Analyzing & Testing

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Dependence of curing kinetics on mass ratio for epoxy/amine systems and on intensity of UV light for photopolymers

Elena Moukhina
Claire Strasser

NATAS,
Dearborn, MI, August 12th, 2025

Agenda

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1. Classical methods of kinetic analysis for curing processes

   Introduction,
   Approaches

2. Actual problems of kinetic analysis:

   Autocatalysis, diffusion control, influence of additional parameter

3. Dependence of two-component curing on mass ratio of reactants

4. Dependence of photocuring on intensity of UV light

5. Conclusion

1 Classic methods of kinetic analysis for curing processes

Material properties, important for curing kinetics

Properties:

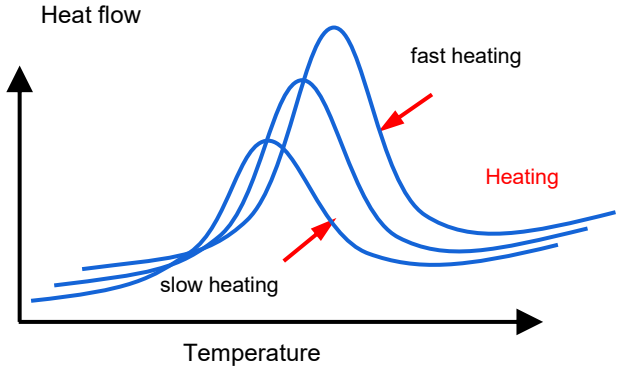
- Enthalpy of reaction
- Gel point,
- Glass transition temperature,
- Heat capacity
- Viscosity

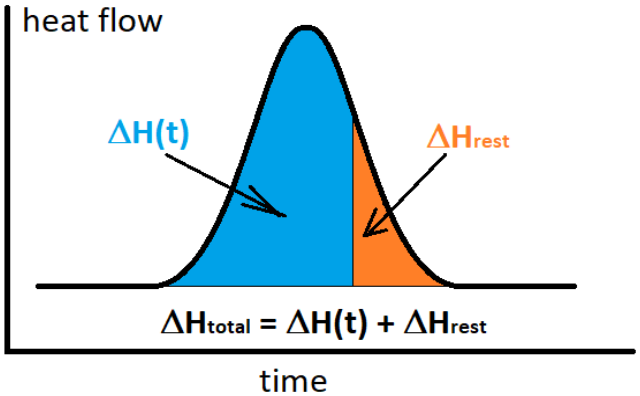
Methods:

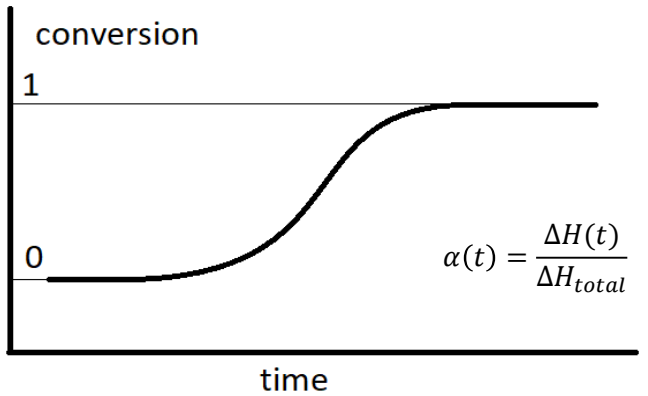
- DSC,
- TM-DSC,
- rheology,
- dielectric analysis

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

DSC







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

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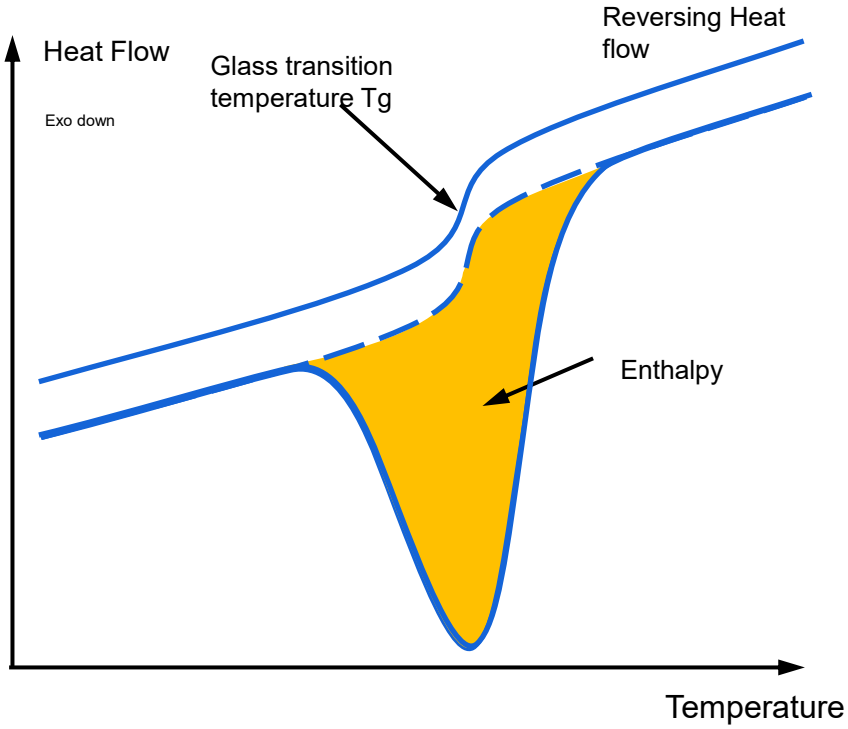
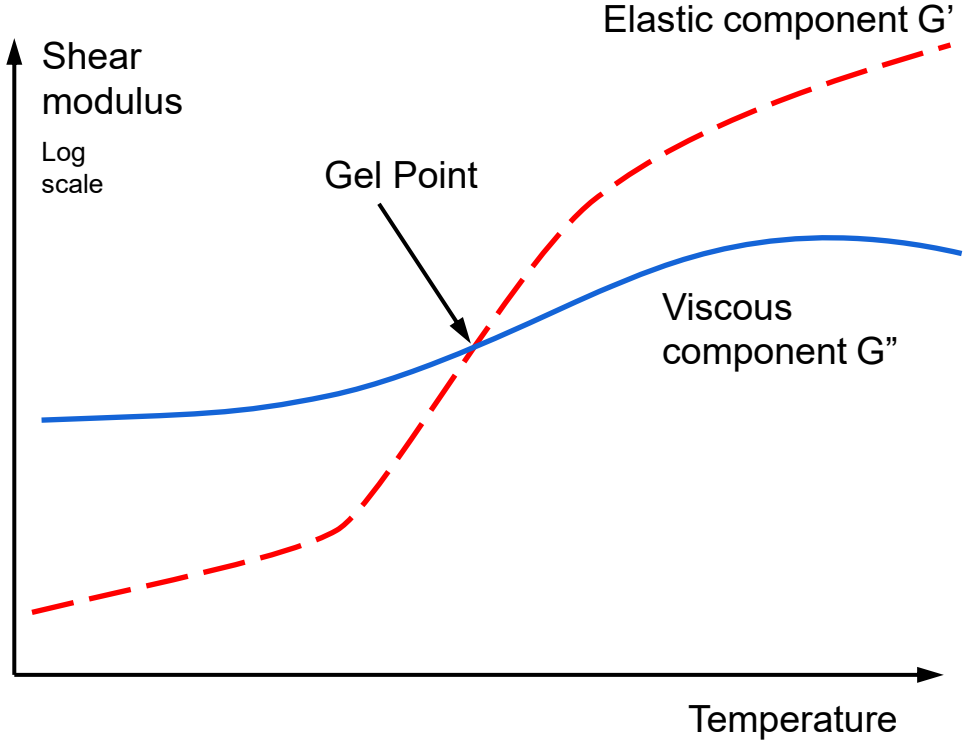
TM-DSC: baseline and glass transition



