NETZSCH

Leading Thermal Analysis

Specificity of Kinetic Modelling and Process Optimization for curing reactions

Elena Moukhina

NATAS 2018
08/08/2018

Production process: Curing

NETZSCH

adhesives, resins, paints, coating, 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/

How to solve the customer's problem?

1. Experimental data
   DSC, DEA — *Instrument is necessary*

2. Kinetics Analysis based on experimental data
   Create kinetic model based on experimental data — *Kinetics Neo*

3. Validation of kinetics Model
   Is the simulation in agreement with any existing isothermal data for this process?
   Instrument and Kinetics Neo

4. Prediction or process optimization — *Kinetics Neo*

Reaction types for curing

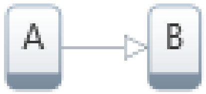
Kinetics Neo: specially for curing

NETZSCH

I. Reaction types for curing reactions

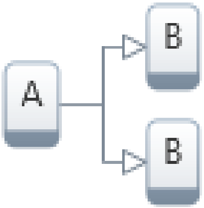
- Bna – autocatalytical reacton of Prout-Tompkins

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



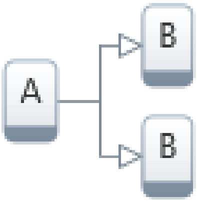
- Cmn – reaction of the n^{th} order with autocatalysis of m^{th} order by product

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



- Kamal-Sourour – two parallel reactions with the same reactant and same product;
  one of them is the reaction of the n^{th} order, the second one is autocatalytical;
  these two reactions have different activation energies

$$\frac{d\alpha}{dt} = A \cdot (1-\alpha)^n \cdot \left[\exp\left(\frac{-E_{a1}}{RT}\right) + K \cdot \alpha^m \cdot \exp\left(\frac{-E_{a2}}{RT}\right)\right]$$



II. Reactions with several steps including different step directions

III. Reactions with diffusion control

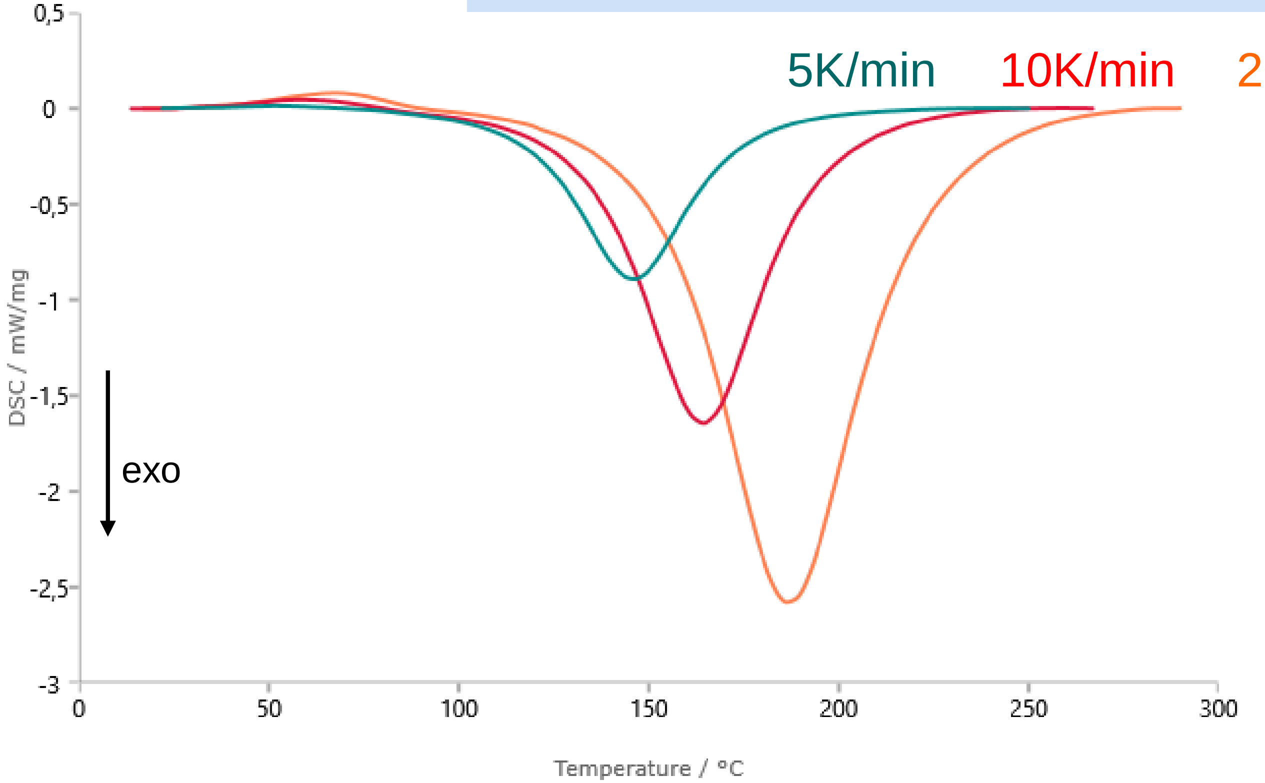
- For curing reactions at the temperatures near glass transition temperature

