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Understanding the Cure Behavior with Rheology Kinetics

How Kinexus and Kinetics Neo work together to better optimize material performance

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NETZSCH Webinar – 24th November 2020

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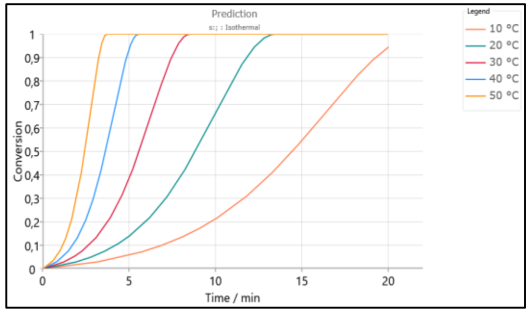
Understanding the Cure Behavior with Rheology Kinetics

- Part 1 – Introduction to Rheology [Adrian Hill]
  - Brief overview of the use of rheology to directly monitor the material change during a cure reaction
- Part 2 – Introduction to Kinetics [Elena Moukhina]
  - Overview of the theory and use of Kinetics for a fuller understanding of curing profiles
- Part 3 – Case Study of a Curing System; Rheology Data, Kinetics Analysis and Predictions [Adrian Hill and Elena Moukhina]
  - An example rheological measurement on the Kinexus rheometer, imported into Kinetics Neo to investigate the changes in conditions affect the reaction kinetics



1. Introduction to Rheology

Typical Cure Measurements

Agenda

1. Basic introduction to rheology; material science measurement
2. Rheolgical terms to describe the material changes during a curing process
3. Typical rheology cure profiles

What is rheology?

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Definition: "The science of deformation and flow"

Rheology is a basic material science for semi-solids & liquids

We measure it, as it needs to be controlled to get needed performance

Rheology is **more** than just viscosity

- Rheology is putting the material properties into context
  - Appropriate flow conditions
  - Even at "rest"
  - Gives us the science & numbers to understand real material performance

Rheometer Principles – Oscillation Testing

Practical Measurements of Curing Reactions

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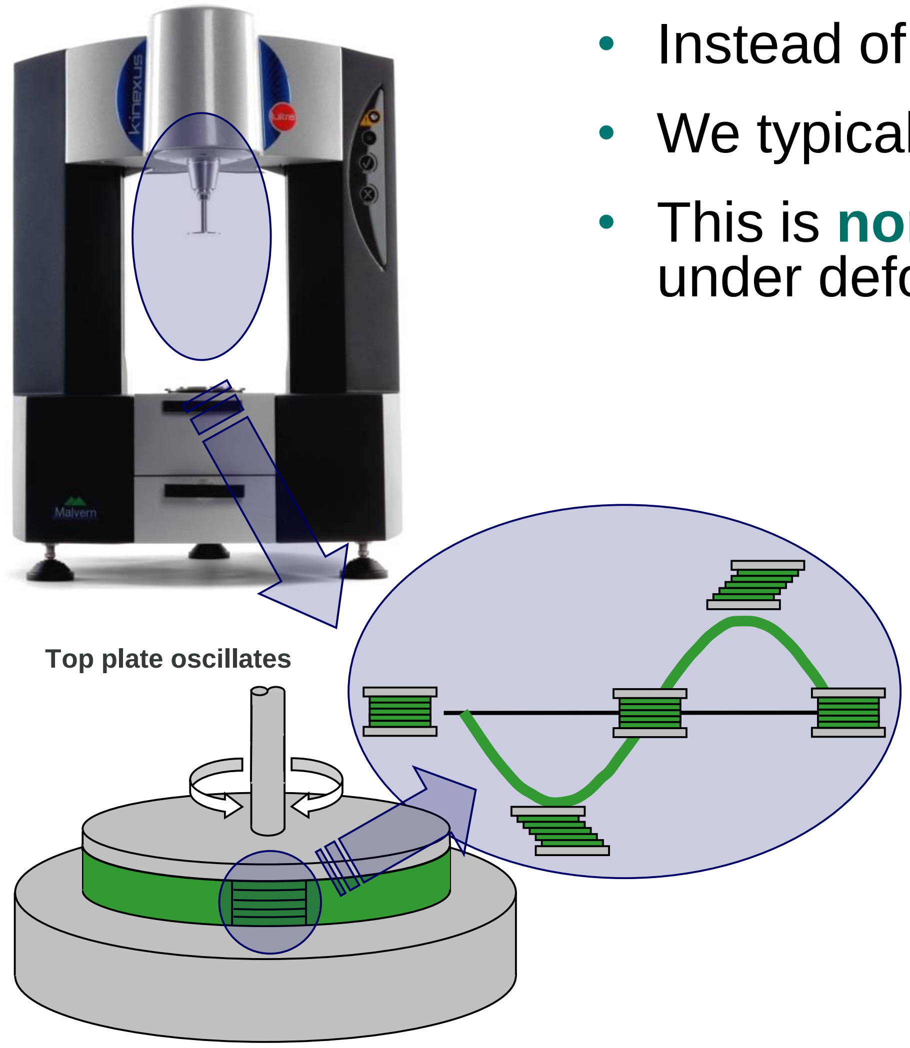


- Instead of rotating on a sample, we now **oscillate back and forth**
- We typically apply a sinusoidal signal to the sample
- This is **non-destructive testing**, so can show the properties under deformation, before flow
  - From this we can predict sample properties
  - Typical variables
    - **Shear Stress, σ [Pa]:** force (f or p) per area (a)
    - **Strain, γ [no units or %]:** displacement (u) divided by height (h)
      - (% strain is the above equation *100)
  - Measures:
    - **Complex Modulus** – the stiffness of material
    - **Phase Angle** – “degree” of fluidity of the sample from 0 to 90°
    - **Complex/Dynamic Viscosity** – Cox-Merz approximation from osc
    - **Elastic (G’) and Viscous (G’’) modulus** - calculated

Disposable Plates for Curing Systems

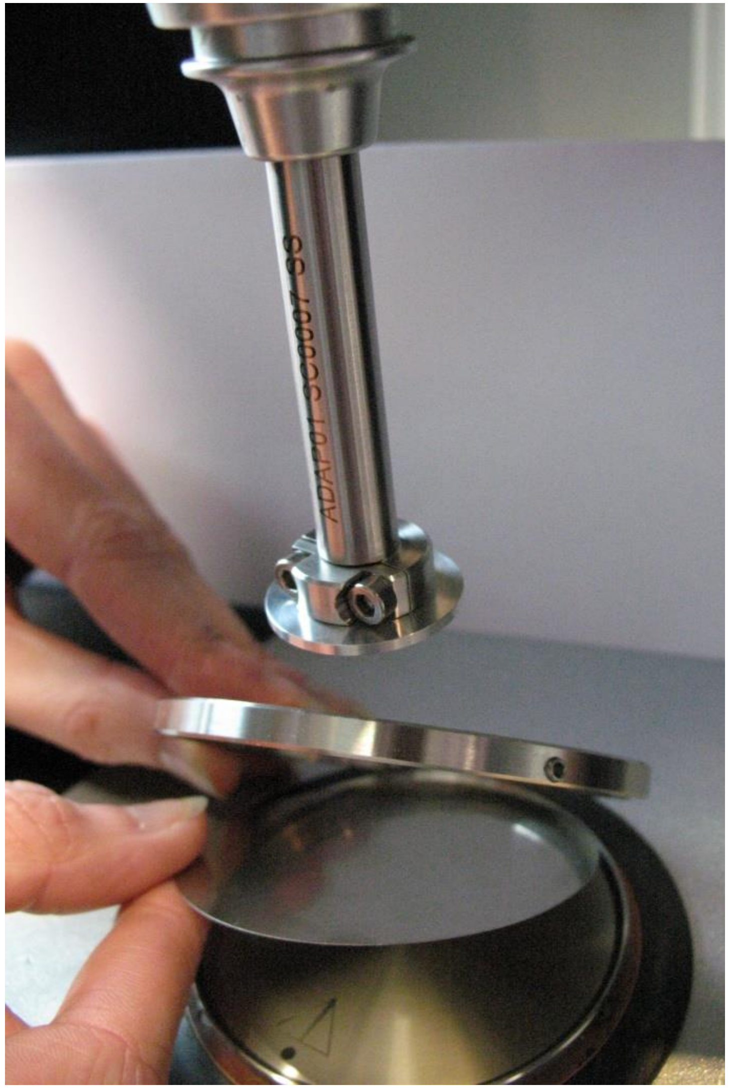
Kinexus Disposable Plate System (KNX2155 Peltier / KNX2263 HTC)

The upper geometry stub and the lower plate are designed to be disposable (at a low price)

The upper geometry is held inside the clamp mechanism

The lower disk is held in place by the clamping ring

Geometry recognition remains with the system configured for the geometry choices



Rheology of Curing/Gelling Reaction Discussion

Overview of typical results

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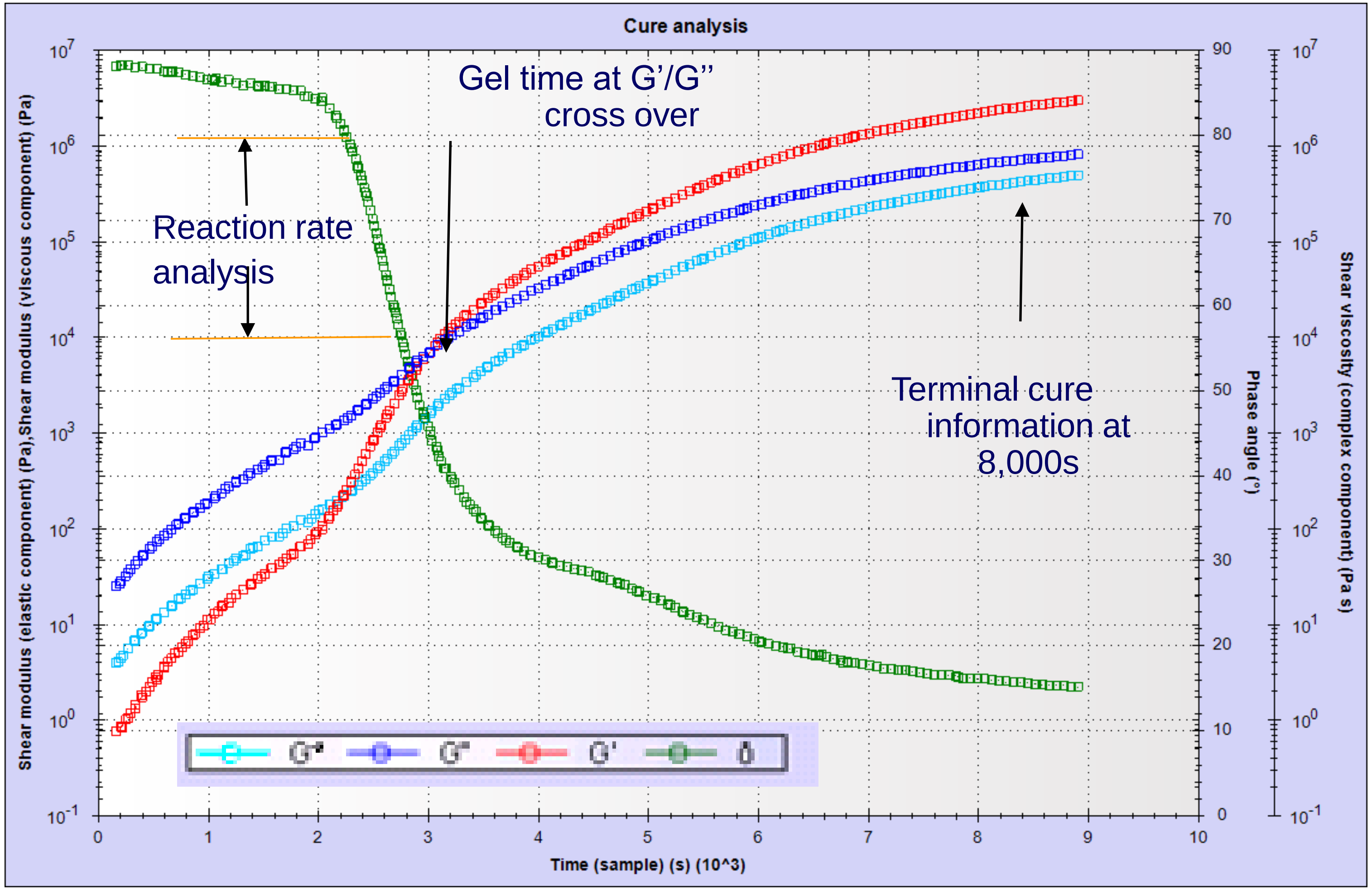
With rheology being the science of deformation and flow, it is an ideal tool to monitor a cure

