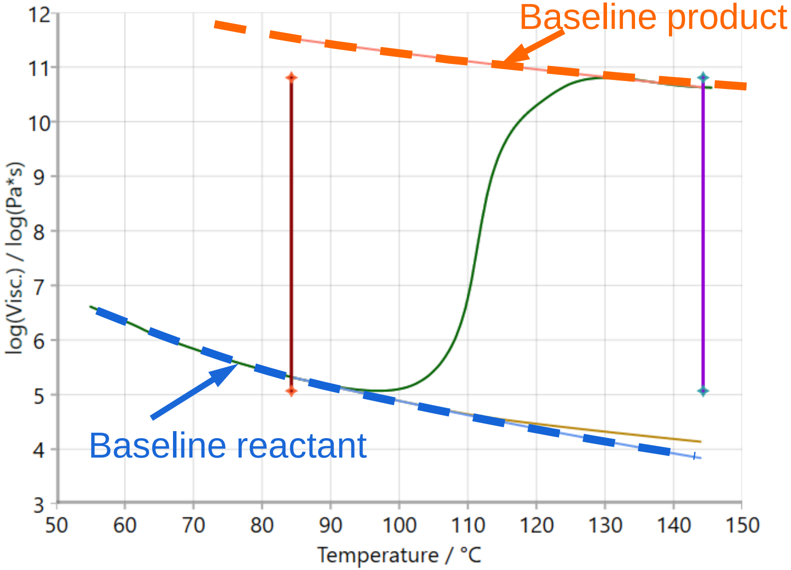
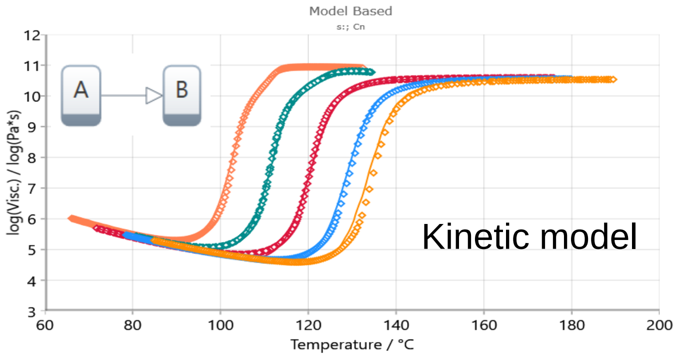
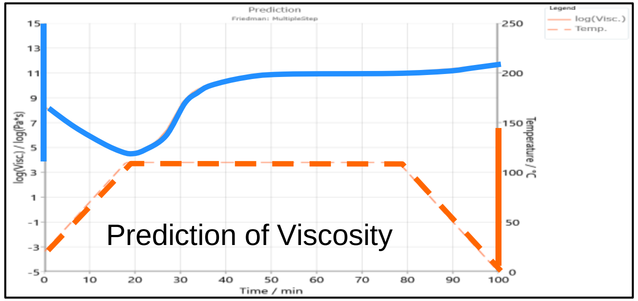


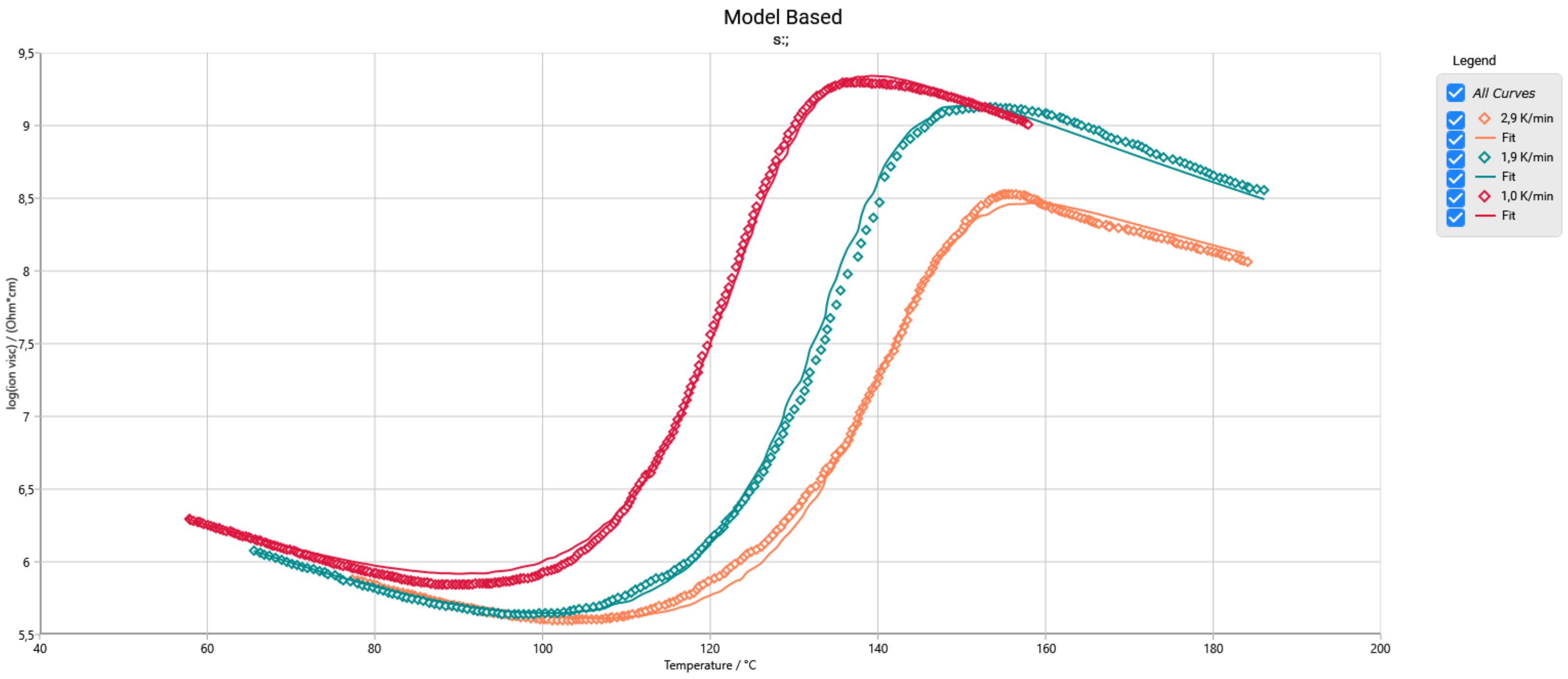






Tangential baseline for heating

Kinetic model for DEA data of epoxy curing



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- Carbon, glass, aramid, hybrid fibres
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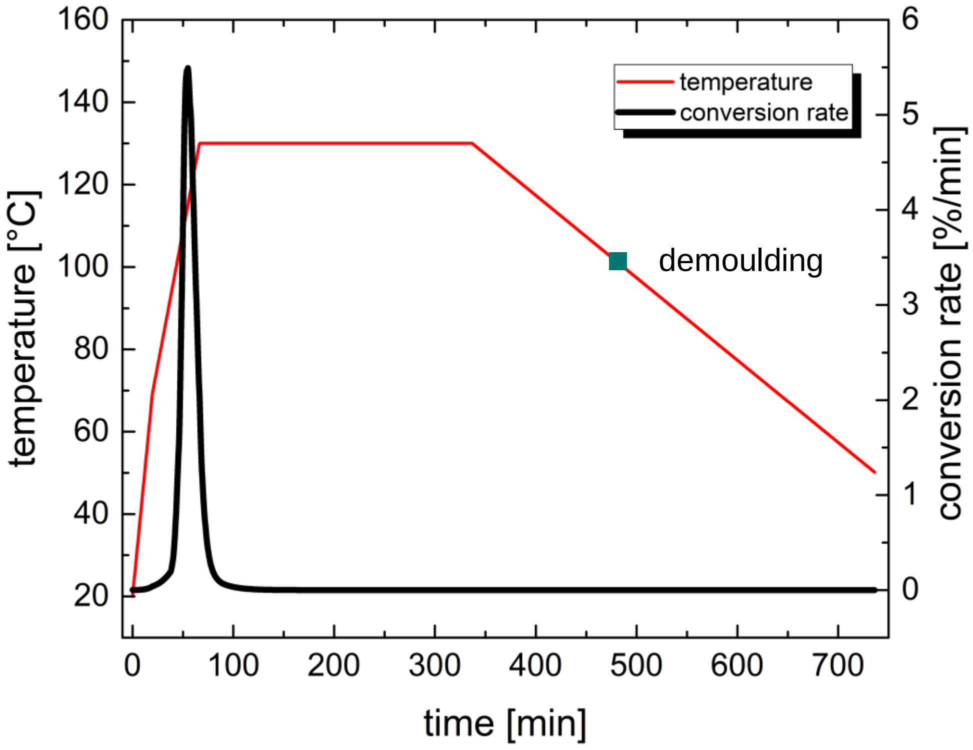
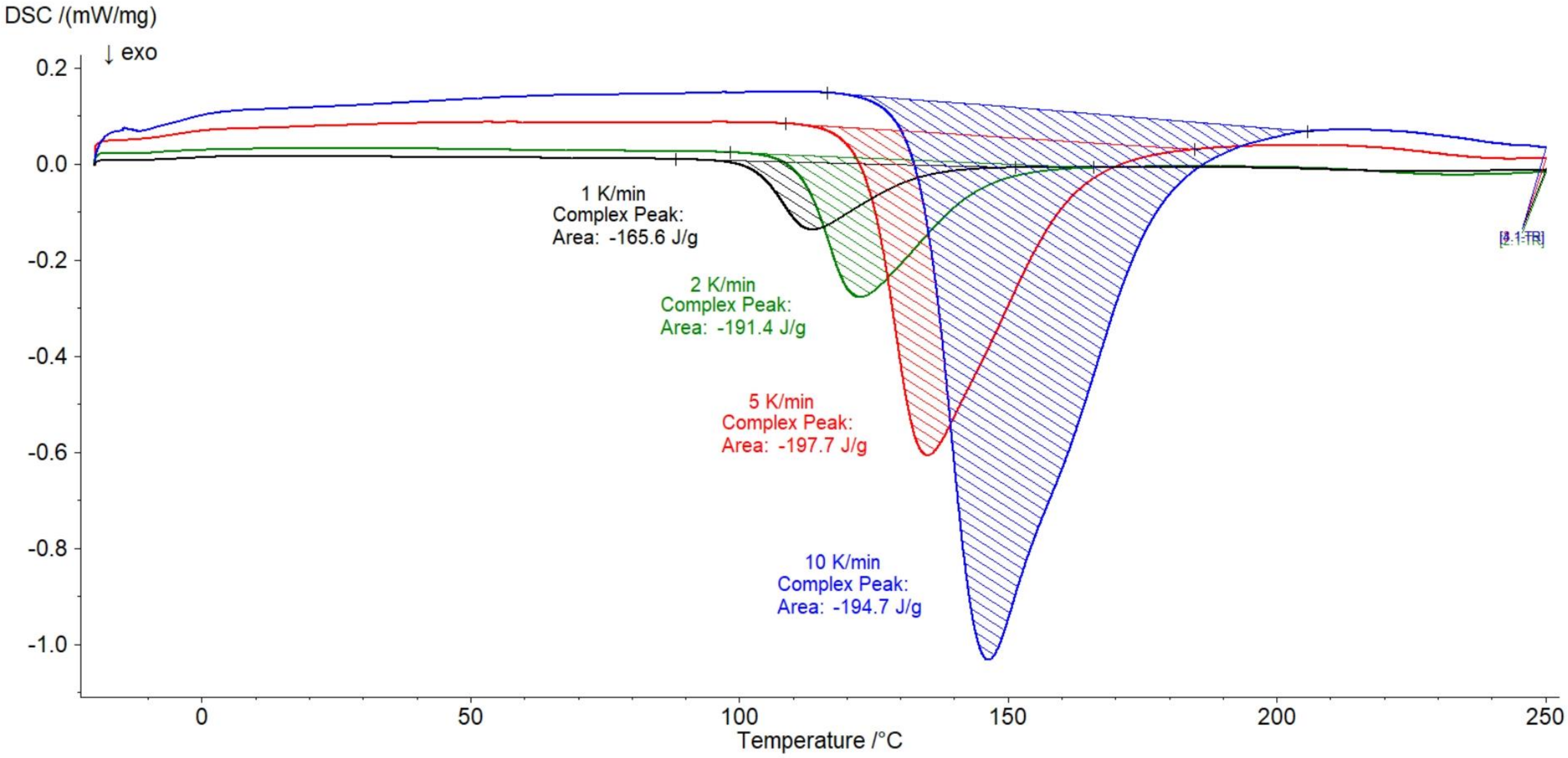
The Challenge: Optimise the Curing a CFRP Bike Rim

- Total cure cycle: 12 hours to reach required 95% conversion, based on material data sheet
- Existing cycle too long and needed optimisation
- Overheating of the material must be avoided due to the curing exotherm

Can the cycle be shortened with the same or a better part quality?