Different directions of reaction steps

Reactions with different direction of reaction steps

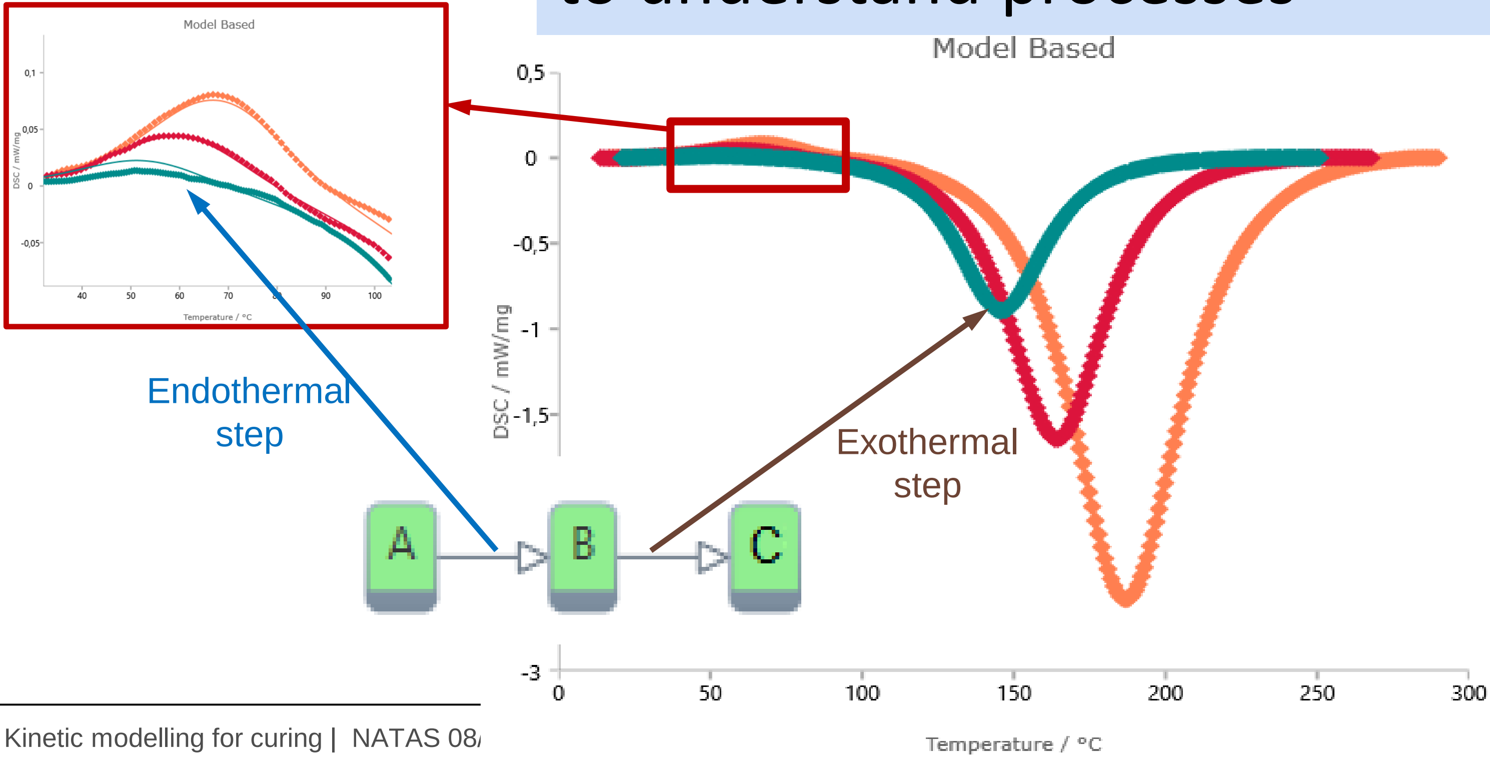
NETZSCH

Differential scanning calorimetry



Reactions with different direction of reaction steps

Use Models
to understand processes