- A lot of this discussion is also relevant to gelling

Typically, we are looking at changes with

- Time
- Temperature, or
- External trigger: UV/light radiation



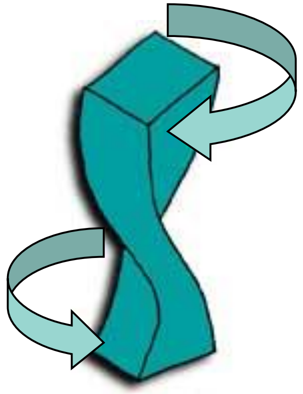
Take this example where the sample starts off low viscosity & gets higher

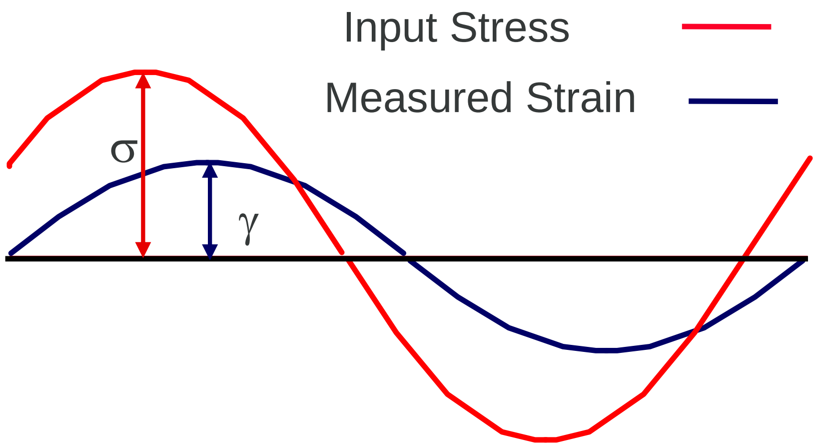
Complex Modulus – G* [Pa]

From oscillation we can measure the materials complex modulus, the **stiffness of a material**

The higher the modulus the tougher the material

Calculated from how much a sample moves for a given force





Units of Pascals (Pa)

$$\text{Modulus} = \frac{\text{Shear Stress}}{\text{Shear Strain}} = \frac{\sigma}{\gamma}$$

Cox Merz "Rule"…

This empirical approximation can indicate a complex or dynamic viscosity from oscillation data which can be preferred:

$$\text{Complex Viscosity} = \frac{\text{Complex modulus}}{\text{Angular frequency}}$$

$$\text{Dynamic Viscosity} = \frac{\text{Viscous modulus}}{\text{Angular frequency}}$$

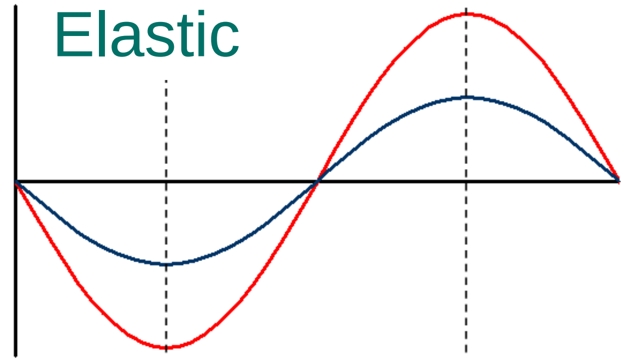
Note: shows the same trends

Phase Angle [°]

For a Purely Elastic Material – Solid-like behaviour

The stress and strain are exactly in phase

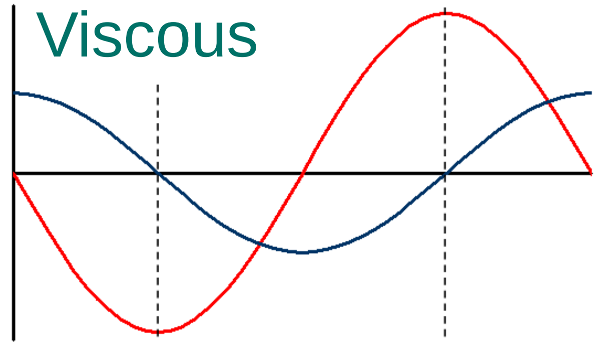
Therefore the phase angle is zero



For a Purely Viscous Material – Liquid-like behaviour

Stress and strain are 1/4 of a cycle out of phase

Therefore the phase angle is 90°



Phase angle can be considered a scale of “fluidity” from 0° (solid like) to 90° (liquid like)

[Tan delta is simple the tan(phase angle), with a range from 0 (solid like) to 0.5 (“gel point”/ d=45°) to infinity (liquid like)]

Storage and Loss Modulus

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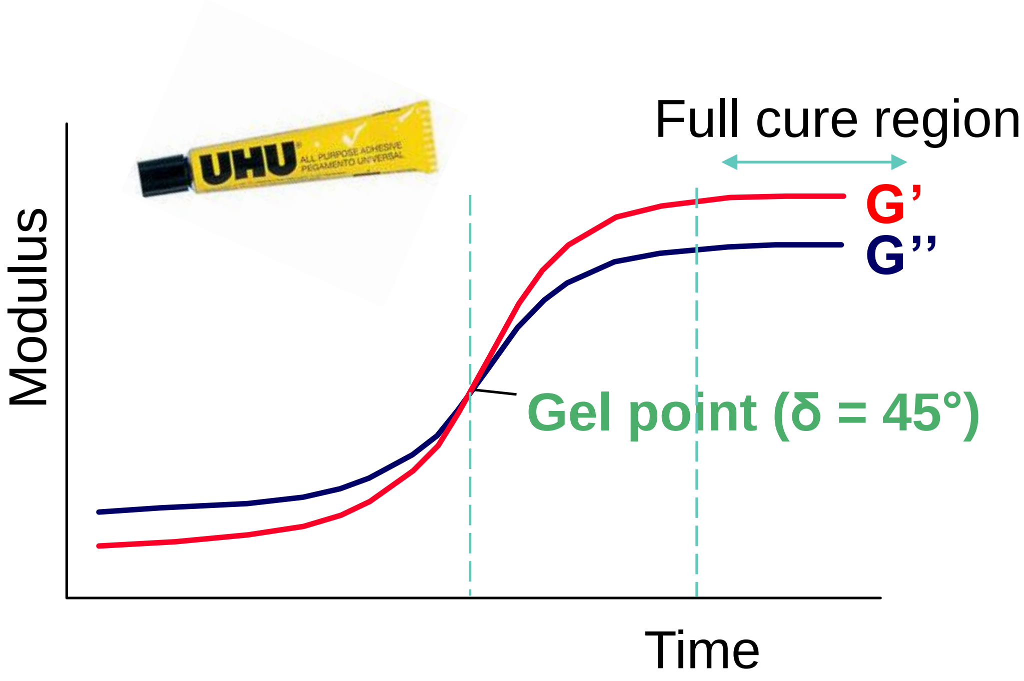
- Rheology language tends to use a combined form of complex modulus and phase angle

- **Storage (elastic) modulus G'**
- **Loss (viscous) modulus G''**

- If **G' > G''**, phase angle less than 45° - **SOLID LIKE**
- If **G'' > G'**, phase angle greater than 45° - **LIQUID LIKE**

- G* - modulus is the overall stiffness of a material



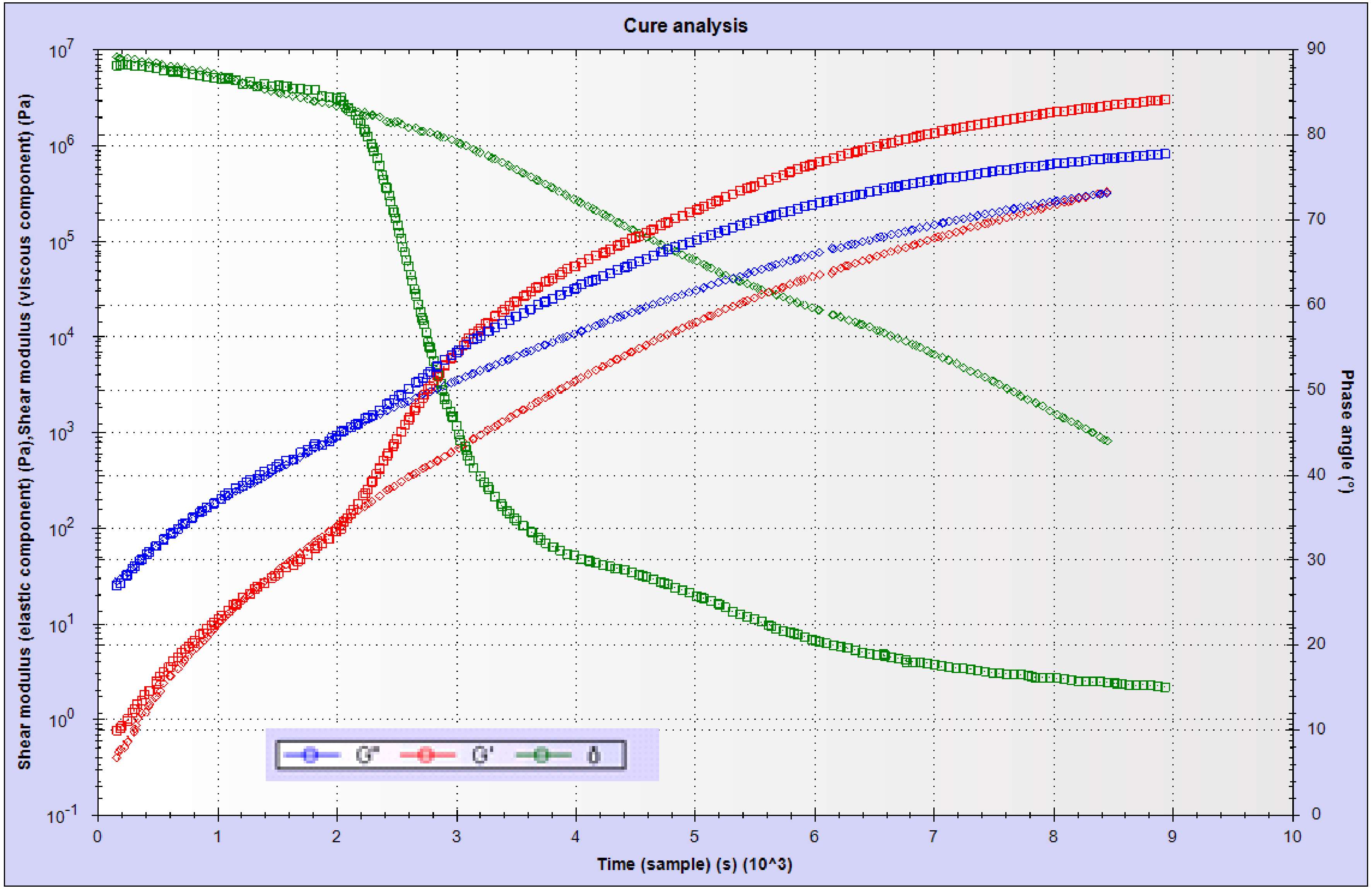
Curing Example

Comparing different samples

Direct measurement of the material changes through a cure

Typically consider:

- Complex modulus, or
- Complex viscosity, or
- Dynamic viscosity
- Elastic/viscous modulus
- Phase angle or tan delta



2. Introduction to Kinetics Neo

Understanding the cure behavior with rheology kinetics

Agenda

1. What is chemical kinetics?
2. Example of curing data, kinetics analysis and predictions

What does chemical kinetics study?