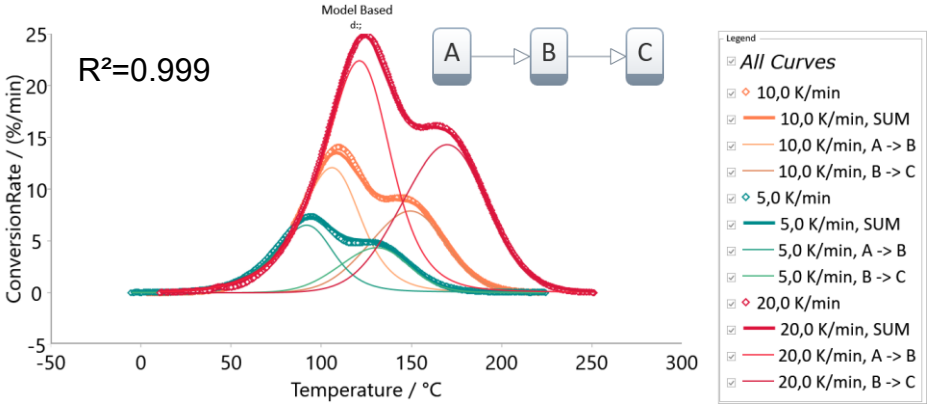
Rheology: gel point



Approaches

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

Model based: several steps with constant parameters

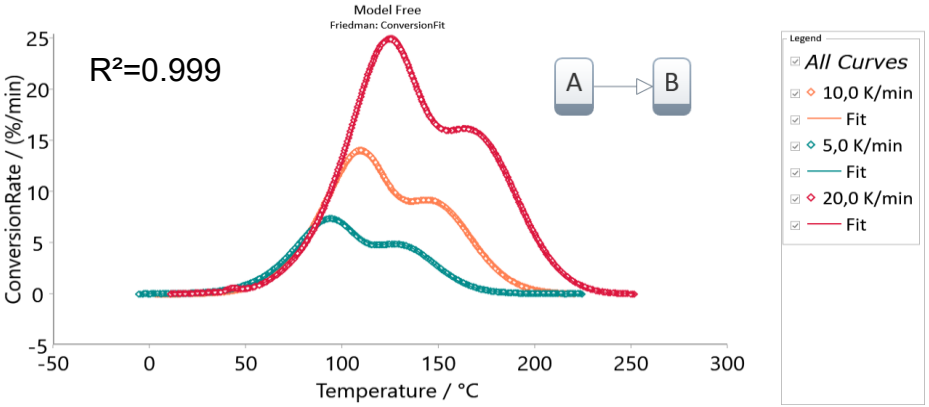


$$\frac{d(a \rightarrow b)}{dt} = A_1 \cdot f_1(a.b) \cdot exp\left(\frac{-E_{A1}}{RT}\right)$$

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

Unknown values: A_1, A_2, Ea_1, Ea_2,n_1, n_2, etc

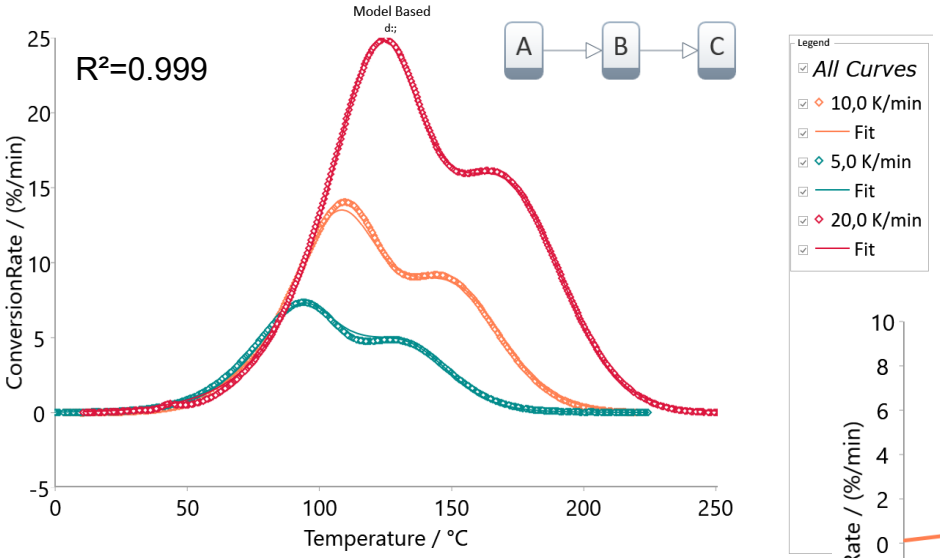
Model free: one step with variable parameters



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

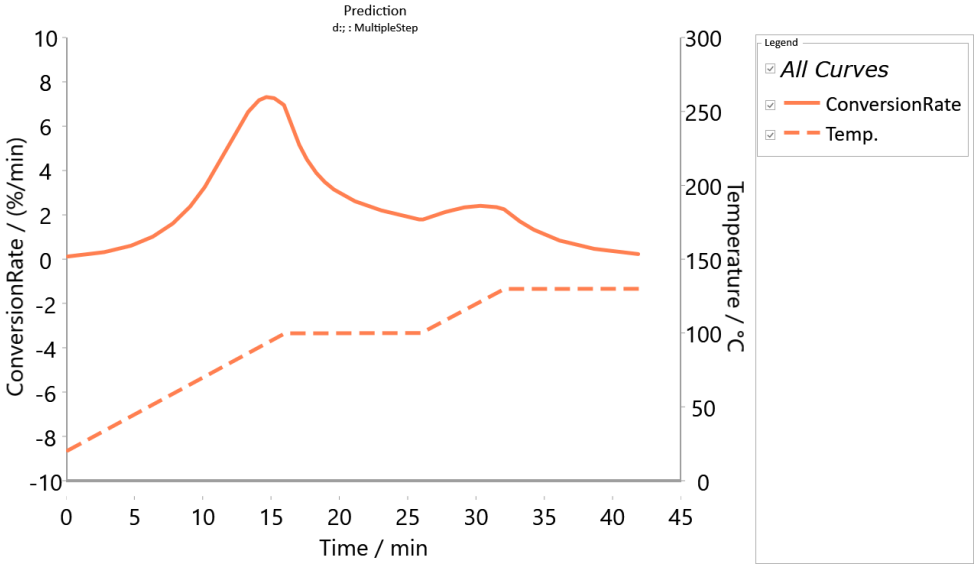
Unknown dependences: Ea(α) and A(α)

Workflow



2. Kinetic Model for the chemical reaction
Simulated curves must fit experimental data,
R^2 must be reported

3. Simulated reaction for new temperatures



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

2 Actual problems of kinetic analysis

Actual problems of kinetic analysis

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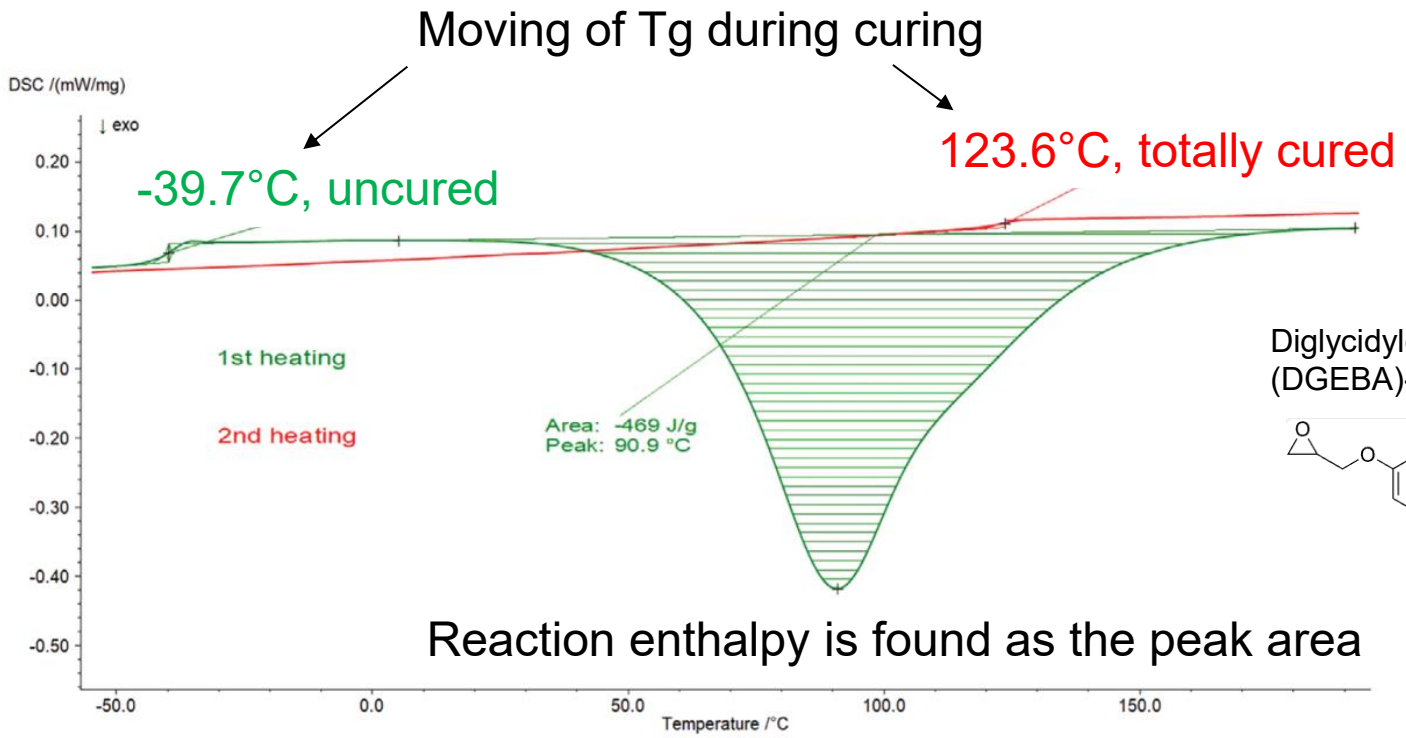
Processes, which exists in nature, but not in the classical approach

- Glass transition and diffusion-controlled reaction near it
- Vitrification
- Gelation

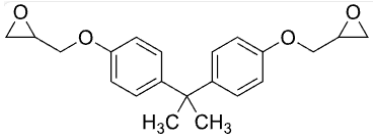
Additional parameter

- Chemical properties of surrounding (presence and concentration of gaseous/liquid reactant)
- Physical properties of surrounding (pressure of inert material)
- Concentration of additive
- Intensity of UV light for photocuring
- Mass ratio for multi-component reactions

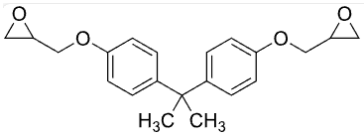
Measurements Step1: enthalpy and glass transition (DSC) for original material



Diglycidylether bisphenol A (DGEBA)-based epoxy resin.