Step 2 - Kinetic Analysis of CFRP Prepreg @ 4 heating rates



Step 3 - *Kinetics Neo* Model Free Analysis: CFRP Prepreg

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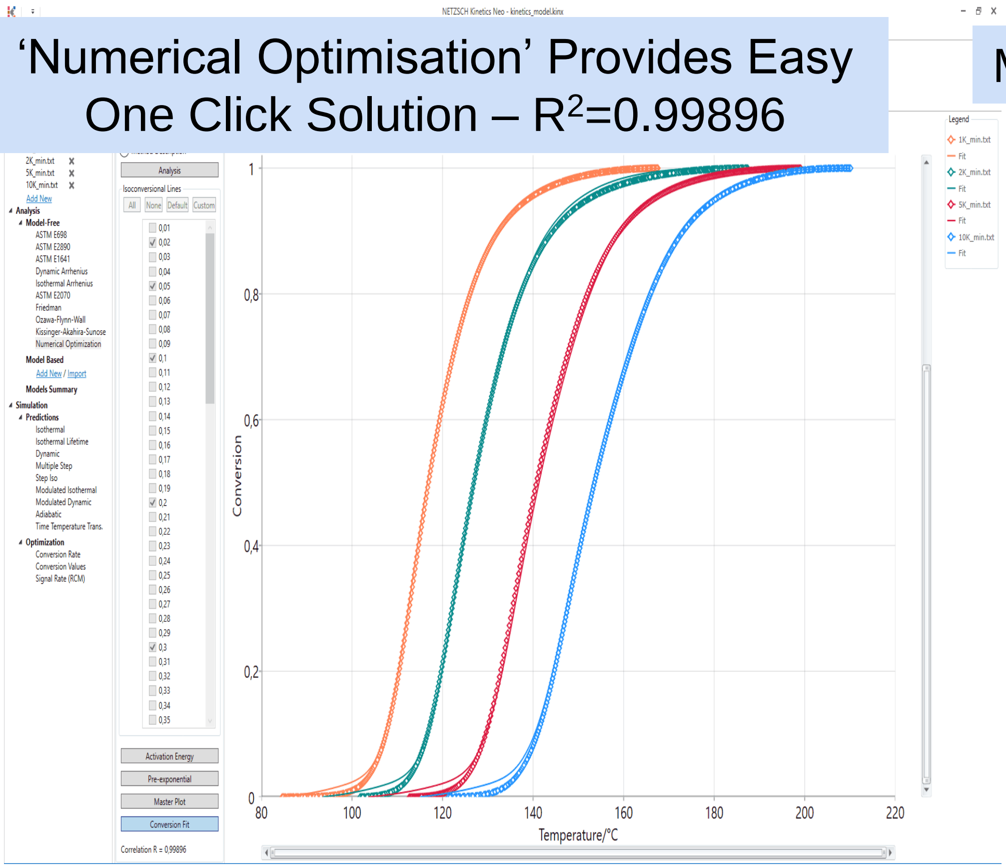
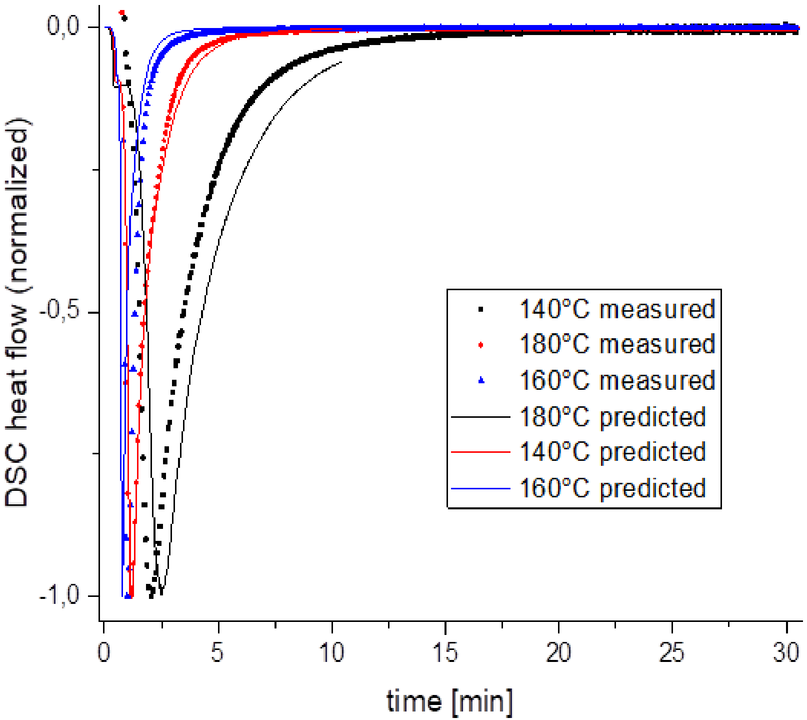
‘Numerical Optimisation’ Provides Easy One Click Solution – R^2=0.99896



Model Validation at isothermal conditions



Results: New Optimised Cycle – 220 Minute Time Saving!

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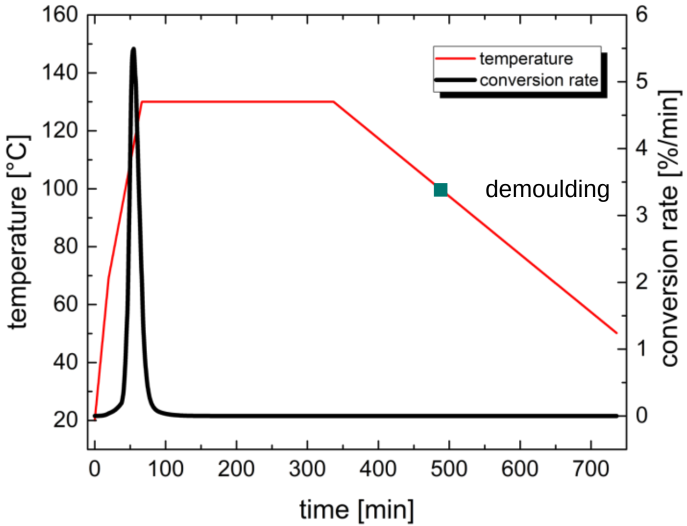
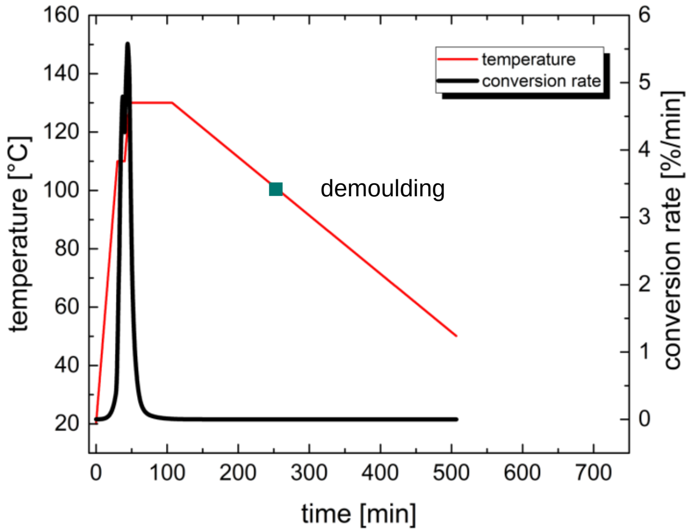
Conventional Cycle



New Cycle



- Maximum conversion rate of new cycle does not exceed conventional cycle

Production time reduced from 460 to 280 minutes

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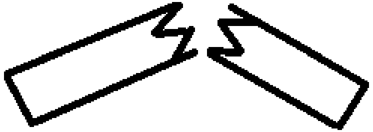
Cold

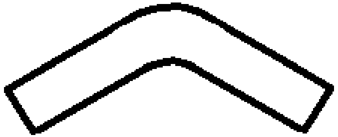


Glassy state

Slow curing
T<Tg

Tg

Warm

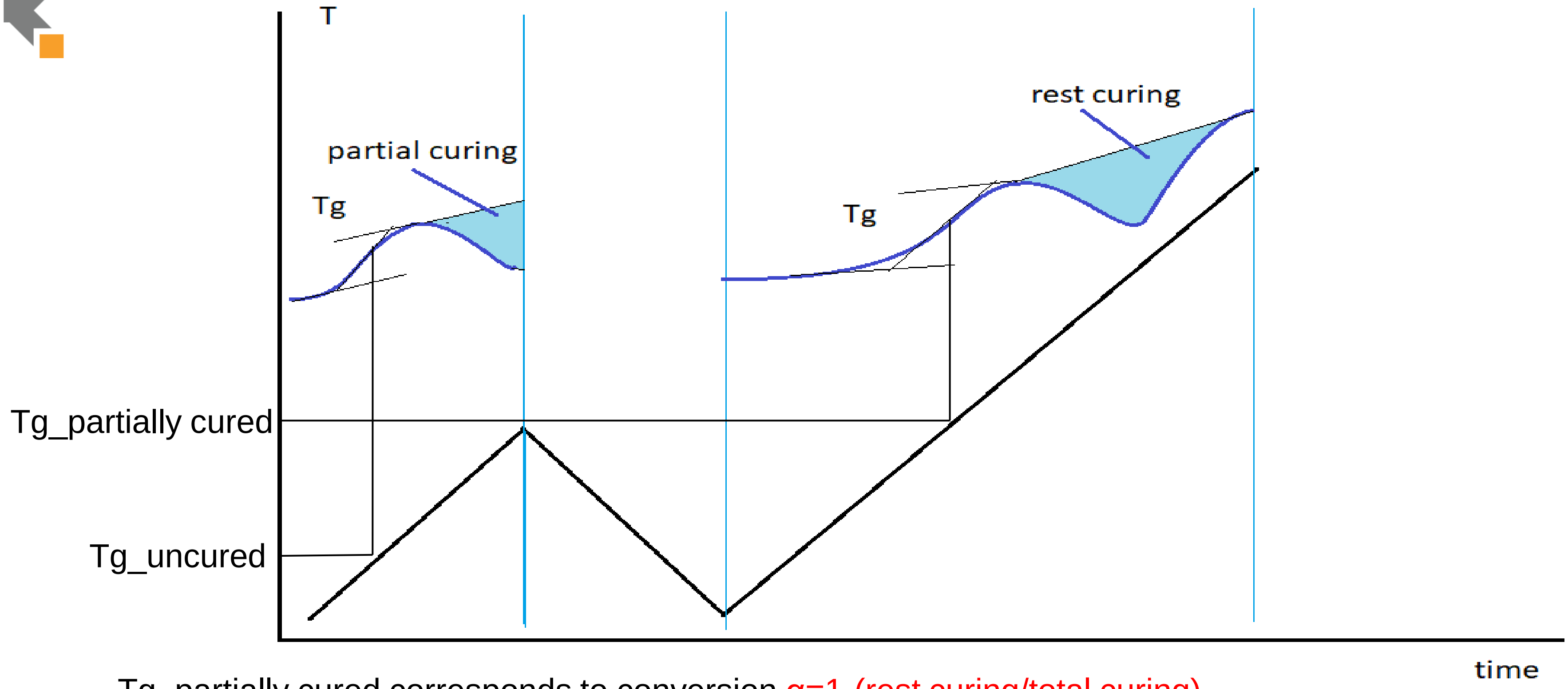


Rubbery or liquid state

Fast curing
T>Tg

Glass transition increases with degree of cure

Determination of glass transition Temperature for partially cured material



Tg_partially cured corresponds to conversion α=1-(rest curing/total curing)

Time-Temperature-Transformation Diagram

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Macromolecular Theory and Simulations

Research Article

Time–Temperature-Transformation (TTT) Cure Diagram of an Epoxy–Amine System

Claire Strasser, Elena Moukhina, Jürgen Hartmann

First published: 15 June 2024 | https://doi.org/10.1002/mats.202400039

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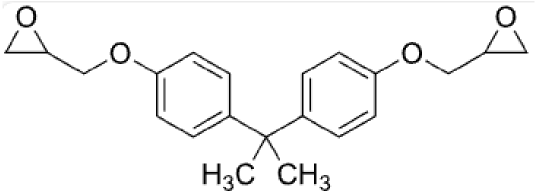
Abstract

A time–temperature-transformation diagram is created for the curing reaction of a diglycidylether bisphenol A (DGEBA)-based epoxy resin. It results from a kinetic analysis performed by means of dynamical differential scanning calorimetry (DSC) measurements; a gelation curve determined with isothermal and dynamical rheological tests; and a vitrification curve obtained from temperature-modulated dynamic DSC measurements. The resulting diagram is validated by comparison of isothermal measurements with the corresponding calculated curves.

