Analyzing & Testing

NETZSCH
Proven Excellence.

Kinetics for Polymers – Decomposition, Curing and Crystallization by Kinetics Neo

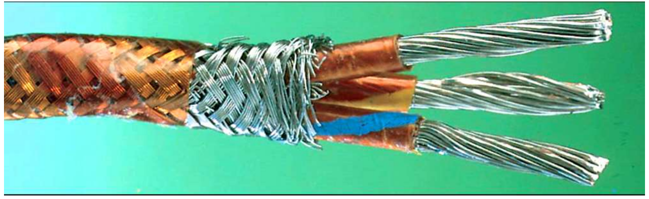
NETZSCH Webinar
Elena Moukhina
03/23/2022

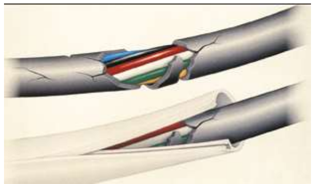
Agenda

1. Introduction into kinetic Analysis
   - 1.1 Problems to solve
   - 1.2 Idea of Kinetic solution
   - 1.3 Theoretical background
     - 1.3.1 Degree of conversion
     - 1.3.2 Arrhenius equation, activation energy, kinetic triplet
     - 1.3.3 Model-free and model-based approaches
2. Applications
   - 2.1 Decomposition
     - 2.1.1 Life time predictions, storage and transportation
     - 2.1.2 Debinding optimization in ceramics sintering and sinter metallurgy
   - 2.2 Curing & cross-linking
     - 2.2.1 Kinetics of DSC data, including UV curing, Autocatalysis, Kamal-Sourour model
     - 2.2.2 Diffusion control, vitrification and TTT diagram
     - 2.2.3 Kinetics of rheological data and predictions for dynamic viscosity
   - 2.3 Crystallization
     - 2.3.1 Isothermal crystallization, Avrami nucleation
     - 2.4.2 Non-isothermal crystallization, Nakamura equation, Sbirrazzuoli equation

1. Introduction into kinetic analysis

Problems solving by Polymer Kinetics: chemical or physical processes





Life time predictions
Recycling, pyrolysis
Thermal stability

Curing, cross-linking

Crystallization

Firing ceramics

Problem: Find reaction mechanism and predict material behavior at the conditions where it is impossible /very hard /expensive to measure

Idea: How to solve the problems

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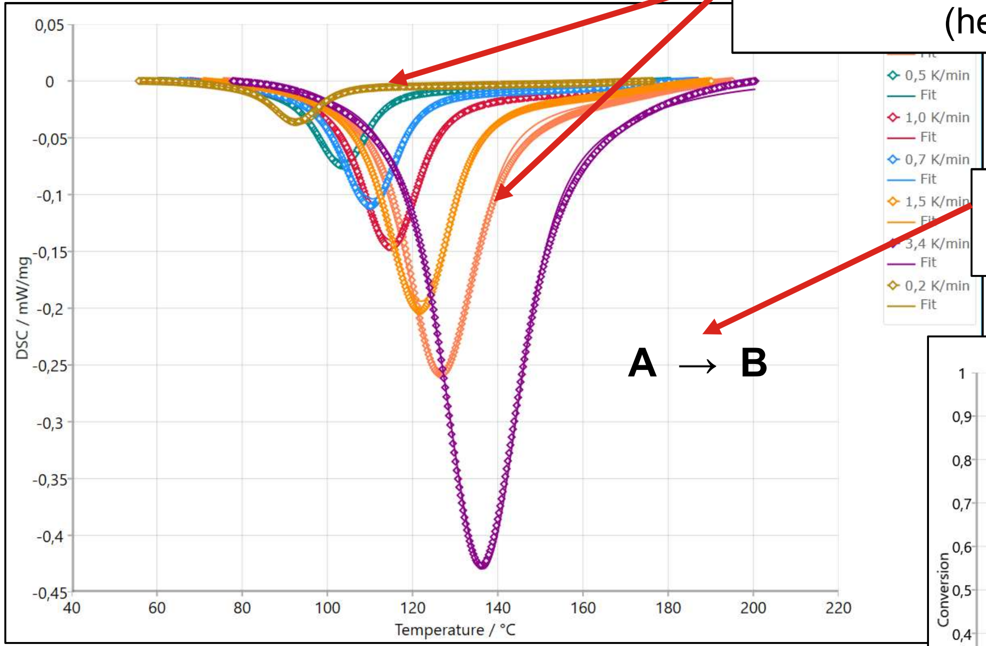
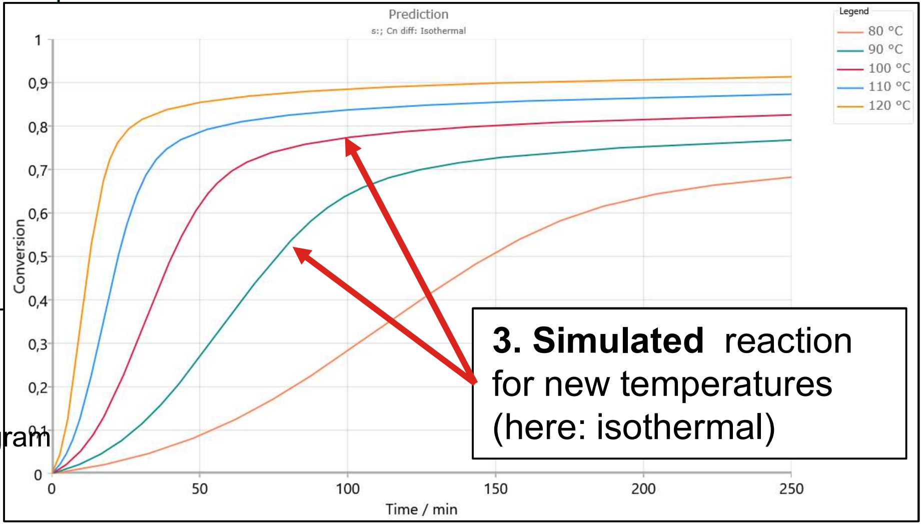
1. **Measured data** for the process
at different temperature conditions
(here: heating for epoxy resin)



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

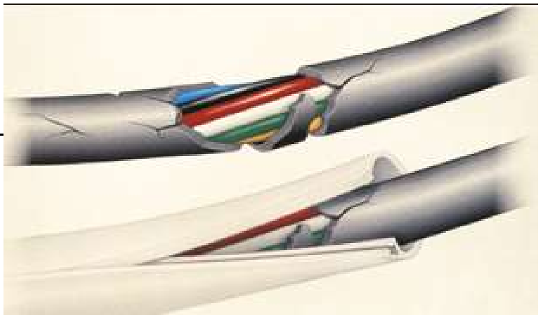
1.3 Theoretical background

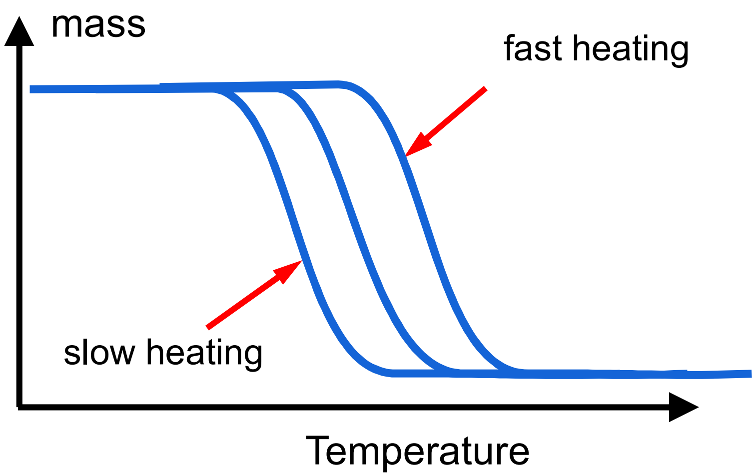
1.3.1 Degree of conversion

1.3.2 Arrhenius equation, activation energy, kinetic triplet

1.3.3 Model-free and model-based approaches

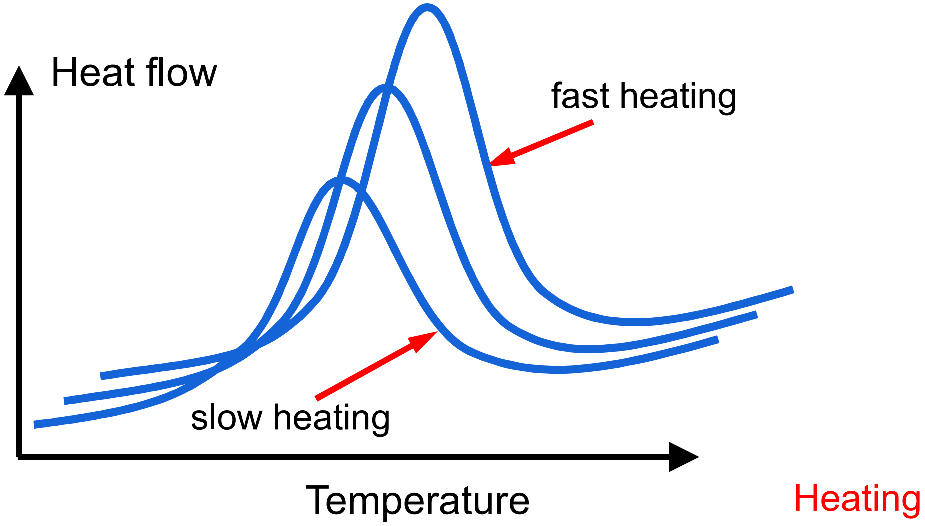
Measurements for kinetic analysis: Thermogravimetry





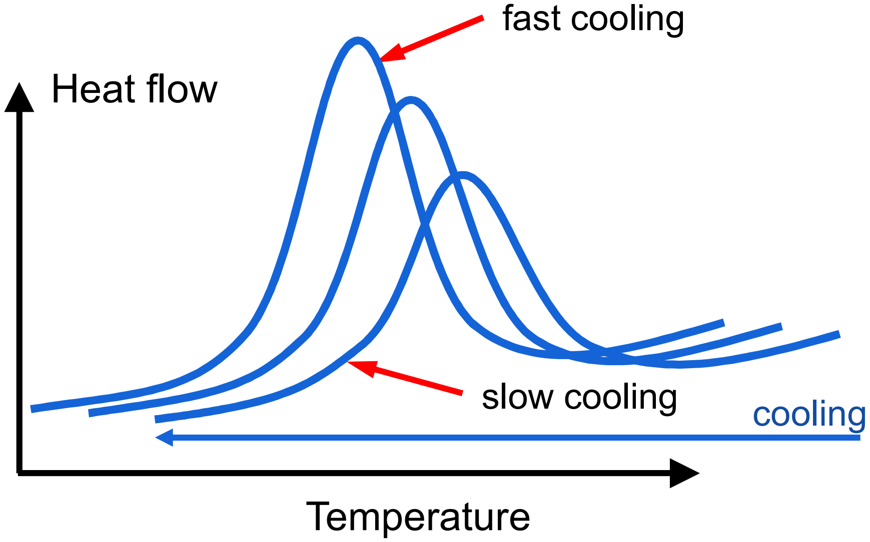
Thermogravimetry: mass change is measured during heating

Measurements for kinetic analysis:
Differential scanning calorimetry



Differential scanning calorimetry: heat flow is measured during temperature

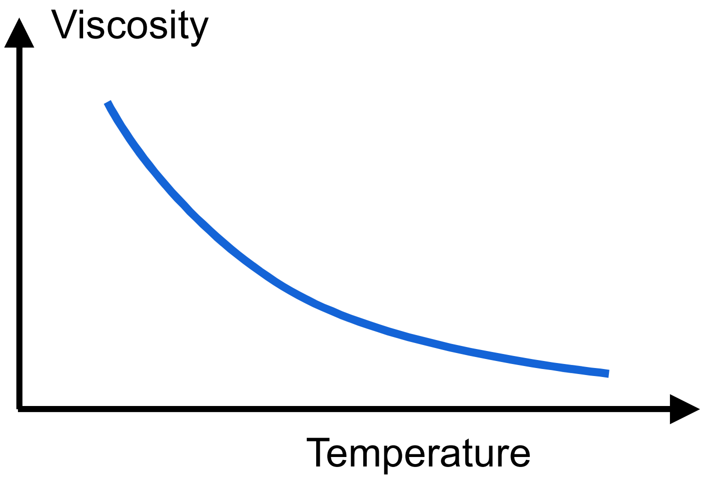
Measurements for kinetic analysis:
Differential scanning calorimetry



Differential scanning calorimetry: heat flow is measured during temperature change

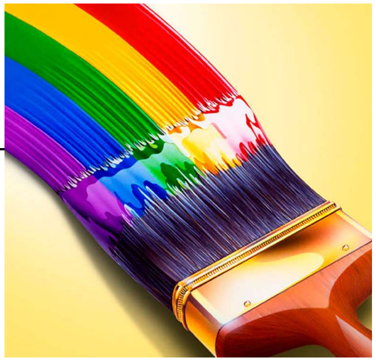
Rheometry: viscosity vs temperature for liquids

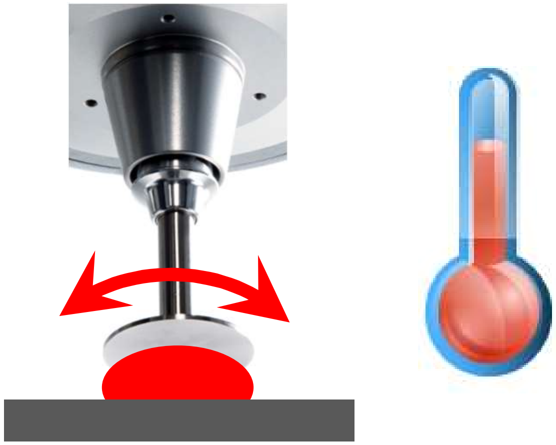
Rheometry: viscosity(t) is measured during heating

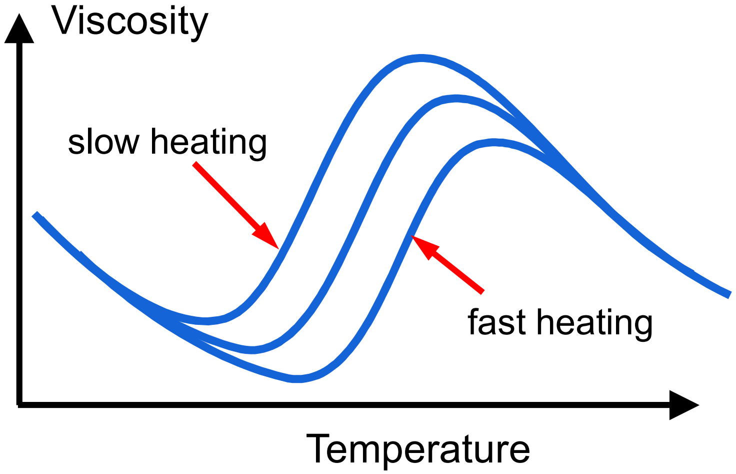


$$\eta = A \cdot \exp(\, B / T \,)$$

Measurements for kinetic analysis:
Rheometry



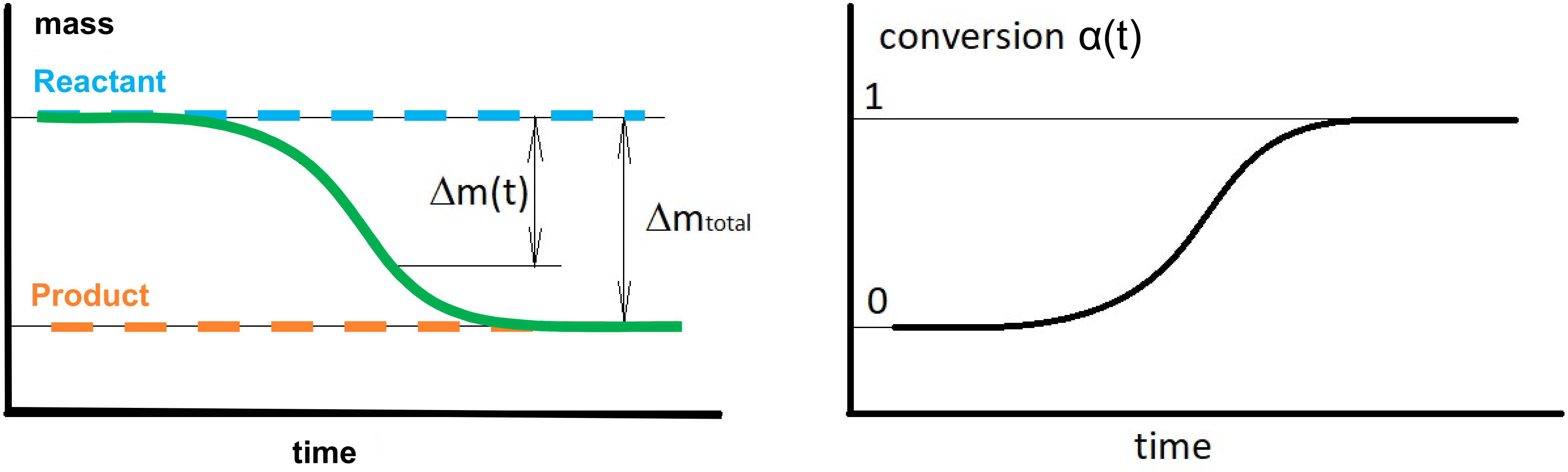




Rheometry: viscosity is measured during temperature

Degree of conversion α(t) for TGA data (extent of conversion, conversion, extent of reaction)

Commonly denoted by **α** and defined as the ratio of the partial to total change of a physical property.