Glass transition, gelation, vitrification: Time-Temperature-Transformation diagram based on DSC data



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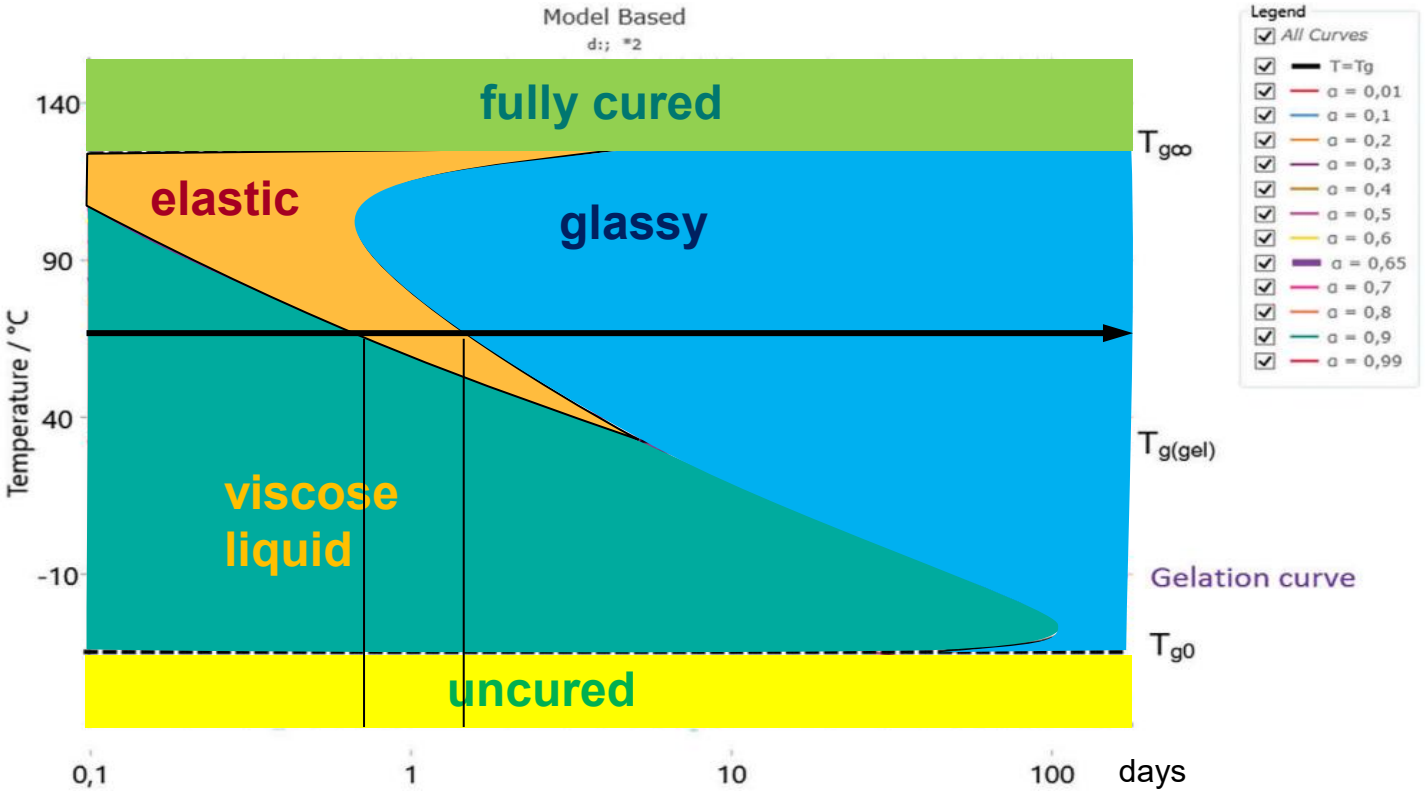
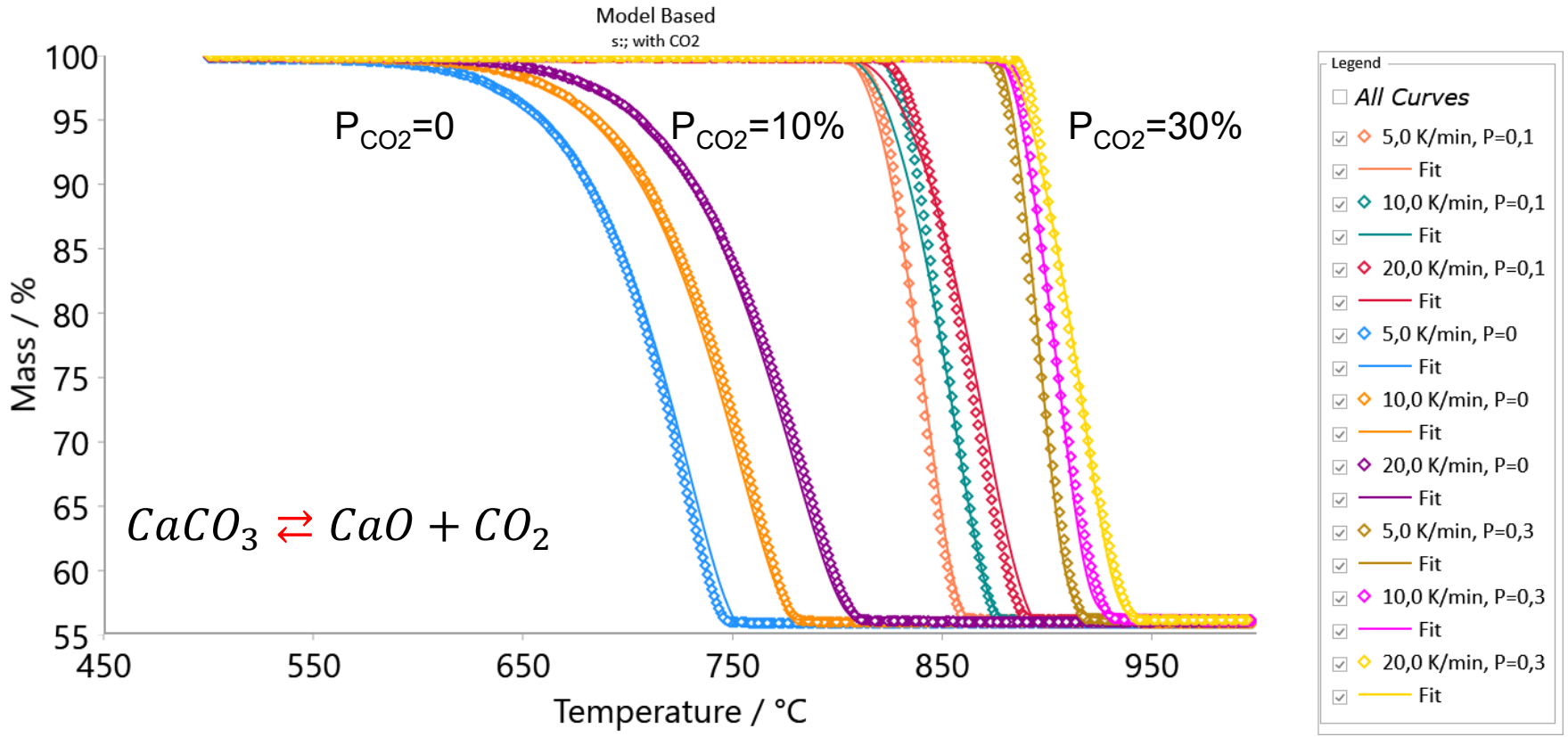