Diglycidylether bisphenol A (DGEBA)-based epoxy resin.



a hardener (e.g., amine) is mixed to the epoxy monomer and this mixture is introduced into a mold containing (or not) a reinforcement.

Measurements Step1: enthalpy and glass transition (DSC) for original material

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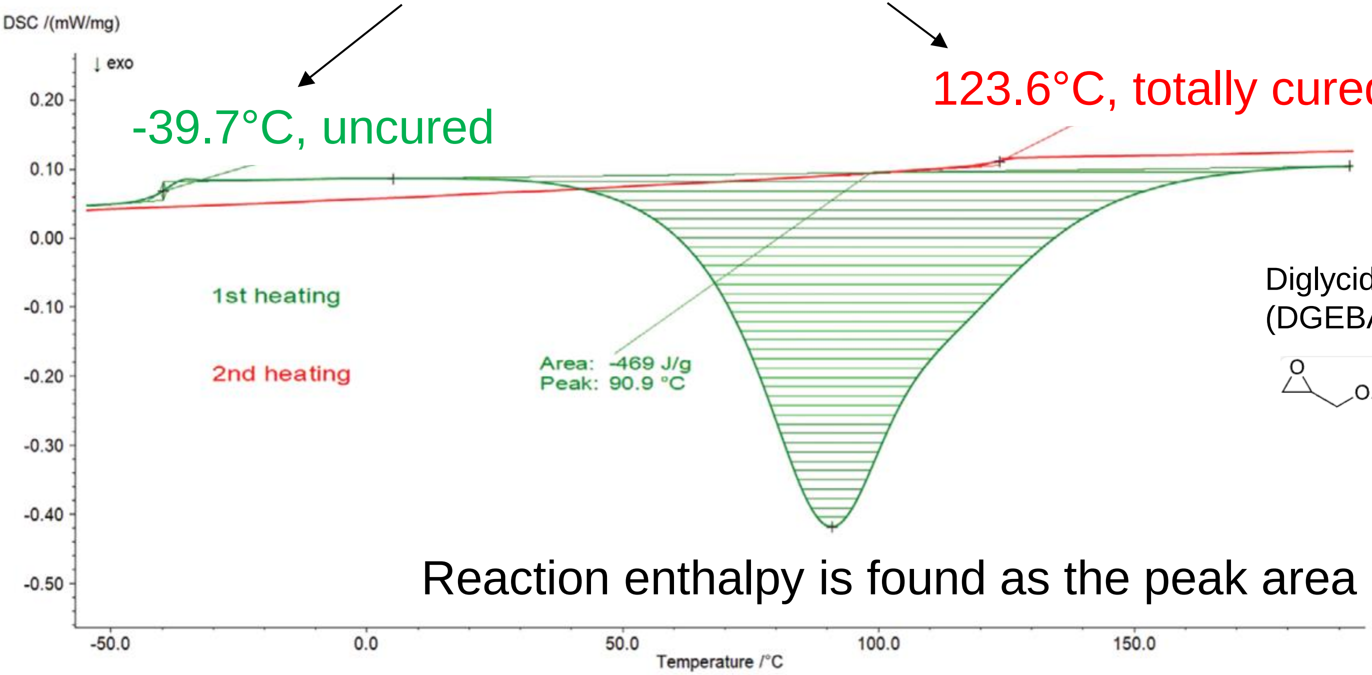
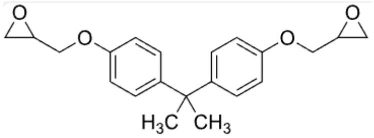
Moving of Tg during curing

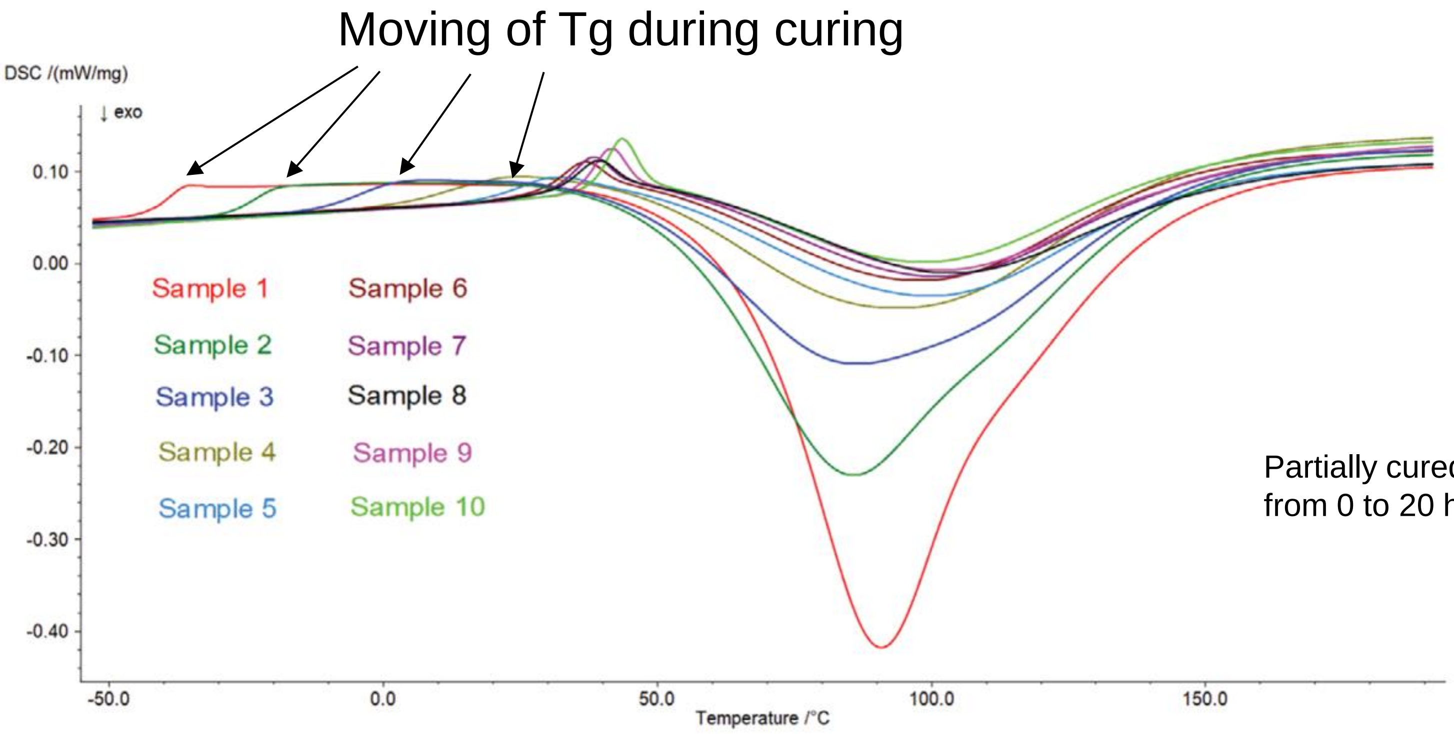


Reaction enthalpy is found as the peak area

Diglycidylether bisphenol A (DGEBA)-based epoxy resin.



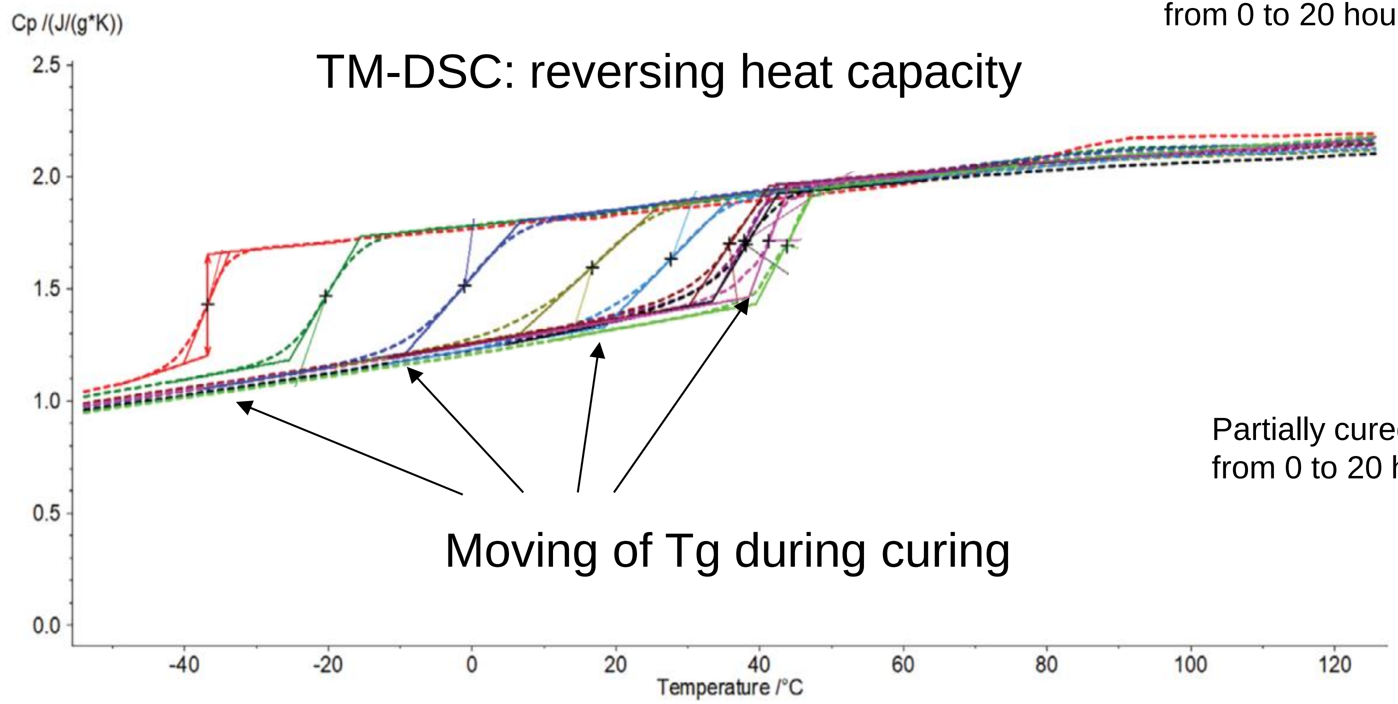
Measurements Step2: enthalpy and glass transition (DSC) for partially cured material



Partially cured material
from 0 to 20 hours at 20°C

Measurements Step3: enthalpy and glass transition (TM-DSC) for partially cured material

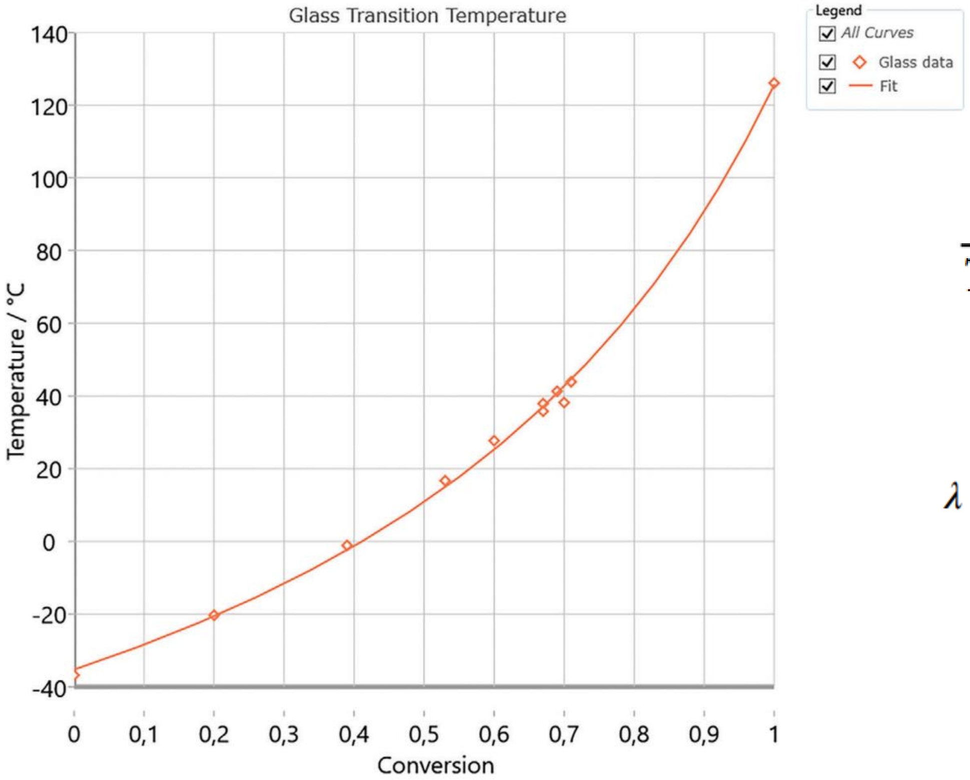
Partially cured material
from 0 to 20 hours at 20°C