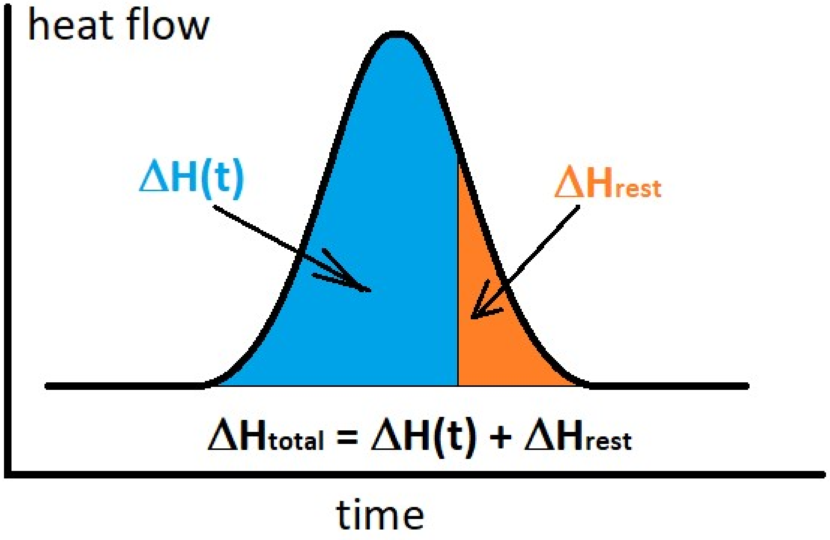


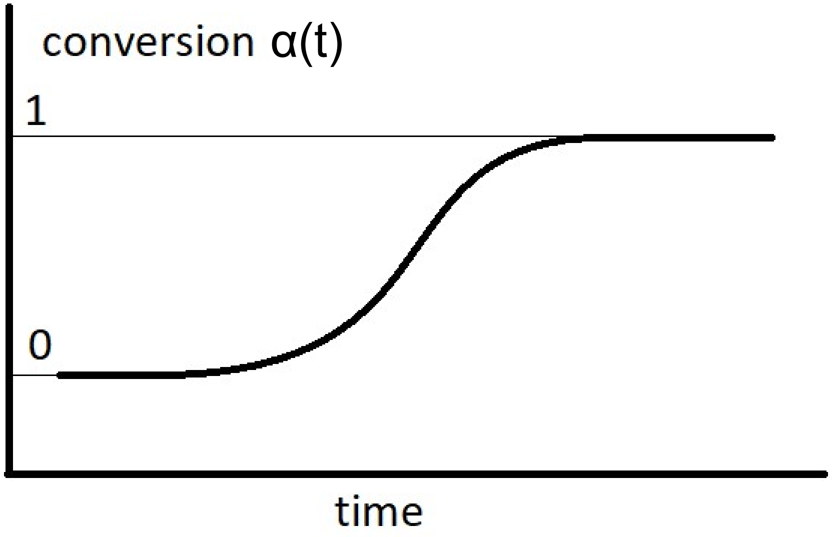
$$\alpha(t) = \frac{\Delta m(t)}{\Delta m_{total}}$$

α=0	before reaction start
α=1	after reaction end

TGA: Conversion is the **ratio of the partial mass loss** at given time point **to the total mass loss** at the final time point

Conversion α(t) for DSC data

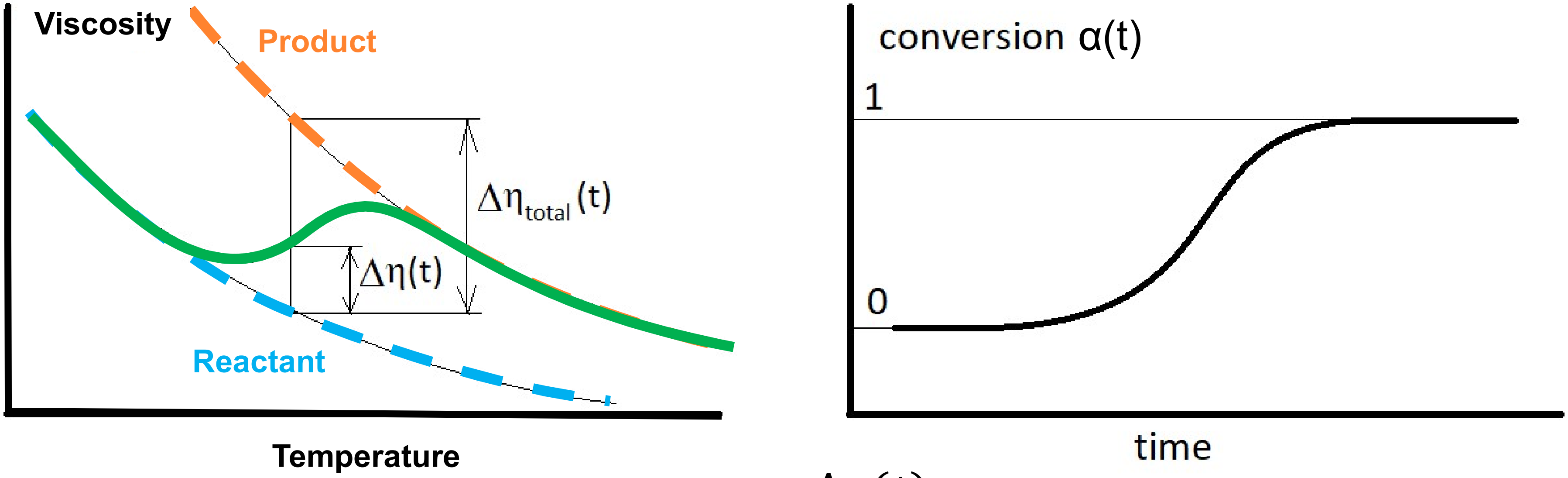




$$\alpha(t) = \frac{\Delta H(t)}{\Delta H_{total}}$$

DSC: Conversion is the ratio of the partial enthalpy change at given time point **to the total enthalpy change** at the final time point

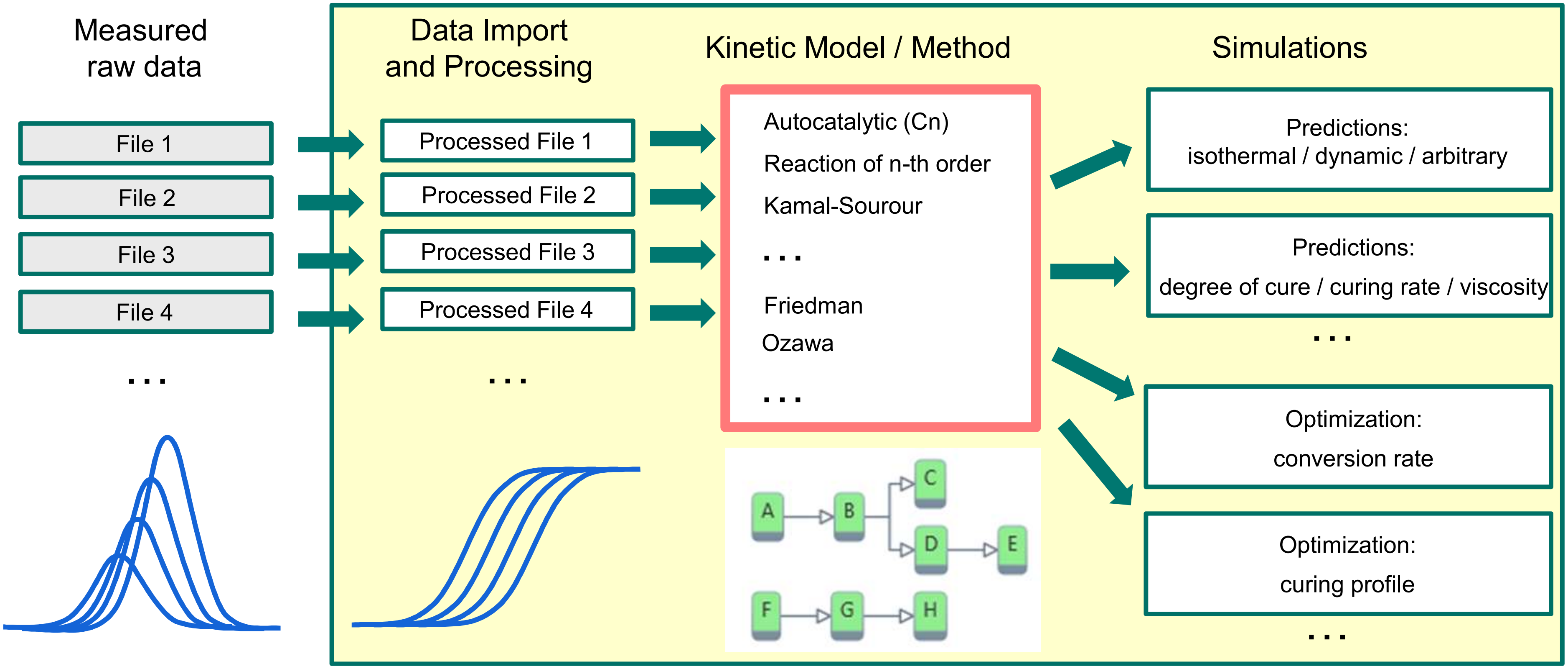
Viscosity measurement for curing
Conversion α(t) for viscosity data



$$\alpha(t) = \frac{\Delta\eta(t)}{\Delta\eta_{total}(t)}$$

Viscosity: Conversion is the ratio of the partial viscosity change at given time point **to the total viscosity change** between extrapolated baselines at the this point

Steps to solve Kinetic Tasks in Kinetics Neo



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 / Method

- 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
- . . .

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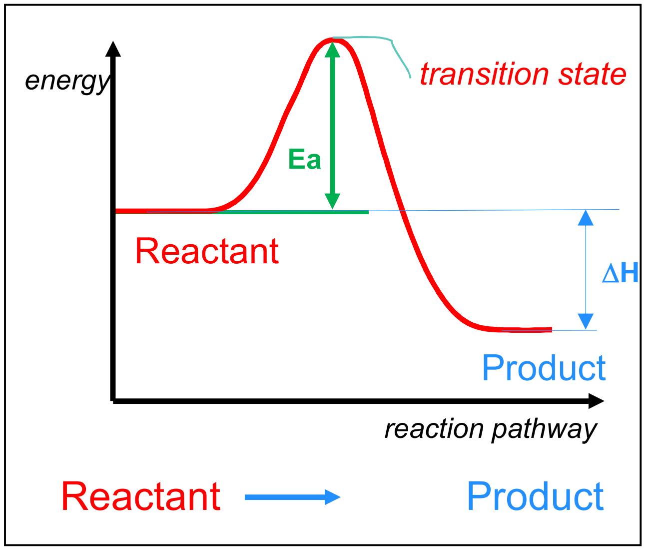
Arrhenius equation. Activation energy. Kinetic triplet



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 …)

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

Approaches: model free (isoconversonal) and model based

Model free

$A \rightarrow B$

α – degree of conversion

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

Unknown: Ea(α) and A(α)
A(α) can be found only with assumption of f(α)

Assumptions:

1. Only **one** kinetic equation
2. Ea and A **depend on α**
3. Reaction rate at the same conversion is only a function of temperature
4. Total effect (total mass loss or total peak area) must be the **same for all curves**
5. **Changes** of mechanism should be at the **same conversion** value

Model based

$A \rightarrow B \rightarrow C \rightarrow \ldots$

a – concentration of A
b – concentration of B
c – concentration of C

$$\frac{d(a \rightarrow b)}{dt} = A_1 \cdot f_1(a.b) \cdot exp\left(\frac{-E_{A1}}{RT}\right)$$

$$\frac{d(b \rightarrow c)}{dt} = A_2 \cdot f_2(b.c) \cdot exp\left(\frac{-E_{A2}}{RT}\right)$$

The number of unknown kinetic triplets equals the number of the steps

Assumptions:

1. Reaction consists of **several individual reaction steps** with own equations.
2. All kinetic parameters which are the **constant values**
3. The **total signal** is the **sum** of the signals of the single reaction steps having **own weight**

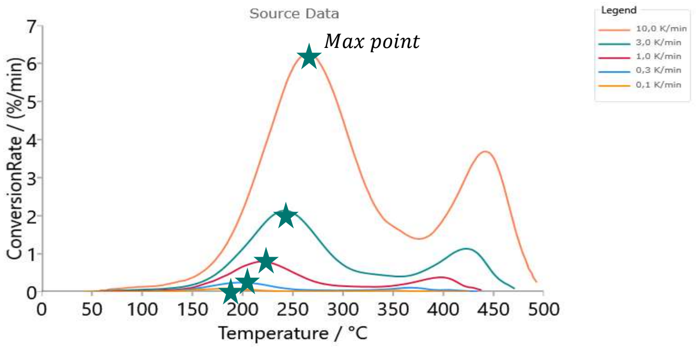
Model free methods

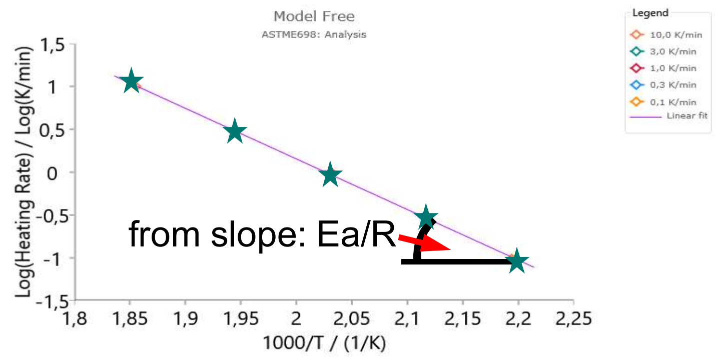
Created in last century before the modern possibilities of personal computers

One-point model free methods

- ASTM E698
- ASTM E2890
- ASTM E1641
- ASTM E2070

Result: **Value Ea**

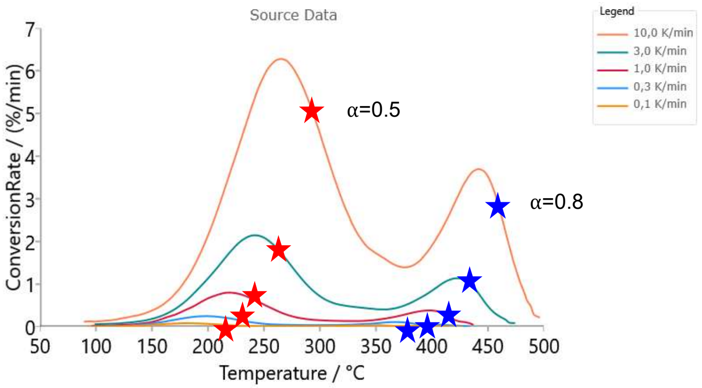


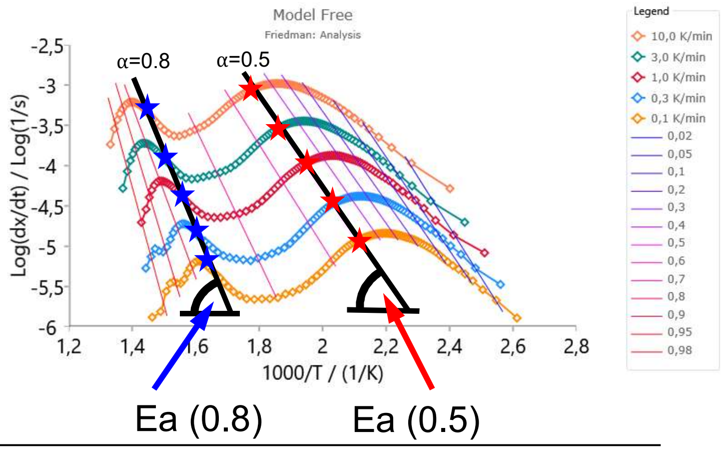


Multi-points model free methods

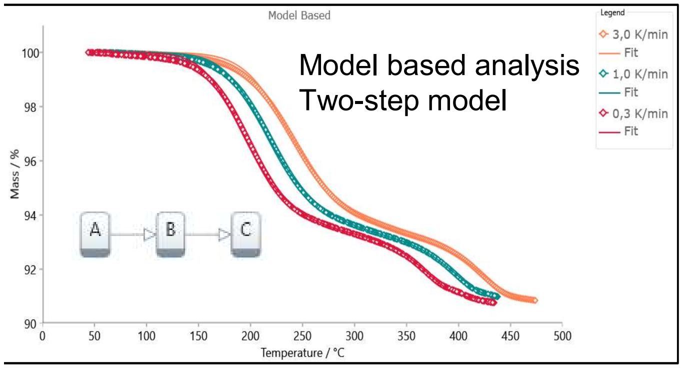
- Ozawa-Flynn-Wall (1965)
- Kissinger-Akahira-Sunose (1956)
- Friedman method (1966)
- Vyazovkin for heating (1996)
- Numerical optimization

Result: **Function Ea(α)**

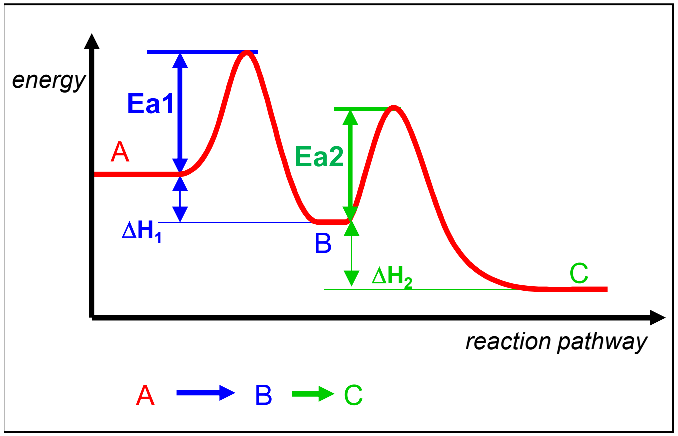




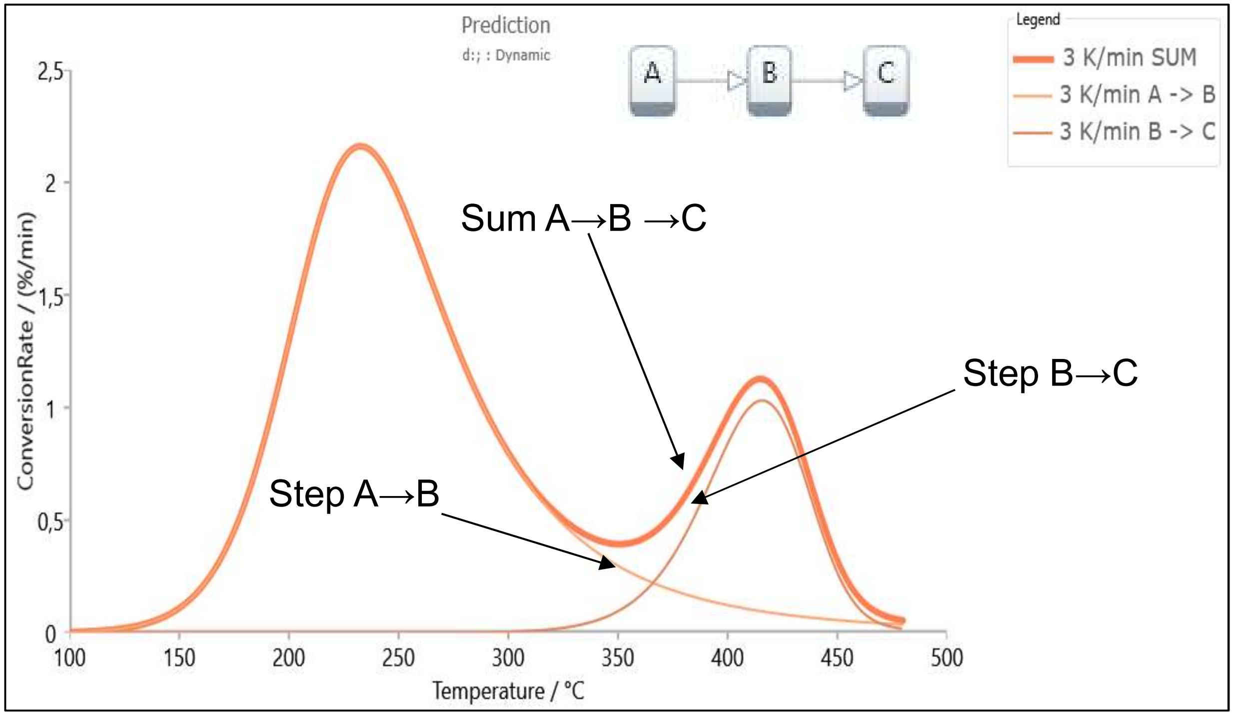
Model based: sum of individual reactions