TTT diagram of the investigated epoxy resin

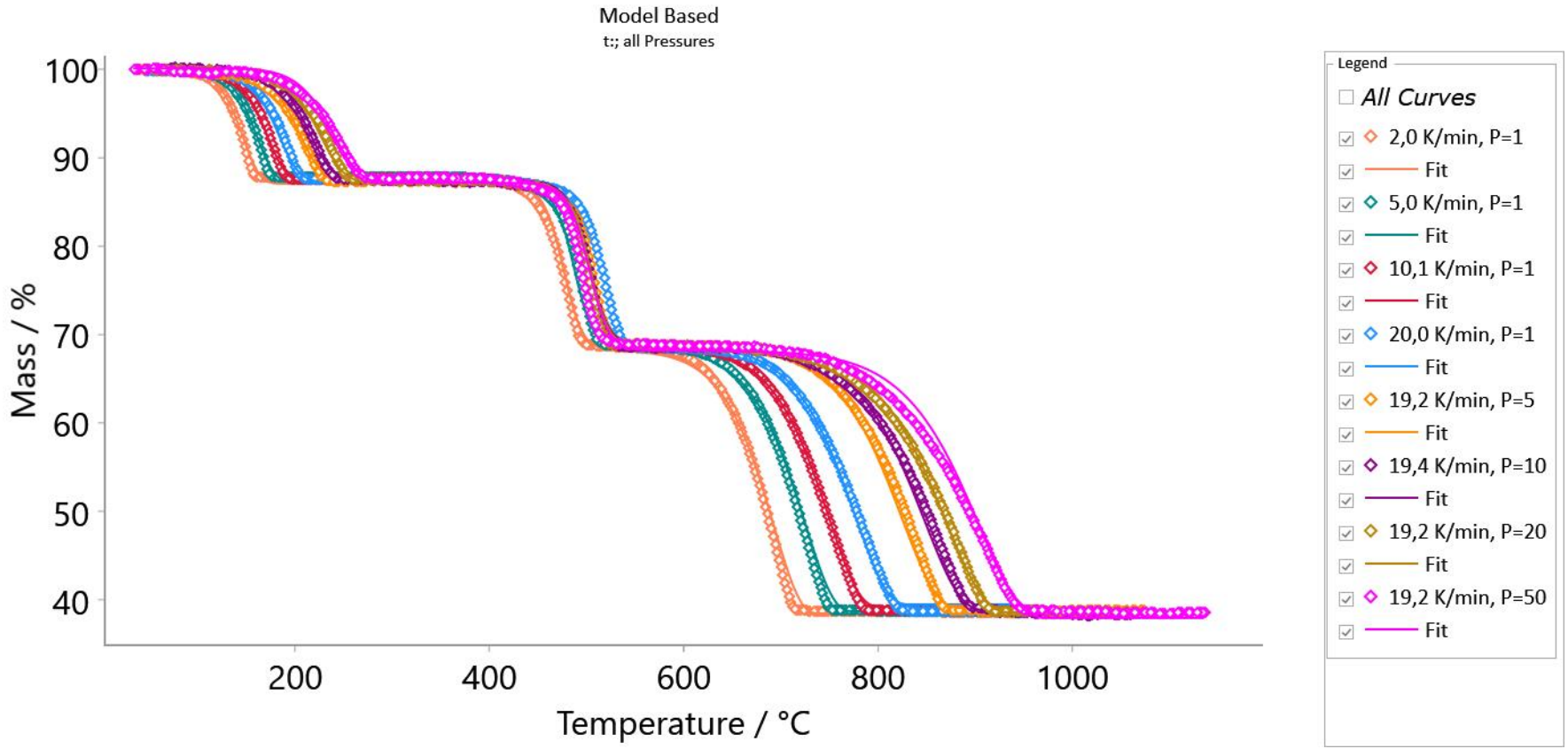
Claire Strasser, Elena Moukhina, and Jürgen Hartmann, Time–Temperature-Transformation (TTT) Cure Diagram of an Epoxy–Amine System, Macromolecules Theory and Simulations, 2024 2400039, https://doi.org/10.1002/mats.202400039

Common kinetic model for decomposition of $CaCO_3$ in Nitrogen with partial pressure CO_2 (total Pressure=1 bar)



Measurements: Jan Hanss, NGB Laboratory

Common kinetic model for decomposition of $CaC_2O_4*H_2O$ in Nitrogen, different pressures from 1 bar to 50 bar, different heating rates: see legend



Actual problems of kinetic analysis

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- Mass ratio for multi-component reactions
- Intensity of UV light for photocuring

3 Dependence of two-component curing on mass ratio of reactants

Curing reaction in solids: why stoichiometry does not work

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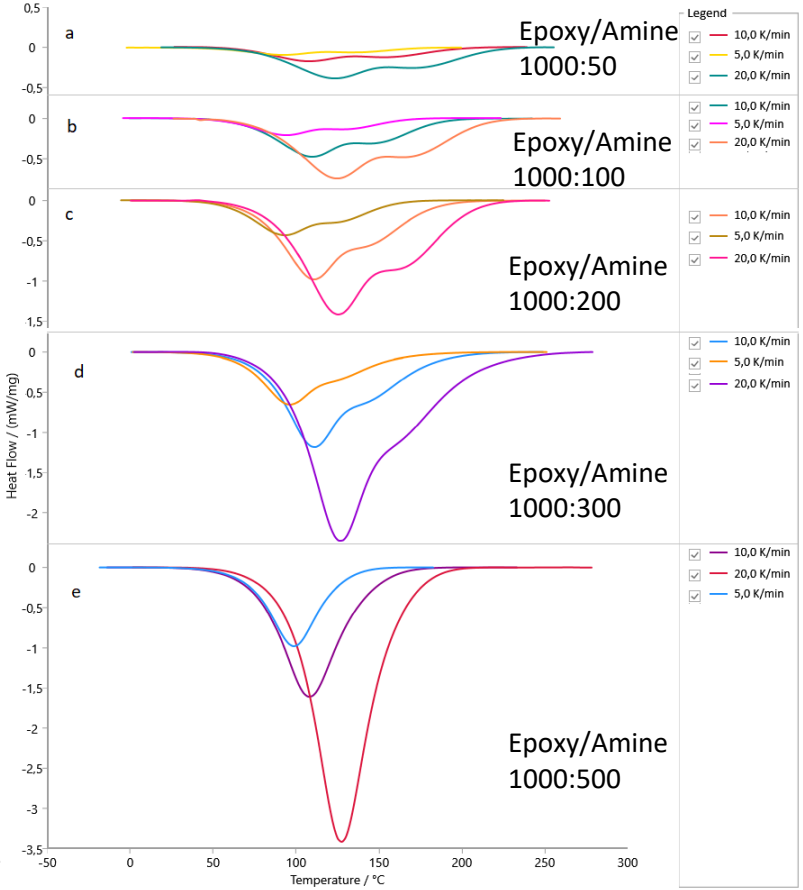
- Morphological effects
  e.g particle shape
- Complex chemical mechanisms
  10 individual reactions are present, but only one peak is seen
- Presence of solvents or additives
- Impurities
- Exact molar masses of oligomers are unknown
- Exact molar concentrations of additives are unknown

Experimental data: DGEBA (double peak)



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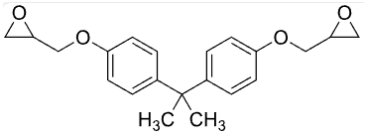
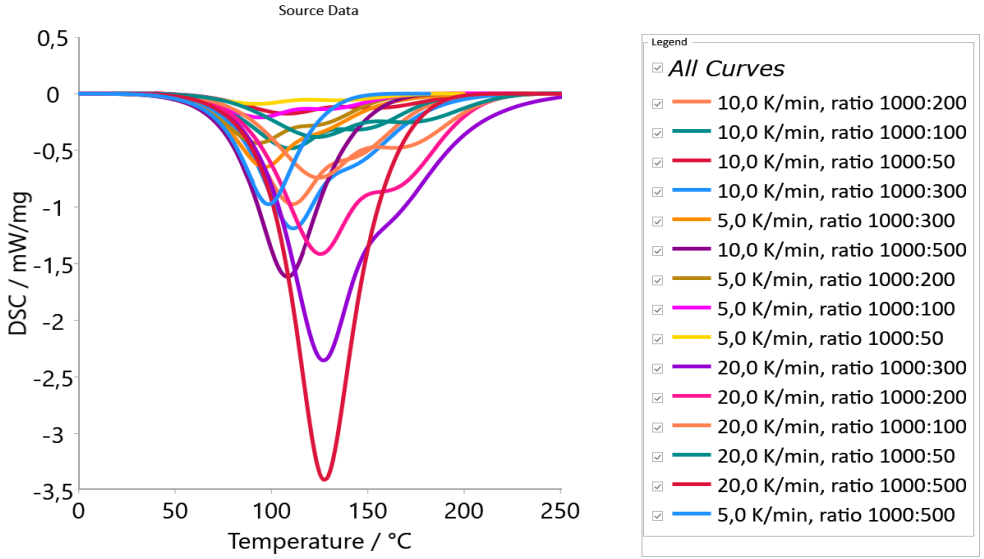
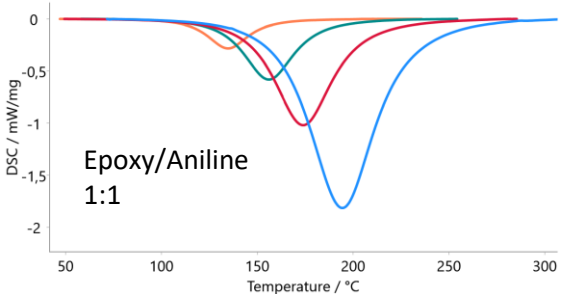
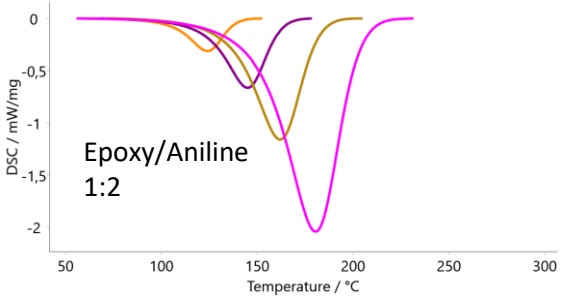
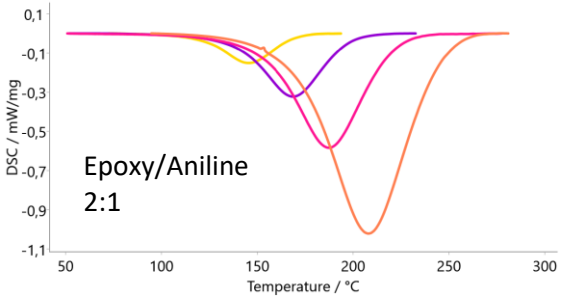