Partially cured material
from 0 to 20 hours at 20°C

Reversing Cp (specific heat capacity) for the samples with different degrees of cure, 3 K min−1

Glass transition Temperature depends on Conversion



Di Benedetto equation

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda \alpha}{1 - (1 - \lambda)\alpha}$$

$$\lambda = \frac{\Delta C_p \text{ (fully cured material)}}{\Delta C_p \text{ (fully uncured material)}} = 0.4$$

Reaction Kinetics for diffusion control

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

f(α): Kamal-Sourour

Chemical rate (slow):
$T_{material} << Tg$

$$k(T) = A \cdot \exp\left(-\frac{E}{RT}\right)$$

Low Pre-exponent A

Diffusion controlled rate
$Tg < T_{material} < Tg+100$

$$\frac{1}{k} = \frac{1}{k_D} + \frac{1}{k_{chem}}$$

$$k(T) = k_{chem} = A \cdot \exp\left(-\frac{E}{RT}\right)$$

Williams-Landel-Ferry:

$$k_D(\alpha, T) = D_0 \exp\left[\frac{C_1 (T - T_g(\alpha))}{C_2 + T - T_g(\alpha)}\right]$$

Chemical rate (fast):
$T_{material} >> Tg$

$$k(T) = A \cdot \exp\left(-\frac{E}{RT}\right)$$

High Pre-exponent A

NETZSCH Kinetics Neo for curing with diffusion control

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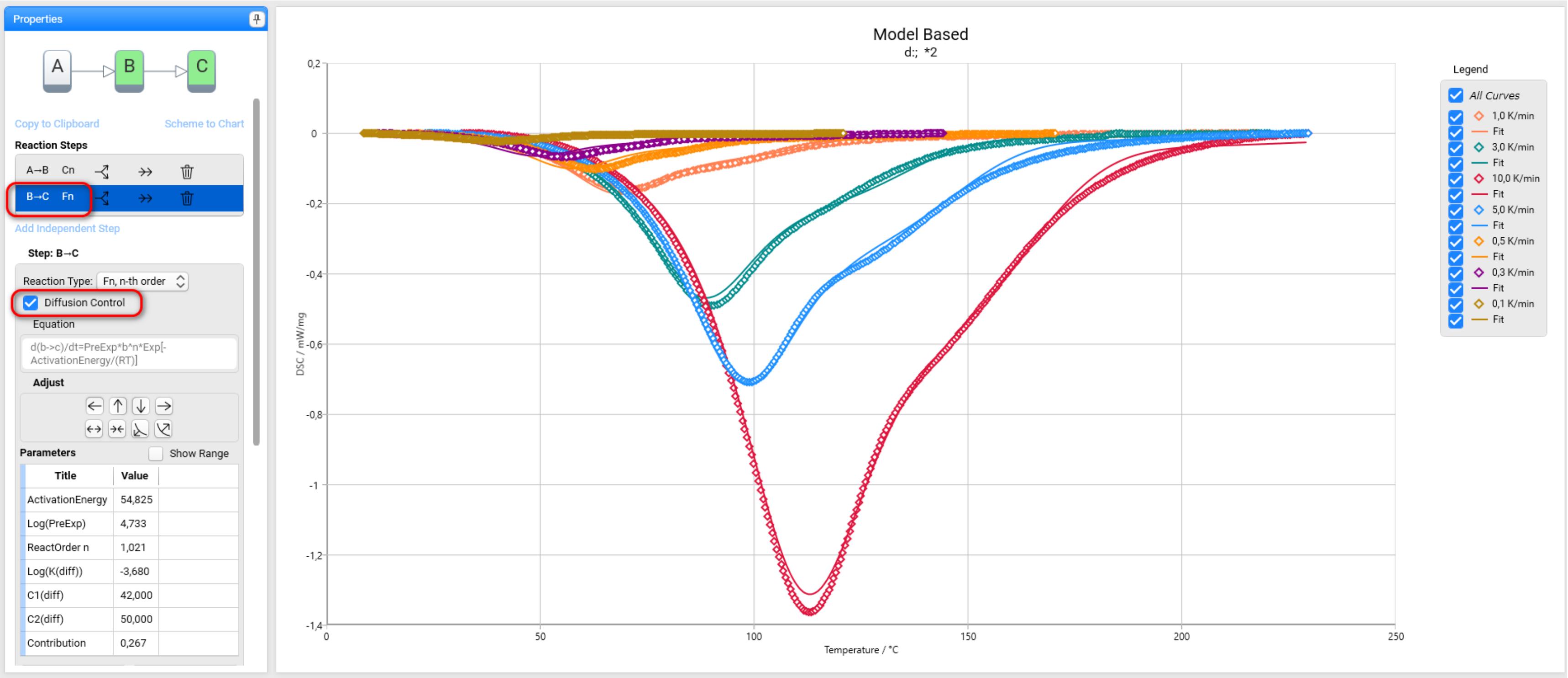
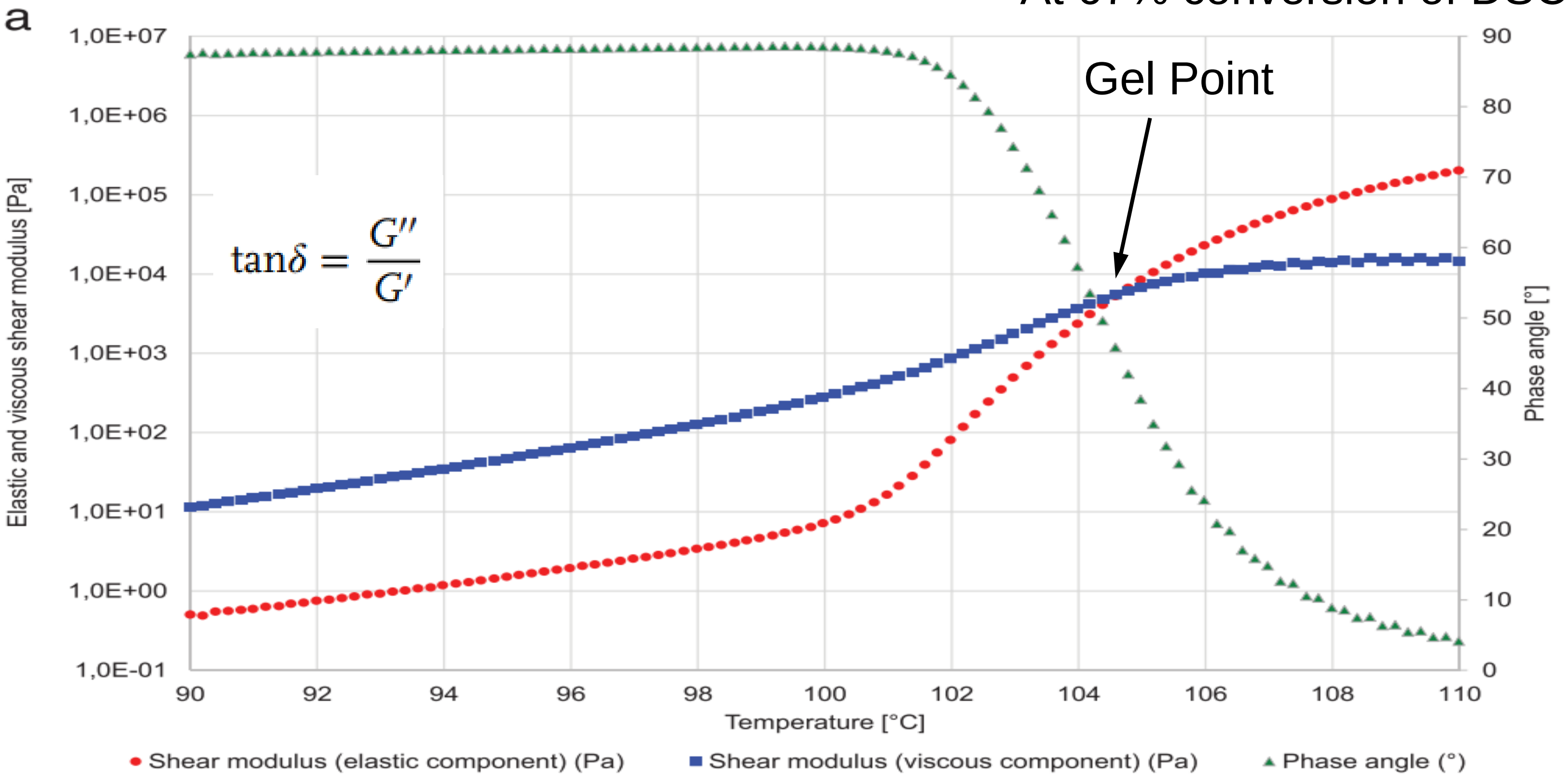


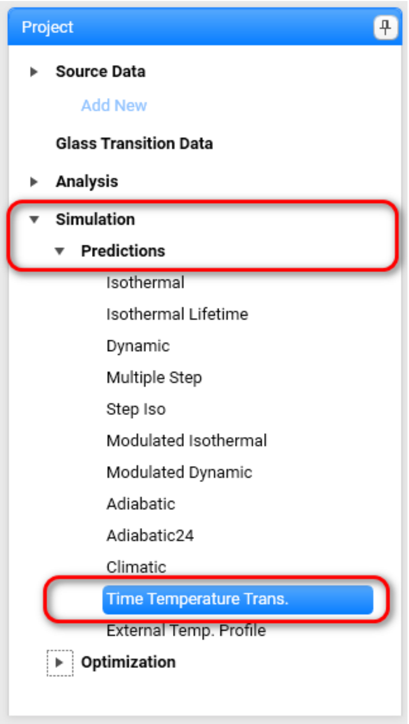
Diffusion control can be switch ON/OFF for each reaction step

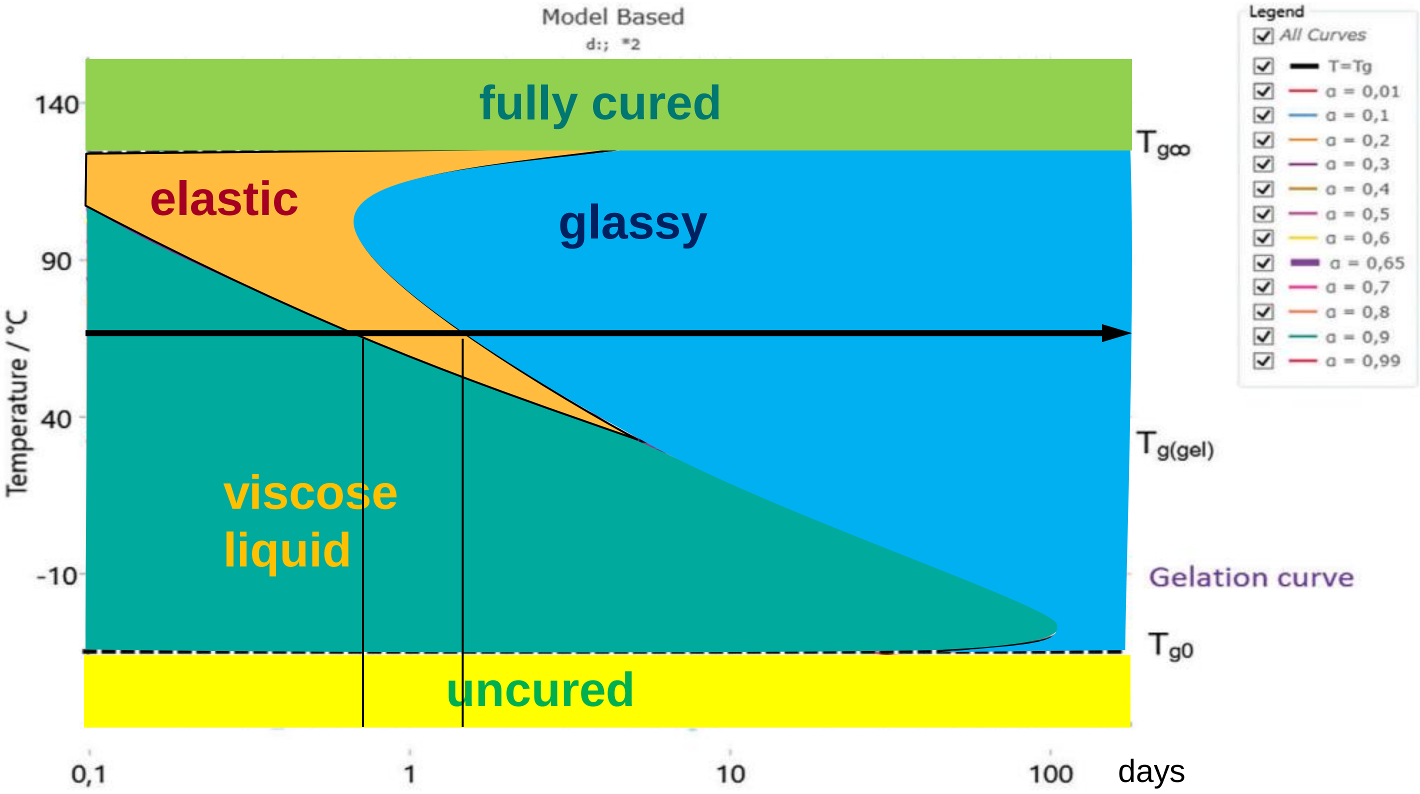
Measurements Step4: Gel point (Rheology) for original material