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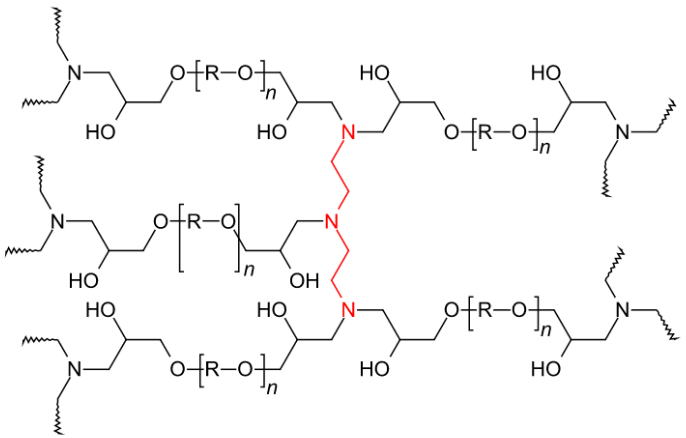

A → **B**

reactant product

Reaction rate depends on

- Temperature
- Concentration
- Pressure
- Catalyst,
- Solvent
- …

Chemical Kinetics answers the following questions**:**

- How fast is the reaction?
- What is the reaction mechanism?
- What is mathematical model of chemical process

NETZSCH Kinetics Neo software

Main problem: how to reduce the costs?

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Ceramics production: What is optimal firing temperature profile?

Morgan Advanced Materials
HALDENWANGER

New material

HALFOAM ALUMINA ™

Problem:

Fast firing: **cracks** and deformations

Slow firing: too **expensive** production process

Laboratory measurements + Kinetic analysis + process optimization:

Production time was reduced more than by 50% from WEEKS to DAYS

Curing, cross-linking

- What happens during curing? How high is the reactivity?
- At which temperature and time curing starts and finished?
- What is the optimum curing process (time/temperature)?
- How high is the degree of curing?
- Where is the glass transition temperature?
- How to reduce costs during production?
- What is the final state of the epoxy after given time at given temperature? (glass /elastic solid/viscose liquid)

Steps to solve Kinetic Tasks in Kinetics Neo

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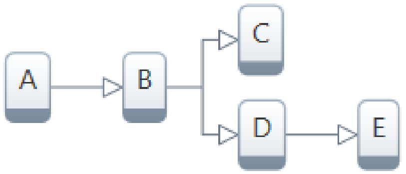
Measured raw data

- File 1
- File 2
- File 3
- File 4
- . . .

Data Import and Processing

- Processed File 1
- Processed File 2
- Processed File 3
- Processed File 4
- . . .

Kinetic Model



Autocatalytic (Cn)

Reaction of n-th order

Kamal-Sourour

. . .

Friedman

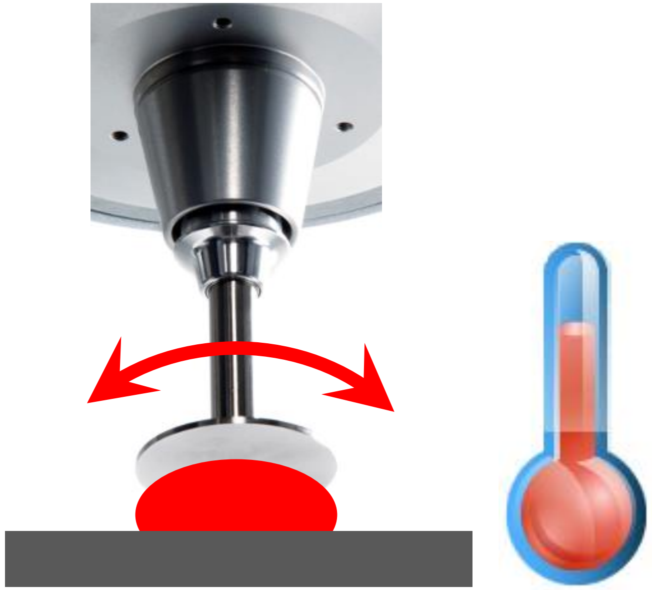
Ozawa

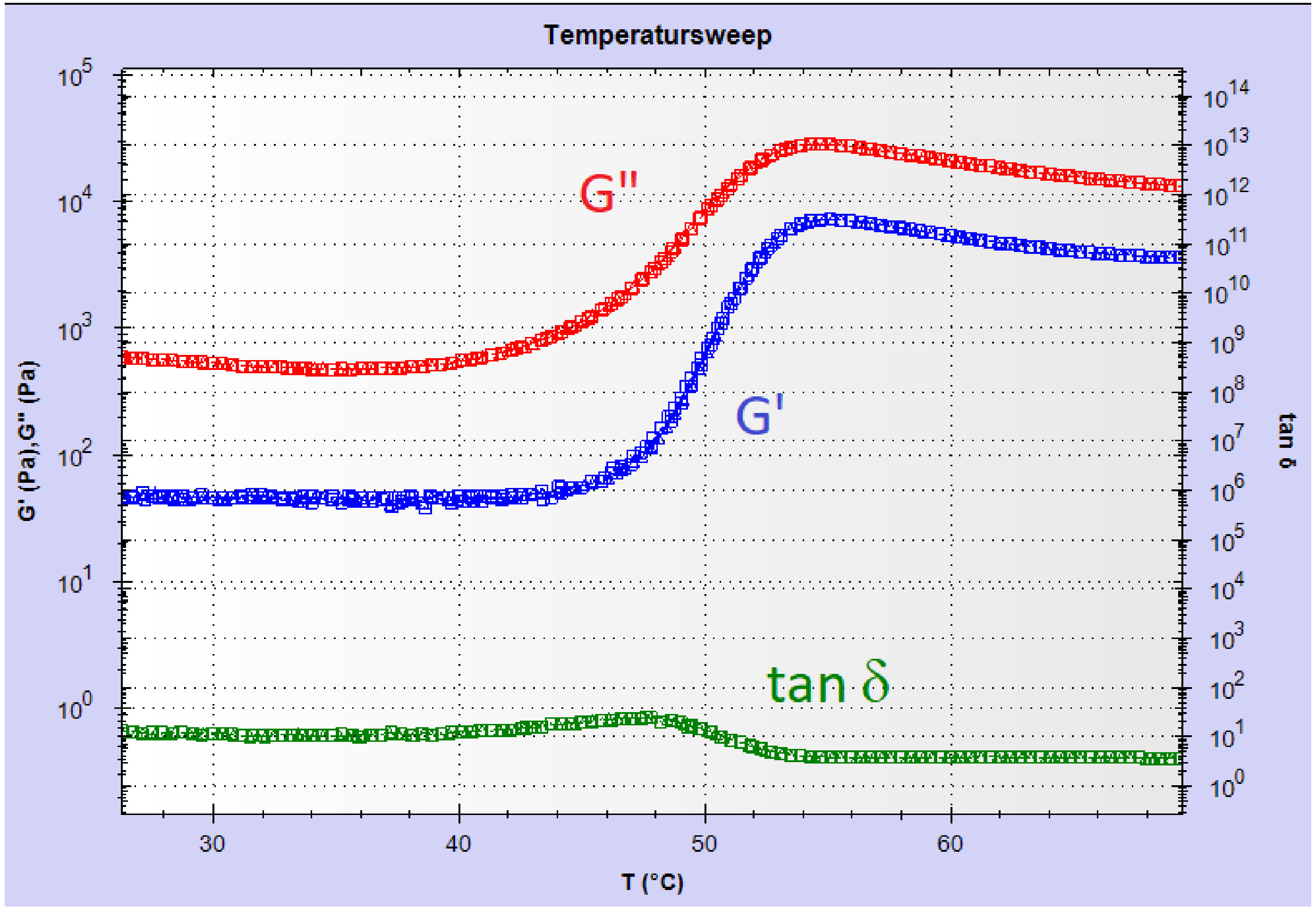
. . .

Simulations

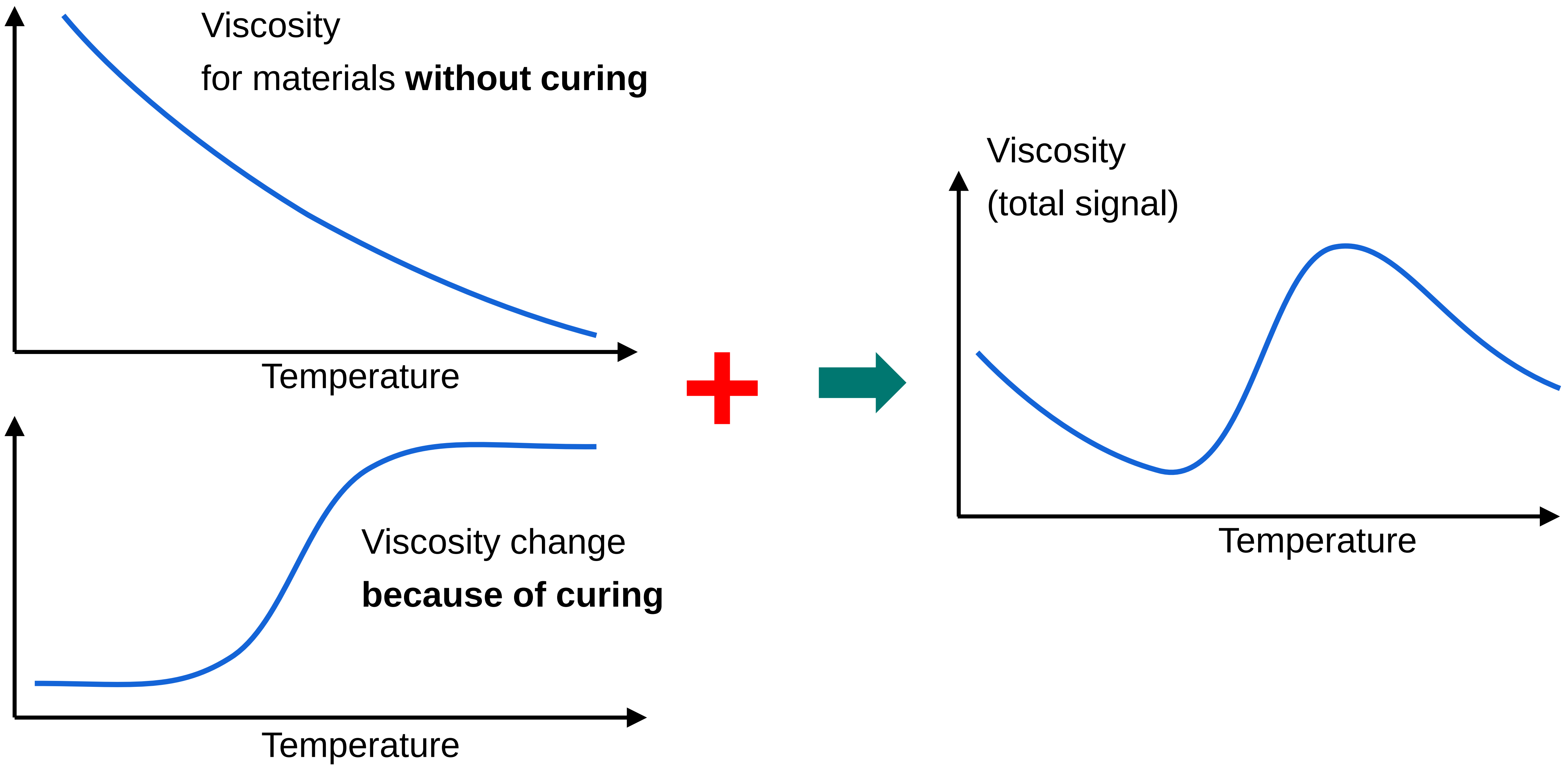
- Predictions: isothermal / dynamic / arbitrary
- Predictions: degree of cure / curing rate / viscosity
- . . .
- Optimization: conversion rate
- Optimization: curing profile
- . . .