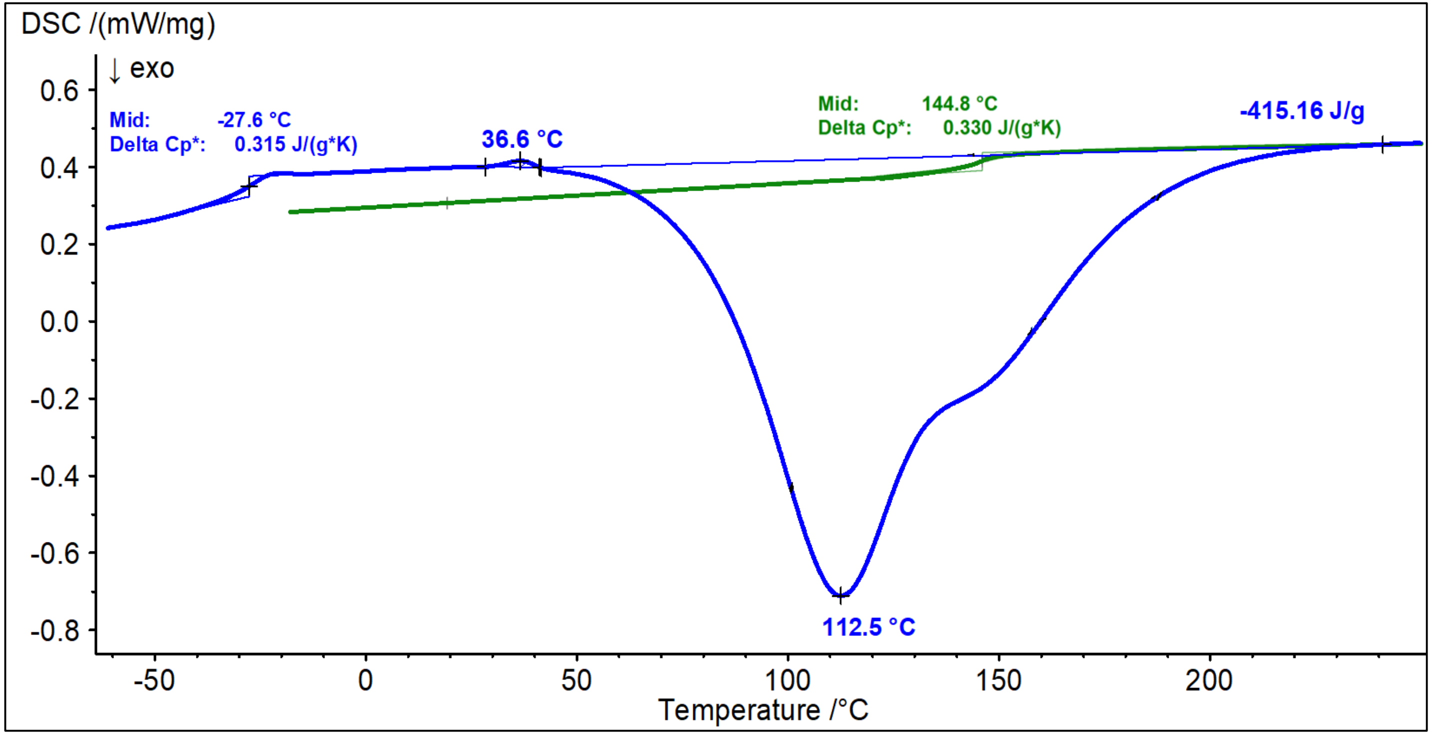


Reactions with diffusion control

Glass transition temperature moves after curing

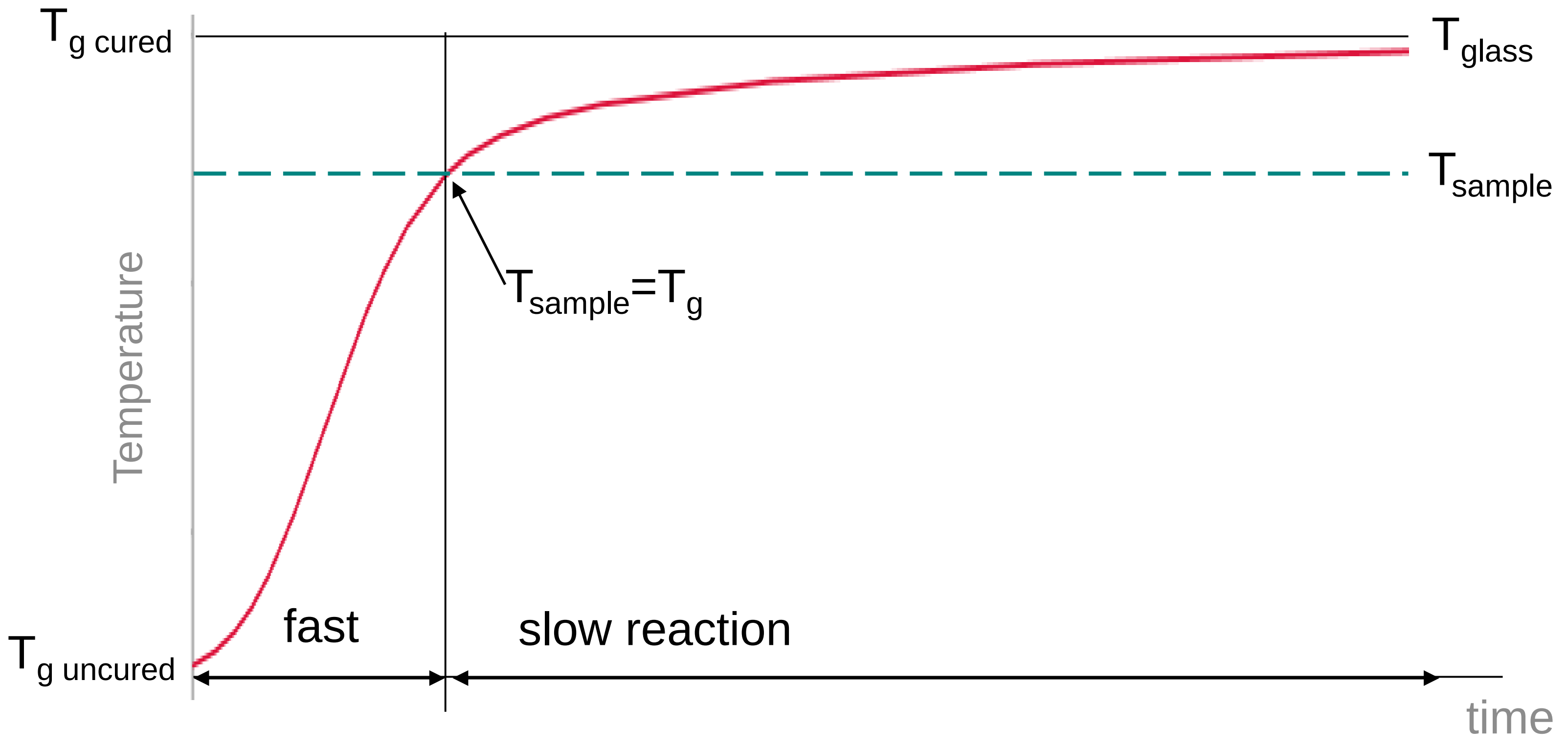
NETZSCH

Fiber-reinforced Plastics



Fast or slow reaction? Isothermal curing

NETZSCH