At 67% conversion of DSC



Time-Temperature-Transformation diagram based on DSC data

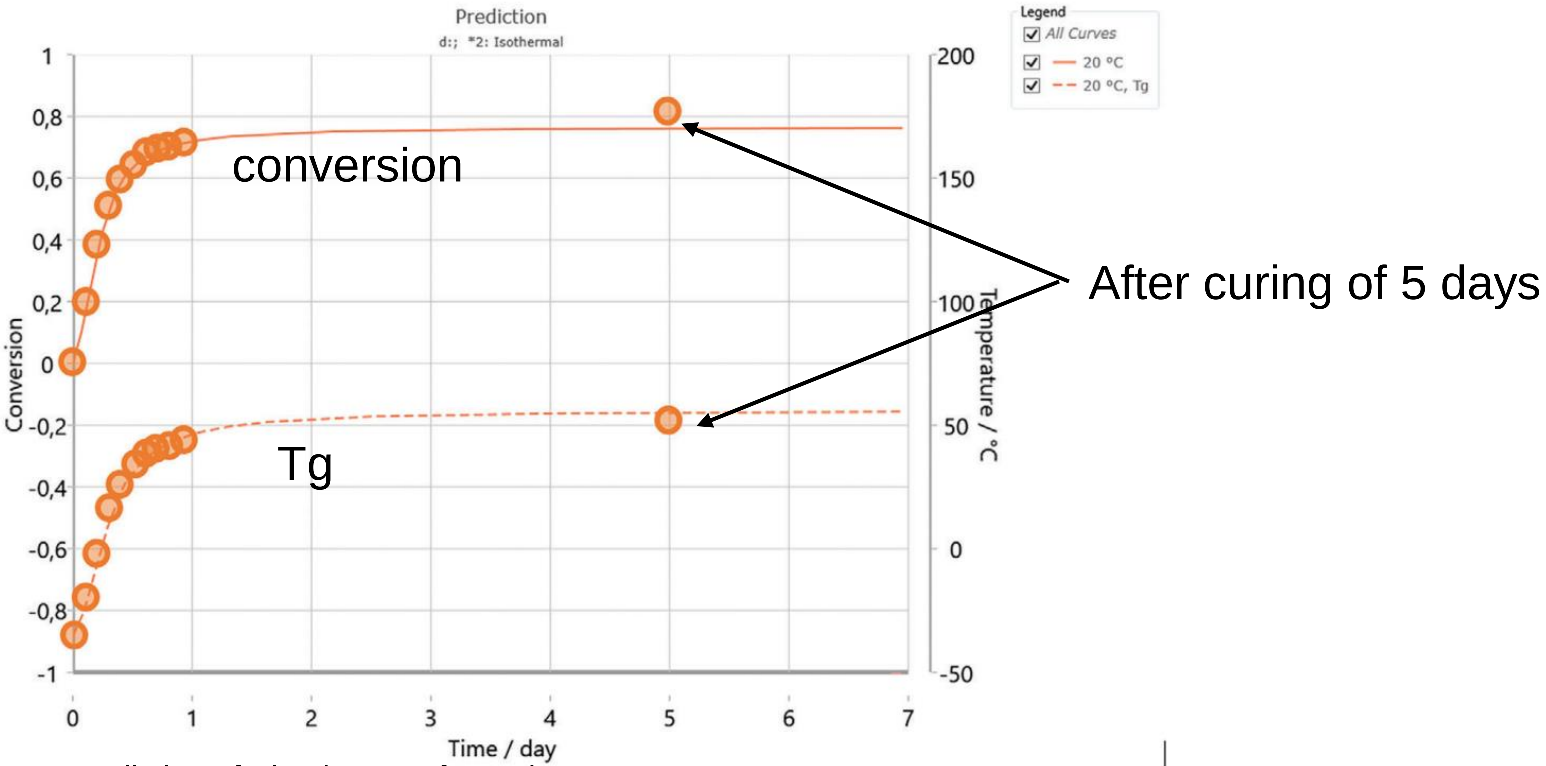




TTT diagram of the investigated epoxy resin

Verification of TTT diagram for 5 days at Room Temperature

DOI: 10.1002/mats.202400039



Prediction of Kinetics Neo for curing at room temperature

Verification of TTT diagram is done for conversion, gel point and glass transition temperature.

3. Dependence on additional parameter

UV curing at different temperatures and different intensities (10kHz)

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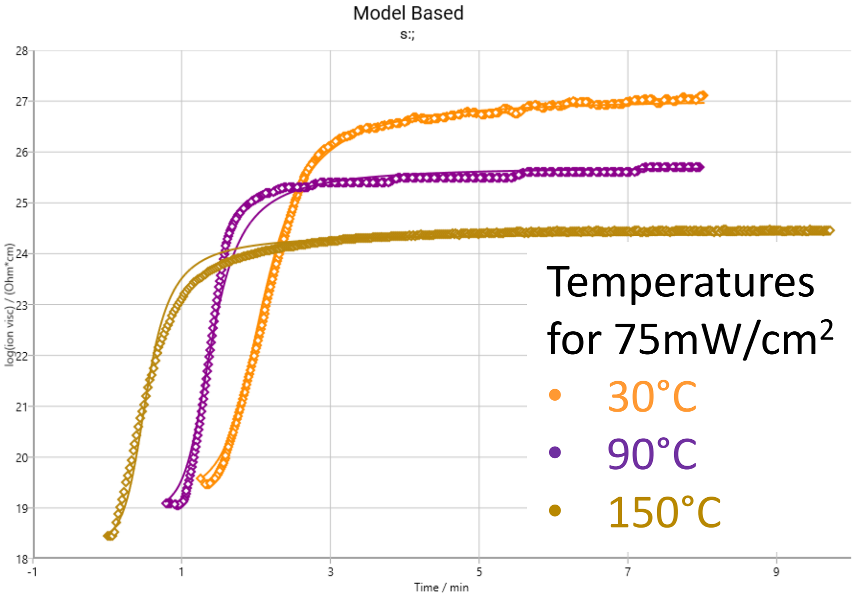

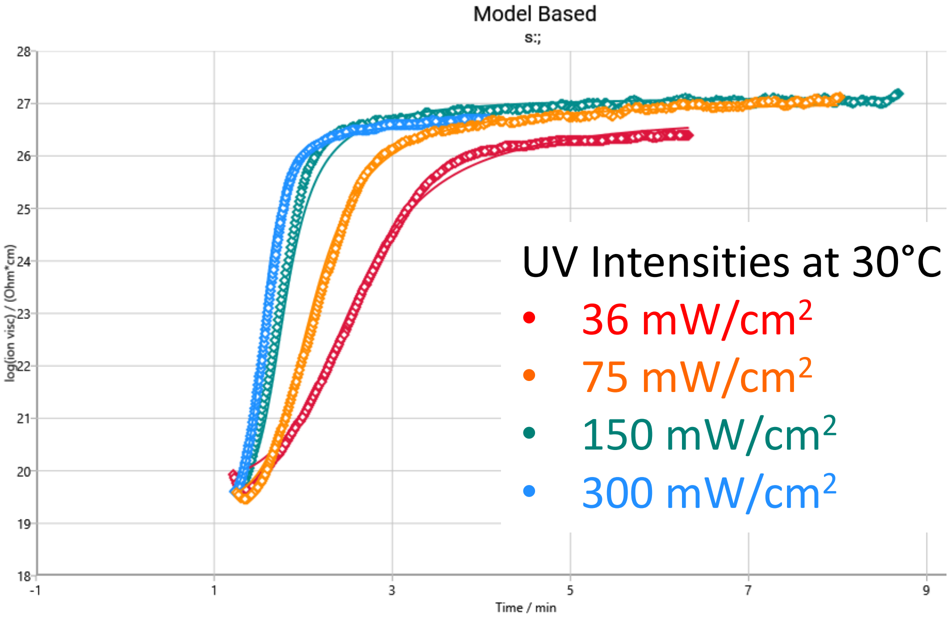

Isothermal DEA measurements at 30°C, 90°C, 150°C for light exposure at 75mW/cm^2

Isothermal DEA measurements at 30°C for light exposure at different intensities from 75mW/cm^2 to 150mW/cm^2

Data: https://4spepublications.onlinelibrary.wiley.com/doi/10.1002/pen.26353

Common model in Kinetics Neo depending on both temperature and the intensity of UV light

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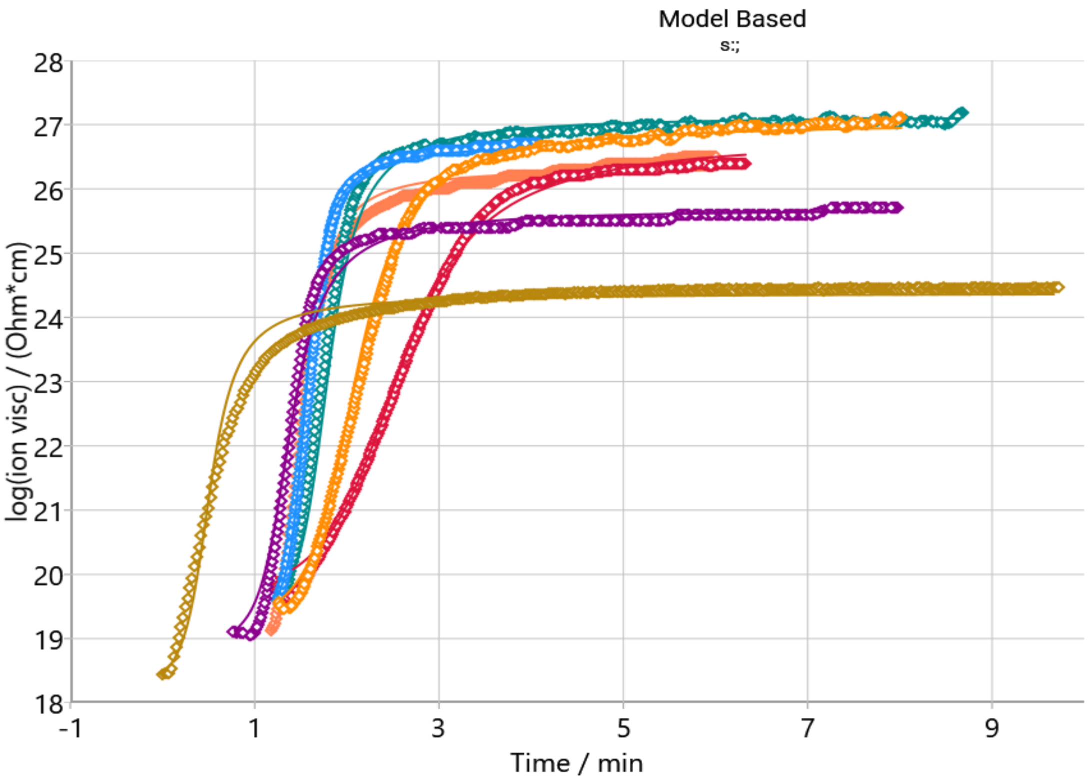
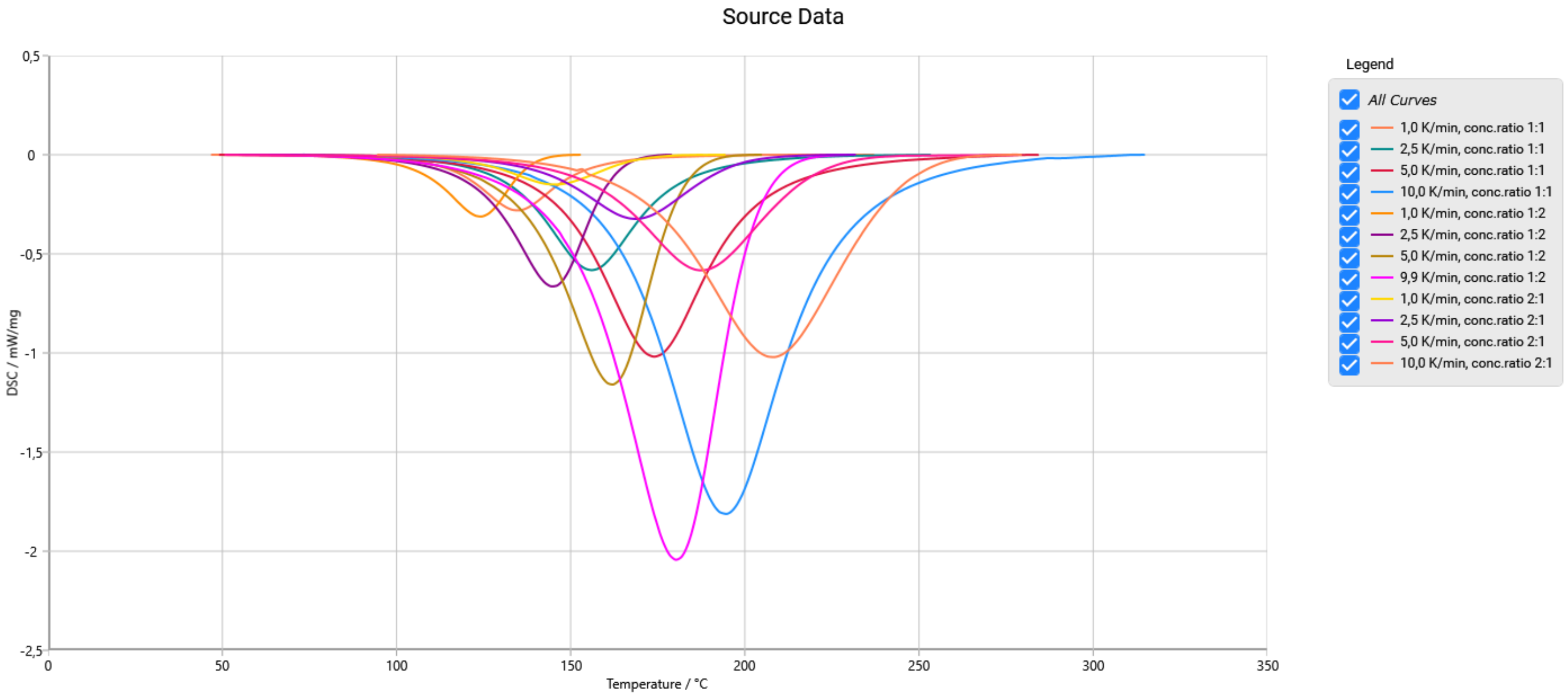