Model based analysis
Two-step model



A → B → C

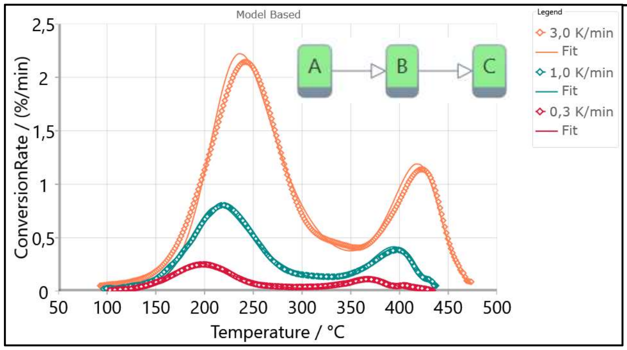


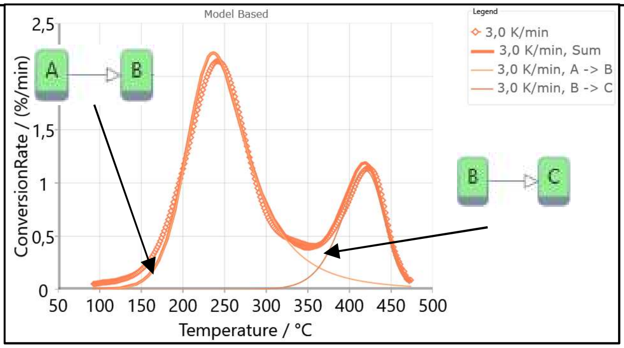
Sum A→B →C

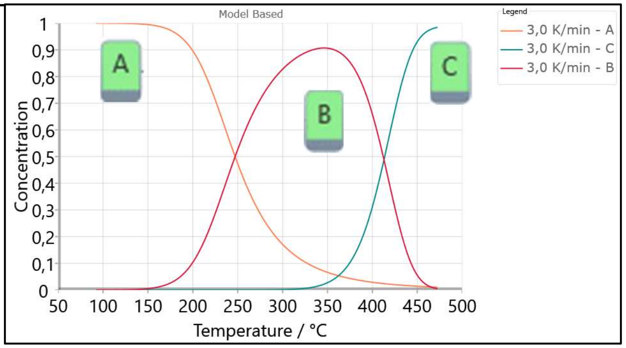
Step B→C

Step A→B

Model based method with reaction steps and concentrations



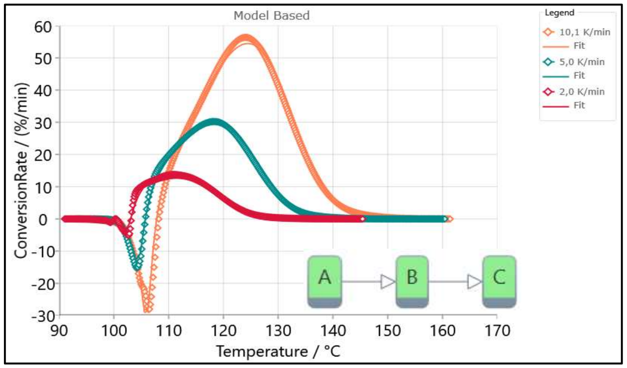


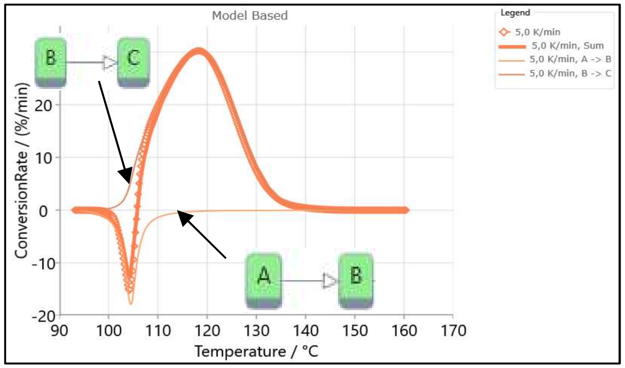


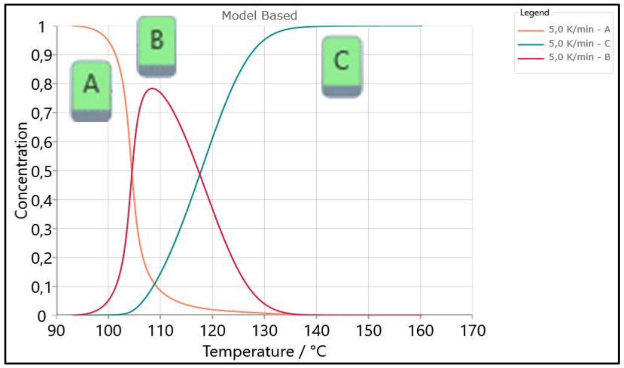
Kinetic model

Individual reaction steps

Concentration of reactants







Advantages and disadvantages

Model free

Advantages:

1. Very fast, one click
2. Easy analytical methods, mostly can be done in Excel

Disadvantages:

1. Does not work for **mixtures** (independent parallel steps)
2. Does not work for **competitive steps**
3. Does not work for **curing with Kamal Sourour** reaction
4. Does not work for **curing with diffusion control**
5. Does not work for **crystallization**
6. Does not work for **the steps of different directions**
7. Does not work for **highly overlapping steps**
8. Does not work if **reaction mechanism changes with heating rate**
9. Has **no** any information about **intermediate steps** and reactants

Model based

Advantages:

1. Works for **mixtures** (independent parallel steps)
2. Works for **competitive steps**
3. Works for **curing with Kamal Sourour** reaction
4. Works for **curing with diffusion control**
5. Works for **crystallization**
6. Works for **the steps of different directions**
7. Works for **highly overlapping steps**
8. Works if **reaction mechanism changes with heating rate**
9. Has information about **intermediate steps** and reactants

Disadvantages:

1. Requires elementary chemical knowledge about the process
2. Number of steps usually should not exceed the number of visible peaks

It is necessary to use ICTAC kinetic recommendations

https://doi.org/10.1016/j.tca.2020.178597

2. Applications

2.1 Decomposition
2.2 Curing and cross-linking
2.3 Crystallization

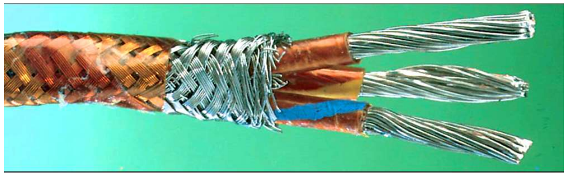
2.1 Decomposition

2.1.1 Life time predictions, storage and transportation
2.1.2 Debinding optimization in sintering processes

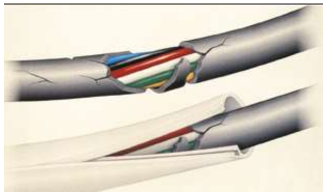
Thermal degradation, life time predictions

How long hold the paint until degradation?

We can not have the measurement
during of several years



How long the cable is flexible in air?



Pipeline coating has different lifetime at different temperatures
How long does is work in different climate?

Photos
https://www.heraldnet.com/business/alaska-pipeline-faces-midlife-crisis-as-flow-of-crude-slows/
https://www.paint.org/article/new-coating-could-prevent-gas-and-oil-pipeline-clogging/

Decomposition

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Arrhenius equation

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

Reaction of n-th order is typical for decomposition

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

Phase-boundary reactions are the partial case of n-th order reaction

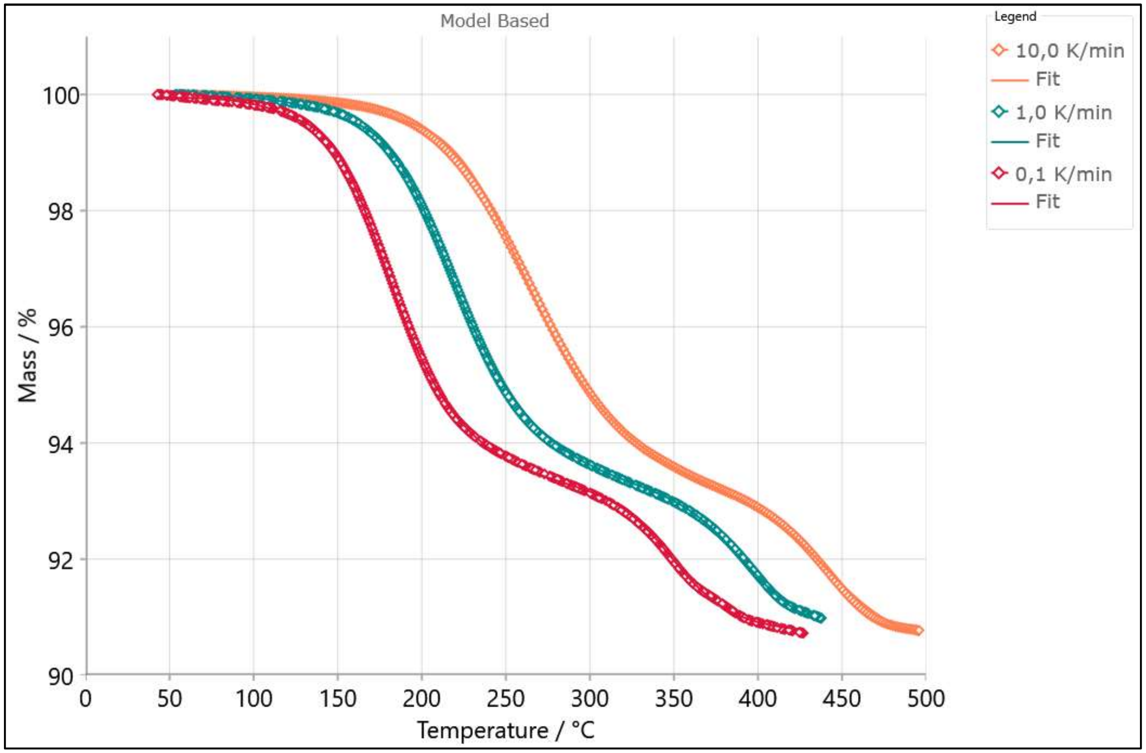
2-dimensional phase-boundary reaction R2: n=1/2

3-Dimensional phase boundary reaction R3: n=2/3

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

Laboratory Measurements for defined temperature program

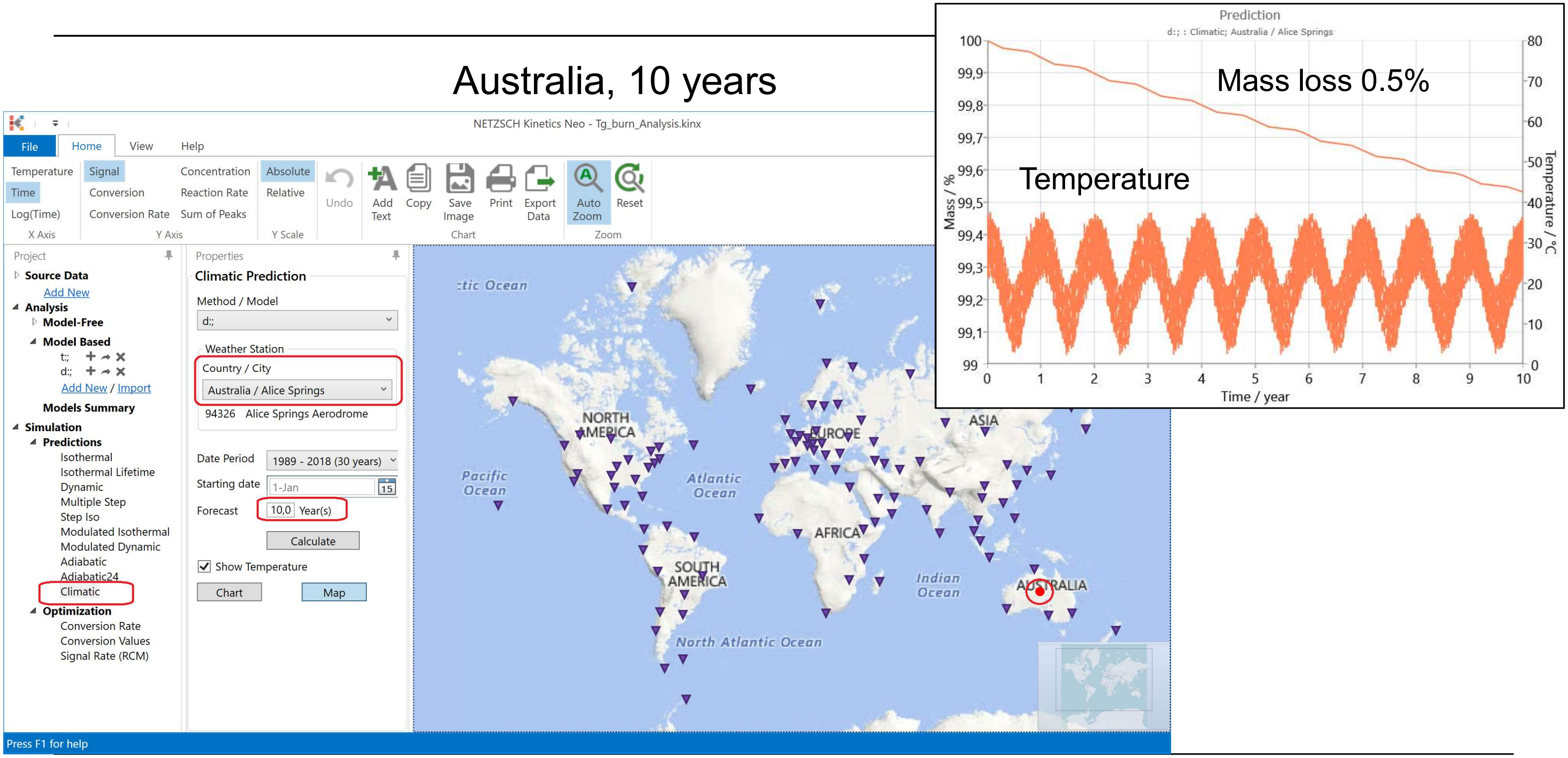
TG 209 Libra:
Measurement at given temperature program



Measurement duration is about 100 hours

Prediction under different climatic conditions:

Australia, 10 years



NETZSCH Kinetics Neo - Tg_burn_Analysis.kinx

Climatic Prediction

Method / Model: d:;

Weather Station

Country / City: Australia / Alice Springs

94326 Alice Springs Aerodrome

Date Period: 1989 - 2018 (30 years)

Starting date: 1-Jan

Forecast: 10,0 Year(s)

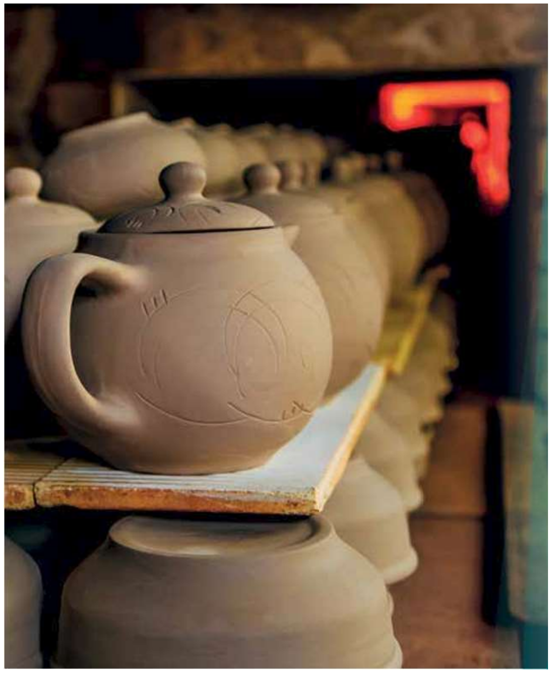
☑ Show Temperature

Press F1 for help

More than 100 weather stations with historical data over last 30 years (including temperature for day and night at each day of the year)

Production: sintering of ceramics

Quality of ceramics depends on the firing temperatures and time
How to improve the quality of product and reduce the production time?



Desired result at unknown production temperature

Photo https://precision-ceramics.com/products/custom-ceramic-parts-components-2/

Two processes during firing: debinding and sintering

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Below 700°C:
Debinding

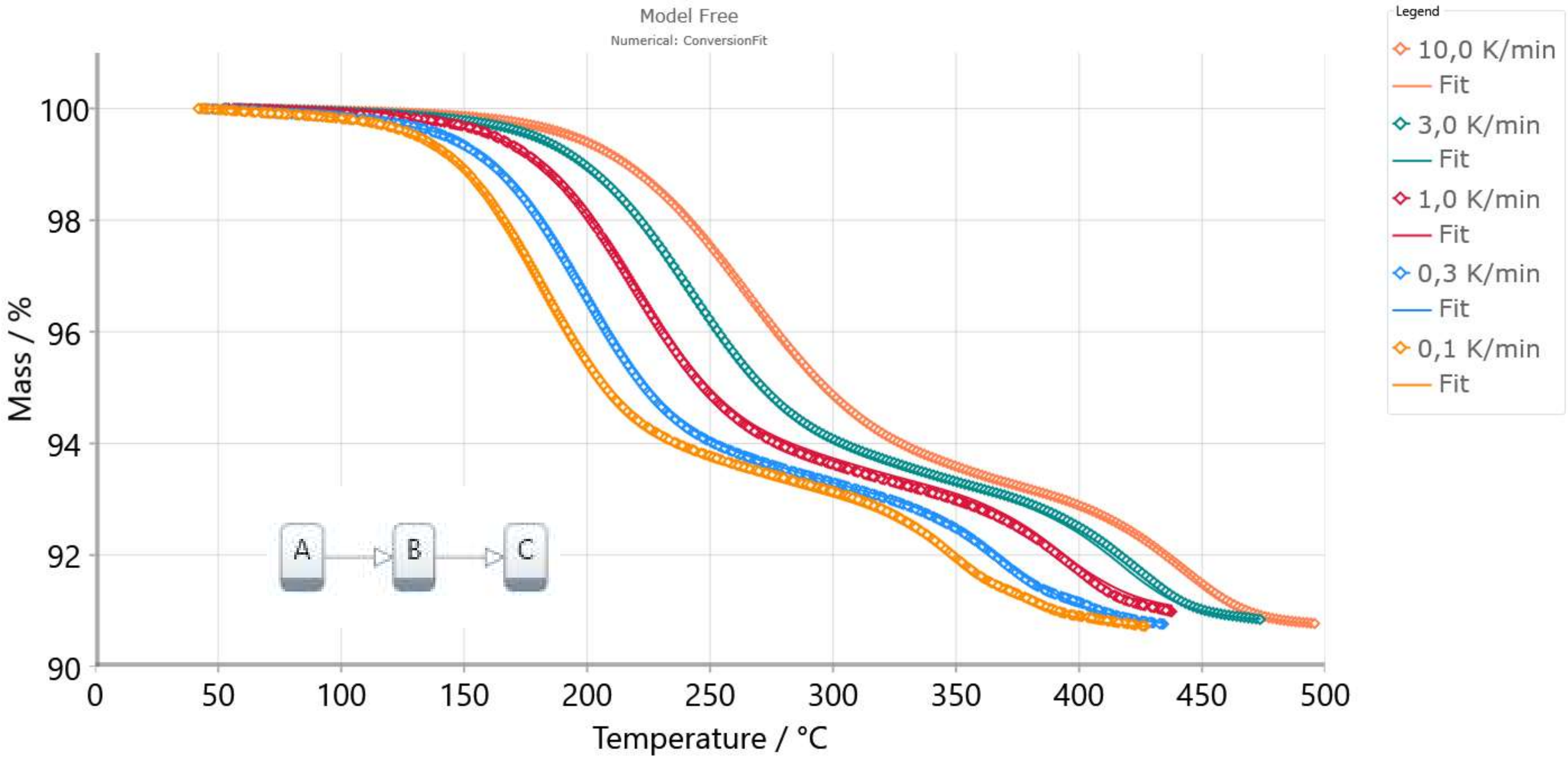
A Thermobalance gives you information about the binder burnout!

Above 700°C:

Densification

A Dilatometer gives you information about the sintering shrinkage and thermal expansion!