Cure Monitoring: Rheometry

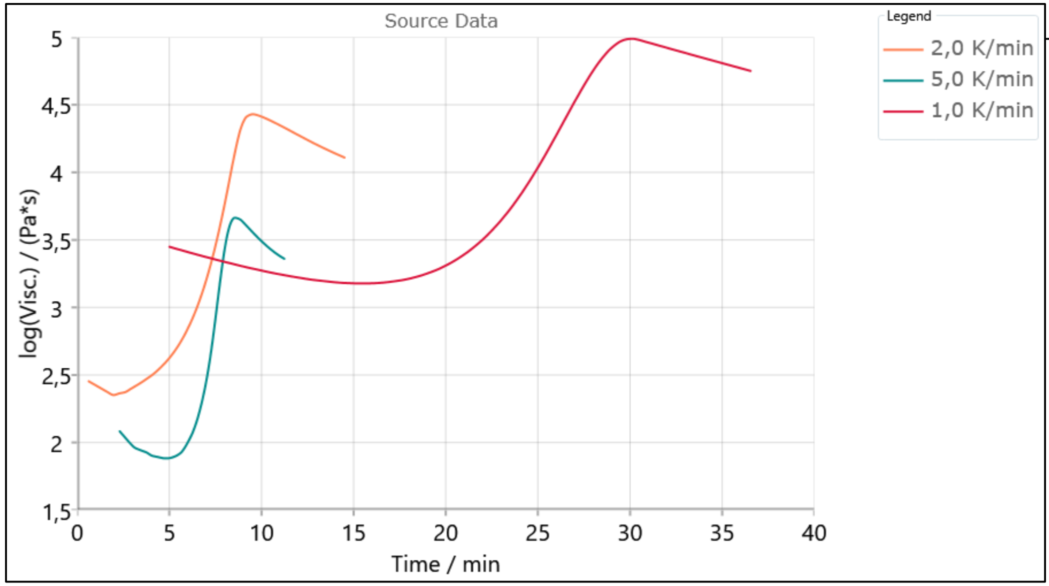


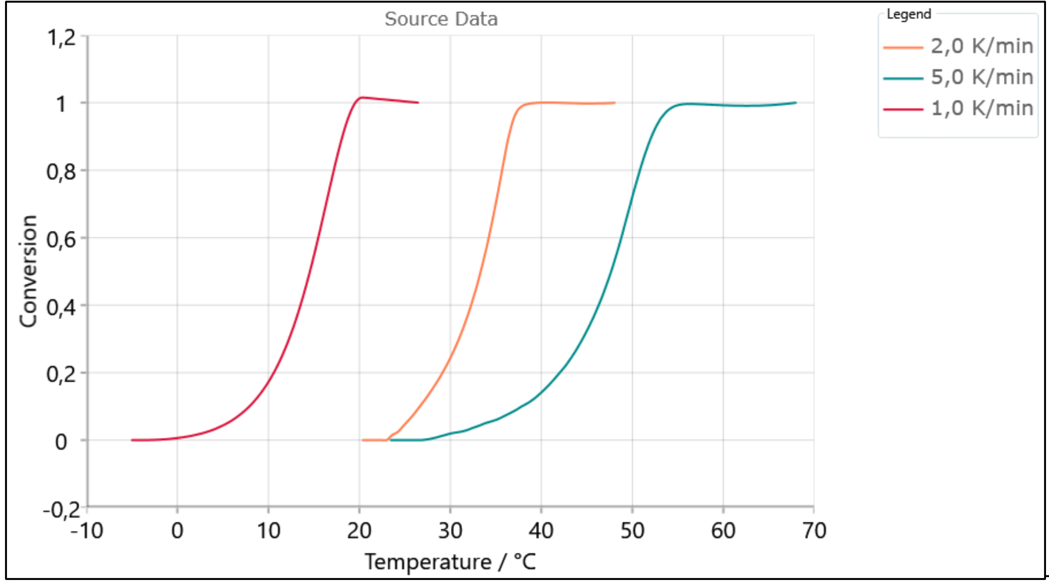


Parts of Measured Viscosity Signal



Kinetics Neo: Data Processing of Complex Viscosity





Target: find degree of curing from the imported data

Steps:

1. Select evaluation range
2. Switch to Temperature scale
3. Remove Viscosity(Temperature) without curing
4. Recalculate to conversion

Kinetic Model for Curing

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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 **Cn** for autocatalytic reaction:

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

This equation with its parameters A, Ea, K, m, n, is the **kinetic model**.

Kinetic parameters are found from the **best fit** for all experimental data

Kinetic Model: Single-Step Autocatalytic Reaction of Cn type

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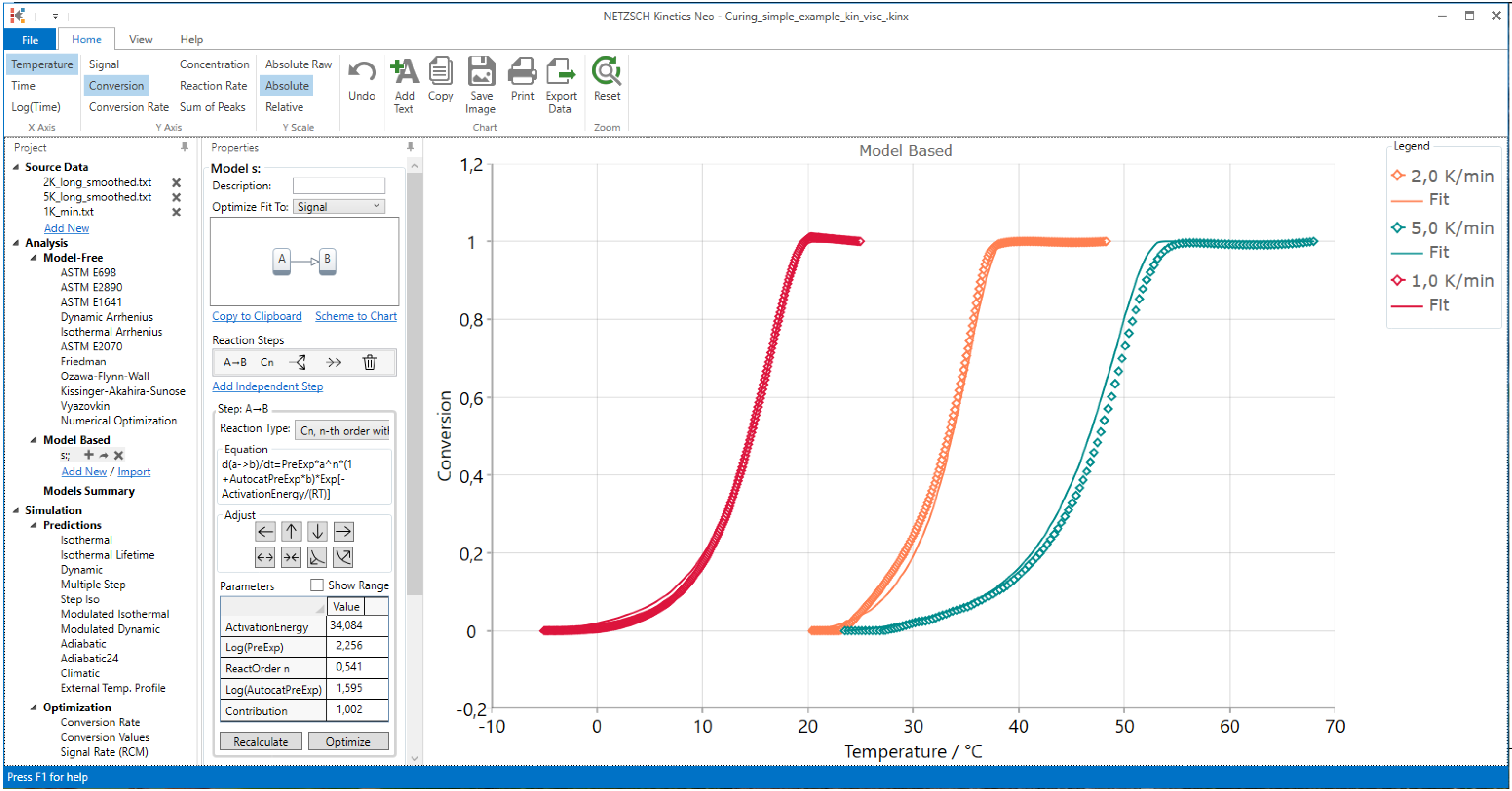
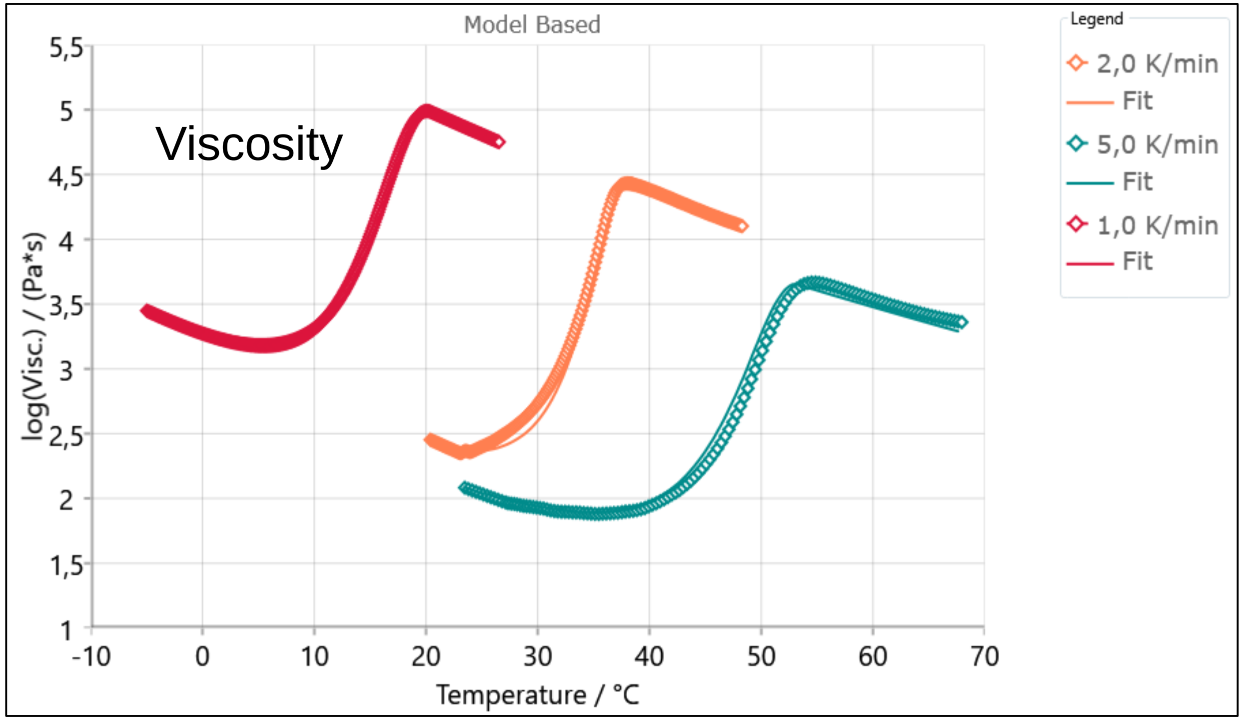
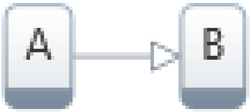