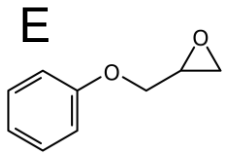
Experimental data: Phenylglycidether (single peak)

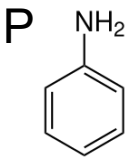




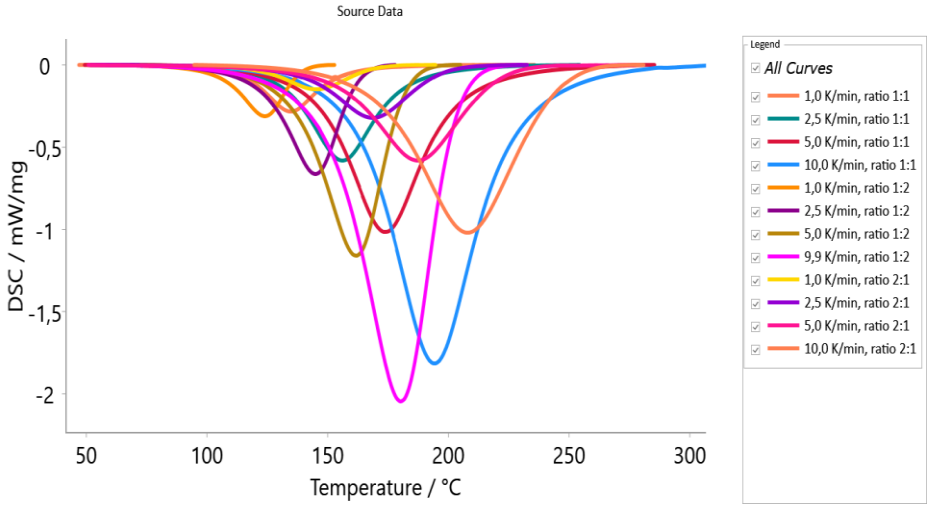


Phenylglycidether (epoxy) and bifunctional amine (aniline)

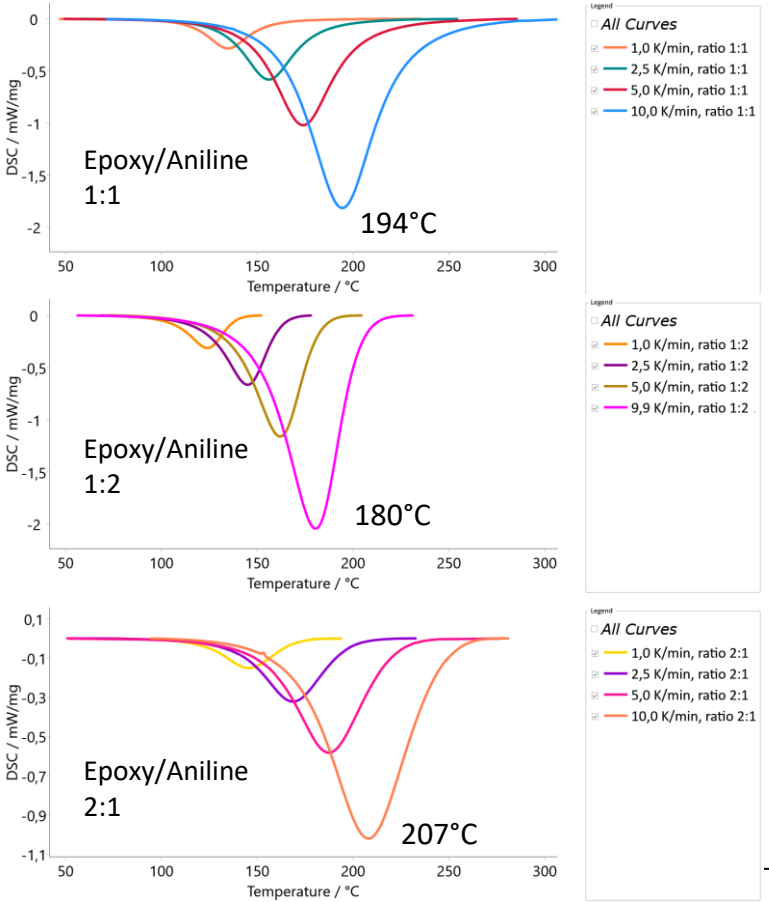




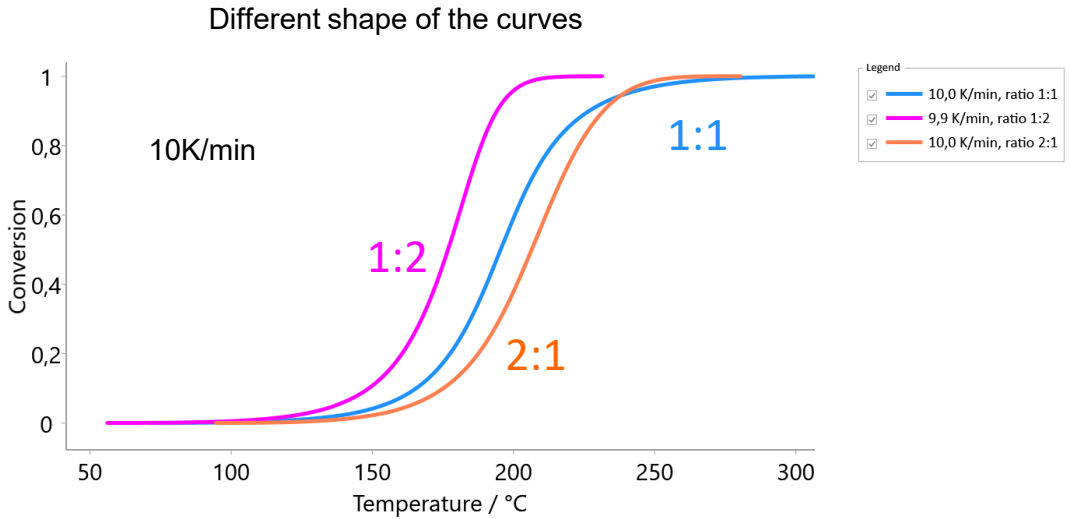
Experiment: single peak



Different shape of the curves

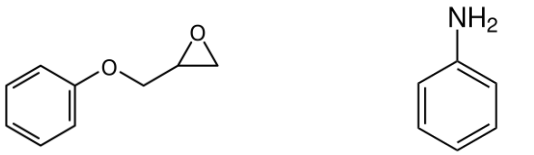


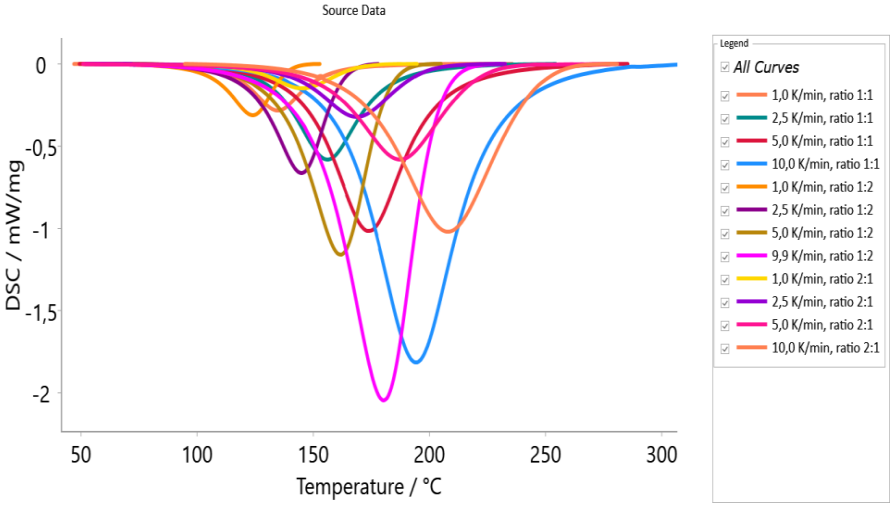
Reactant ratio		Kinetic parameters				
Epoxy	Amine	Log(Pre-exp) log(1/s)	Ea kJ/mol	n -	Log(kCat) log(1/s)	Enthalpy J/g
1	1	2.9	54	1.8	1.3	538
1	2	3.3	54	1.1	1.1	453
2	1	3.0	54	1.0	1.1	313