Debinding beow 700°C: Kinetic Analysis



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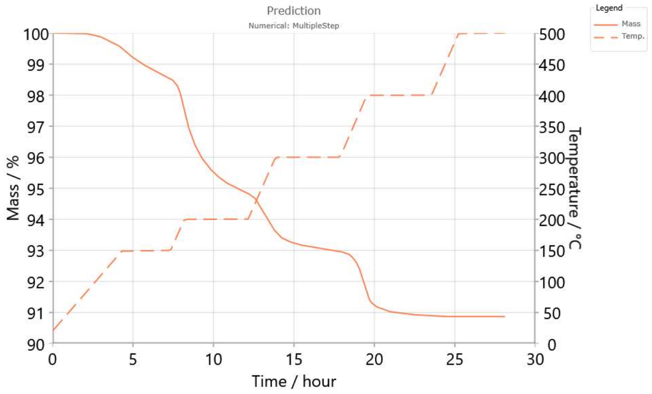
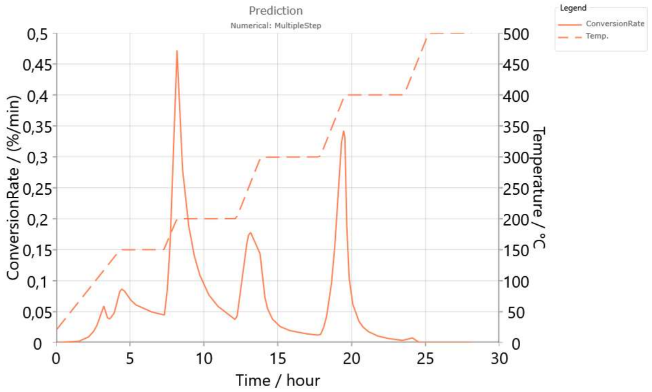
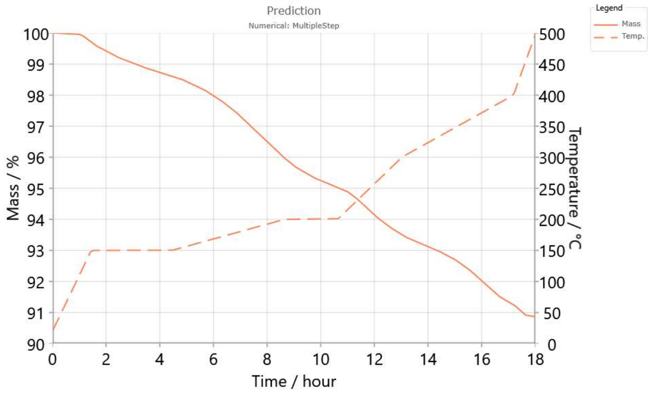
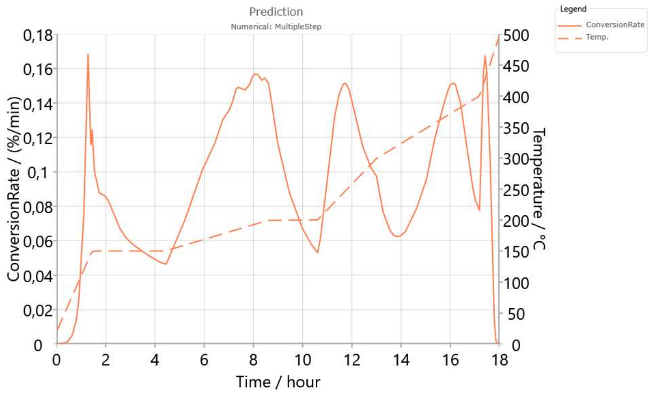
Optimization of temperature below 700°C based on TG





Non-optimized 29 hrs, max 0.5%/min





Optimized 18 hrs, max 0.16 %/min

New material

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HALFOAM ALUMINA ™

by

Morgan
Advanced Materials
HALDENWANGER

Production time was reduced more than by 50%

By applying of process optimization in kinetics

2.2 Curing and cross-linking

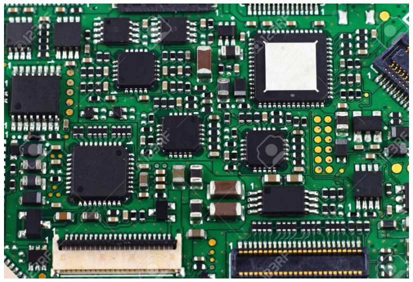
2.2.1 Kinetics of DSC data, UV curing, Autocatalysis, Kamal-Sourour model

Production process: Curing, cross-linking

adhesives, resins, paints, from microchips and automotive to wind power stations

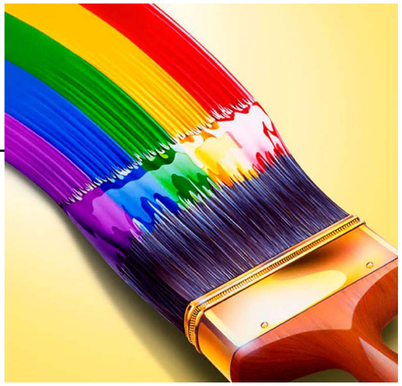
How to make the best painting in shortest time?
What happens during curing process?
How to reduce costs during production?

What is the **final state** of the epoxy after given **time** at given **temperature**?



Photos
http://www.businesskorea.co.kr/news/articleView.html?idxno=14620
http://www.swada.co.uk/applications/solvent-borne-paints-and-coatings/

Kinetic Modelling for Curing

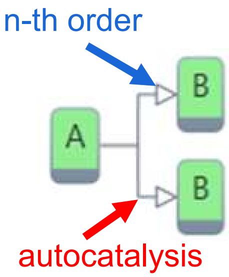


Chemical process is **generally** described by Arrhenius equation:

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

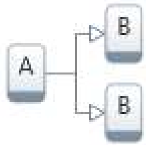
Curing can be described by the equation **Kamal-Sourour** for autocatalytic reaction:

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



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

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

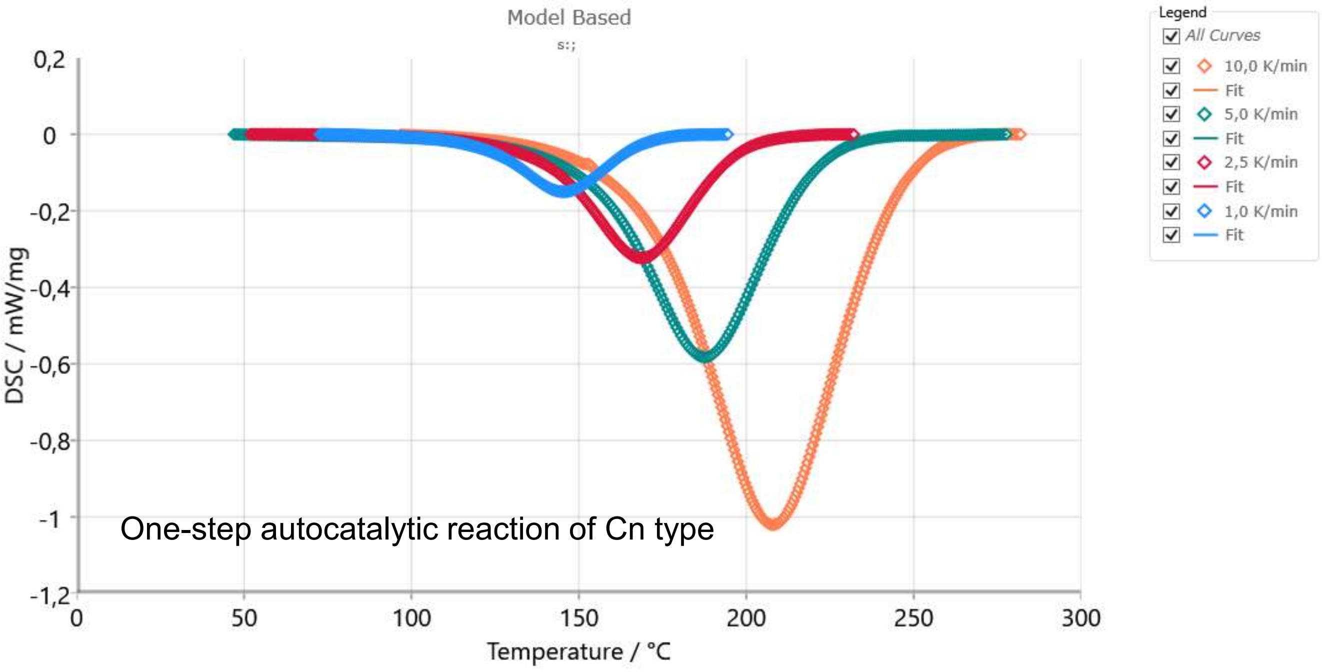


Bna – autocatalytical reacton of Prout-Tompkins

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

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

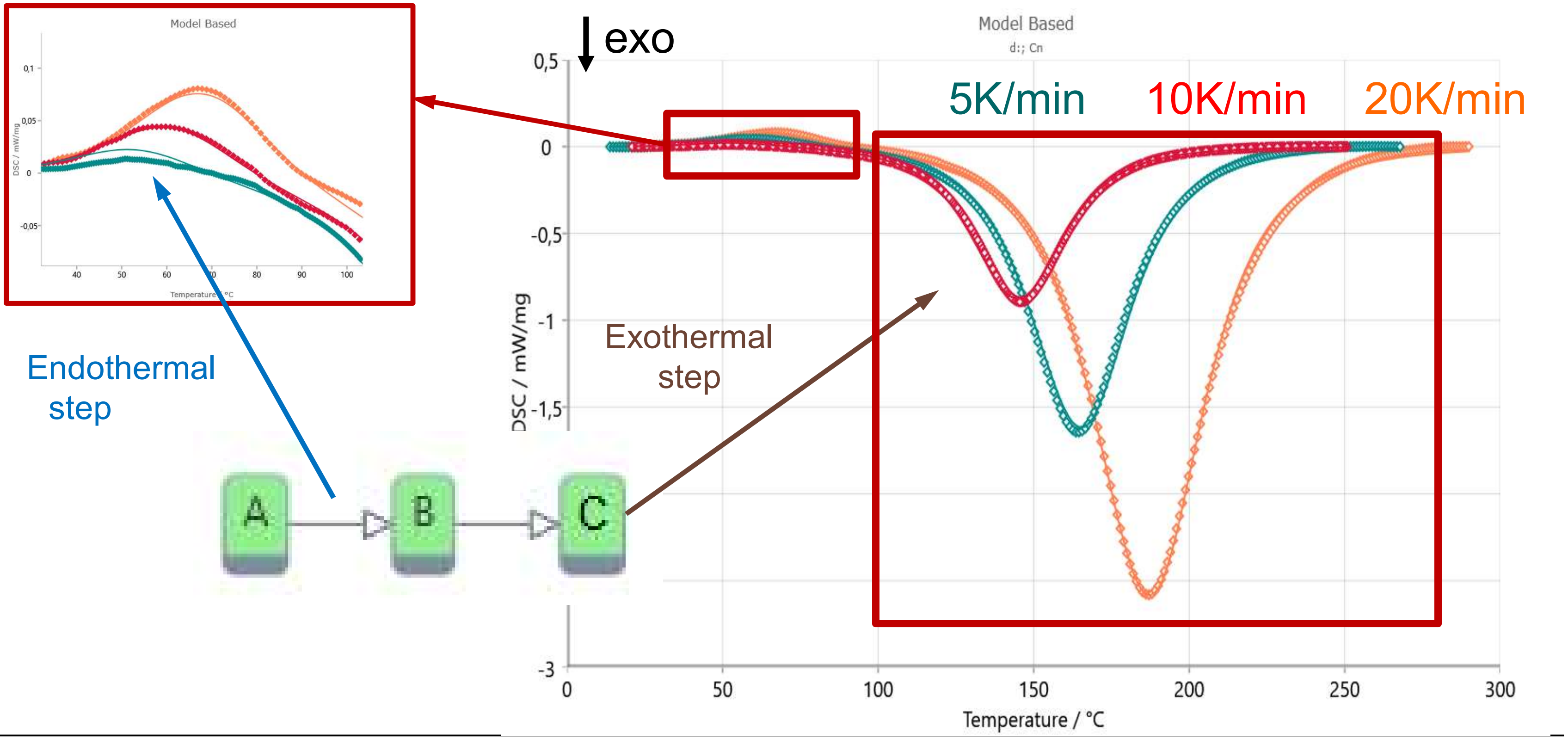
Autocatalytic model for mono-functional epoxy (phenyl glycidyl ether with aniline)



One-step autocatalytic reaction of Cn type

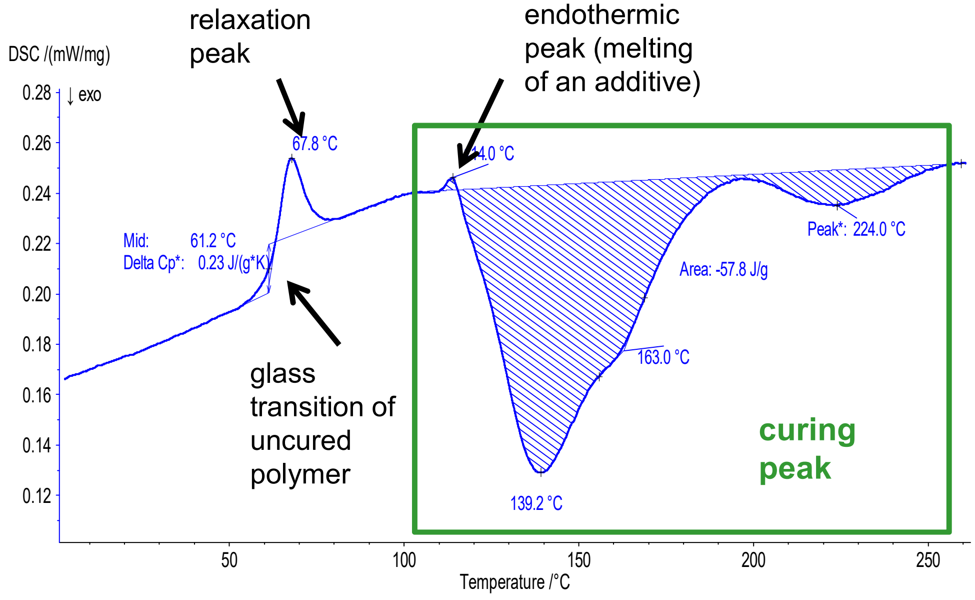
Hans-Jürgen Flammersheim, Johannes R.Opfermann, Macrmol.Mater.Eng.,2001, 286, 143-150

Epoxy curing reaction with different direction of reaction 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

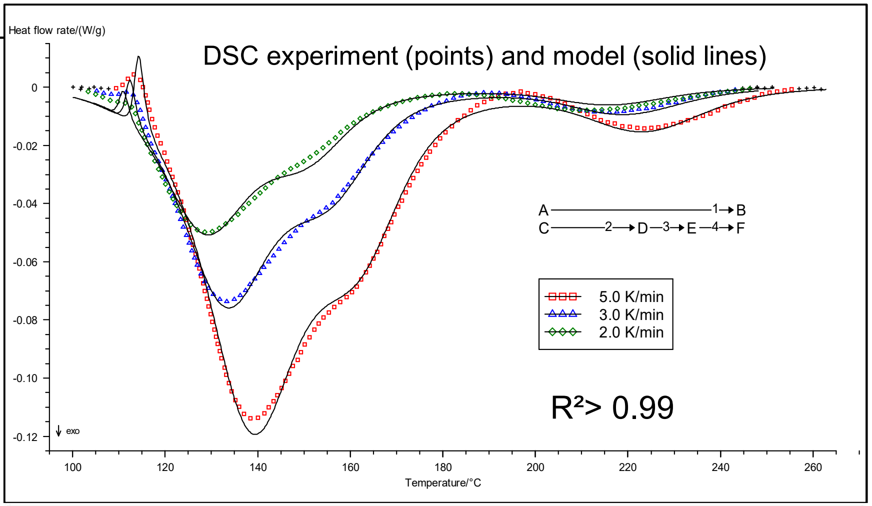


relaxation peak

endothermic peak (melting of an additive)

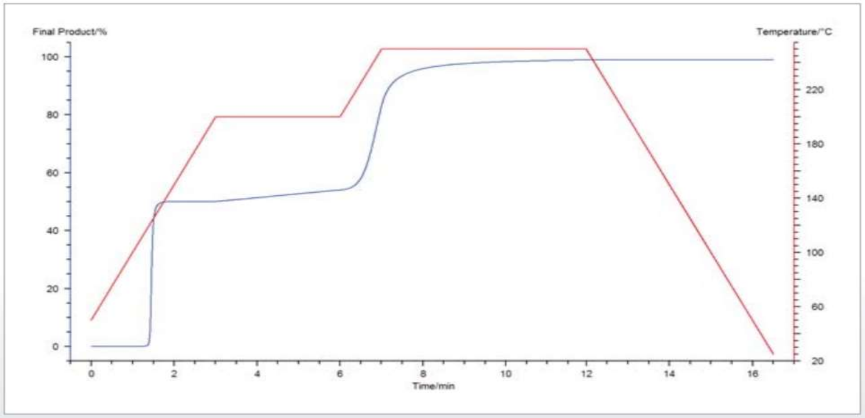
glass transition of uncured polymer

curing peak



DSC experiment (points) and model (solid lines)

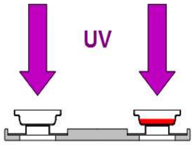
R²> 0.99



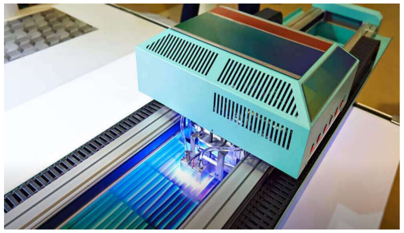
4 Prediction of degree of conversion for a user-defined temperature program. A degree of conversion of 98% is achieved during the second isothermal segment (250°C) after 9.5 minutes.

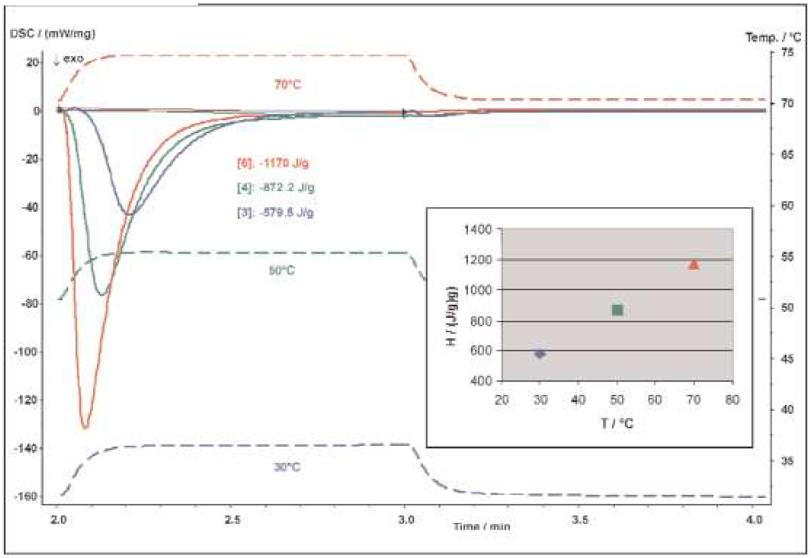
AN 056, Claire Straßer, Dr. Elena Moukhina and Dr. Stefan Schmölzer

UV curing: 1-Component Epoxy Resin Delo-Katiobond KB 554

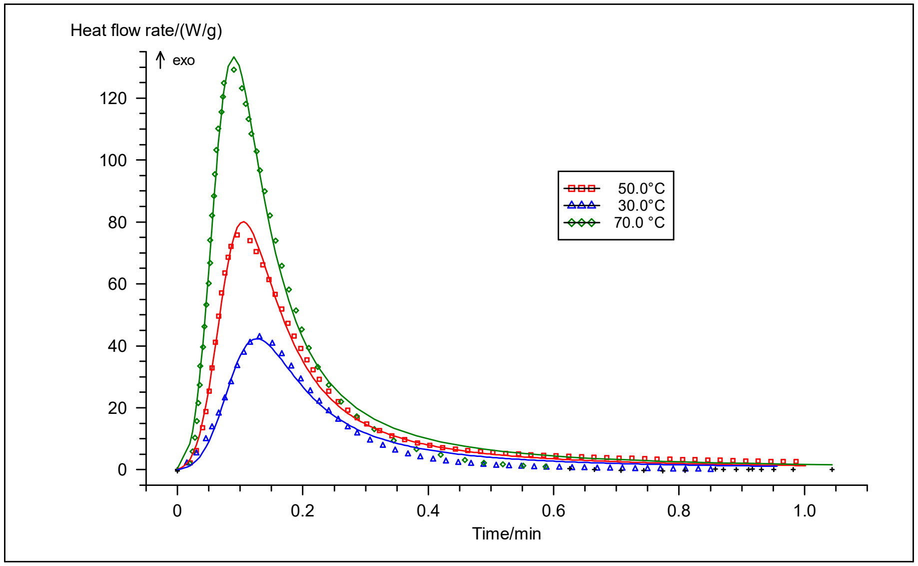


- Cationic UV-curing mechanism,
- Free radical UV-curing system





Temperature range:	30°C/50°C/70°C	**Crucible:**	open Al
Heating/cooling rates:	0 K/min	**UV device:**	Delolux 04
Atmosphere:	Nitrogen 50 ml/min	**Radiation time:**	60 s
Sample mass:	approx. 8.5 mg		