Temperatures
- 30°C
- 90°C
- 150°C

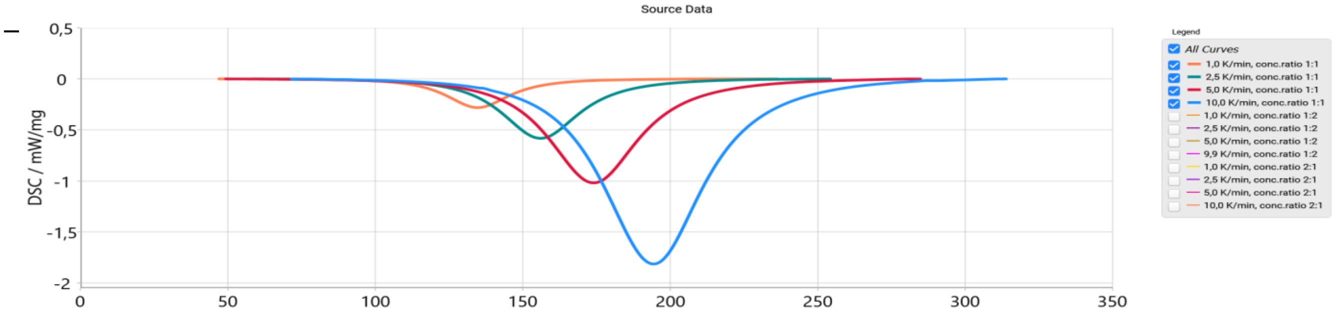
UV Intensities
- 36mW/cm^2
- 75mW/cm^2
- 150mW/cm^2
- 300mW/cm^2

Data: https://4spepublications.onlinelibrary.wiley.com/doi/10.1002/pen.26353

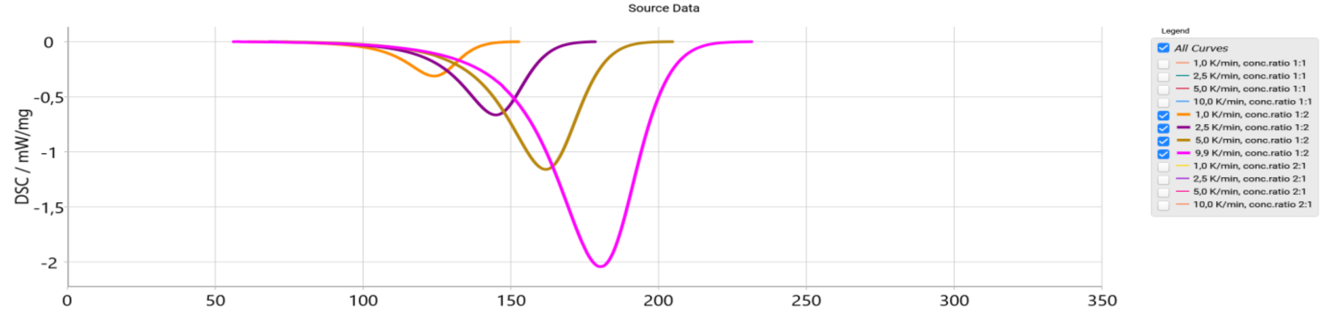
Different concentration ratios: data for analysis



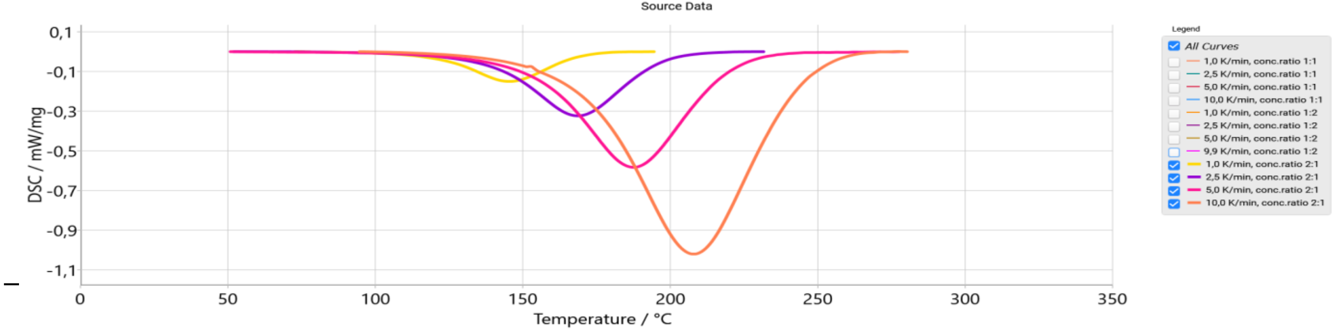
Peak position for different concentrations



Epoxy/Aniline 1:1
Peak 10K/min 194°C

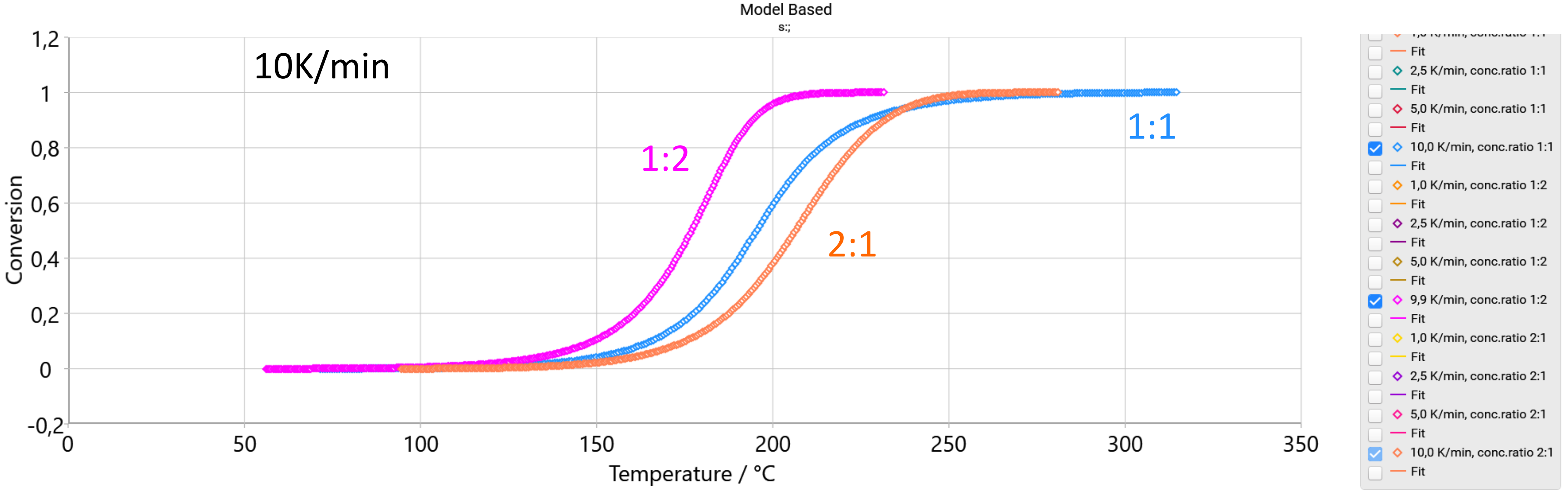


Epoxy/Aniline 1:2
Peak 10K/min 180°C



Epoxy/Aniline 2:1
Peak 10K/min 207°C

Different shape of the curves



Independent kinetic analysis for each concentration ratio

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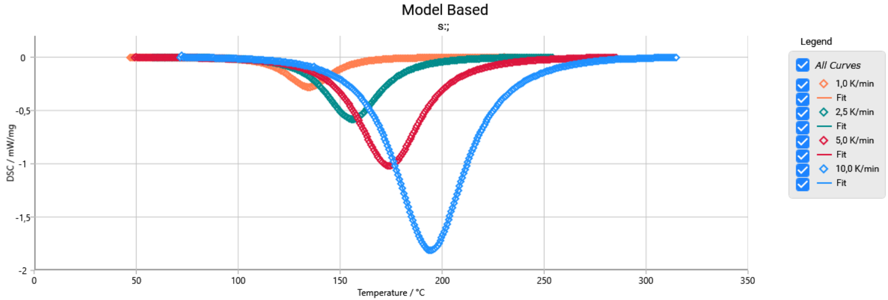
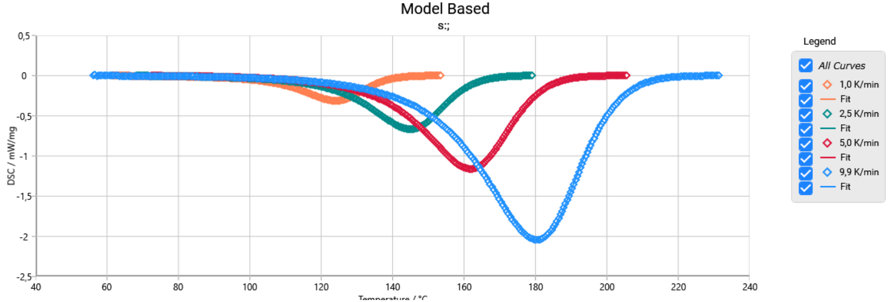
Title	Value
ActivationEnergy	53,583
Log(PreExp)	2,931
ReactOrder n	1,806
Log(AutocatPreExp)	1,389
Contribution	1,000



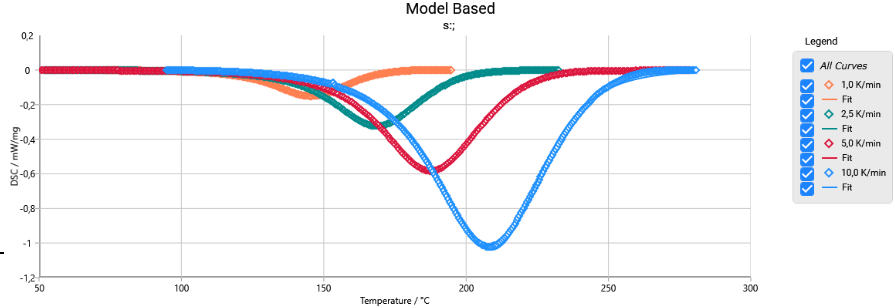
Epoxy/Aniline 1:1
logA=2.9
n=1.8

Title	Value
ActivationEnergy	54,148
Log(PreExp)	3,368
ReactOrder n	1,108
Log(AutocatPreExp)	1,142
Contribution	1,000