Glass transition temperature vs Conversion

Properties

Glass Transition Temperature

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

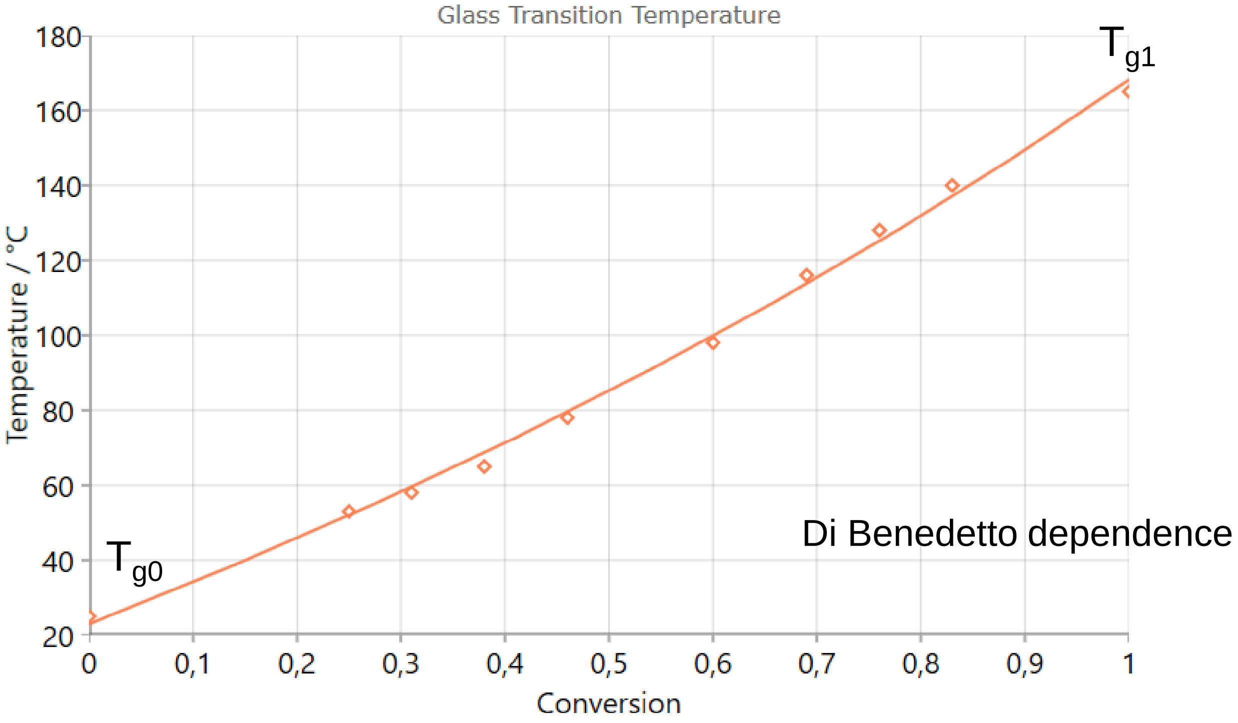
Add Point Calculate

Interpolation

Spline Di Benedetto

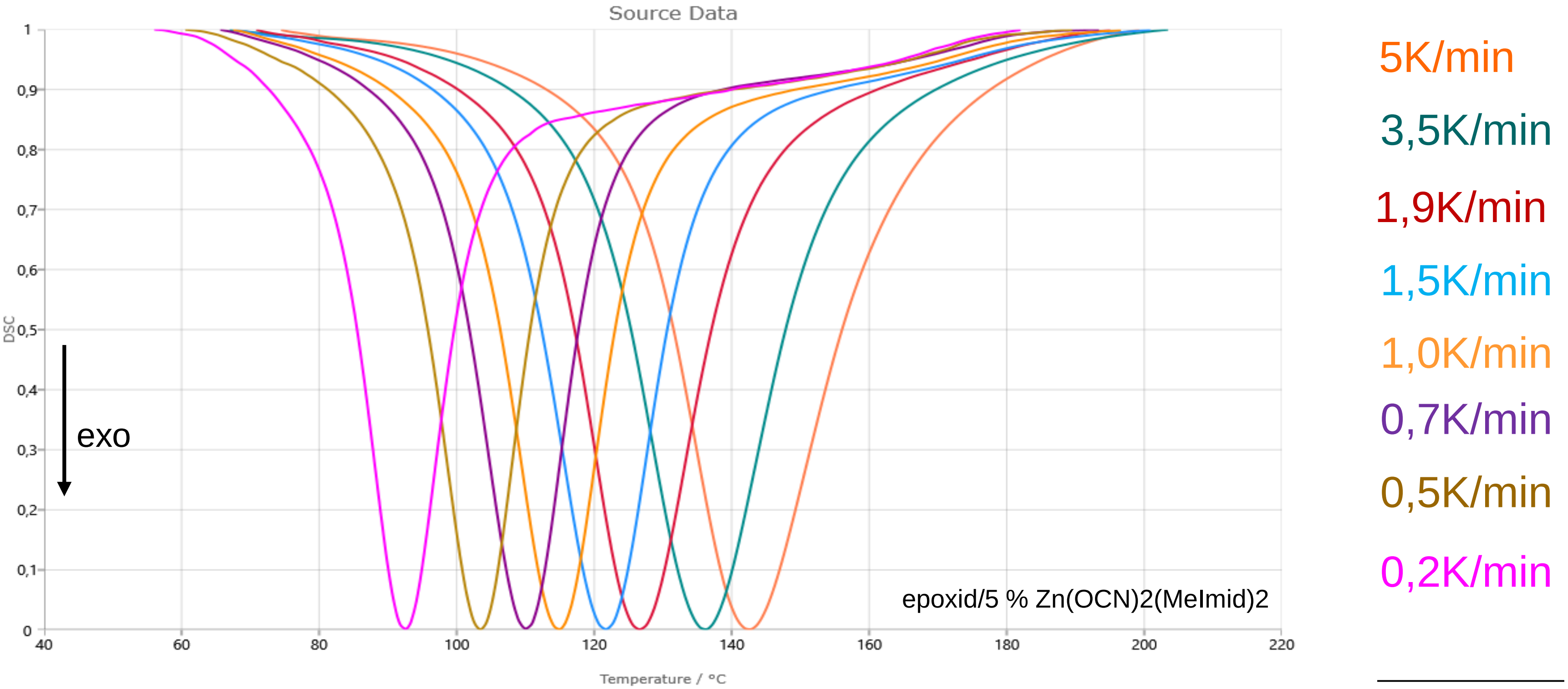
Parameters:

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



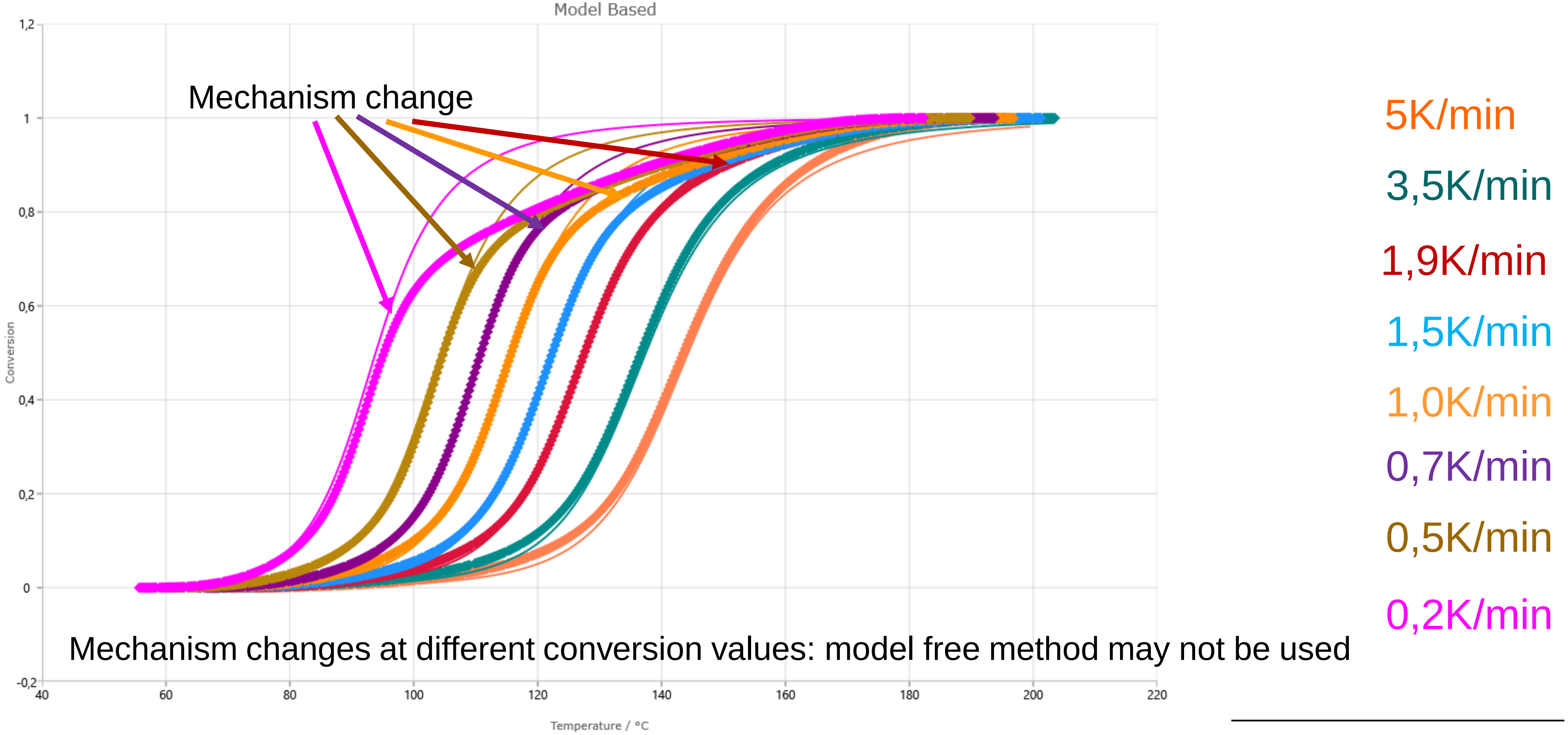
epoxid/5 % Zn(OCN)2(MeImid)2

DSC Measurements



Model without diffusion control

NETZSCH



Mechanism changes at different conversion values: model free method may not be used

Reaction with diffusion control: Theory

NETZSCH

Rabinovich equation for entire rate constant:

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

k_{chem} is the chemical reaction rate

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

k_{diff} is the diffusion rate, calculated by WLF (Williams – Landel - Ferry) equation:

Above glass transition (T > Tg):

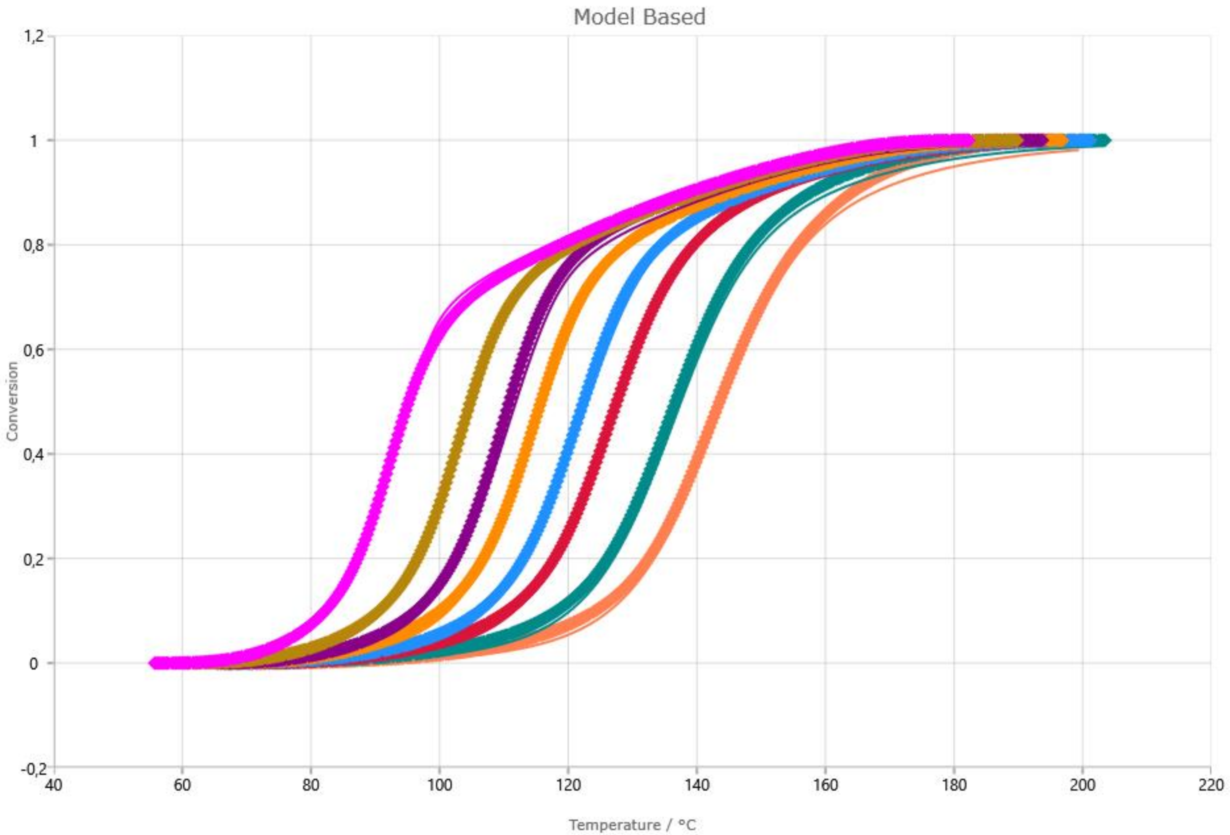
$$k_{diff}(T) = k_{diff}(T = T_g) \cdot \exp\left[\frac{C_1 \cdot (T - T_g)}{C_2 + T - T_g}\right]$$

Below glass transition (T < Tg):

$$k_{diff}(T) = k_{diff}(T = T_g) \cdot \exp\left[-\frac{E(T_g)}{R}\left(\frac{1}{T} - \frac{1}{T_g}\right)\right]$$