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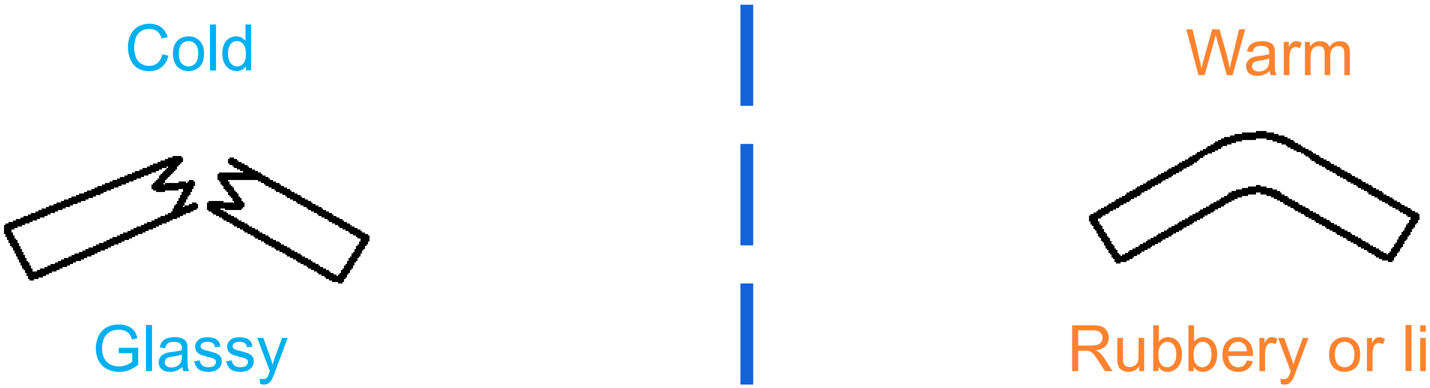
1. E. Füglein, AS-106-2006, Cationic UV-curing mechanism
2. 39th NATAS conference, August, 7-10, 2011, Des Moines, Elena Moukhina , Stefan Schmoelzer, free-radical System

2.2 Curing and cross-linking

2.2.2 Diffusion control, vitrification and TTT diagram

Amorphous material (Polymer)



Reaction finished

Cold

Warm

Glassy state

Rubbery or liquid state

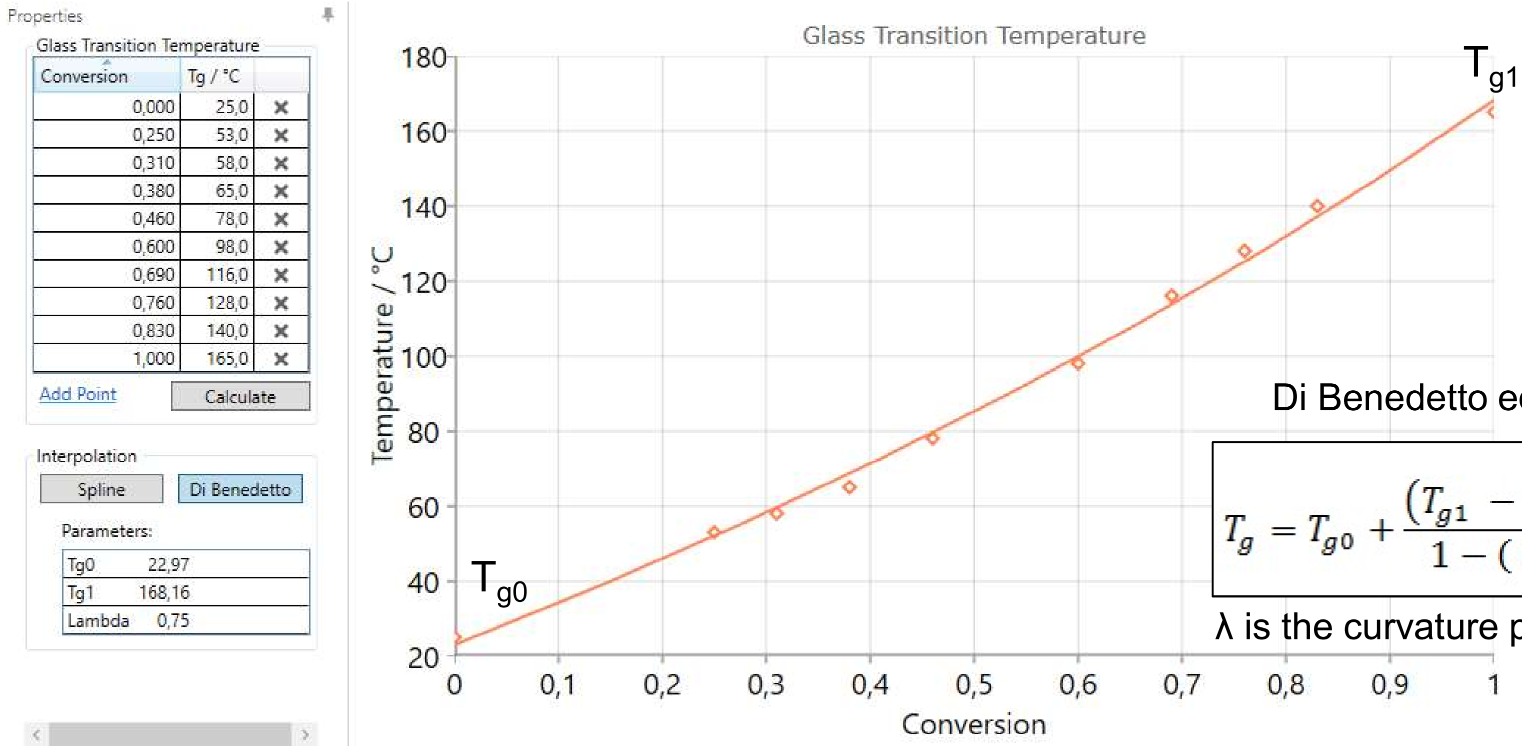
Tg

Slow curing
T<Tg

Fast curing
T>Tg

Glass transition

Glass transition temperature vs Conversion



Conversion	Tg / °C
0,000	25,0
0,250	53,0
0,310	58,0
0,380	65,0
0,460	78,0
0,600	98,0
0,690	116,0
0,760	128,0
0,830	140,0
1,000	165,0

Tg0	22,97
Tg1	168,16
Lambda	0,75

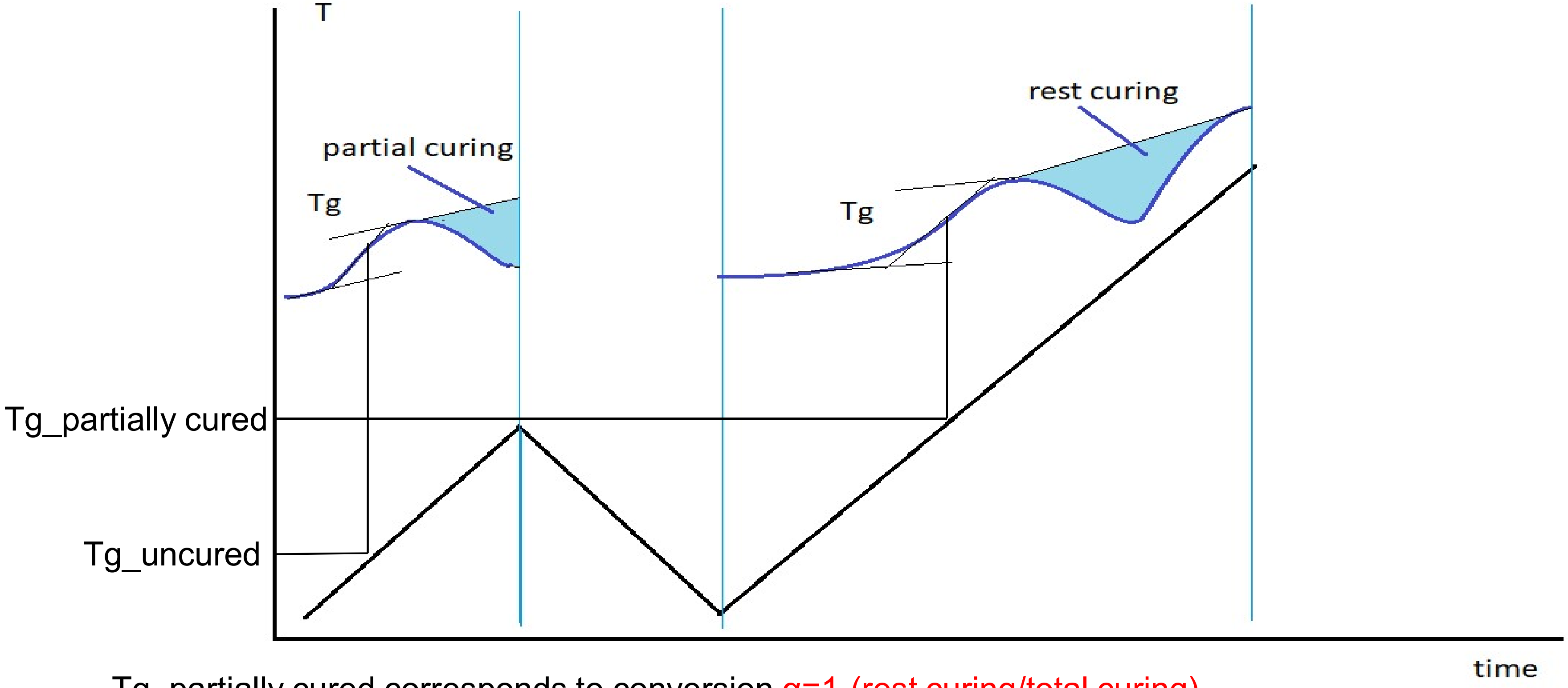
Di Benedetto equation:

$$T_g = T_{g0} + \frac{\left(T_{g1} - T_{g0}\right) \cdot \lambda \cdot \alpha}{1 - (1 - \lambda) \cdot \alpha}$$

λ is the curvature parameter

epoxid/5 % Zn(OCN)2(MeImid)2

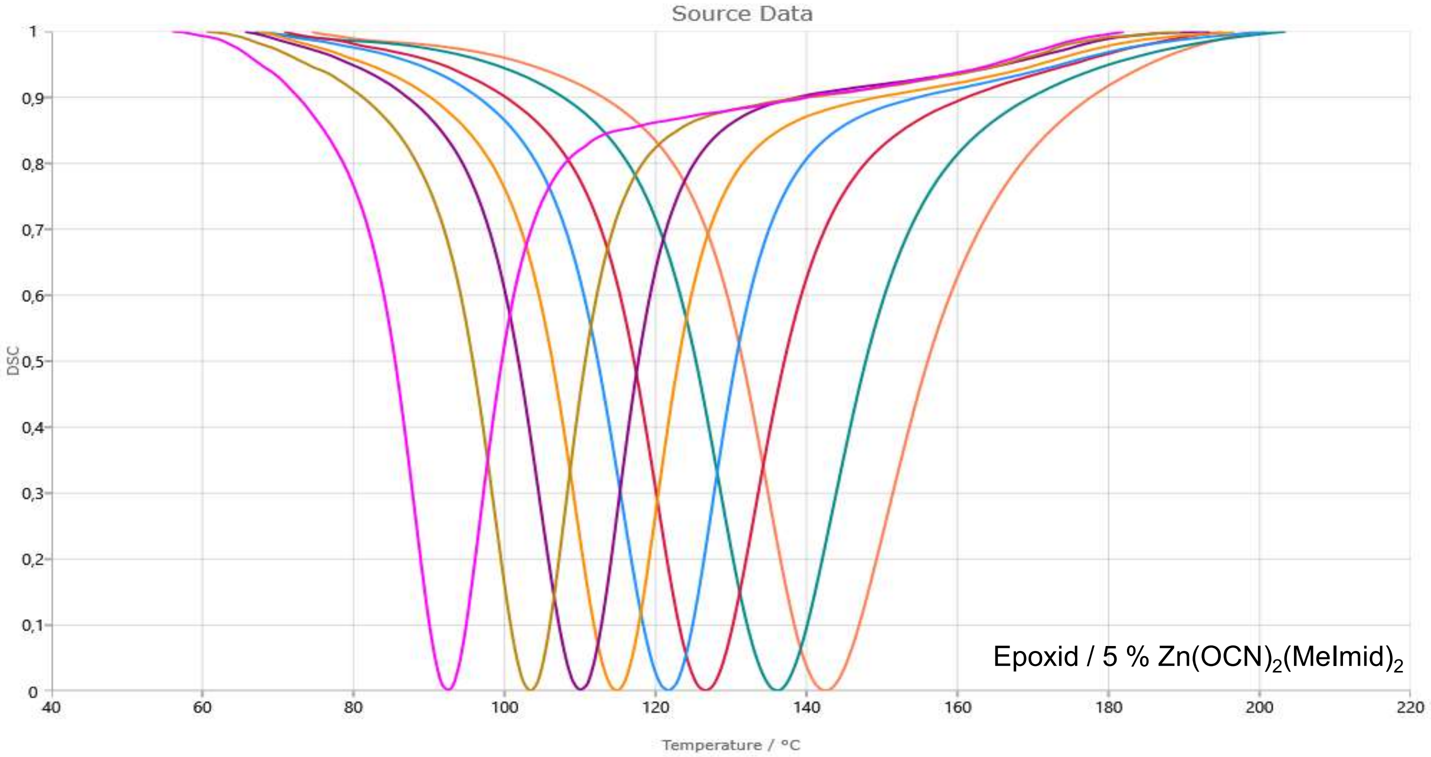
Determination of the points for glass transition Temperature



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

DSC Measurements

Heat Flow: relative scaling



Epoxid / 5 % $Zn(OCN)_2(MeImid)_2$

5K/min

3,5K/min

1,9K/min

1,5K/min

1,0K/min

0,7K/min

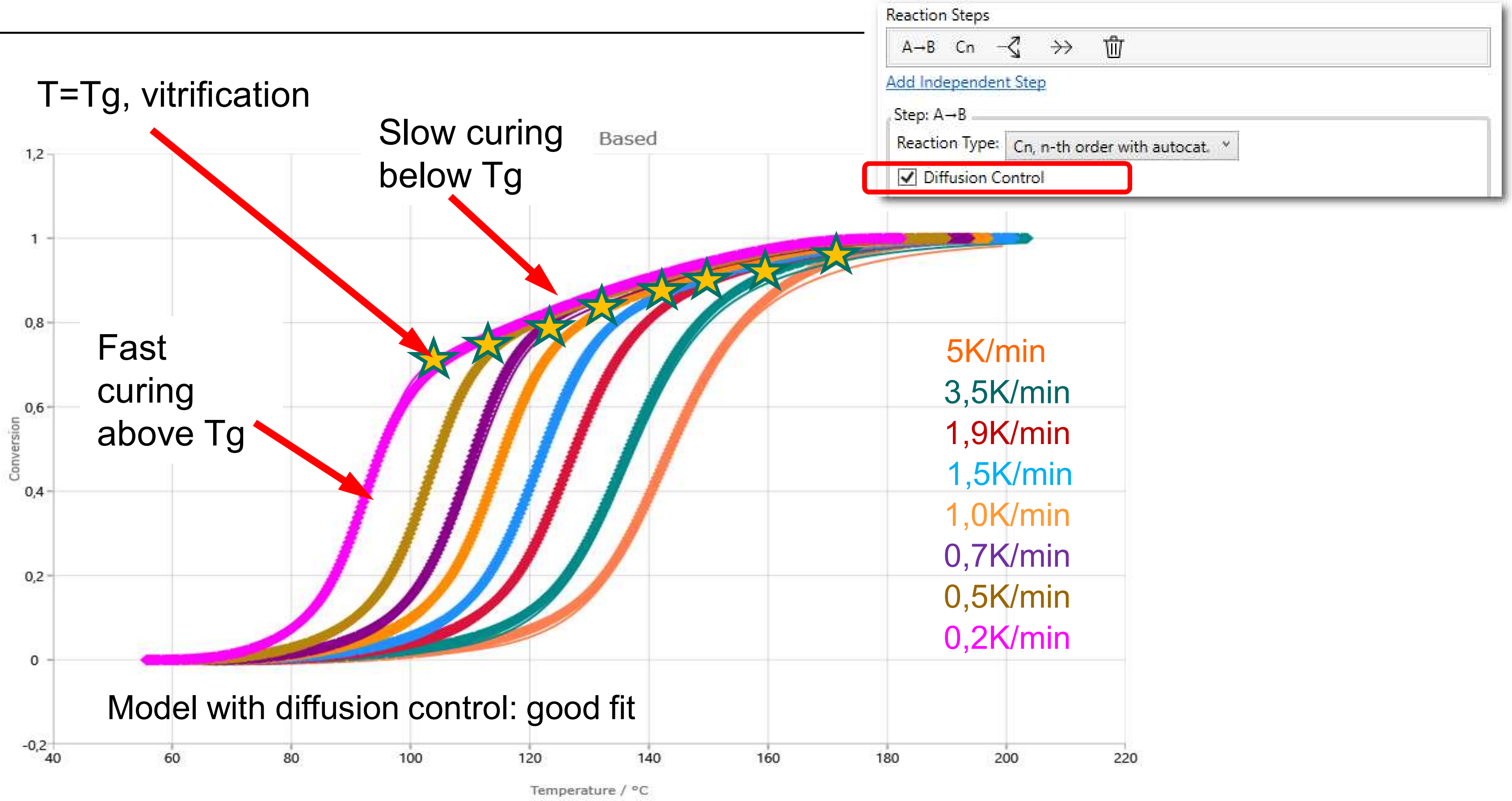
0,5K/min

0,2K/min

H.J. Flammersheim and J. Opfermann, Thermochimica Acta 337 (1999) 141 - 148

Experiment and Model Fit for diffusion control

NETZSCH



Reaction Steps

Step: A→B

Reaction Type: Cn, n-th order with autocat.