Epoxy/Aniline 1:2
logA=3.3
n=1.1

Title	Value
ActivationEnergy	54,258
Log(PreExp)	3,015
ReactOrder n	1,398
Log(AutocatPreExp)	1,068
Contribution	1,000



Epoxy/Aniline 2:1
logA=3.0
n=1.0

Kinetics Neo: common kinetic model for all concentration ratios and all heating rates

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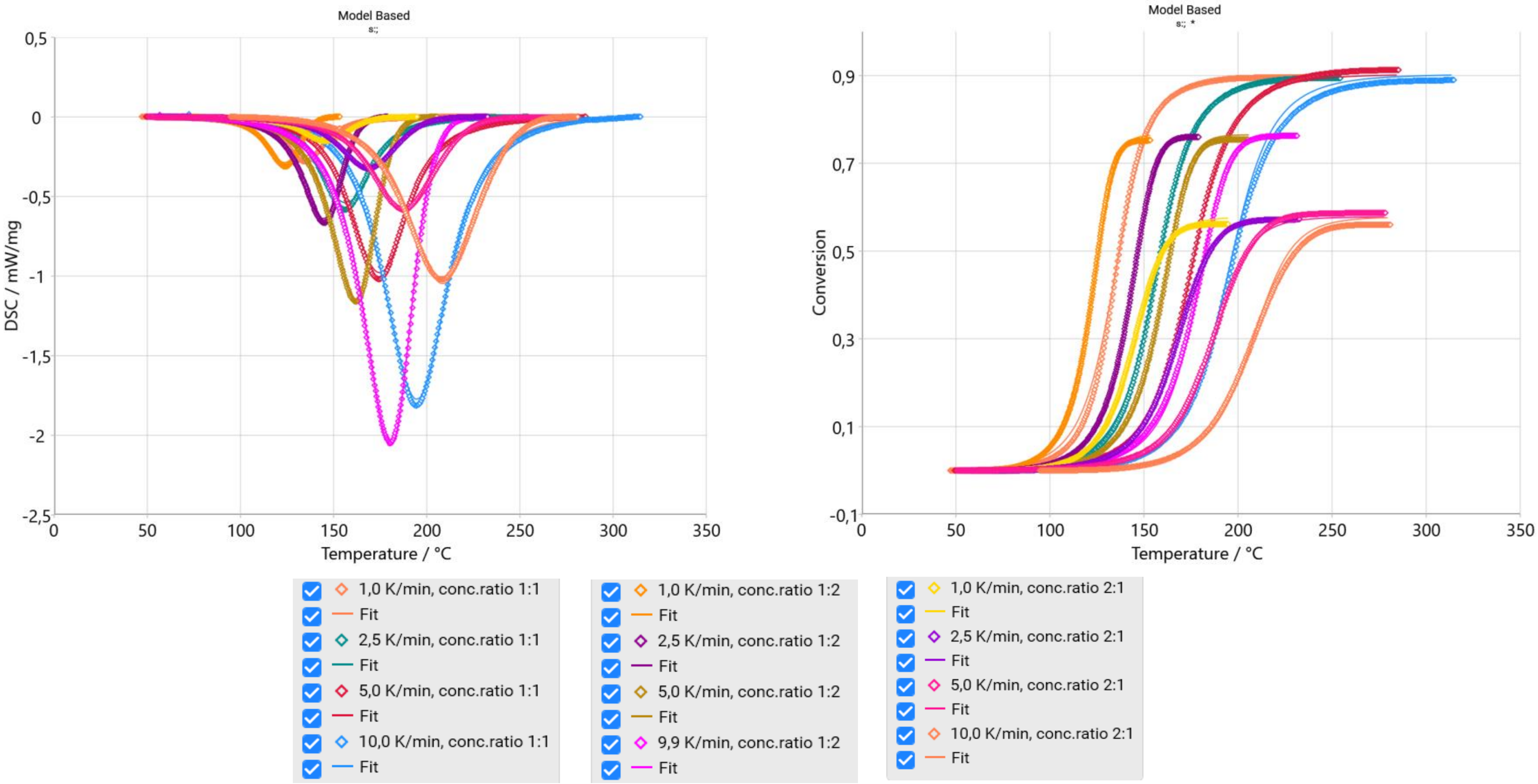
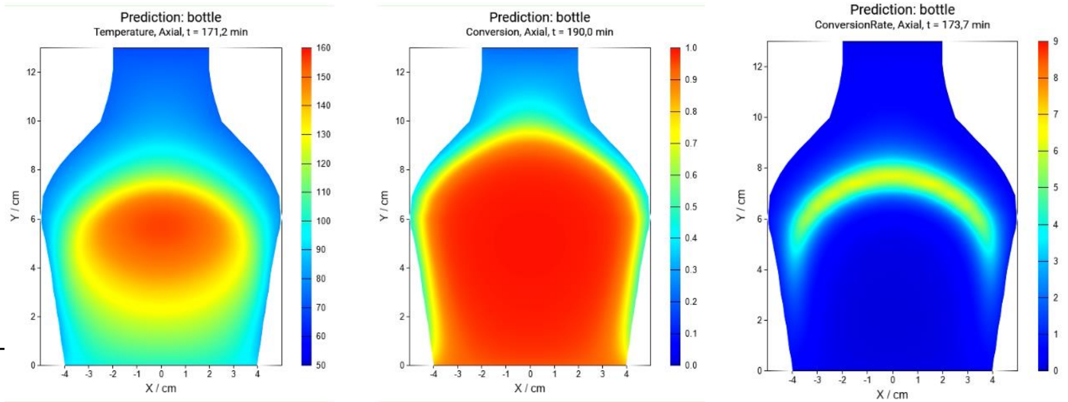


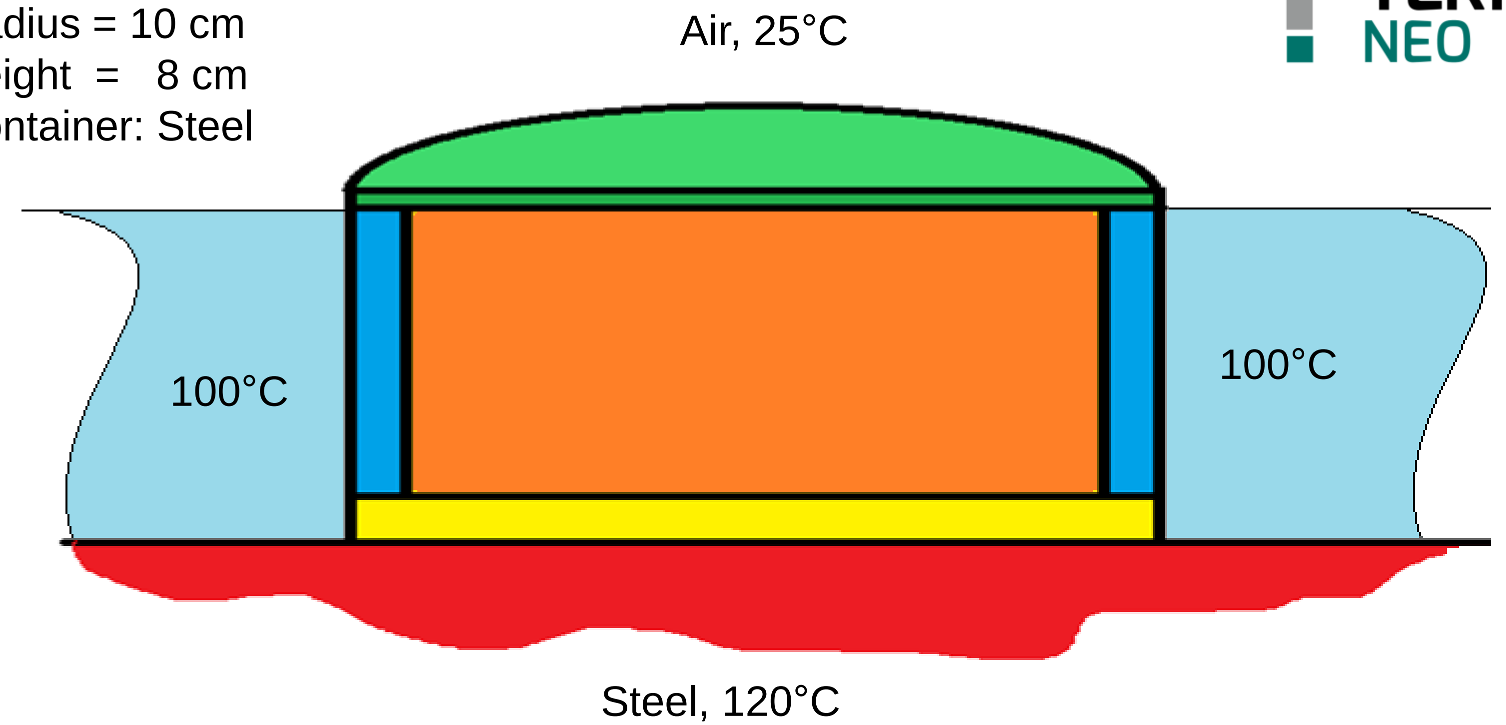
5

Simulation and optimization for thick layers Dependence on thickness and surrounding Termica Neo software

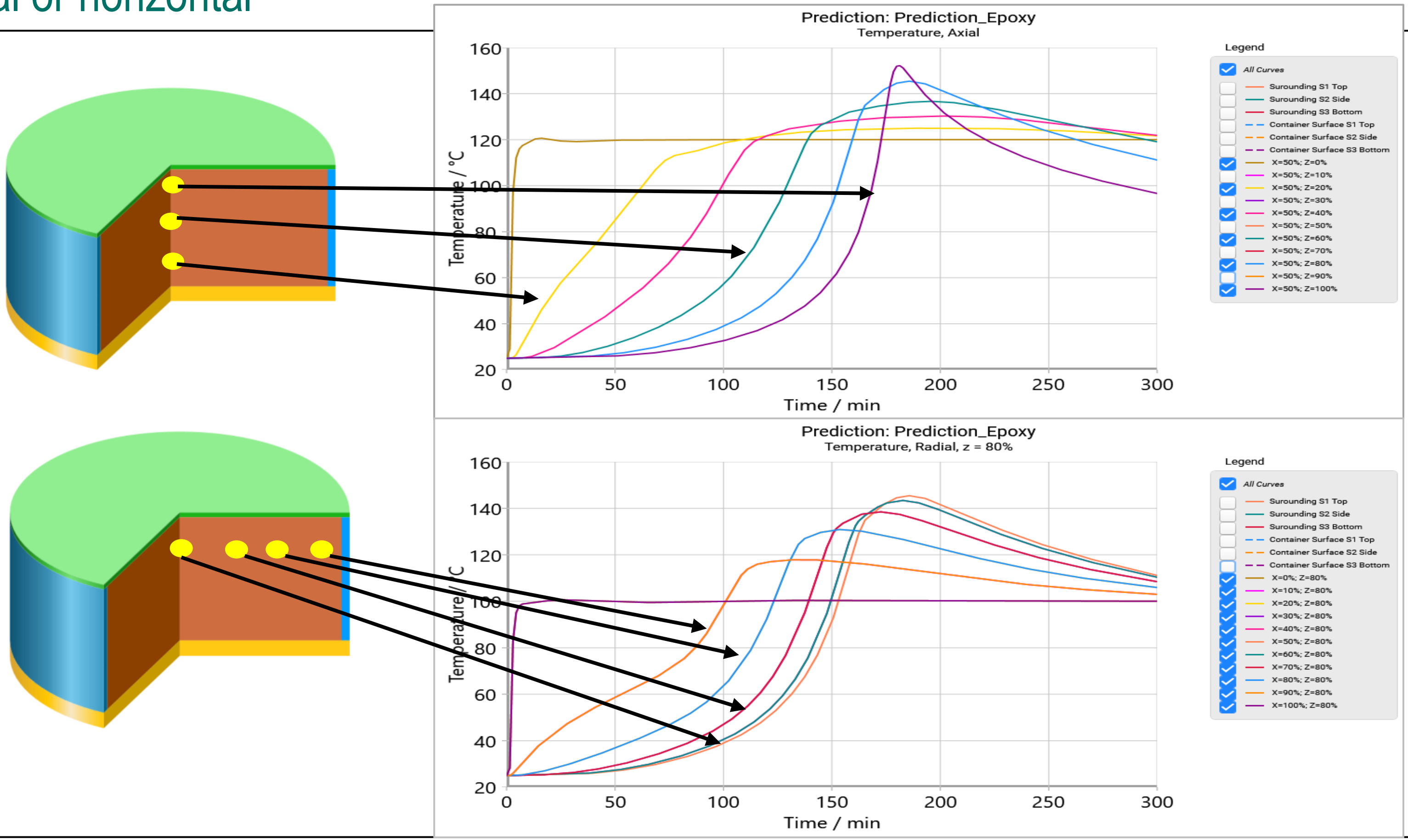


Simplest example for epoxy curing: Is the curing reaction complete after 2 hours?