Peak position for different concentrations

Phenylglycidether (epoxy) and bifunctional amine (aniline)





Experiment: single peak

Brutto reaction: $P + E \xrightarrow{k_P} S$, $S + E \xrightarrow{k_S} T$

P: Anilin, $C_6H_5\text{-}NH_2$

E: Phenylglycidether, $C_6H_5\text{-}O\text{-}CH_2\text{-}CH\text{-}CH_2$ (O)

S: $C_6H_5\text{-}N(H)\text{-}CH_2\text{-}CH(OH)\text{-}CH_2\text{-}O\text{-}C_6H_5$

T: $C_6H_5\text{-}N(CH_2\text{-}CH(OH)\text{-}CH_2\text{-}O\text{-}C_6H_5)_2$

Stoichiometry

$E + OH \xleftrightarrow{K_1} E\cdots OH$

$P + OH \xleftrightarrow{K_2} P\cdots OH$

$S + OH \xleftrightarrow{K_3} S\cdots OH$

$E + P \xleftrightarrow{K_4} E\cdots P$

$EOH + P \xrightarrow{k_1} S + 2\,OH$

$EOH + POH \xrightarrow{k_2} S + 3\,OH$

$EOH + S \xrightarrow{k_3} T + 2\,OH$

$EOH + SOH \xrightarrow{k_4} T + 3\,OH$

$EP + P \xrightarrow{k_5} S + P + OH$

Analysis of single peak can not be used for 13 reactions

Problem and theoretical solution

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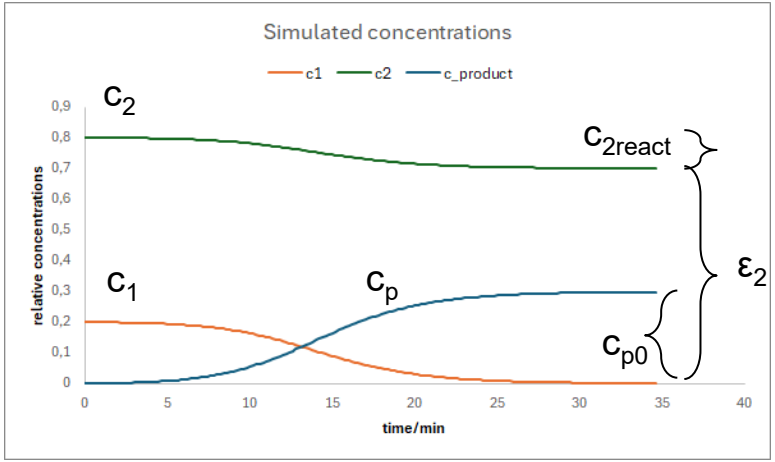
Problem:

$$n_1 R_1 + n_2 R_2 \rightarrow P$$

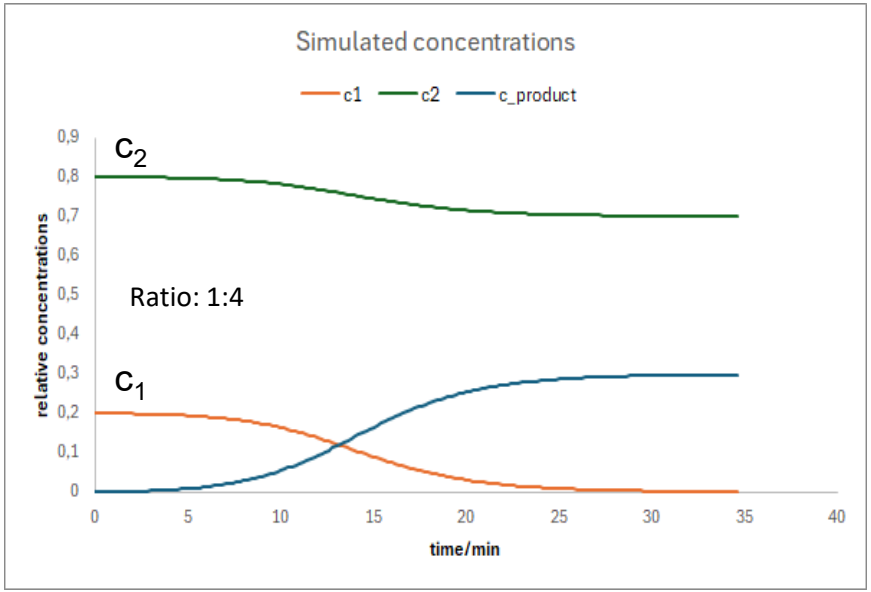
$$\frac{d\alpha}{dt} = A \cdot (1-\alpha)^n \cdot \exp\left(\frac{-E_a}{RT}\right)$$

$$\frac{dc_P}{dt} = A_o * {c_1}^{n_1} * {c_2}^{n_2} \exp\left(\frac{-E_a}{RT}\right)$$

$$c_1 = c_{1react} + \varepsilon_1 \qquad c_2 = c_{2react} + \varepsilon_2$$



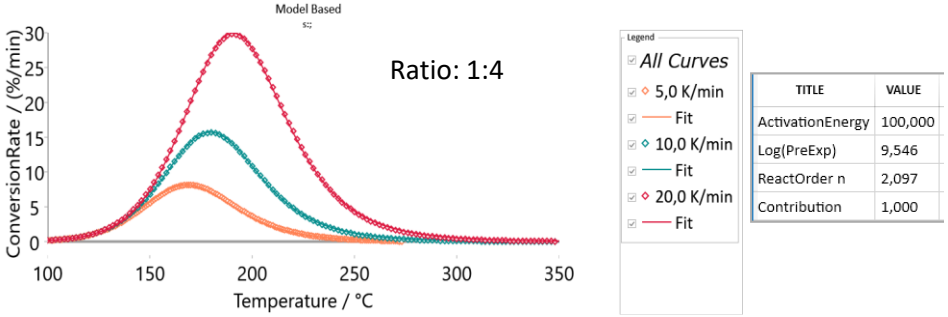
Data for verification of theoretical solution



Simulation with known parameters
n_1=2, n_2=1, Log(A)=10, E=100, Kcat=1

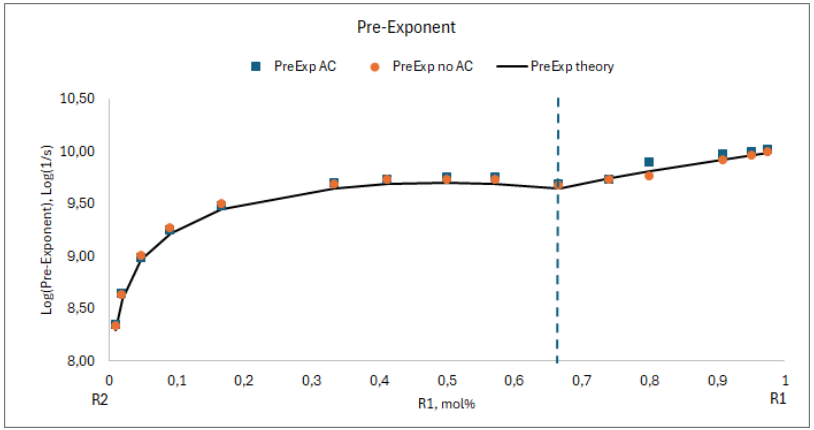
Kinetic analysis must find those parameters