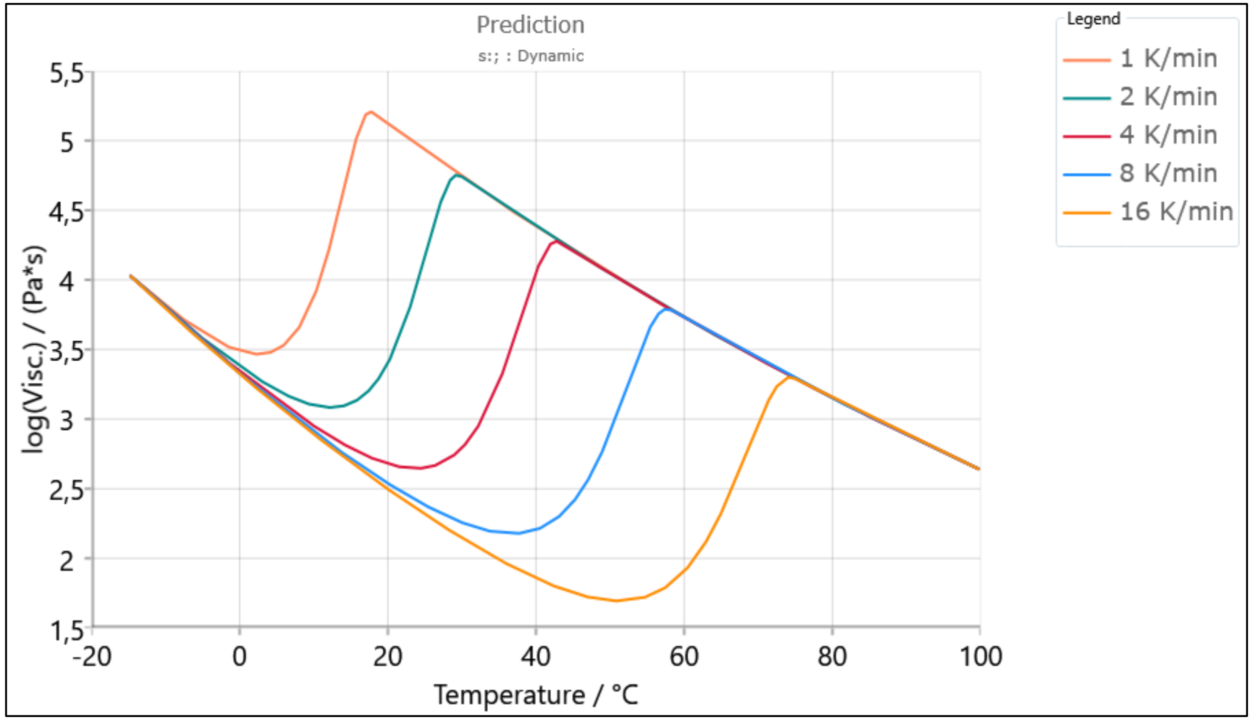
Predictions 1
What is **viscosity** for user-defined temperature program?

Constant heating: measured reaction rate





New temperature program: Unknown **viscosity**

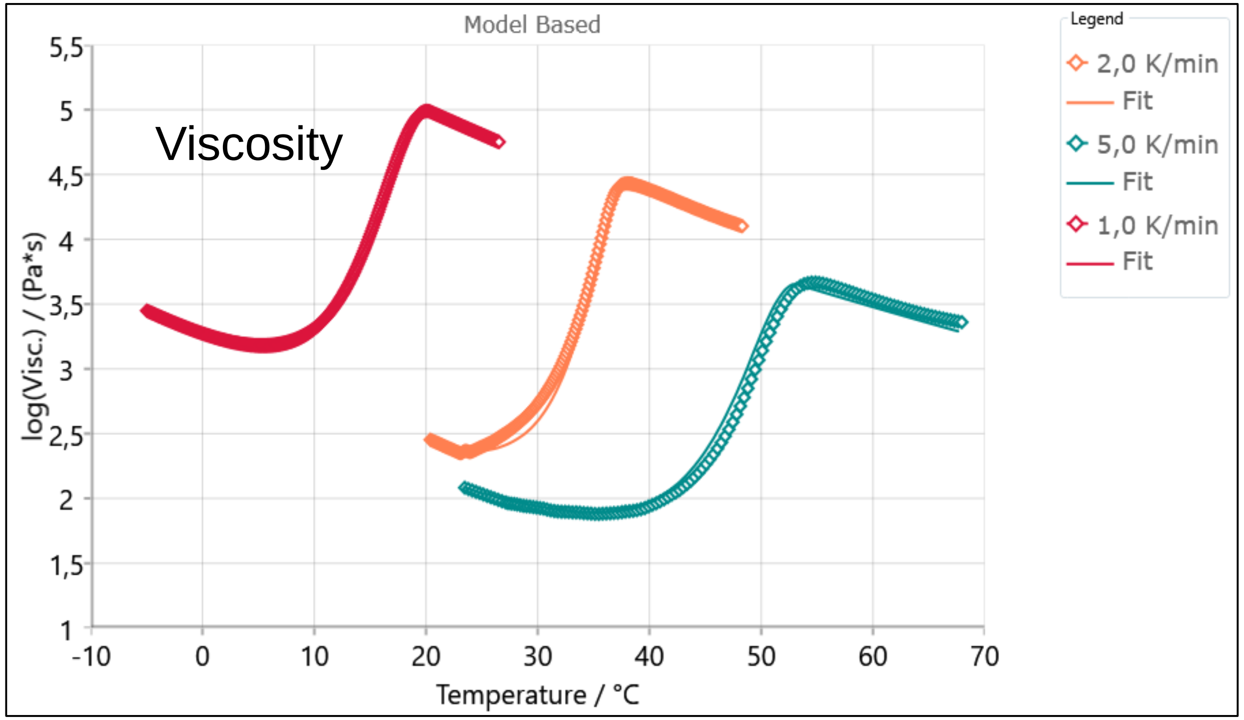


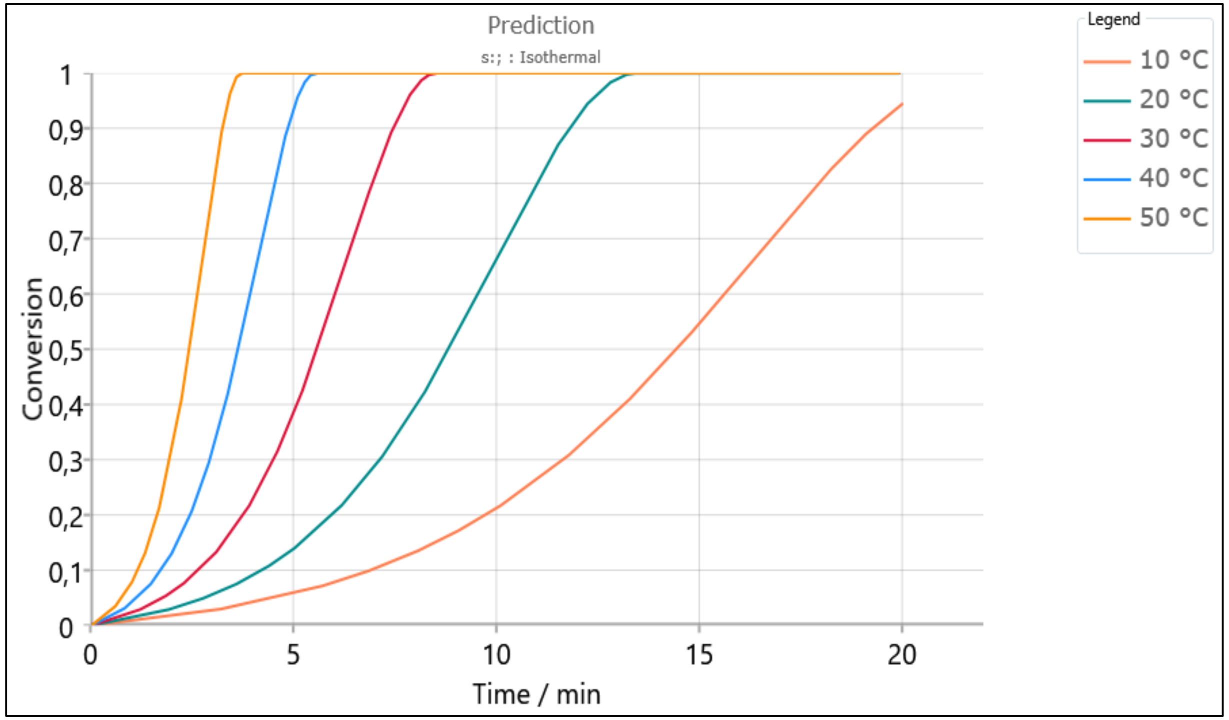
No new measurement
Calculation with Kinetics Neo

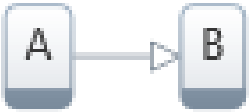
Predictions 2
What is **degree of cure** for user-defined temperature program?

Constant heating: measured reaction rate

New temperature program: Unknown **degree of cure**



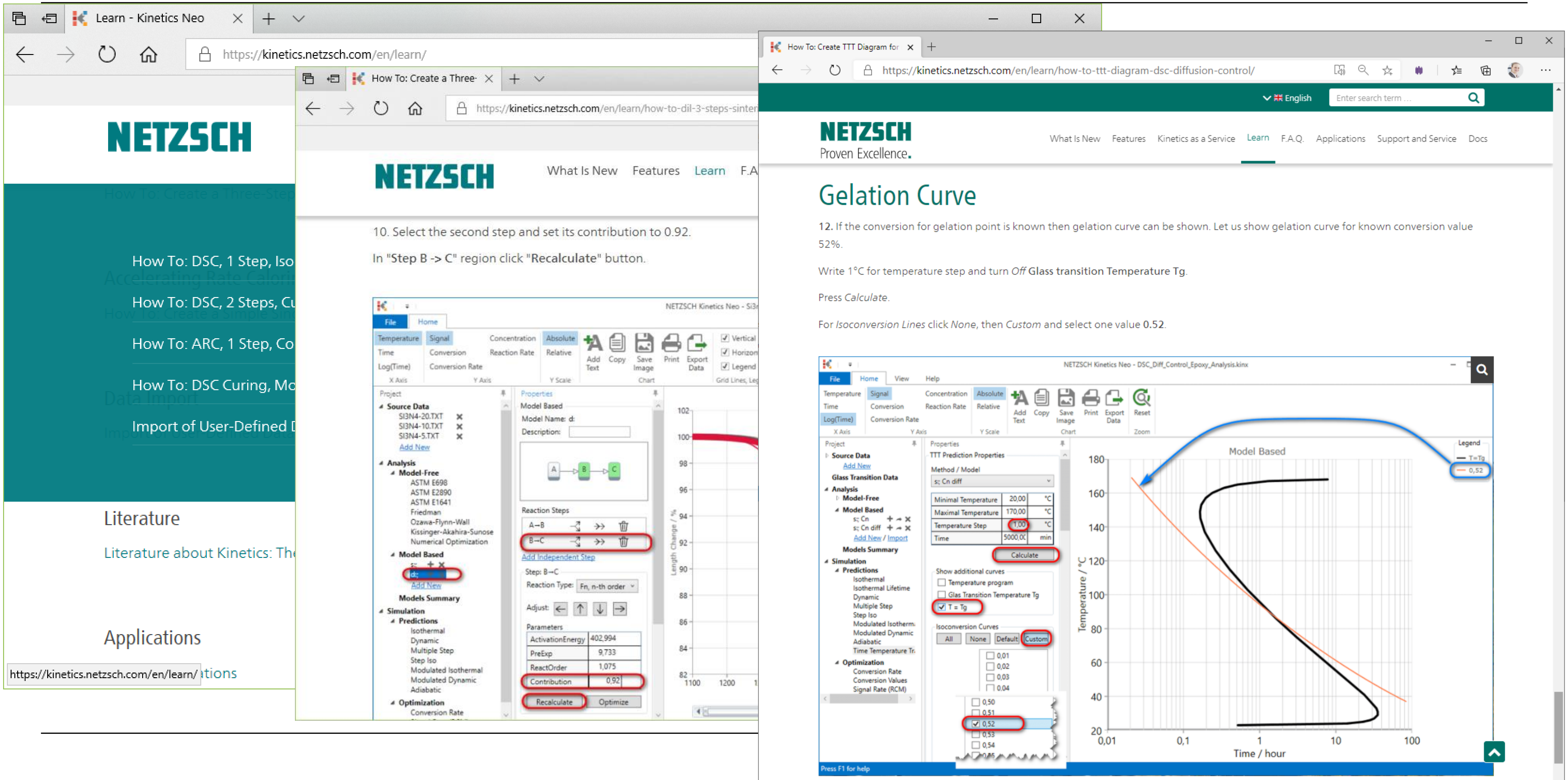




No new measurement
Calculation with Kinetics Neo

NETZSCH Kinetics Neo Web Site including User Guides

https://kinetics.netzsch.com



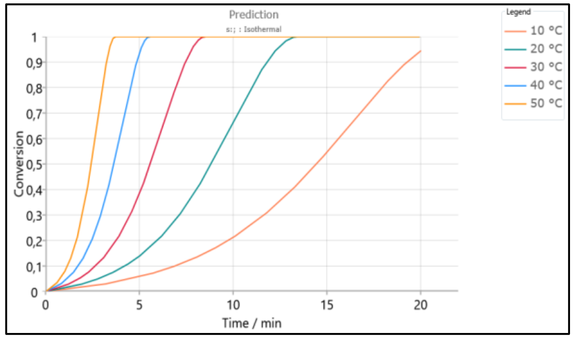
Conclusion

Kinetics Neo Software help to do:

1. Calculation of one mathematical kinetic model for several measurements
2. Prediction of degree of cure for the new temperature profile
3. Prediction of viscosity for new temperature profile
4. Prediction and glass transition temperatures (temporary DSC only)
5. Optimization of curing process. Find the concentrations in order to have what we want to have

3. Case Study of a Curing System

Rheology Data, Kinetics Analysis and Predictions



Curing example: ARALDITE

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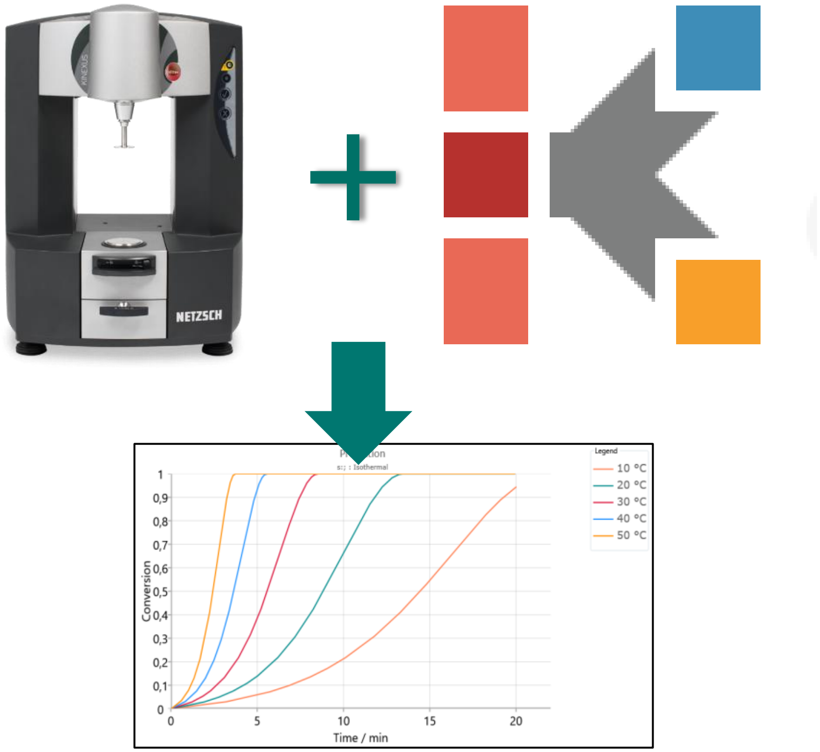
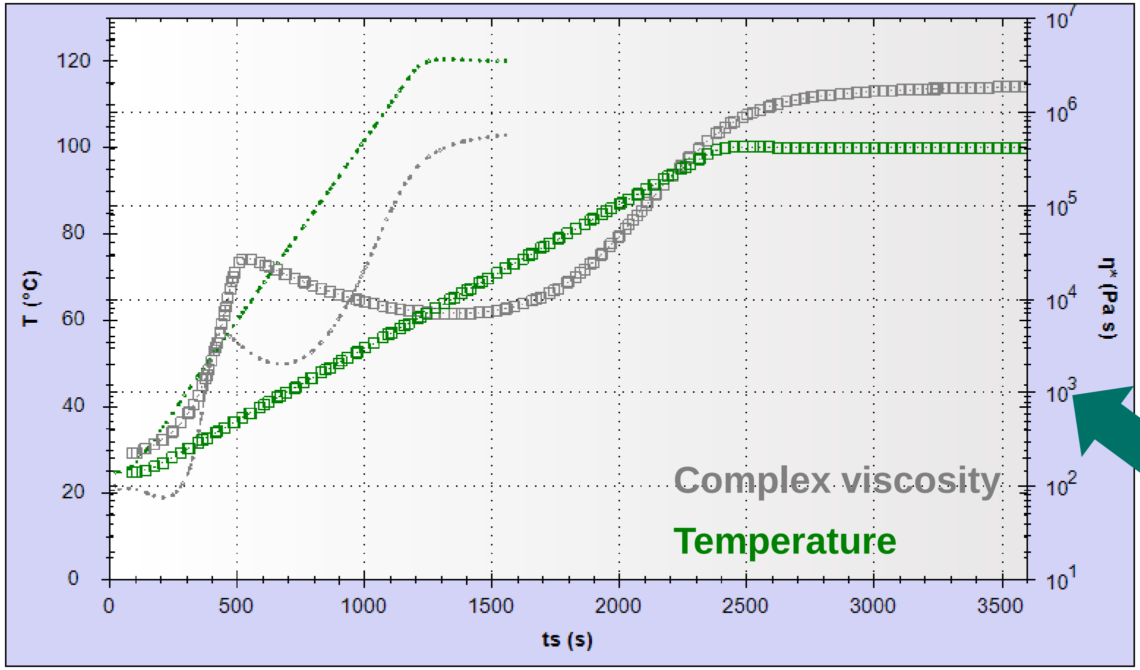
2-component adhesive

"Very fast setting": 5 minutes…

Complete curing 24 hours

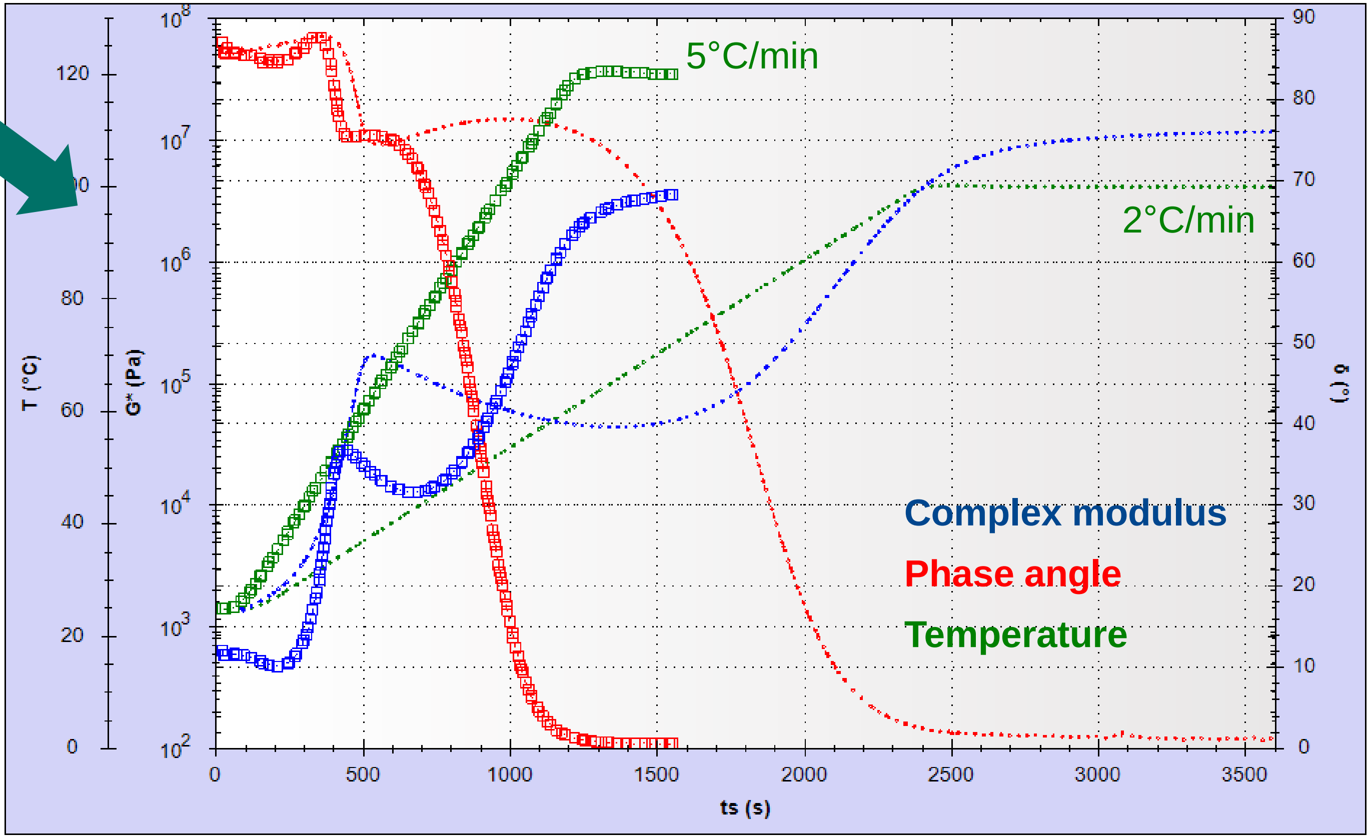


Kinexus Measurements



Araldite measured at two different temperature ramps

Same data presented in different ways



ARALDITE, Rheometry measurements

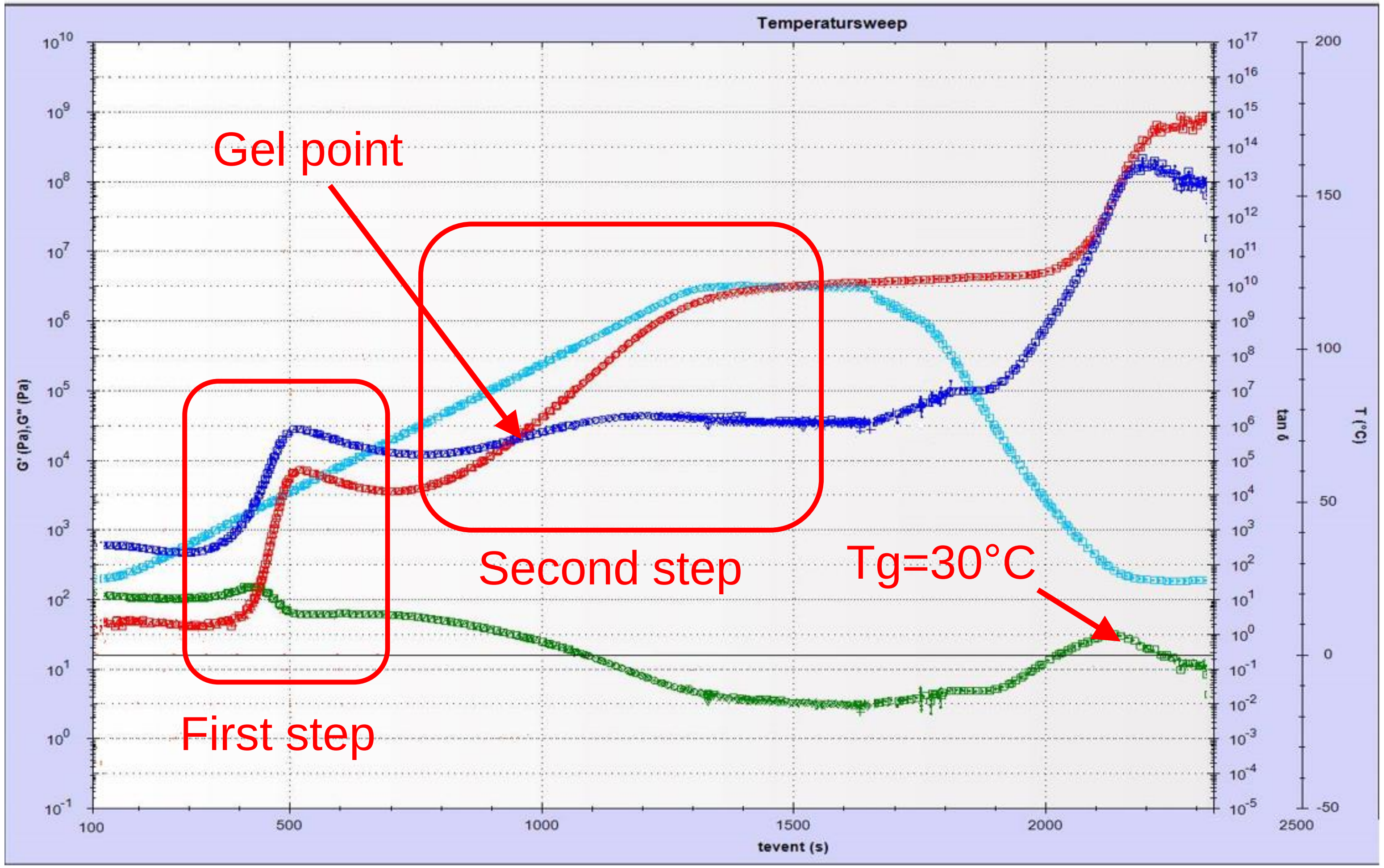
Temperature program consists of

1. Heating
2. Isotherm
3. Cooling

Measured data:

1. shear stress (*)
2. shear strain (*)
3. shear modulus (elastic component) G’
4. shear modulus (viscose component) G”
5. shear modulus (complex component (*)
6. shear viscosity (complex component) (*)
7. tan(Delta)

(*) not shown on the graph



ARALDITE, DSC measurements

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1. DSC measurements contain 2 peaks

First peak is 49.7°C

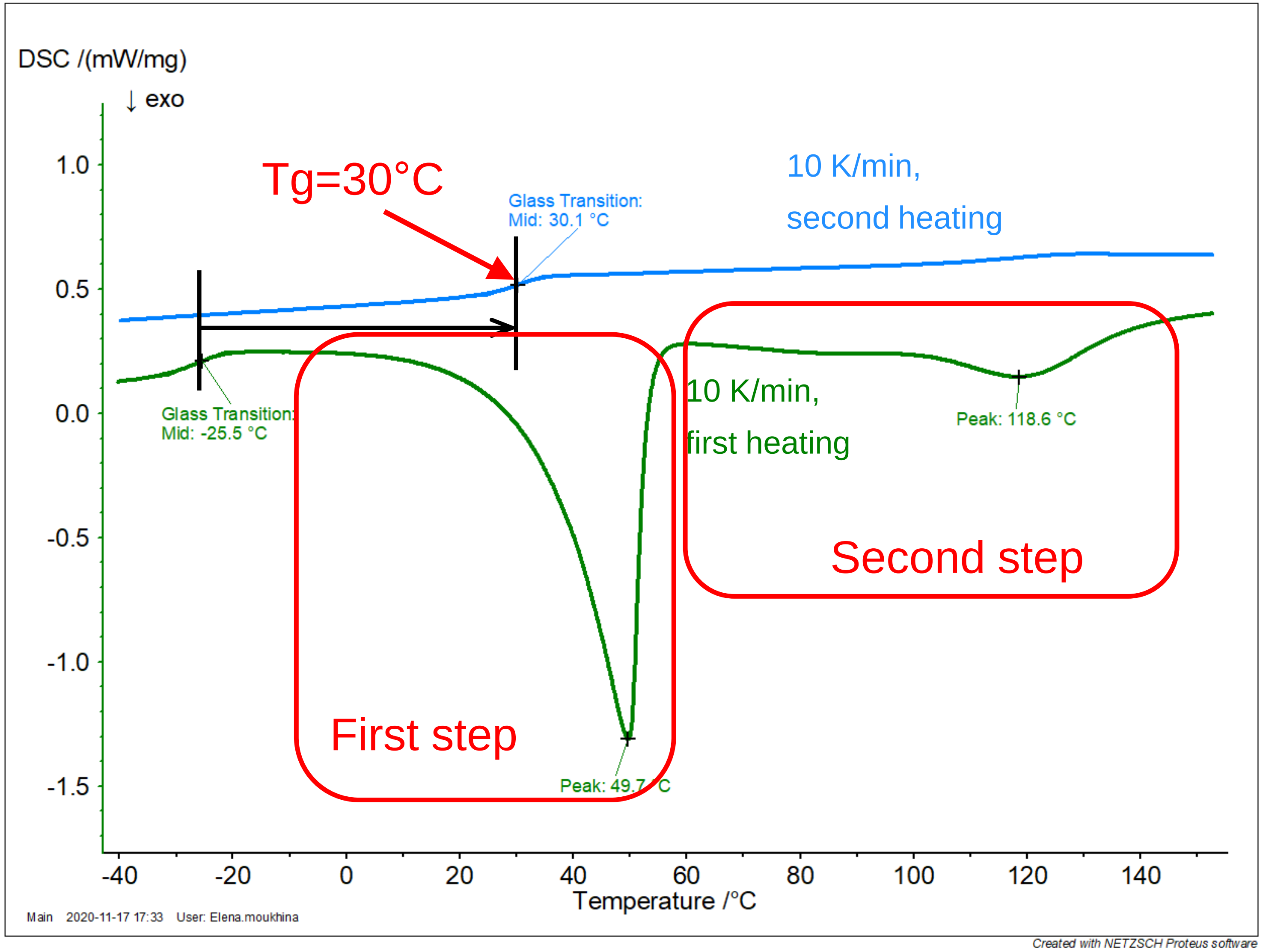
Second peak is 118.6°C

2. Glass transition

   for uncured material: -25.5°C

   for totally cured material 30.1°C

This is in agreement with Tg from Rheometric measurement



ARALDITE, Rheometry measurements for kinetic analysis

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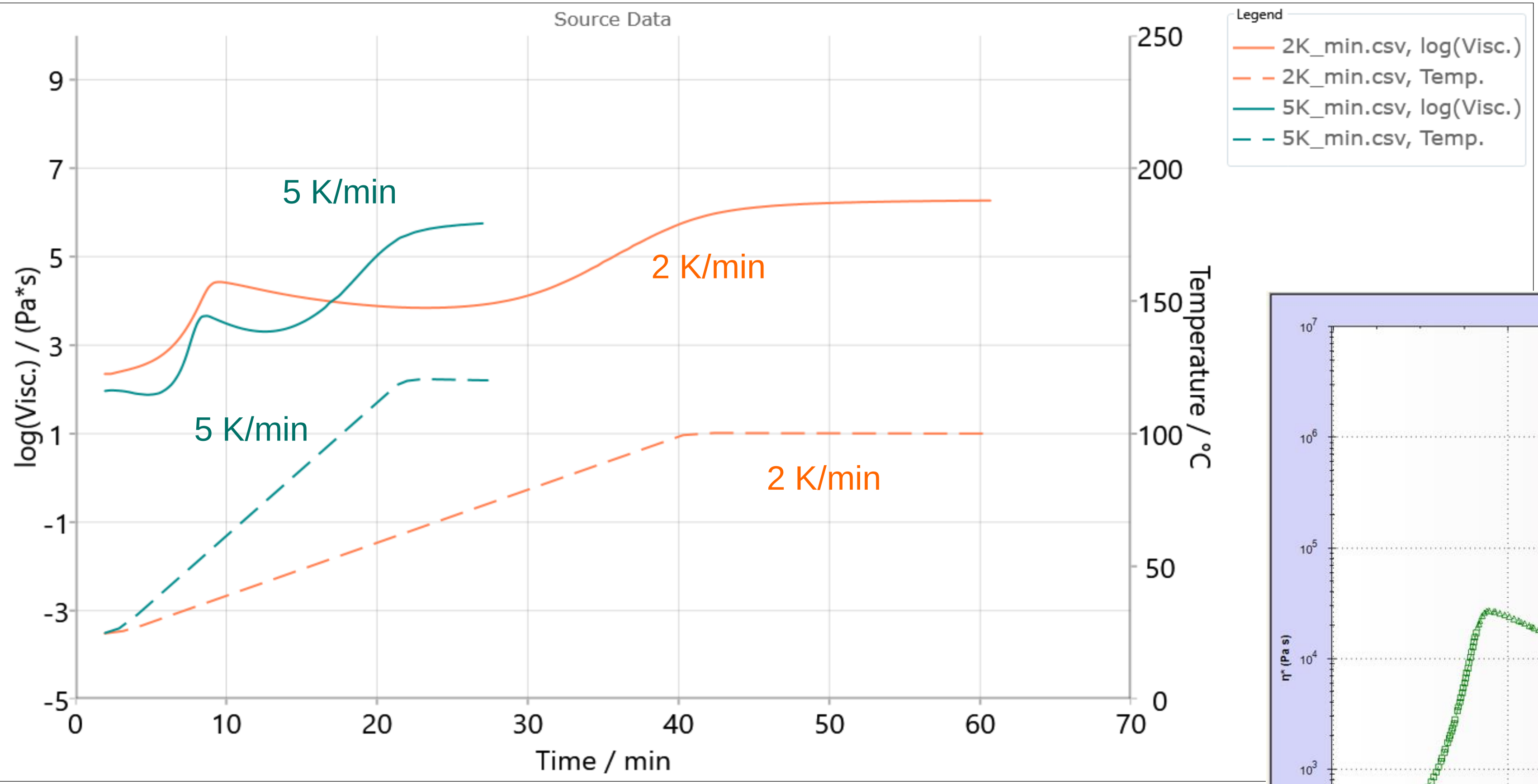
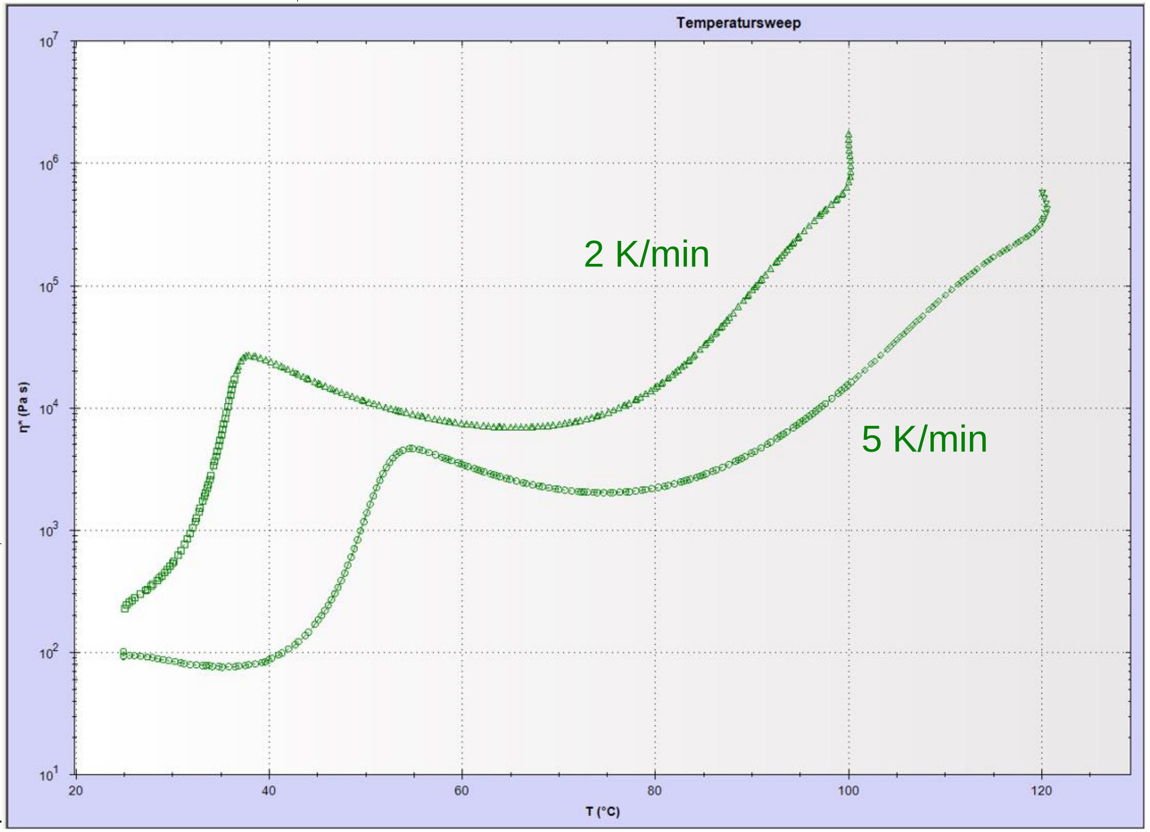
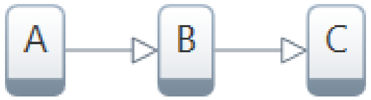