Model with diffusion control

NETZSCH



5K/min

3,5K/min

1,9K/min

1,5K/min

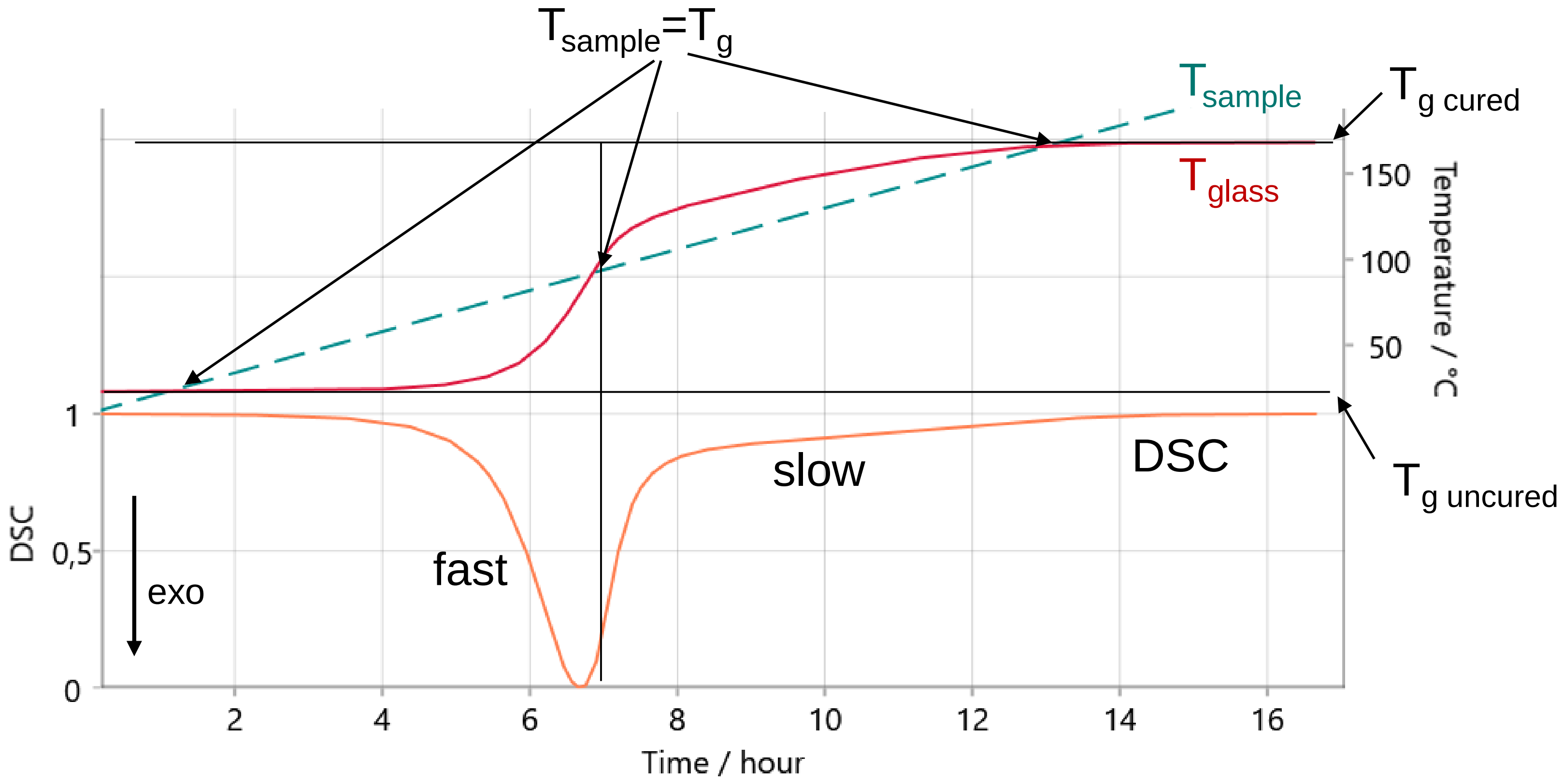
1,0K/min

0,7K/min

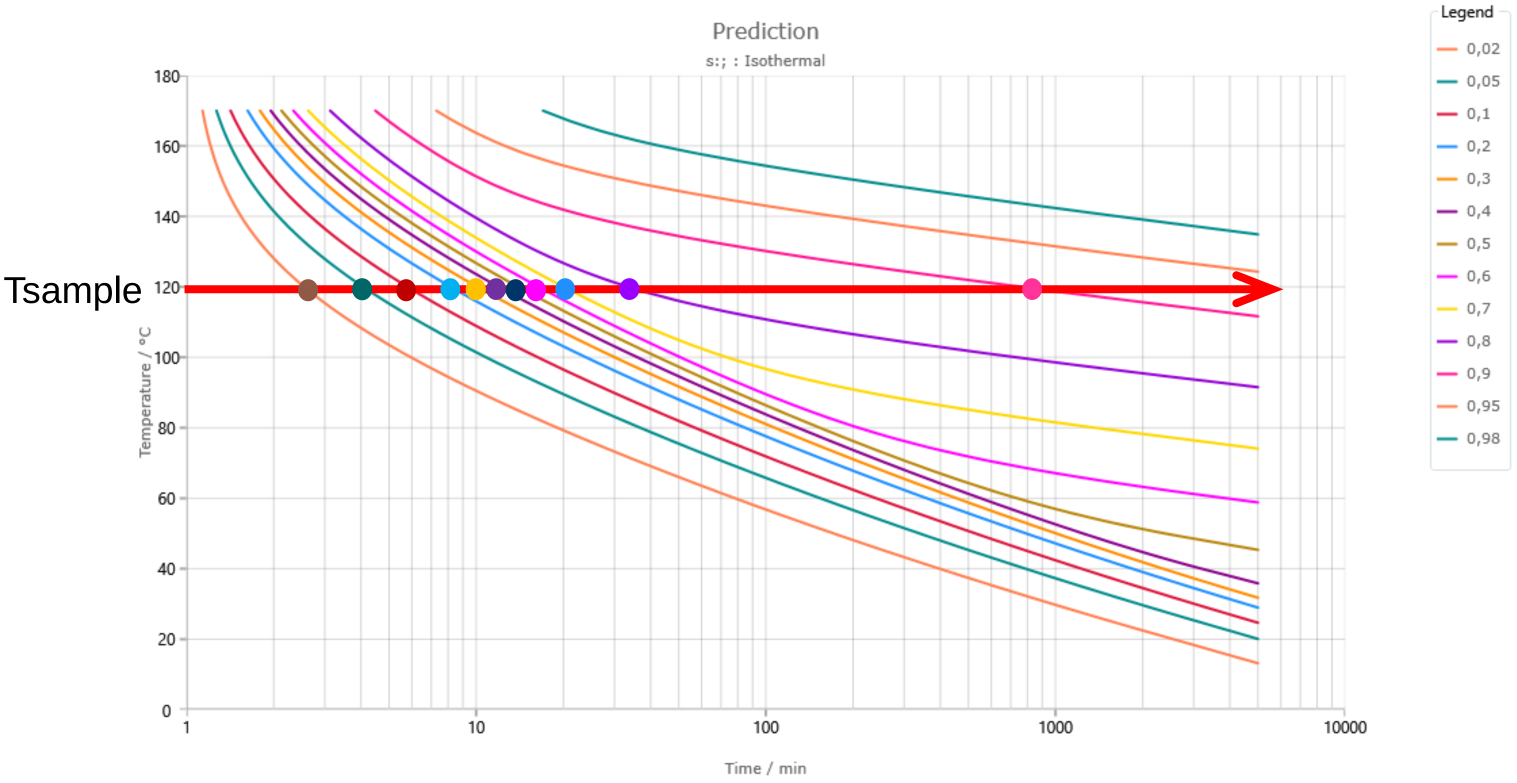
0,5K/min

0,2K/min

Predictions of glass transition

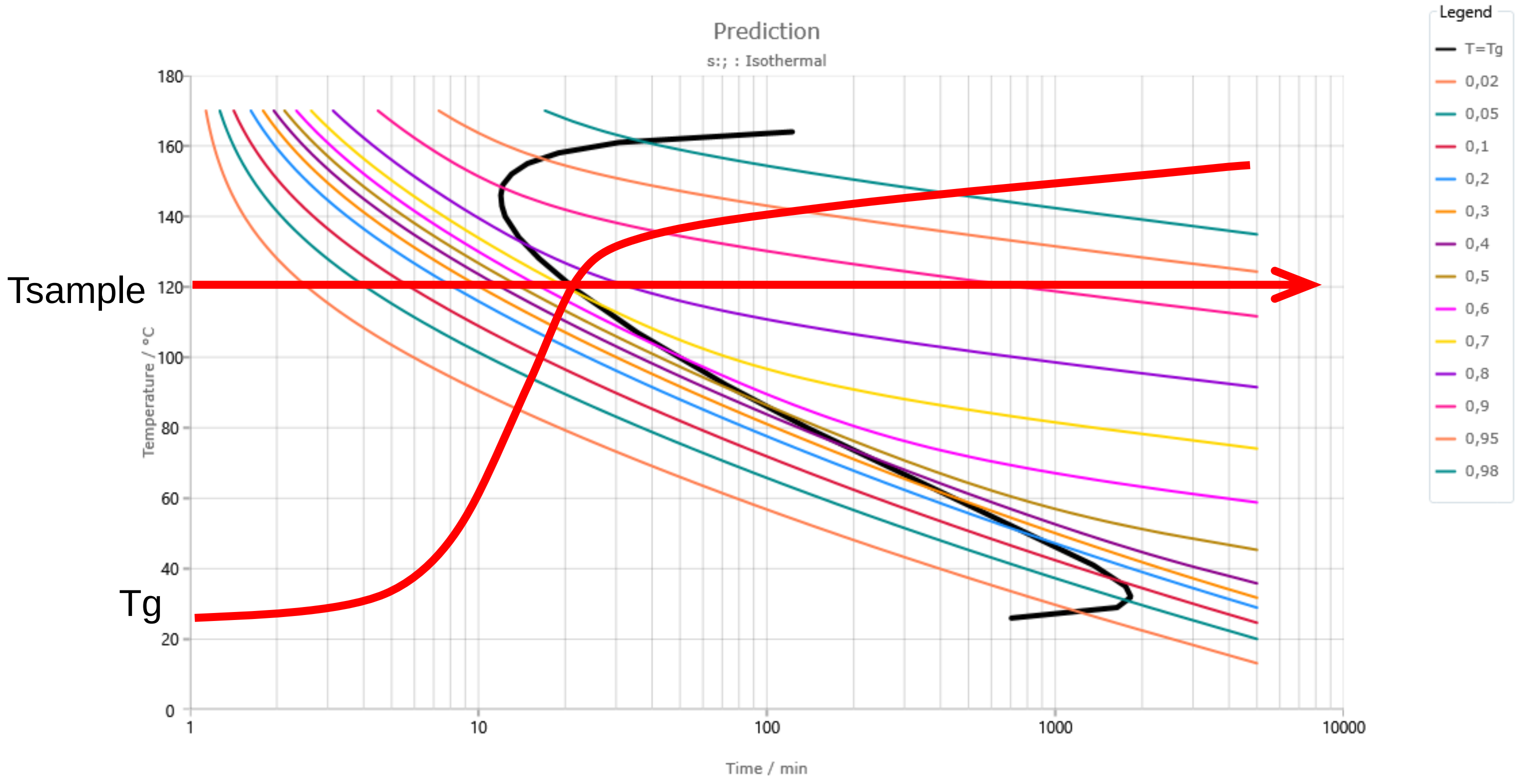


Predictions of conversion



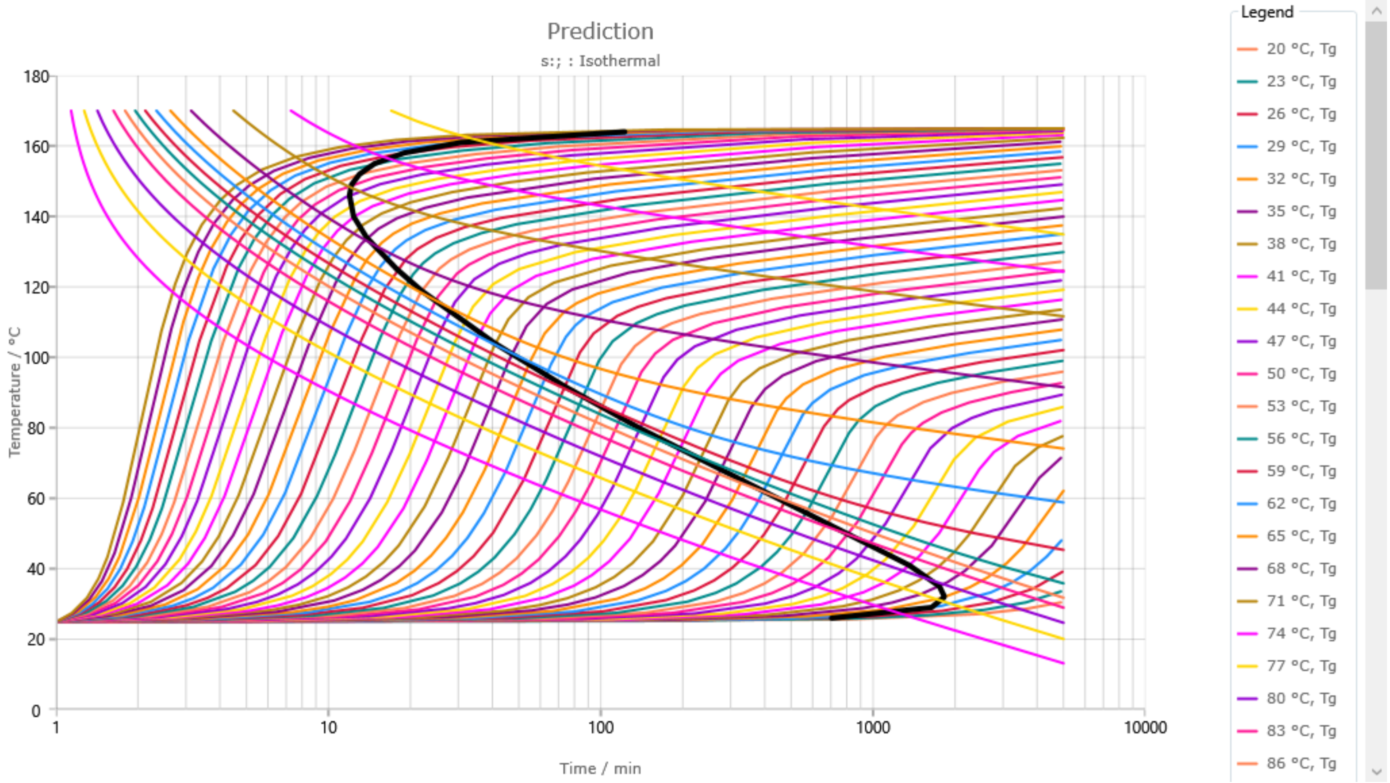