Radius = 10 cm
Height = 8 cm
Container: Steel

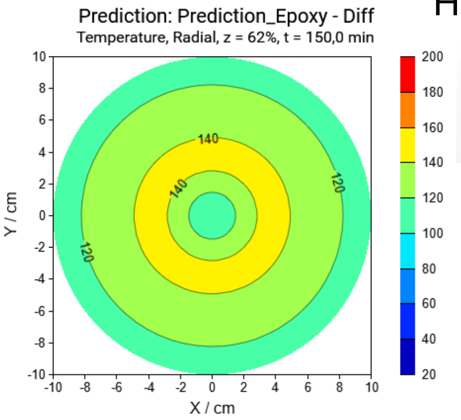


Results: Temperature vs time at any point of the reacting volume: Vertical or horizontal

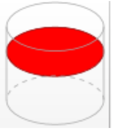


Possible to show: Temperature, conversion, conversion rate, concentrations vs time

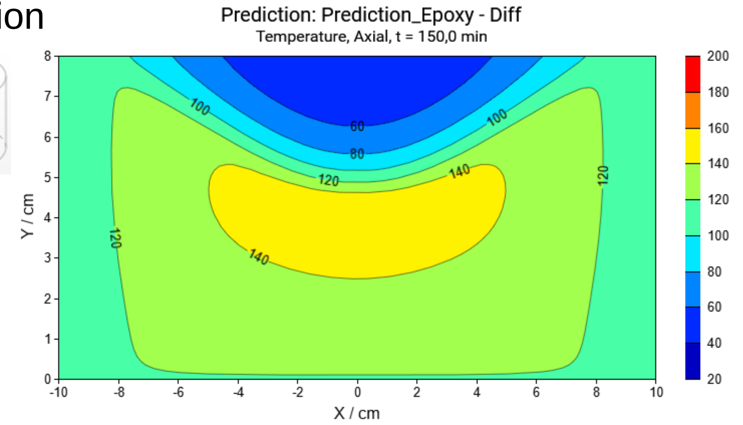
Simulation Example: Find Tg during Curing of epoxy
Horizontal and vertical cross-sections for cylinder



Horizontal

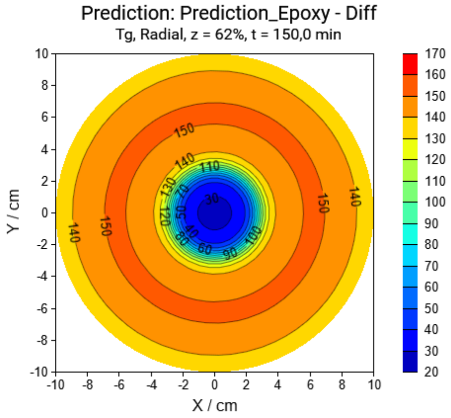


Vertical Section



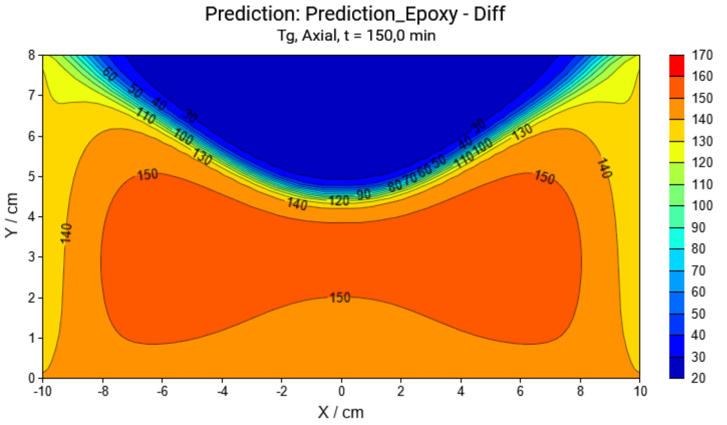
Material temperature T

time=150min



Glass transition temperature Tg

time=150min

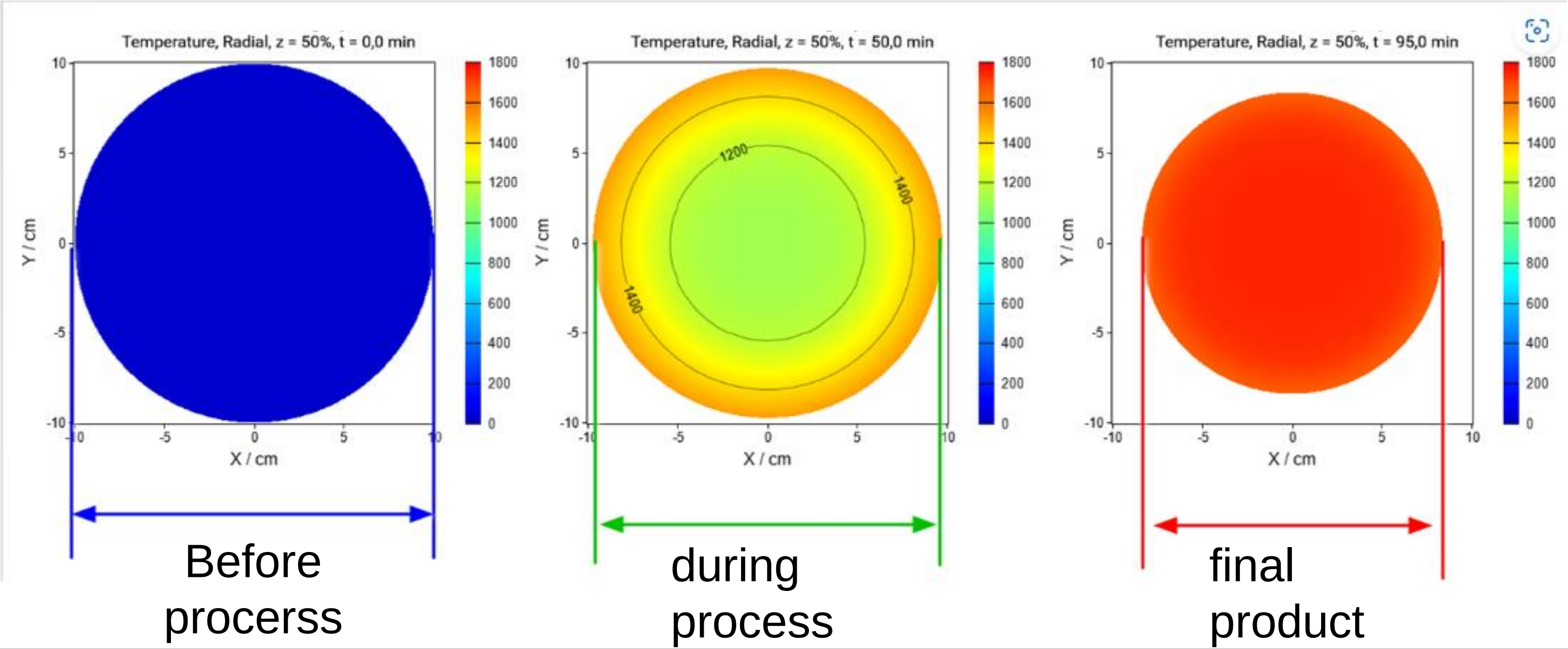


T<Tg: glass

T>Tg: viscose liquid/gel

Simulation Example: changing of length

Reasons for linear changes:
1. thermal expansion
2. different density properties for reactant and final product (here)



NETZSCH Kinetics Neo Web Site

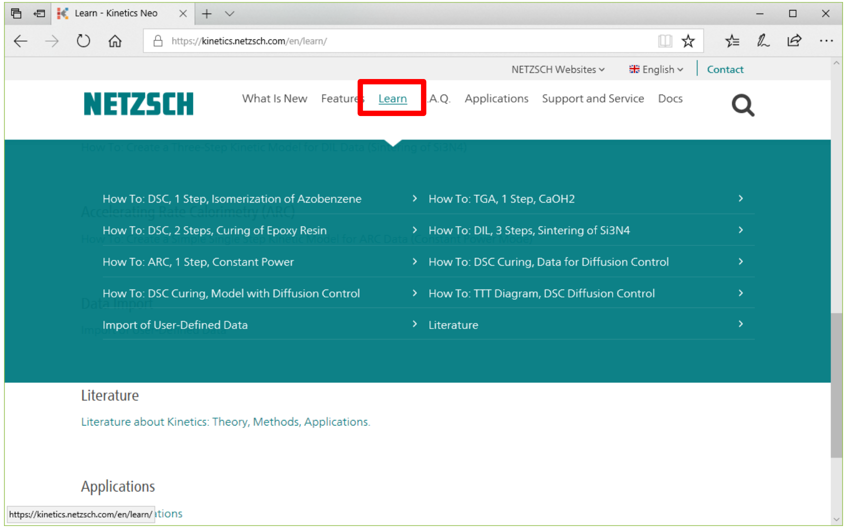
https://kinetics.netzsch.com

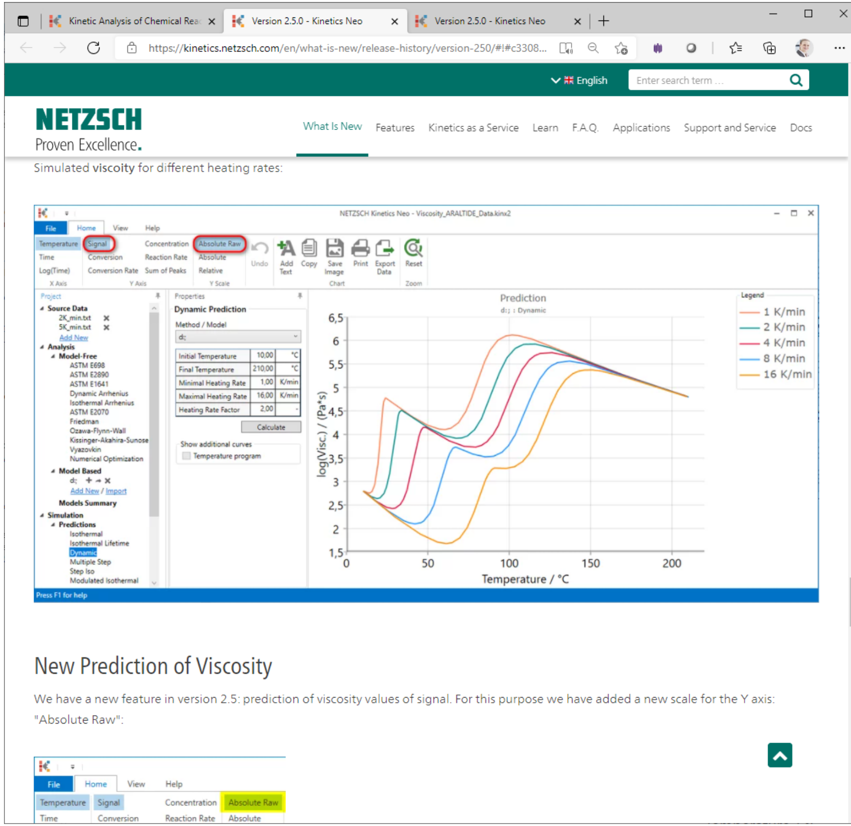
Users Guide, Training examples,

Webinars: (pdf and video):

- *Advantages and disadvantages of different kinetics approaches.*
- *Unique and powerful features of NETZSCH Kinetics Neo software*
- *Crystallization*
- *Polymers*

Trial Version 30 days





Unique: Kinetics Analysis must fulfils ICTAC kinetics recommendations

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International Confederation for Thermal Analysis and Calorimetry

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Review

ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics

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ABSTRACT

The present recommendations have been developed by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC). The recommendations provide guidance on kinetic analysis of multi-step processes as measured by thermal analysis methods such as thermogravimetry (TGA) and differential scanning calorimetry (DSC). Ways of detecting the multi-step kinetics are discussed first. Then, four different approaches to evaluation of kinetic parameters (the activation energy, the pre-exponential factor, and the reaction model) for individual steps are considered. The approaches considered include multi-step model-fitting as well as distributed reactivity, isoconversional, and deconvolution analyses. For each approach practical advice is offered on its effective usage. Due attention is also paid to the typical problems encountered and to the ways of resolving them. The objective of these recommendations is to help a non-expert with efficiently performing multi-step kinetic analysis and interpreting its results.

- Model free analysis
- Multi-step model-fitting (model based)
- Diffusion control for curing
- Crystallization kinetics
- Kamal model for curing
- Deconvolution analysis (sum of peaks)

KINETICS NEO