☑ Diffusion Control

T=Tg, vitrification

Slow curing below Tg

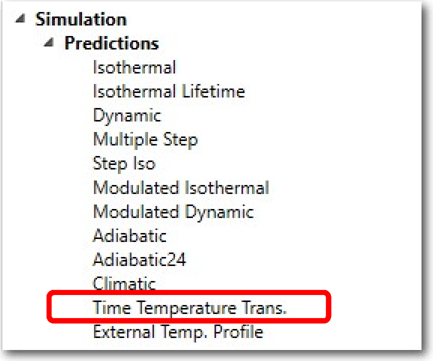
Fast curing above Tg

Model with diffusion control: good fit

See Theory of diffusion control in

S.Vyazovkin, A.K.Burnham, L.Favergeon, N.Koga, E.Moukhina, L.A.Perez-Maqueda, N. Sbirrazuoli.
Thermochimica Acta 689 (2020) 1785977, ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics

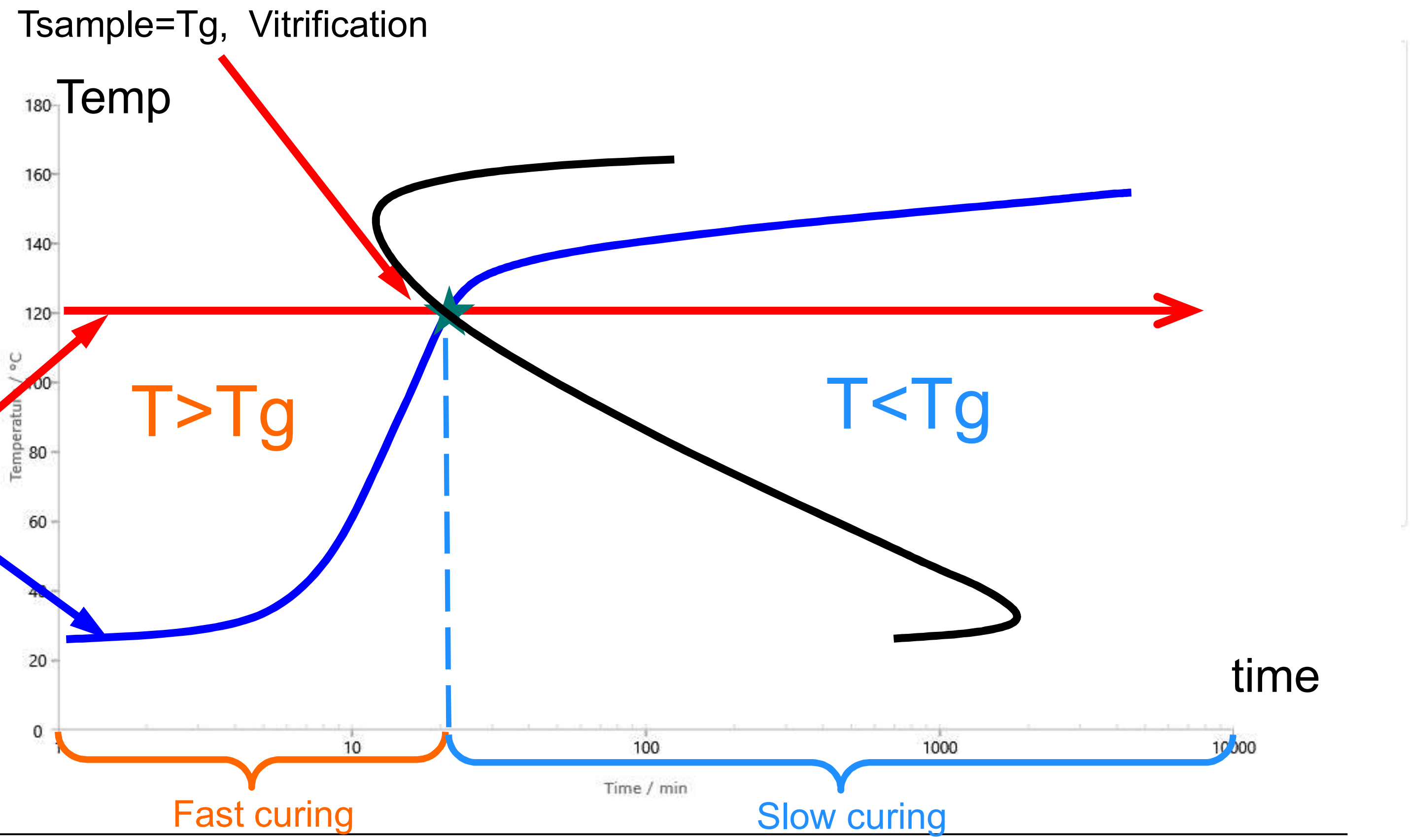
Isothermal Predictions of glass transition for Time-Temperature-Transition diagram



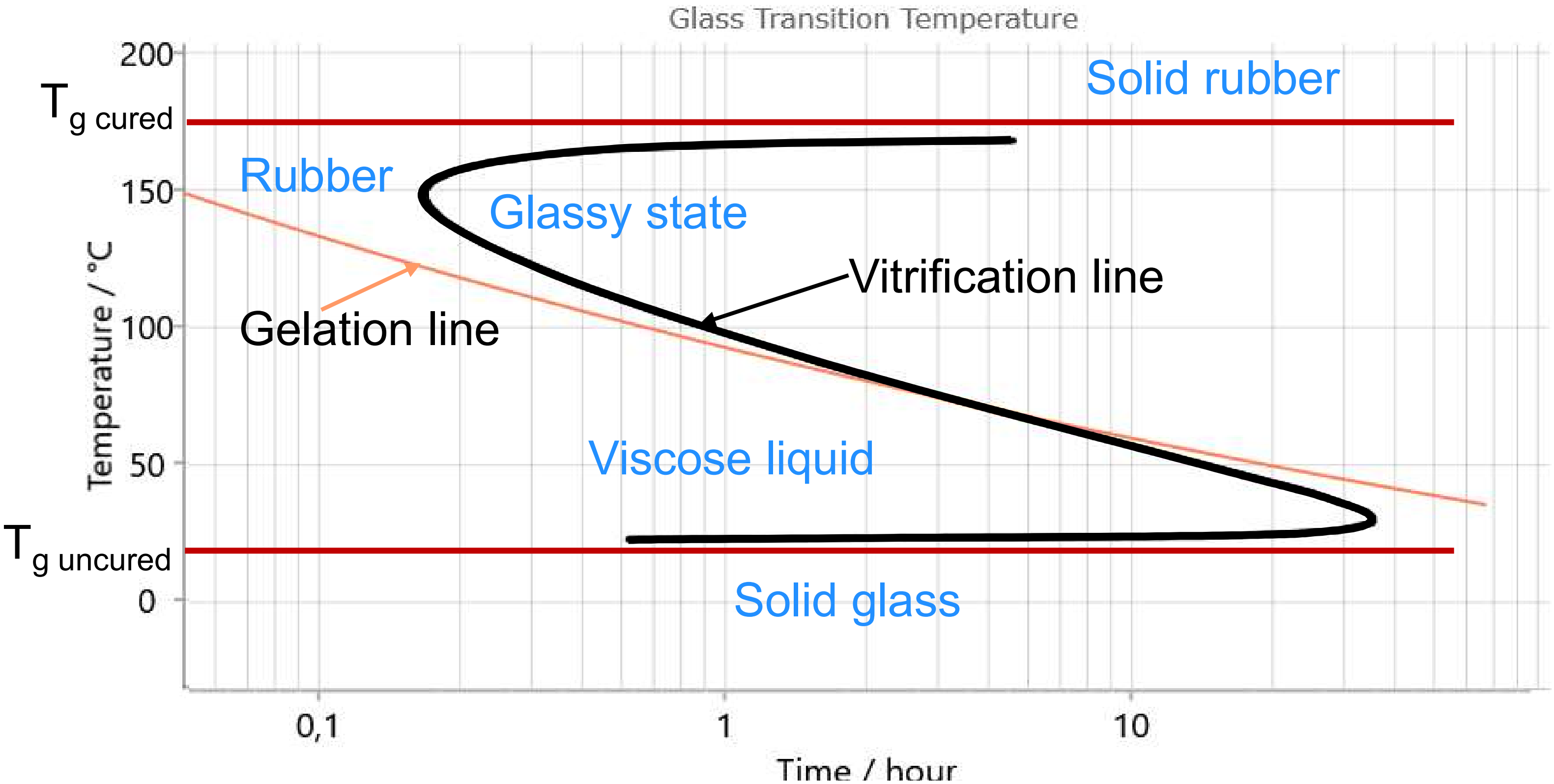
- Simulation
  - Predictions
    - Isothermal
    - Isothermal Lifetime
    - Dynamic
    - Multiple Step
    - Step Iso
    - Modulated Isothermal
    - Modulated Dynamic
    - Adiabatic
    - Adiabatic24
    - Climatic
    - Time Temperature Trans.
    - External Temp. Profile

Tsample = const

Tg



Time-Temperature-Transition diagram for curing

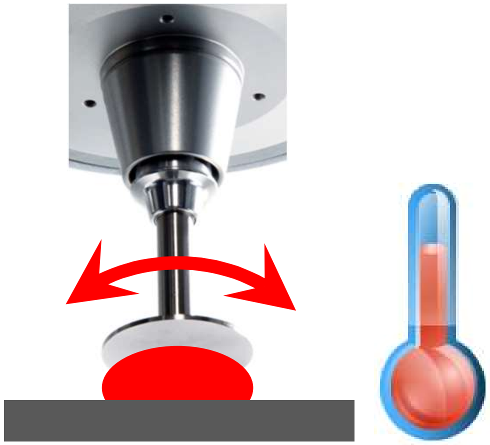


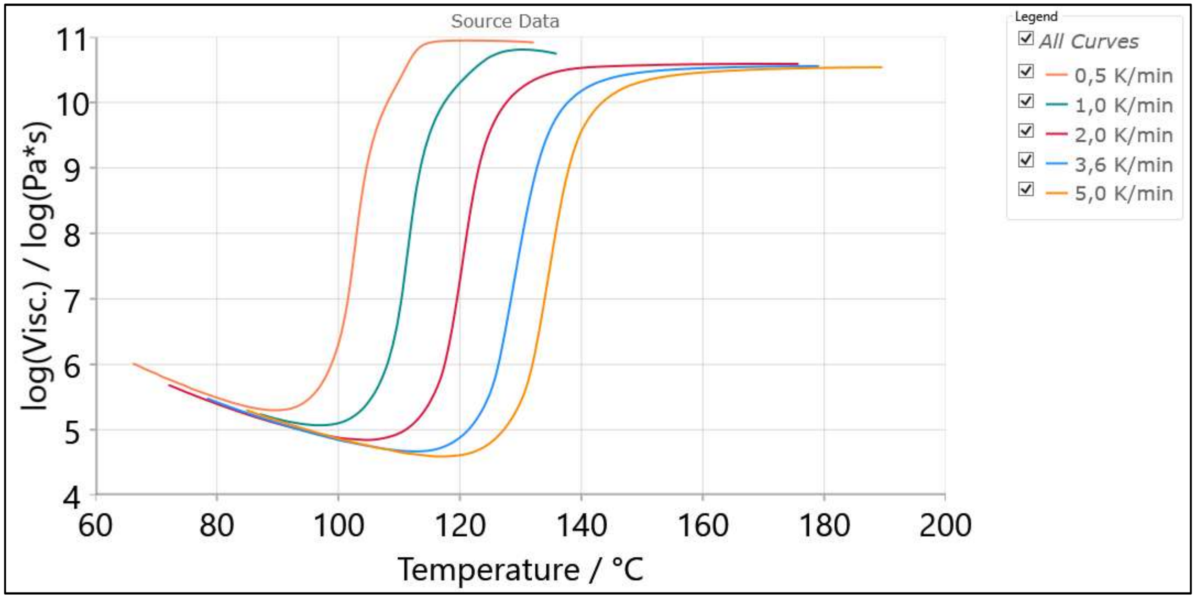
TTT Diagram shows the state of the material (glass, liquid, rubber) for isothermal conditions with known temperature and time

2.2 Curing and cross-linking

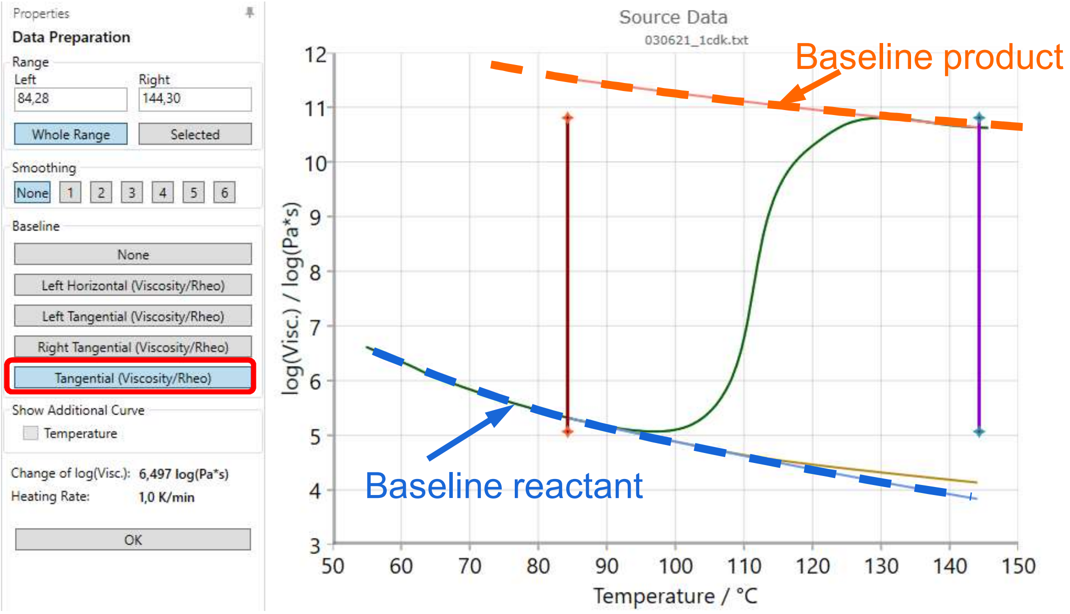
2.2.3 Kinetics of rheological data for dynamic viscosity

Kinetic analysis of rheological data
and prediction of dynamic viscosity





SPMKOMPOZIT: epoxy system



Range Left: 84,28 Right: 144,30

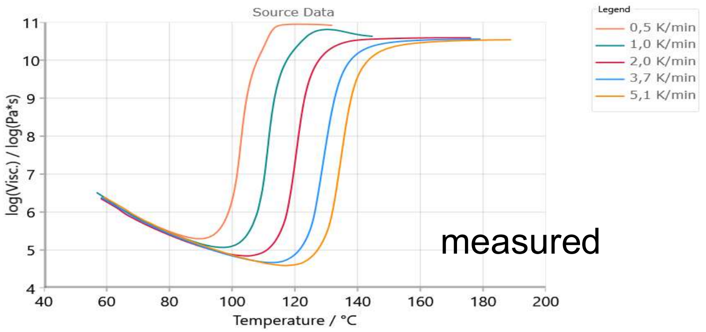
☐ Temperature

Change of log(Visc.): 6,497 log(Pa*s)
Heating Rate: 1,0 K/min

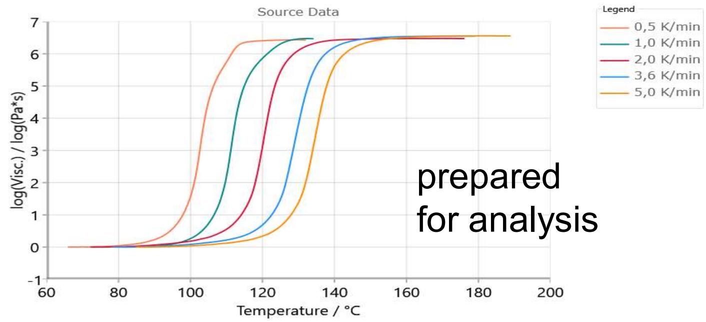
Baseline product

Baseline reactant

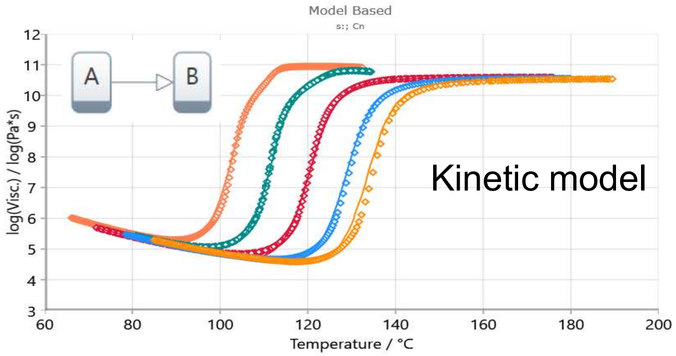
Tangential baseline for heating



measured

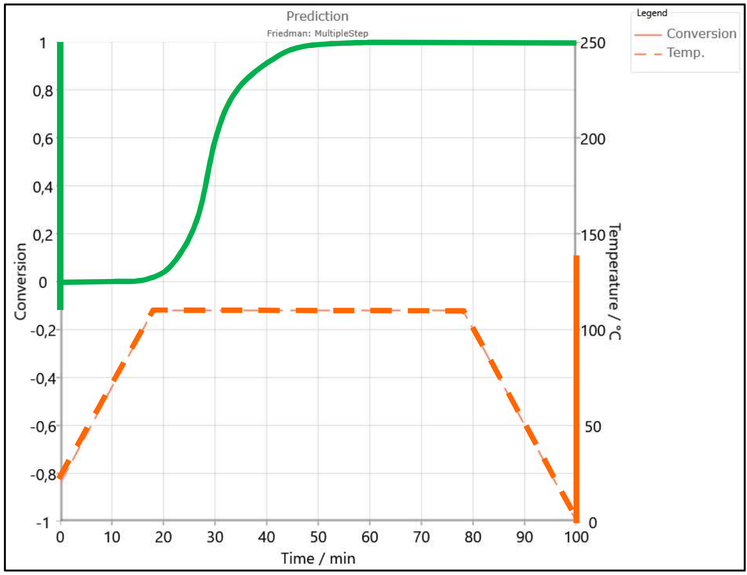


prepared
for analysis

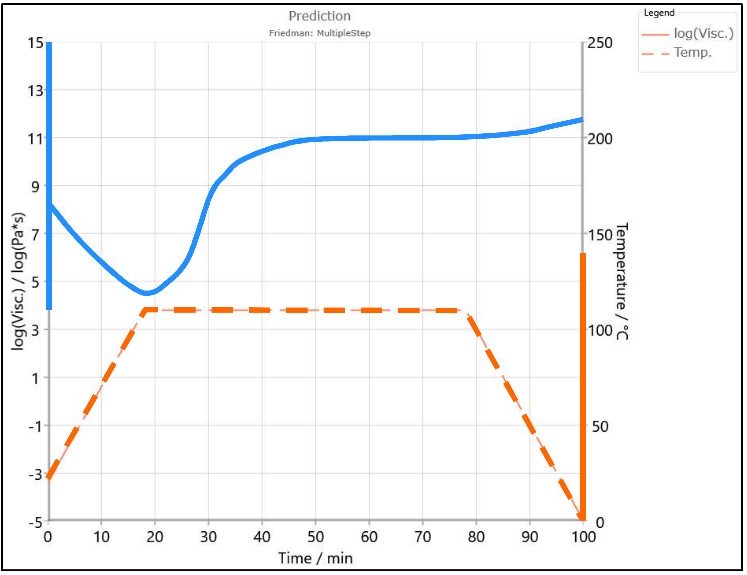


Kinetic model

Predictions of viscosity and conversion



Prediction of Conversion



Prediction of Viscosity

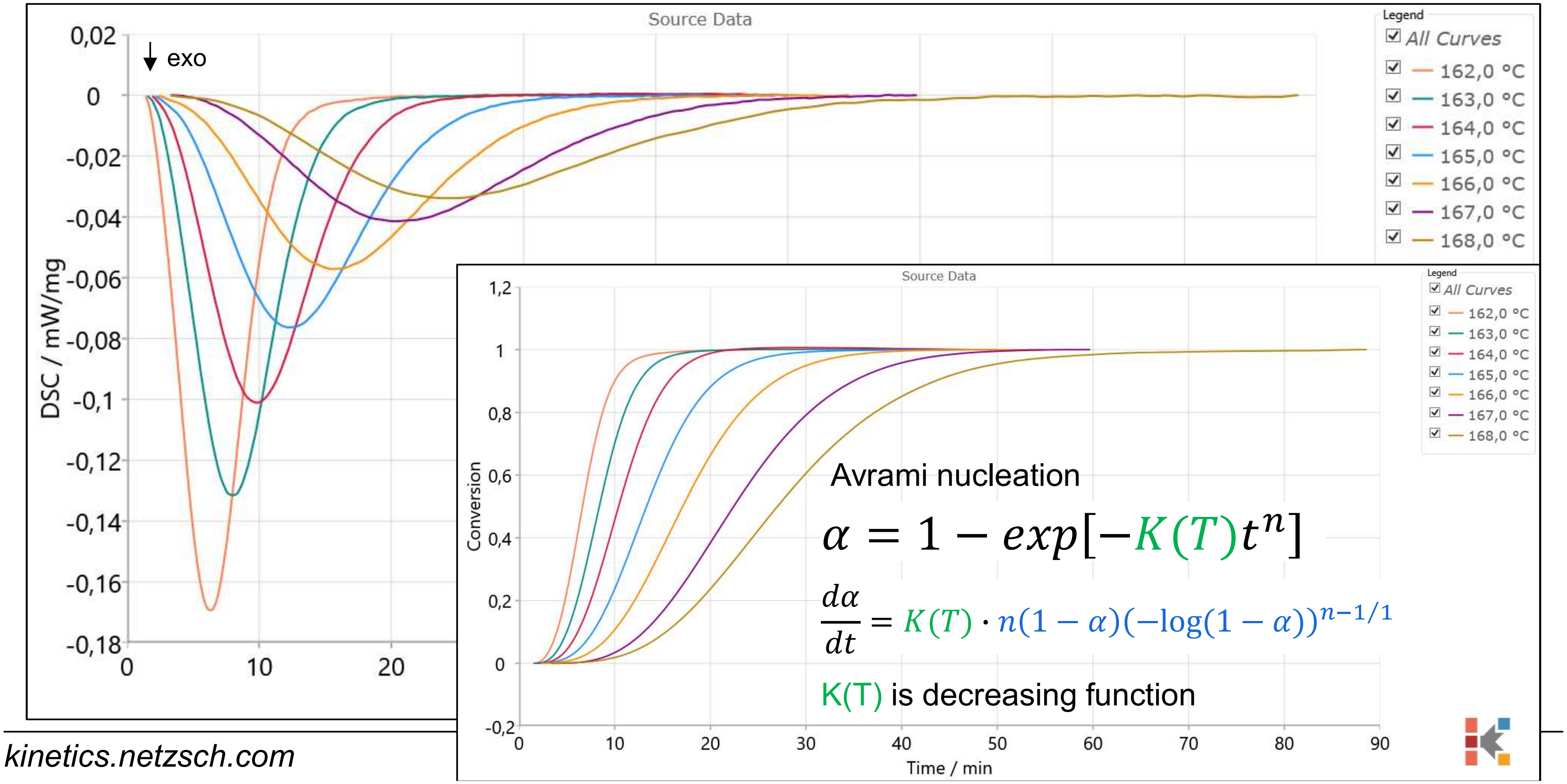
kinetics.netzsch.com

NETZSCH

2.3 Crystallization

2.3.1 Isothermal crystallization, Avrami nucleation
2.4.2 Non-isothermal crystallization,
Hoffman-Lauritzen theory,
Nakamura crystallization,
Sbirrazzuoli crystallization