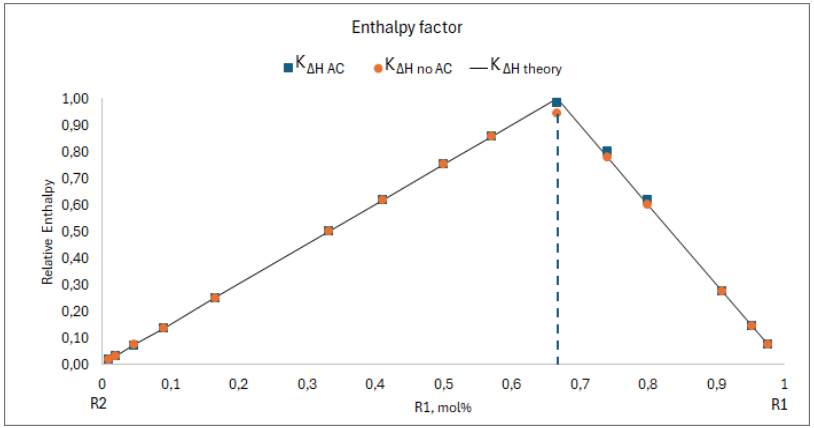
which were used for simulation

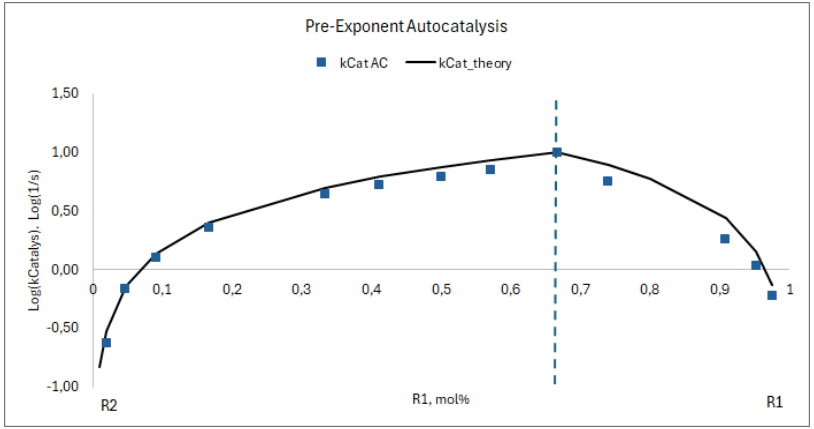


Ratios		No Autocatalysis				Autocatalysis			
c_{10}	c_{20}	Ea kJ/mol	PreExp no AC log(1/s)	n no AC	Peak Area no AC	PreExp $_{AC}$ log(1/s)	n $_{AC}$	kCat $_{AC}$ log(1/s)	Peak Area $_{AC}$
40	1	100	9.99	1.05	0,07	10.01	1.01	-0.23	0,07
20	1	100	9.96	1.09	0,14	9.99	1.03	0.03	0,15
10	1	100	9.91	1.20	0,27	9.97	1.10	0.26	0,28
2	1	100	9.67	2.99	0,95	9.68	3.00	0.99	0,95
4	3	100	9.72	2.59	0,86	9.74	2.49	0.85	0,81
1	1	100	9.73	2.40	0,75	9.75	2.30	0.79	1,00
7	10	100	9.72	2.26	0,62	9.73	2.18	0.72	0,63
1	2	100	9.68	2.18	0,5	9.69	2.11	0.64	0,51
1	5	100	9.49	2.08	0,25	9.48	2.02	0.35	0,25
1	10	100	9.26	2.05	0,14	9.25	2.01	0.10	0,14
1	20	100	9.00	2.03	0,07	8.98	2.01	-0.17	0,07
1	50	100	8.63	2.02	0,03	8.63	2.00	-0.63	0,03
1	100	100	8.33	2.02	0,02	8.34	2.00		0,02

Solution: theoretical curves

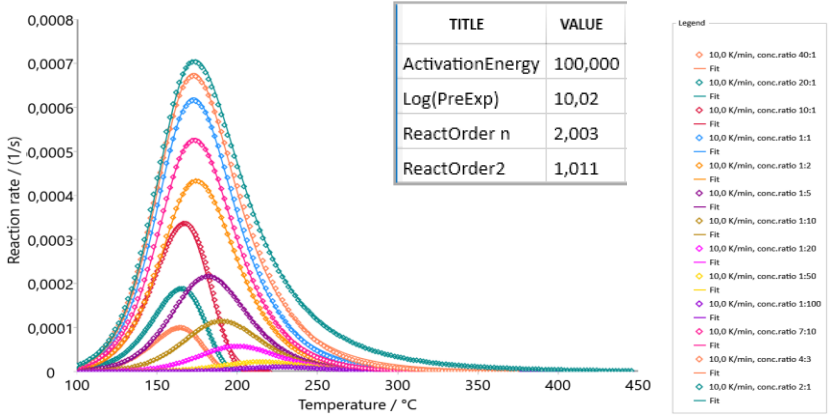


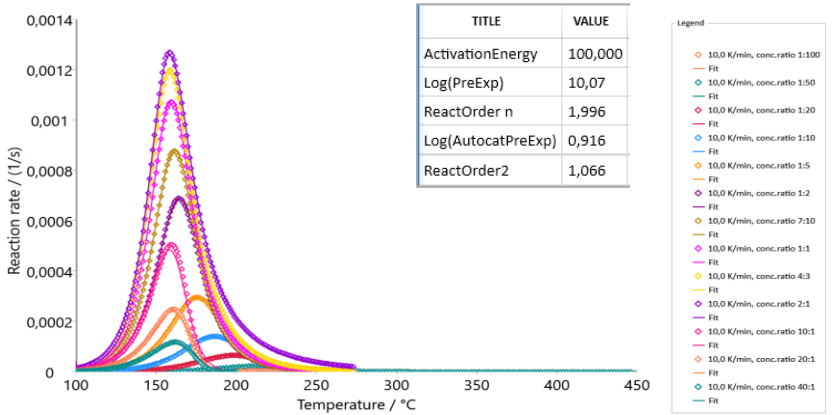


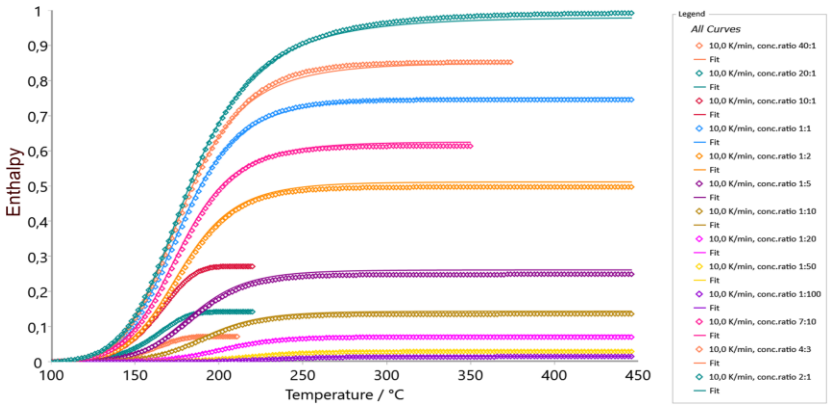


Vertical dashed line presents the optimal ratio

Verification of theory on simulated data: common kinetic model





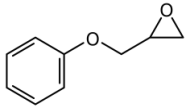


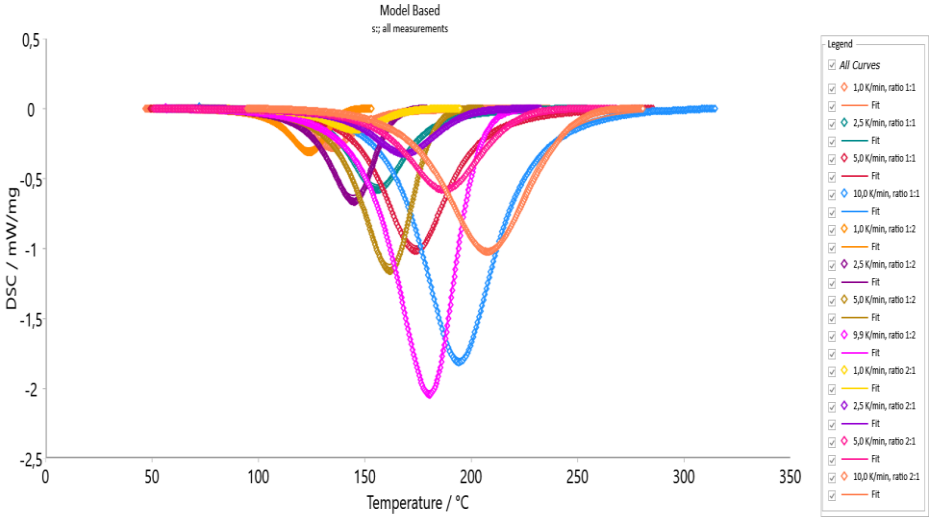
Simulation with known parameters
n_1=2, n_2=1, Log(A)=10, E=100, Kcat=1

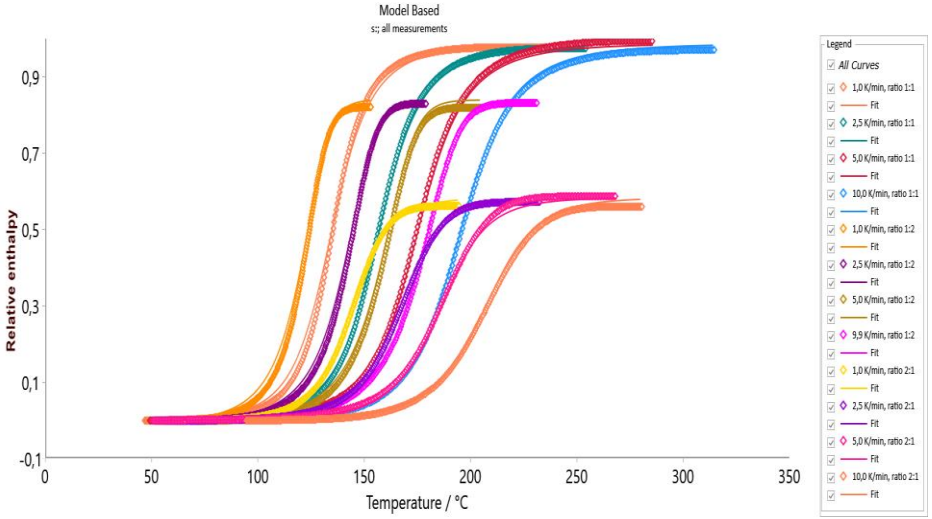
Verification procedure provide expected parameters