Predictions of glass transition

NETZSCH

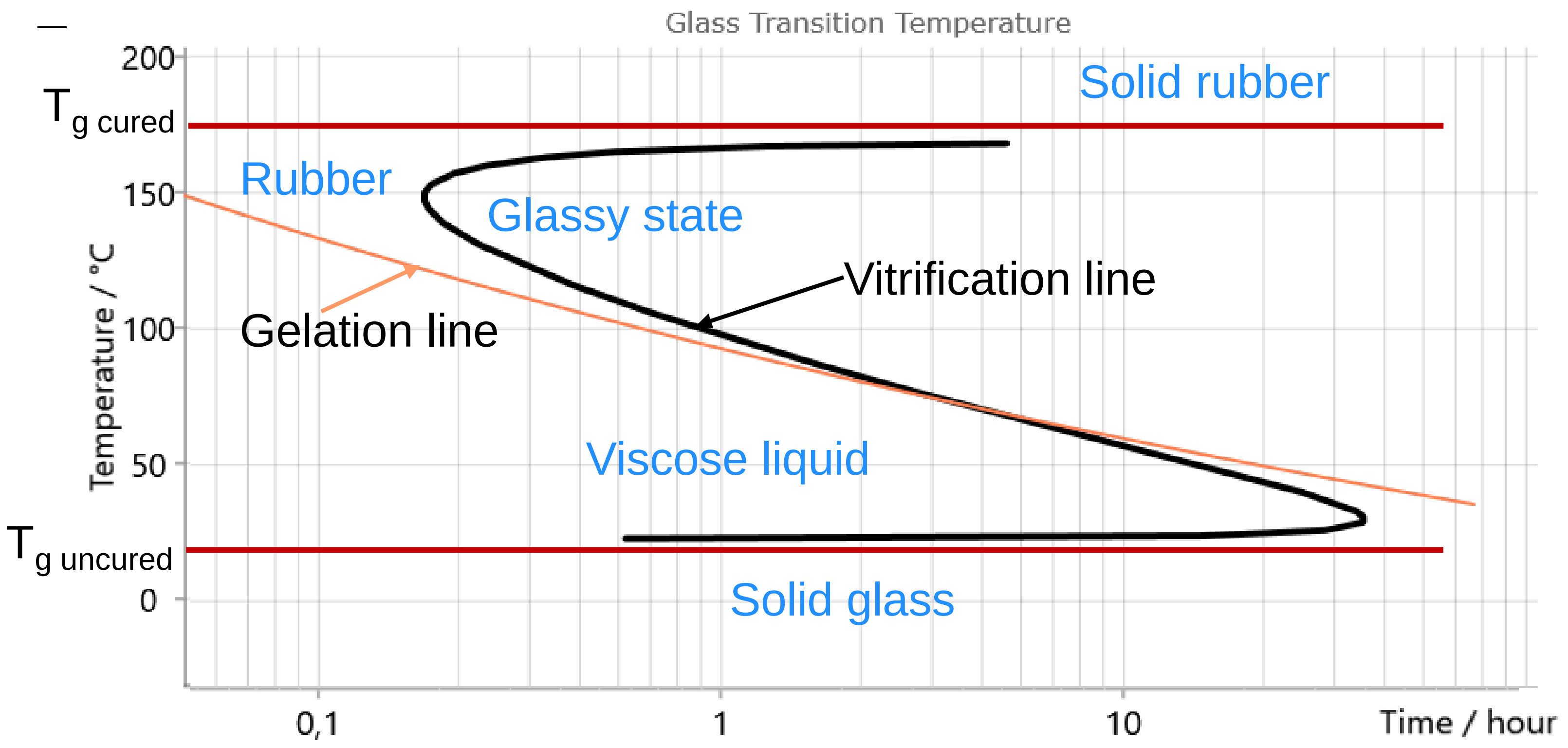


Time-Temperature-Transition diagram

NETZSCH



TTT: Time Temperature Transition diagram



What is the final state of the curing material after given time at given temperature?

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

Conclusion

NETZSCH

Special features for curing analysis

- Autocatalytical reactions including Kamal-Sourour with two different activation energies
- Kinetic models for reactions with several individual steps including the steps with different directions of exotherm
- Curing reactions with glass transition and partial diffusion control

Additional information: *kinetics.netzcsh.com*