Isothermal crystallization PA12



Avrami nucleation

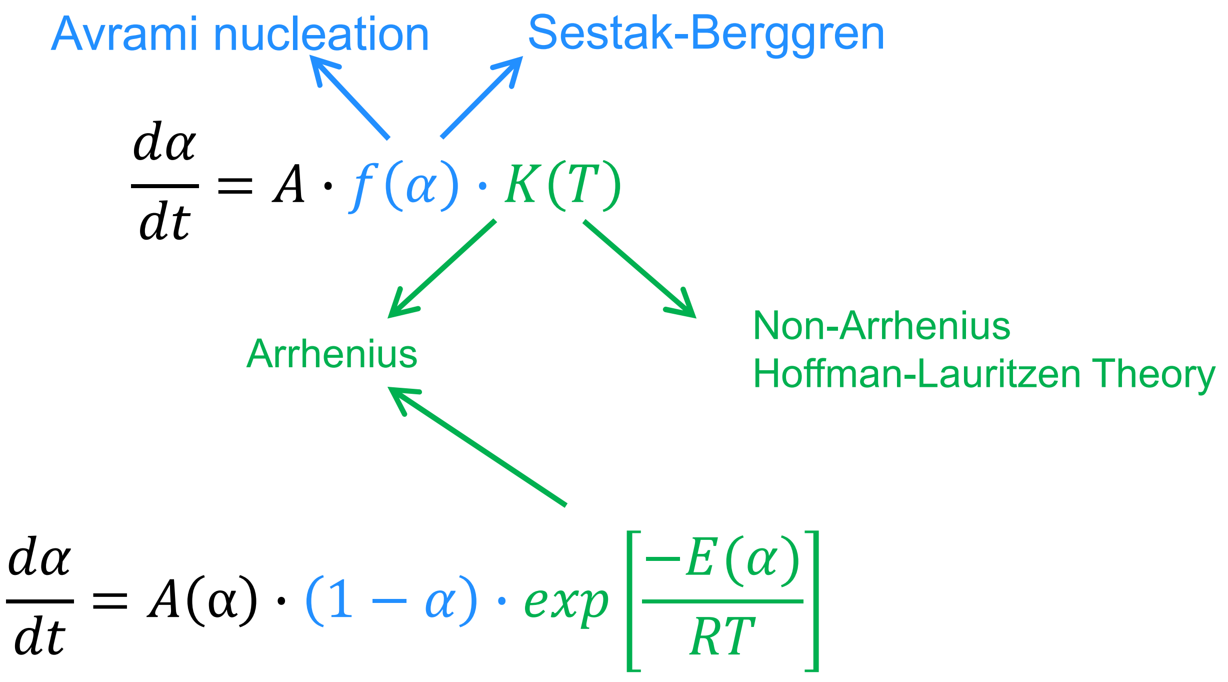
$$\alpha = 1 - exp[-K(T)t^n]$$

$$\frac{d\alpha}{dt} = K(T) \cdot n(1-\alpha)(-\log(1-\alpha))^{n-1/1}$$

K(T) is decreasing function

Crystallization kinetics in Kinetics Neo

Crystallization rate



Avrami nucleation

Sestak-Berggren

Model based

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

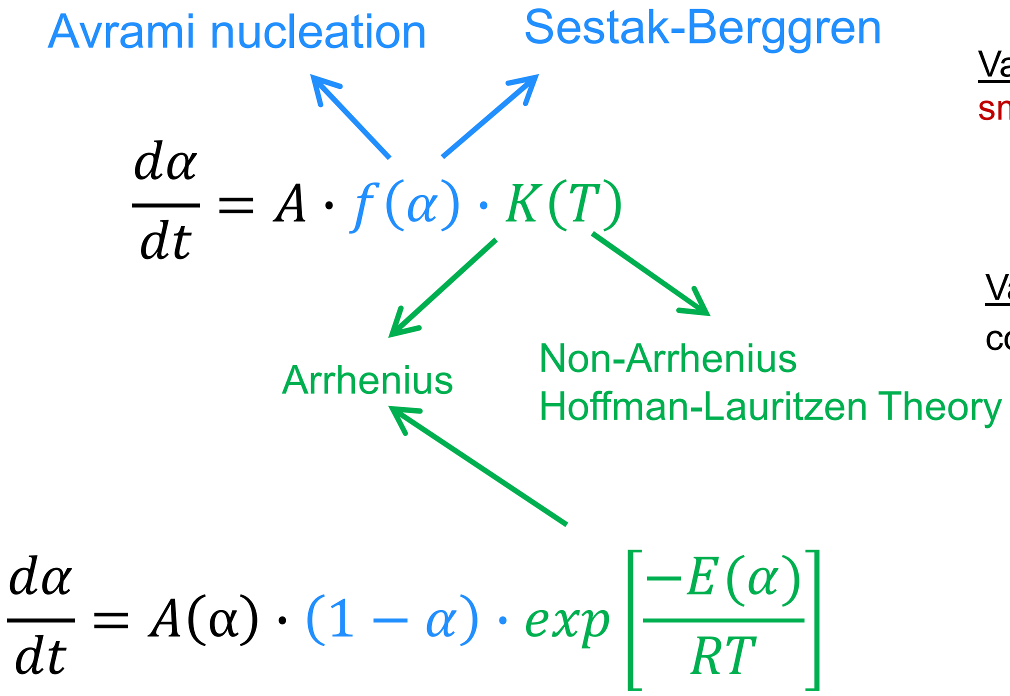
Arrhenius

Non-Arrhenius
Hoffman-Lauritzen Theory

Model free

$$\frac{d\alpha}{dt} = A(\alpha) \cdot (1 - \alpha) \cdot exp\left[\frac{-E(\alpha)}{RT}\right]$$

Crystallization kinetics



Avrami nucleation

Sestak-Berggren

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

Arrhenius

Non-Arrhenius
Hoffman-Lauritzen Theory

$$\frac{d\alpha}{dt} = A(\alpha) \cdot (1-\alpha) \cdot exp\left[\frac{-E(\alpha)}{RT}\right]$$

Model based reaction type:

An: Avrami+ Arrhenius
SB: Sestak Berggren + Arrhenius

Valid: isothermal crystallization,
small temperature range

Nakamura: Avrami+ Hoffman-Lauritzen
Sbirrazzuoli: Sestak-Berggren+ Hoffman-Lauritzen

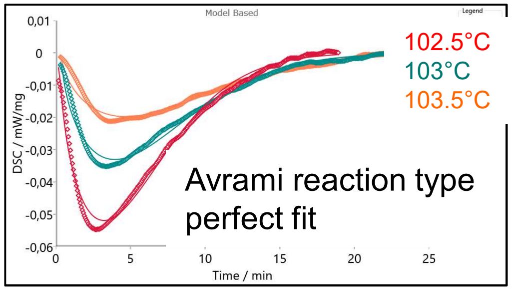
Valid: both isothermal and cooling crystallization
complete temperature range between T_∞ and Tm

Model free:

ASTM2070
Friedman
Numerical Optimization

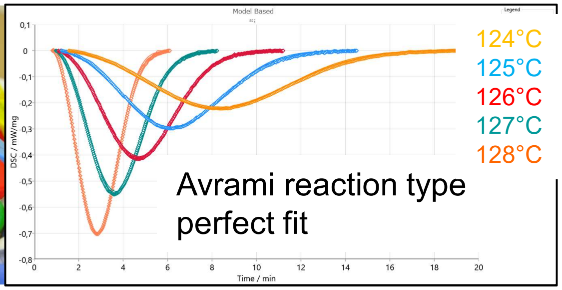
Valid: isothermal crystallization,
small temperature range

Arrhenius: Isothermal crystallization: LDPE and PP



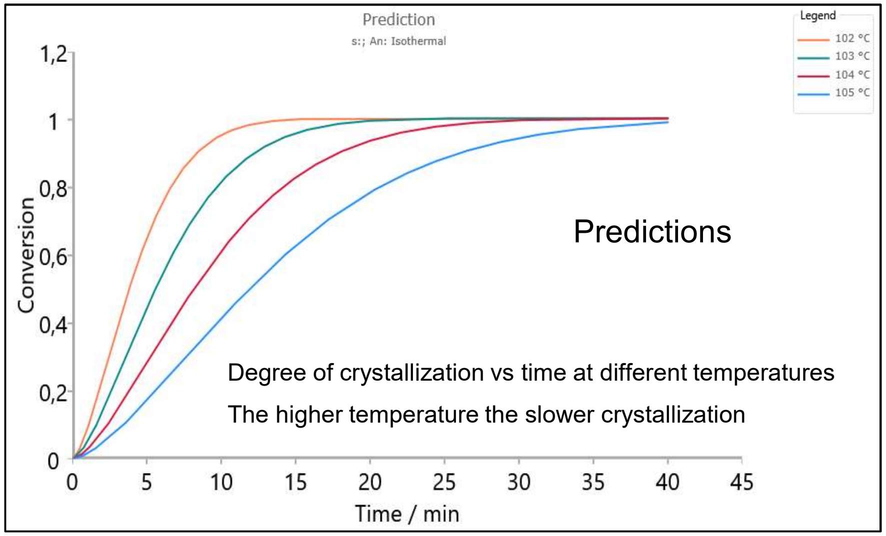
102.5°C
103°C
103.5°C

Avrami reaction type perfect fit



124°C
125°C
126°C
127°C
128°C

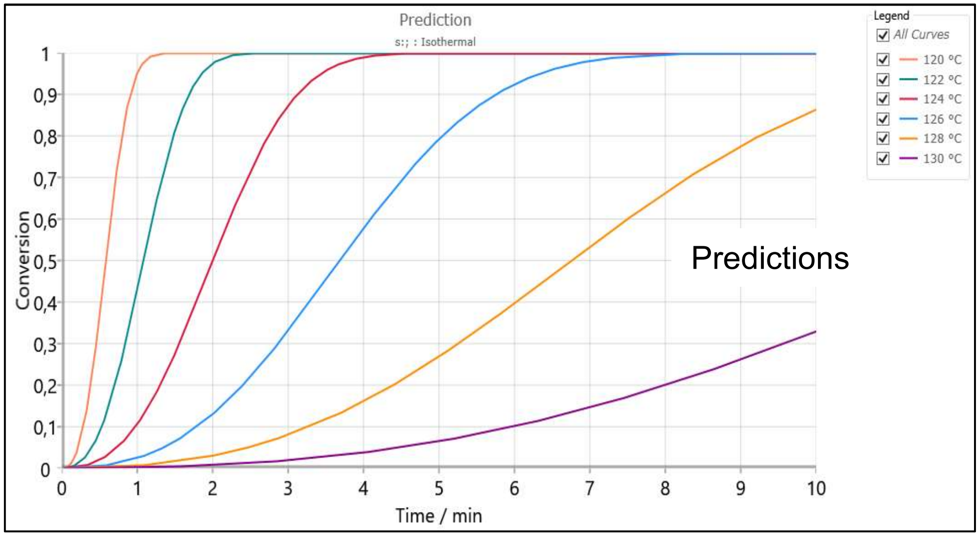
Avrami reaction type perfect fit



Predictions

Degree of crystallization vs time at different temperatures

The higher temperature the slower crystallization



Predictions

Isothermal Crystallization: Arrhenius approach

Advantage:

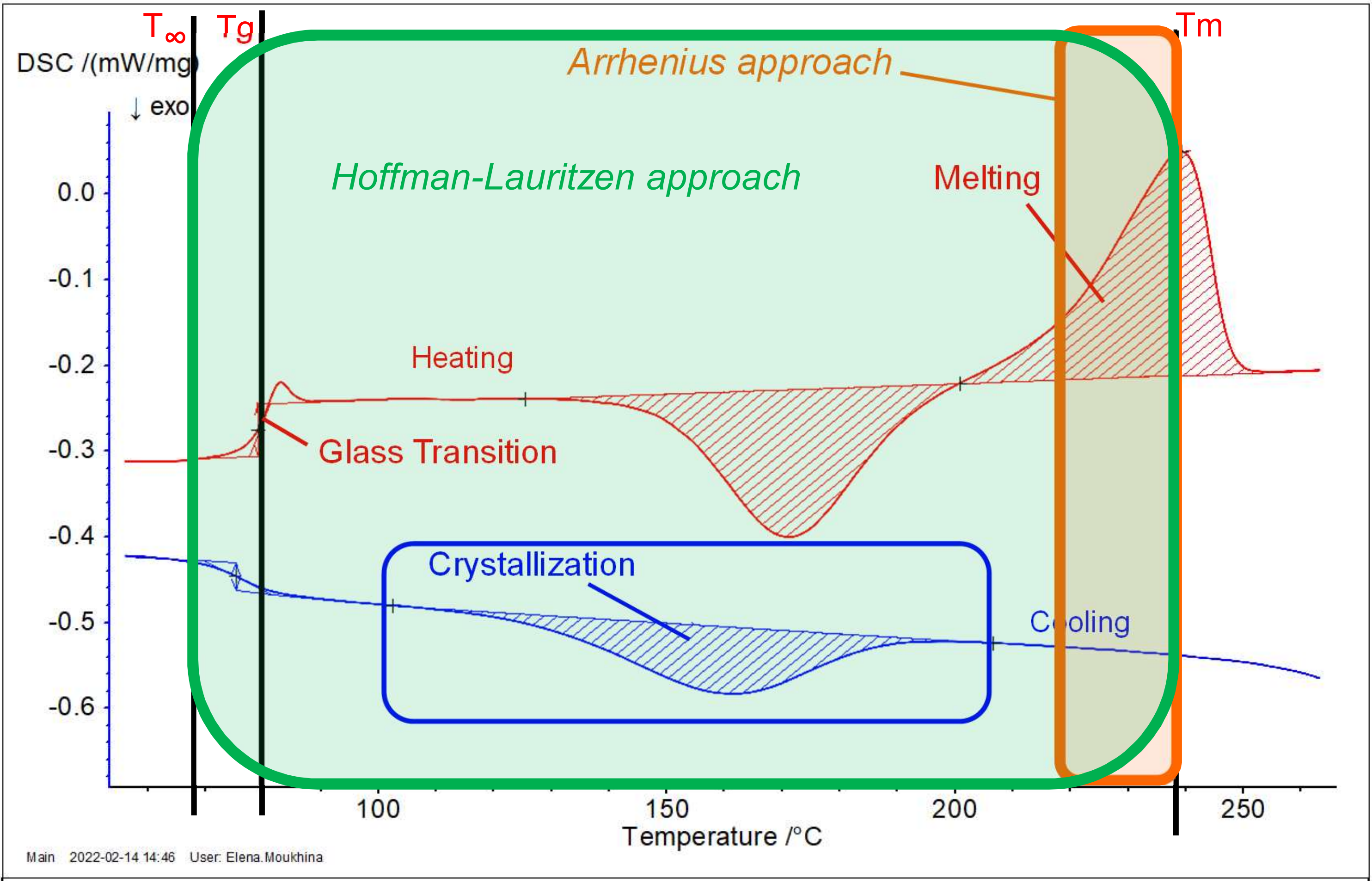
very simple and fast, mathematics of chemical kinetics can be used.

Disadvantages:

1. Arrhenius approach has no physical background. Activation energy is just the apparent value.
2. Does not take into account diffusion near glass transition temperature
3. Enables only for very small temperature range near melting point. Produces incorrect predictions outside of this range.