ARALDITE, Rheometry measurements and kinetic model



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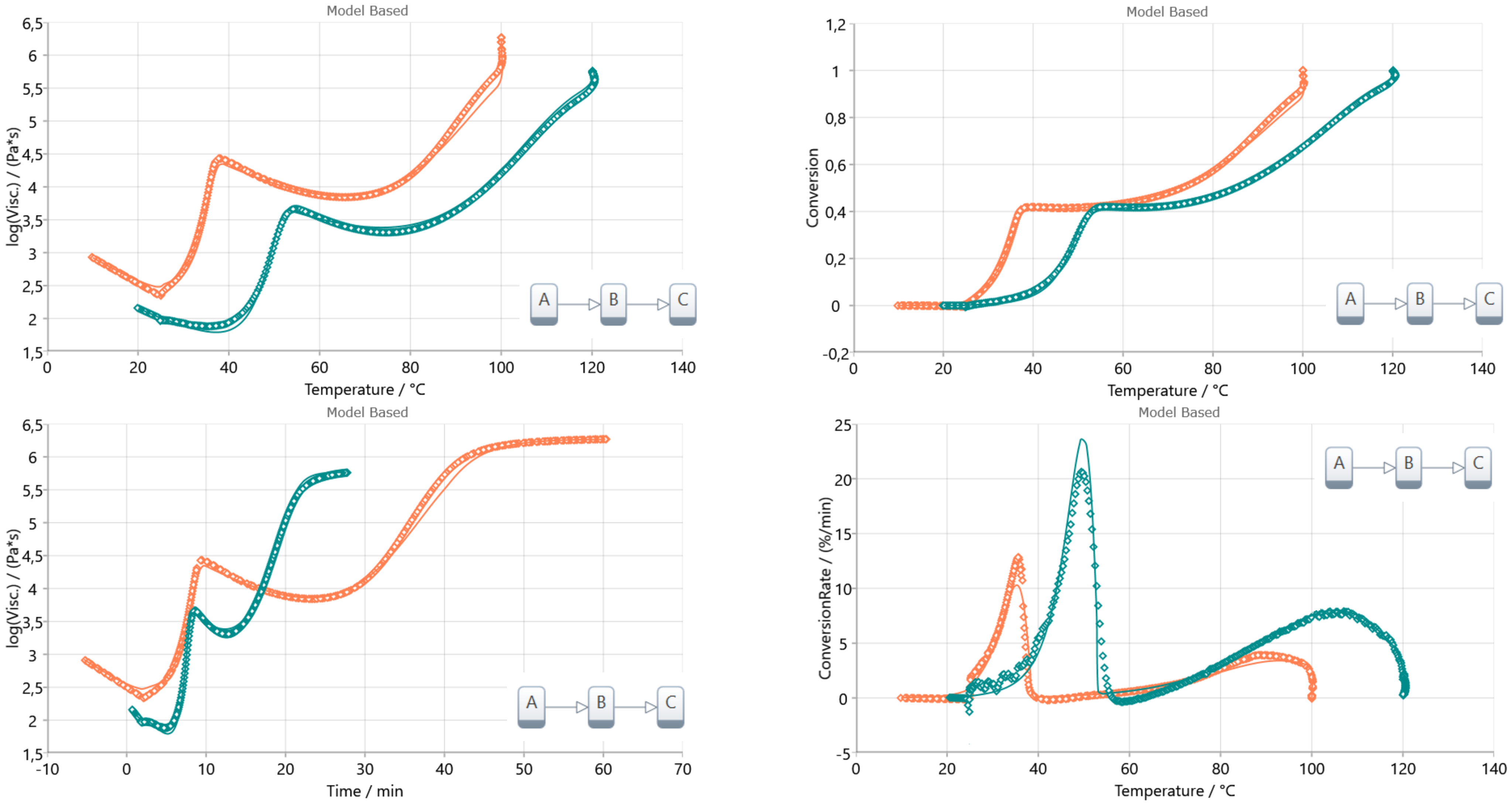

Two-step kinetic model can describe raw measurements, conversion and conversion rate. Fit quality R^2=0.999

Prediction of conversion and viscosity for complex temperature program

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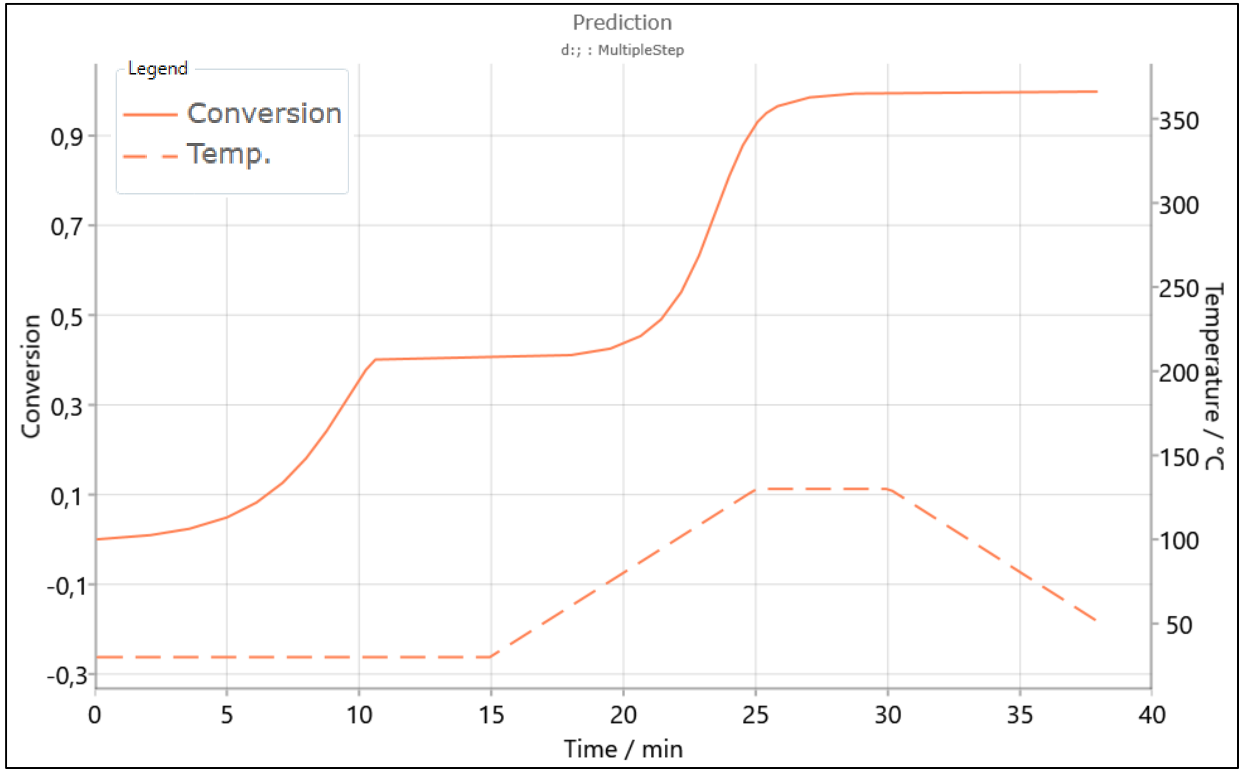

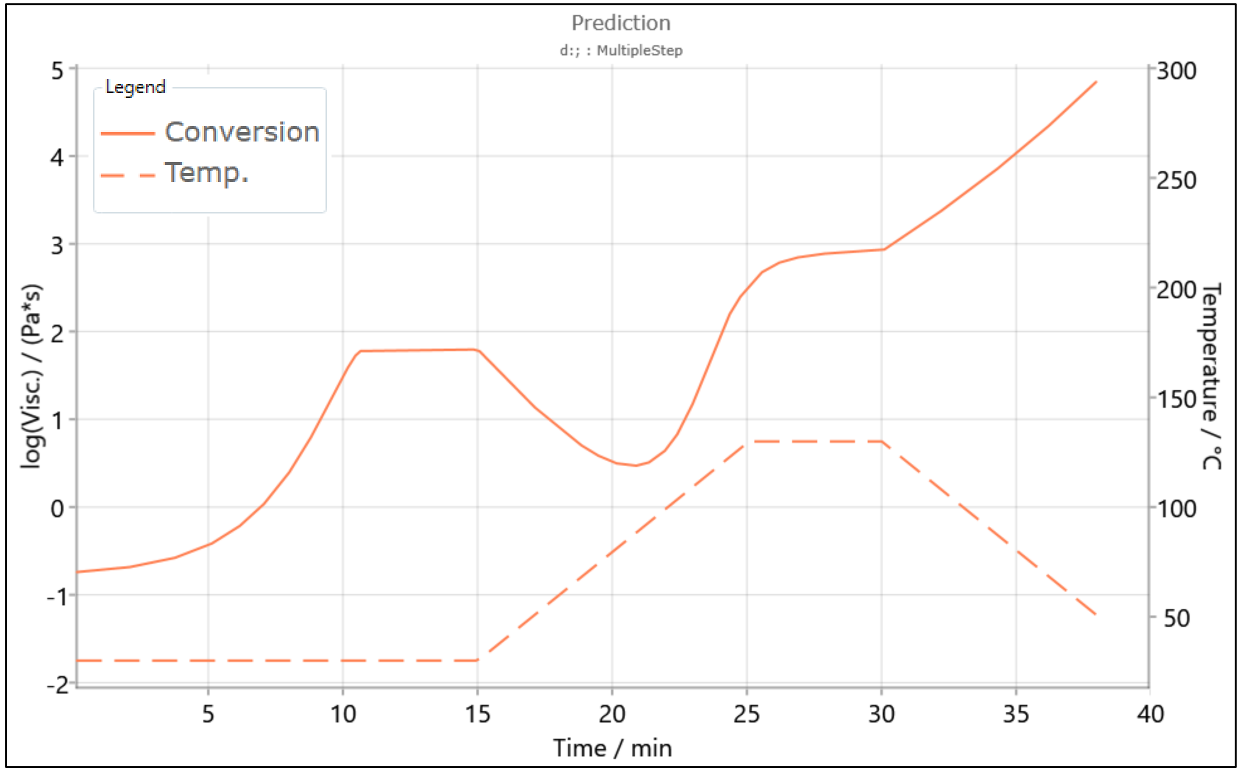

Start T/°C	End T/°C	H.R./K/min	Time/min
30,000	30,000	0,000	15,000
30,000	130,000	10,000	10,000
130,000	130,000	0,000	5,000
130,000	50,000	-10,000	8,000

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5. Kinetics Neo and Kinexus; Curing Partners

Concluding remarks

Concluding remarks

Material analysis and kinetic analysis to give the bigger picture

Disposable Plate Systems available for rheometers to enable to monitoring of curing systems

The rheology of curing systems is a demanding test, which is usually carried out with a single frequency oscillation

Curing / gelling reactions can be analyses over time, temperature and/or UV exposure

There are several key rheological features such as minimum viscosity, gel point and final cure that can be determined to assist with QC testing and development of these systems

Kinetic analysis takes rheology data and enables reaction profiles to be understood over many conditions

Kinetics Neo creates one mathematical kinetic model for several measurements

Kinetics Neo uses this model for simulation of viscosity and degree of cure for the new user-defined temperature profile

Kinetics Neo helps to optimization the temperatures and times of curing process.

You can rely on NETZSCH.

Thank you for your attention.
Any questions?

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https://www.netzsch-thermal-analysis.com/en/products-solutions/rheology/
https://kinetics.netzsch.com/

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