Conclusion: this approach is very simplified, and has very limited working temperature range

Polymer: Heating and Cooling



Crystallization kinetics

Crystallization rate $$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

1. Arrhenius approach

(model free and model based)

$$K(T) = exp\left(\frac{-E_a}{RT}\right)$$

$E_a<0$

Partial solution only for isothermal crystallization
Works in small range below melting temperature

2. Non-Arrhenius approach

(model based only)

- Hoffman-Lauritzen Theory

$$K(T) = exp\left(\frac{U^*}{R(T-T_\infty)}\right) \cdot exp\left(\frac{-K_G}{T\Delta T f}\right)$$

Solution for both isothermal and cooling crystallization
Works for complete crystallization range

Crystallization kinetics:
non-Arrhenius approach: Nakamura und Hoffman-Lauritzen

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

Diffusion term

Nucleation term

$$K(T) = exp\left(\frac{-U^*}{R(T - \boxed{T_\infty})}\right) \cdot exp\left(\frac{-K_G}{T \cdot \boxed{\Delta T} \cdot f}\right)$$

No viscose flow below Tg

Supercooling

U*	activation energy of segmental jump in polymers, this parameter has universal value 6.3kJ/mol
K_G	kinetic parameter for nucleation
$\Delta T = Tm - T$	undercooling from the equilibrium ***melting point Tm***
$T_\infty = Tg - 30$	temperature at which crystallization transport is finished, this temperature is 30K below the ***glass transition temperature Tg***.
f=2T/(T+Tm)	correction factor

This method defined for total temperature range between T_∞ and $T_{melting}$

Sbirazzuoli* crystallization model SbC with Sestak-Berggren reaction type

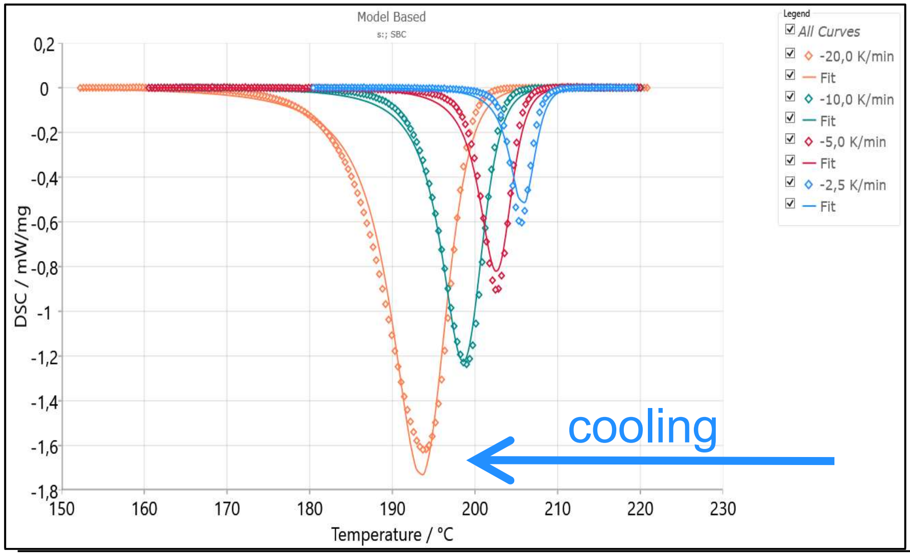
$$\frac{d\alpha}{dt} = A \cdot f(\alpha) \cdot K(T)$$

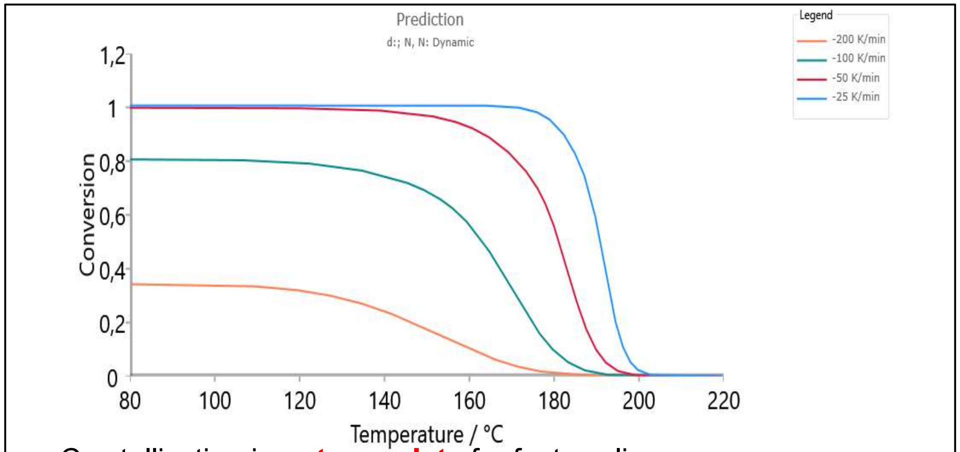
Hoffman-Lauritzen Theory

Sestak-Berggren Crystallization

$f(\alpha)=(1-\alpha)^n \cdot \alpha^m \cdot [-\ln((1-\alpha))]^q$

PBT Tg= 40-60°C, Tm=220-230°C





Crystallization is **not complete** for fast cooling

because of **glass transition.** Polymer is partially **amorphous**

* Nathanael Guigo, Jesper van Berkel, Ed de Jong , Nicolas Sbirrazzuoli, Thermochimica Acta 650 (2017) 66-75

Crystallization for Polyethylene Terephthalate (PET)

PET

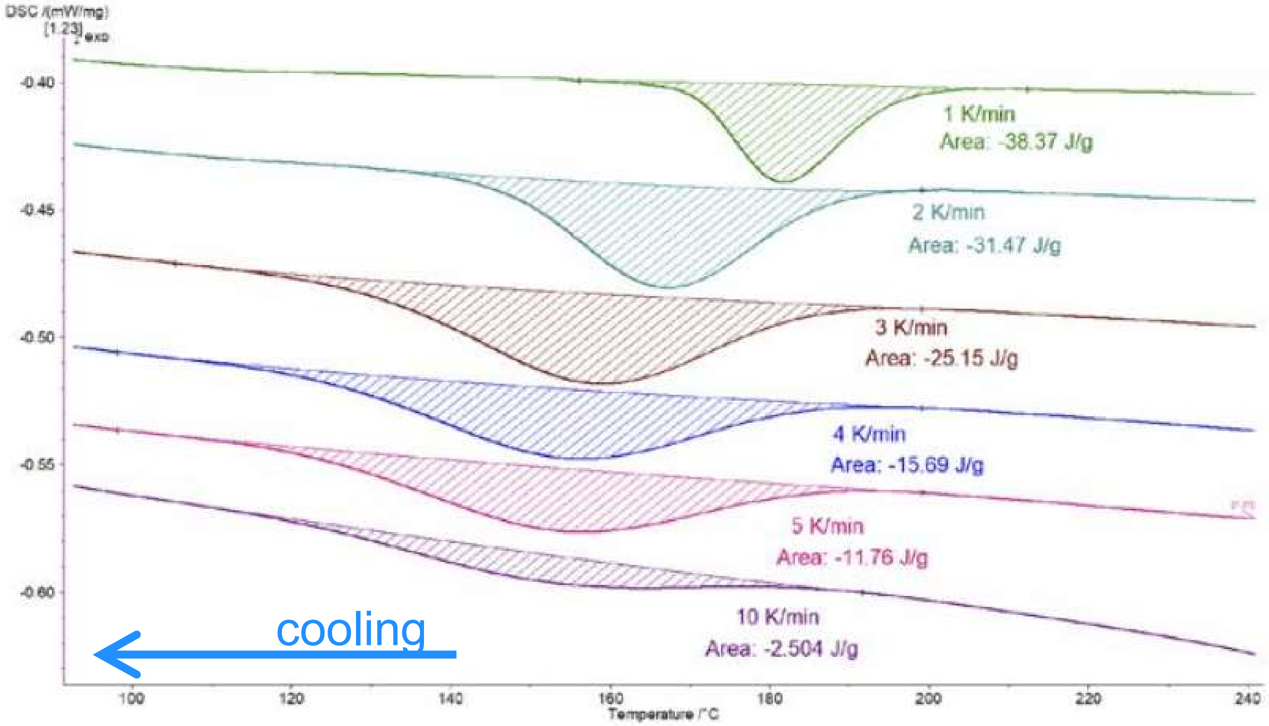
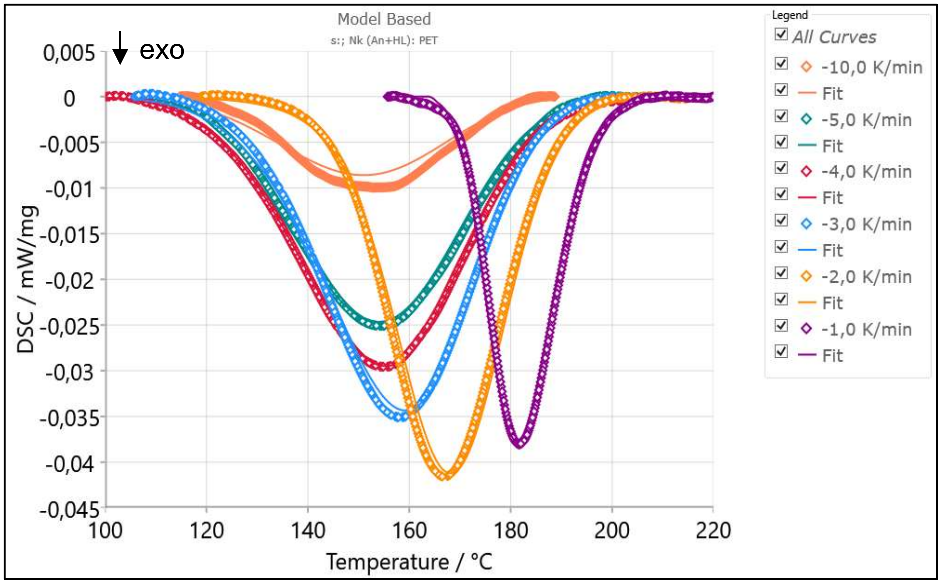
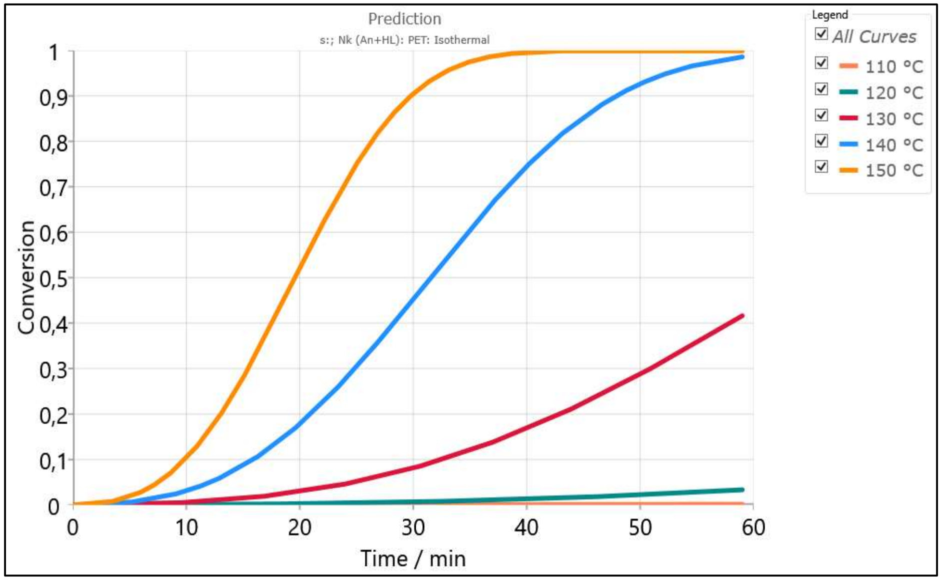


Fig. 1. Crystallization curves for polyethylene terephthalate (PET) measured at cooling rates from 1 to 10 K/min

Crystallization Prediction for Polyethylene Terephthalate (PET)



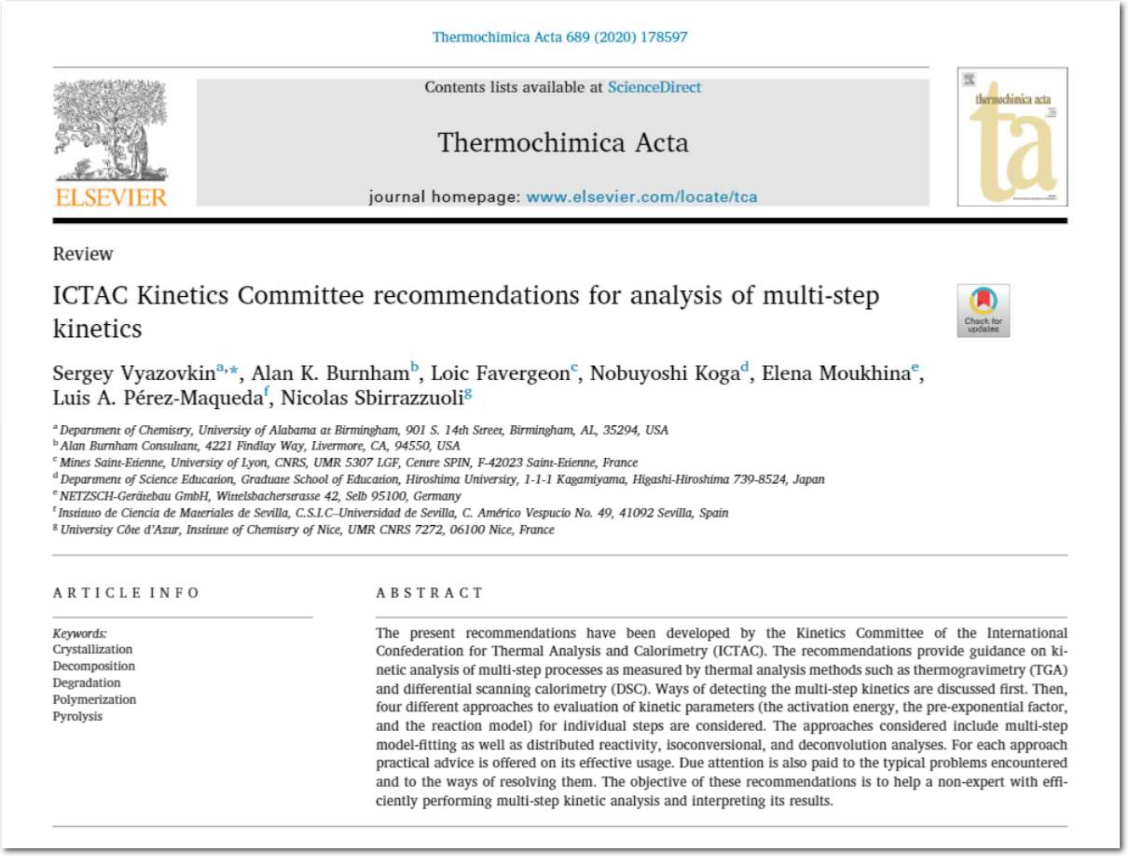


One can observe that at temperatures of 110°C to 120°C, no crystallization occurs and the bottles remain in the glassy state and transparent. If the production temperature is too high – e.g., 140°C – then crystallization starts earlier, and the bottles get turbid.

PET:
stretch
blow
molding

Unique: Kinetics Analysis must fulfils ICTAC kinetics recommendations

International Confederation for Thermal Analysis and Calorimetry



Thermochimica Acta 689 (2020) 178597

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Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Review

ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics

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Polymerization
Pyrolysis

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.

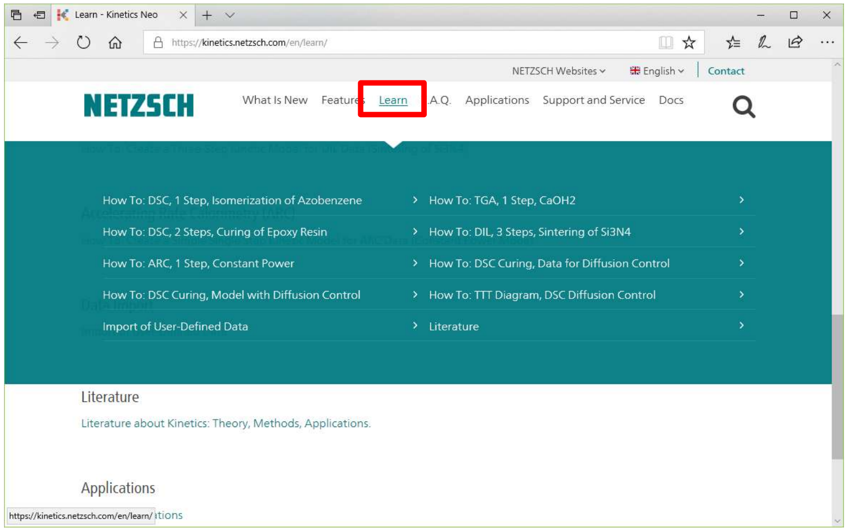
- Model free analysis
- Multi-step model-fitting (model based)
- Diffusion control for curing
- Crystallization kinetics
- Kamal model for curing
- Deconvolution analysis (sum of peaks)

NETZSCH Kinetics Neo Web Site
https://kinetics.netzsch.com

Users Guide, Training examples,

Webinars: Thermokinetics (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



How To: DSC, 1 Step, Isomerization of Azobenzene

How To: DSC, 2 Steps, Curing of Epoxy Resin

How To: ARC, 1 Step, Constant Power

How To: DSC Curing, Model with Diffusion Control

Import of User-Defined Data

How To: TGA, 1 Step, CaOH2

How To: DIL, 3 Steps, Sintering of Si3N4

How To: DSC Curing, Data for Diffusion Control

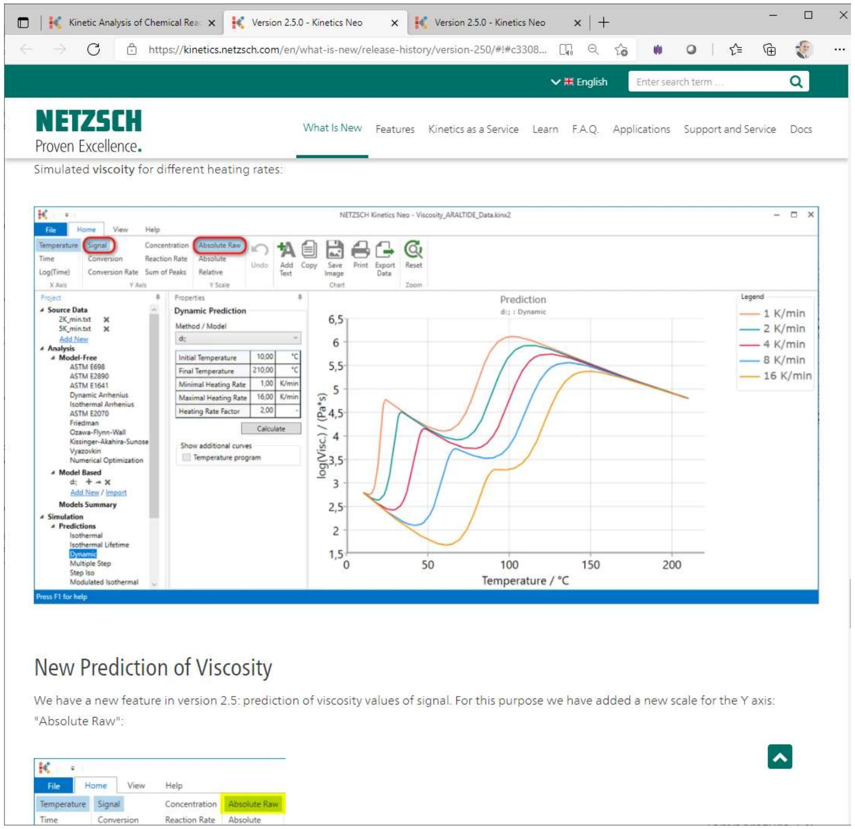
How To: TTT Diagram, DSC Diffusion Control

Literature

Literature

Literature about Kinetics: Theory, Methods, Applications.

Applications



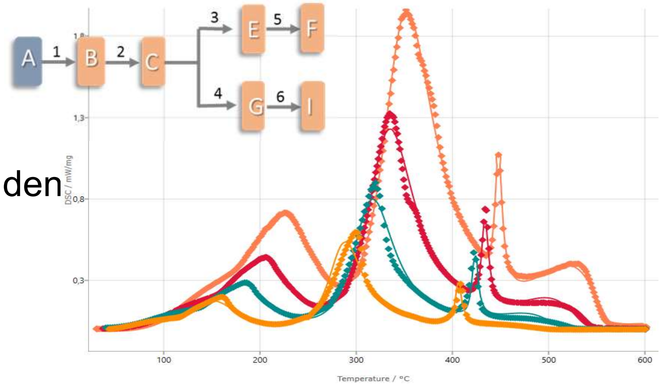
Simulated viscoity for different heating rates:

New Prediction of Viscosity

We have a new feature in version 2.5: prediction of viscosity values of signal. For this purpose we have added a new scale for the Y axis: "Absolute Raw":

Conclusion

KINETICS NEO is used to analyze kinetics of temperature dependen chemical processes.



Analysis

- one mathematical kinetic description for several measurements
- different approaches: model free (11 methods) and model based (unlimited number of models)
- model based: individual reaction steps, concentrations, kinetic triplet for each step, reaction mechanism
- standard reaction types (n-th order, Autocatalysis, diffusion, Avrami nucleation)
- unique reaction types (Kamal-Sourour, diffusion control, Nakamura nucleation, Hoffman-Lauritzen theory)
- Standard data types like TG or DSC
- Unique data types (Dilatometry, Rheometry, DEA)

Predictions and optimizations

- optimization of industrial chemical processes like debinding, curing, sintering
- standard predictions (isothermal, heating, multi-step, user-defined, TD24, climatic for 100 weather stations)
- unique predictions of individual peaks, concentrations, Tg, TTT diagram, temperature presets like fire presets)
- prediction of viscosity or ion viscosity for new temperature profile
- Optimization of temperature profile for constant or predefined conversion rate

- DSC
- DTA
- TGA
- DIL
- DEA
- ARC
- Rheology

You can rely on NETZSCH.

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