Maximal enthalpy is for optimal ratio

Kinetics Neo: common kinetic model: Phenylglycidether (single peak) for all concentration ratios and all heating rates







Kinetics Neo: common kinetic model: DGEBA (double peak) for all concentration ratios and all heating rates

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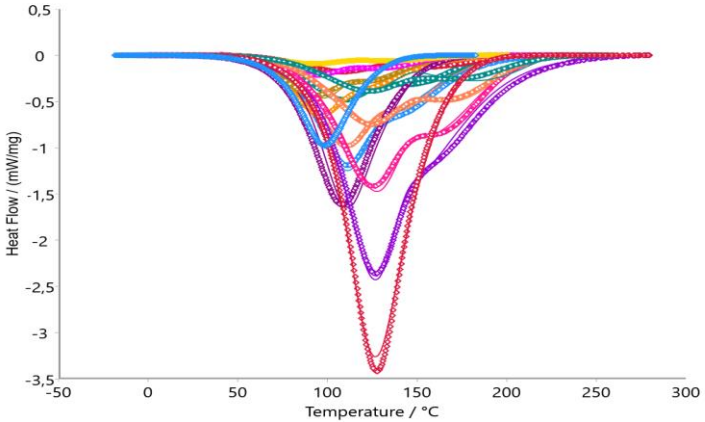
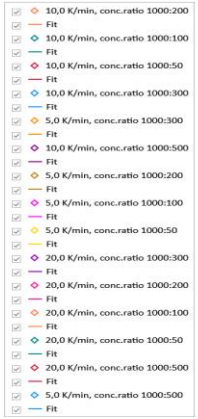
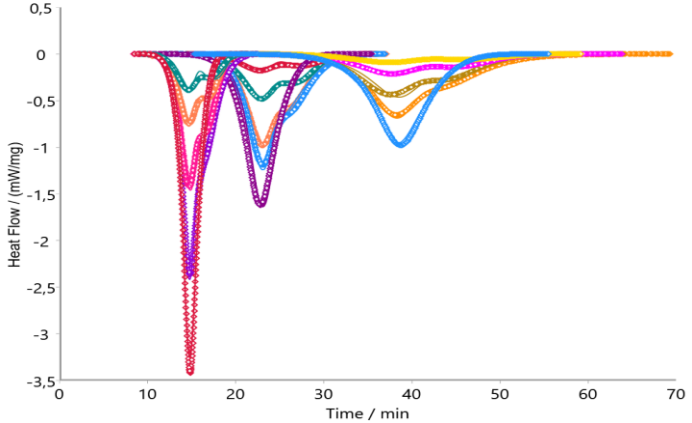
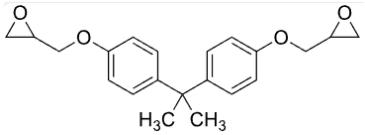
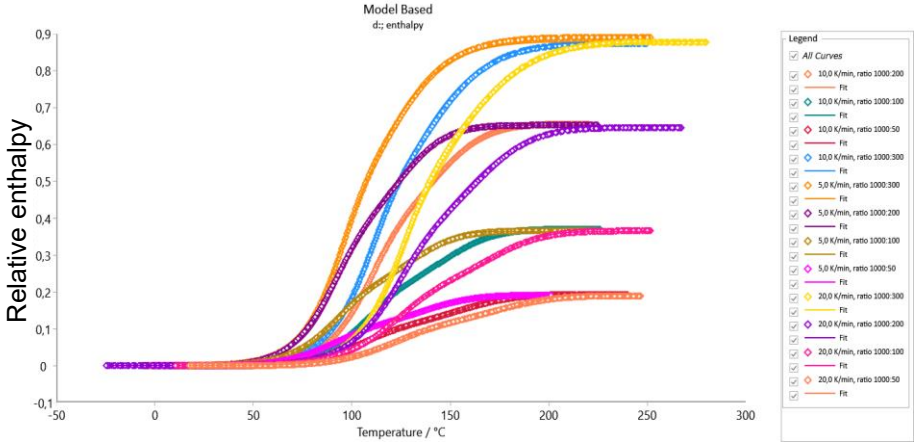






Diglycidylether bisphenol A (DGEBA)-based epoxy resin.





4 Dependence of photocuring on intensity of UV light

Experimental

Photocentric

Measurement by NETZSCH DEA 288

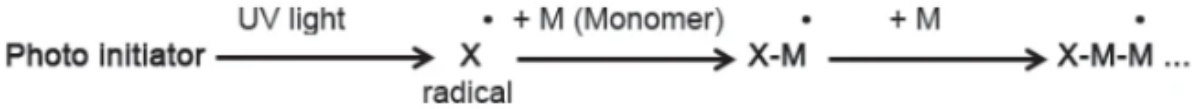
Light source: OmniCure® S 2000,
wave length: 320 nm to 500 nm

IDEX sensor for DEA cure monitoring

Polymers for Additive Manufacturing
Acrylate based photopolymers
tradename “UV DLP Firm”
from company Photocentric 3D

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

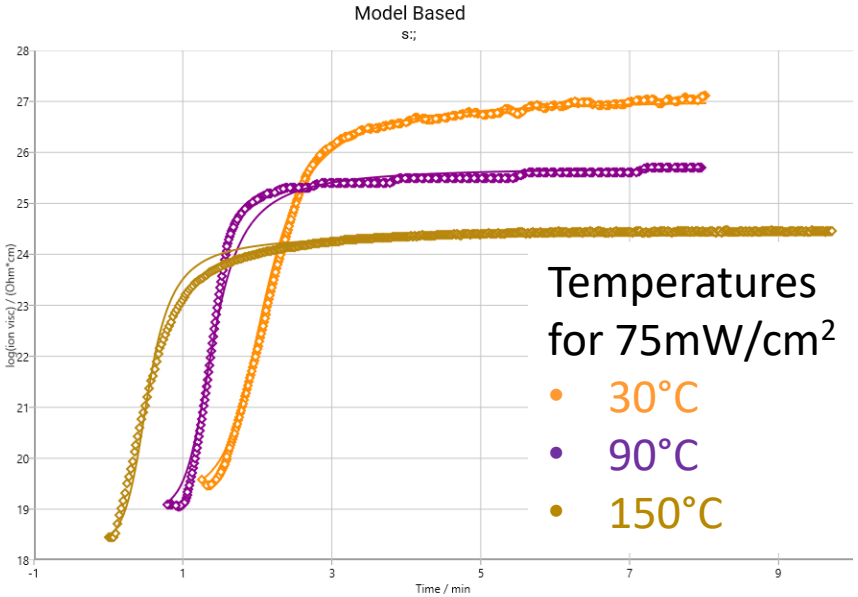
Free-radical polymerization



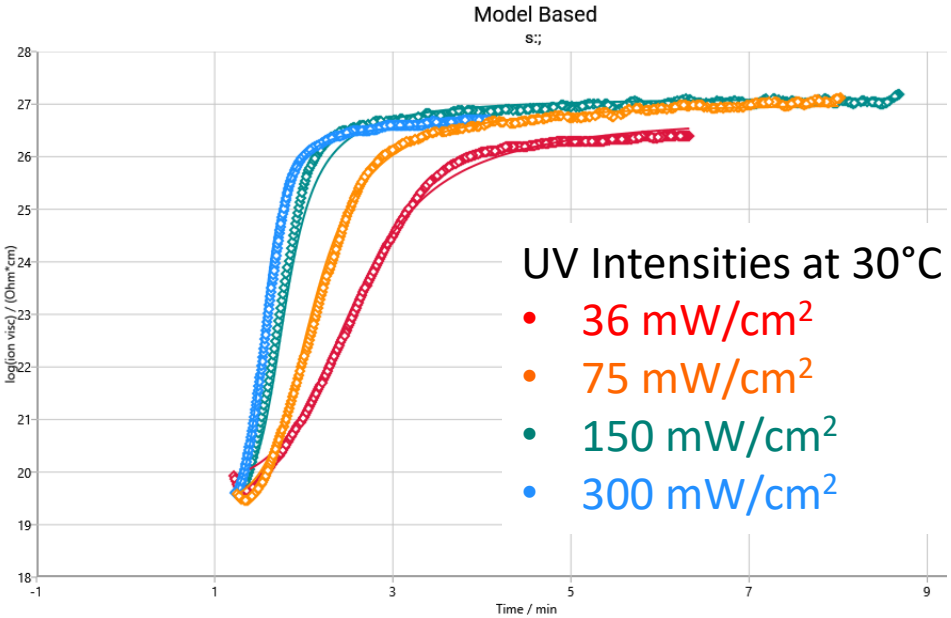
$$\frac{d\alpha}{dt} = Intensity^{n} A \, exp\left(\frac{-E_A}{RT}\right) f(\alpha)$$

Applications: coating, electronic materials, printing, additive manufacturing and packaging by using of UV curable resins or UV inks.

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



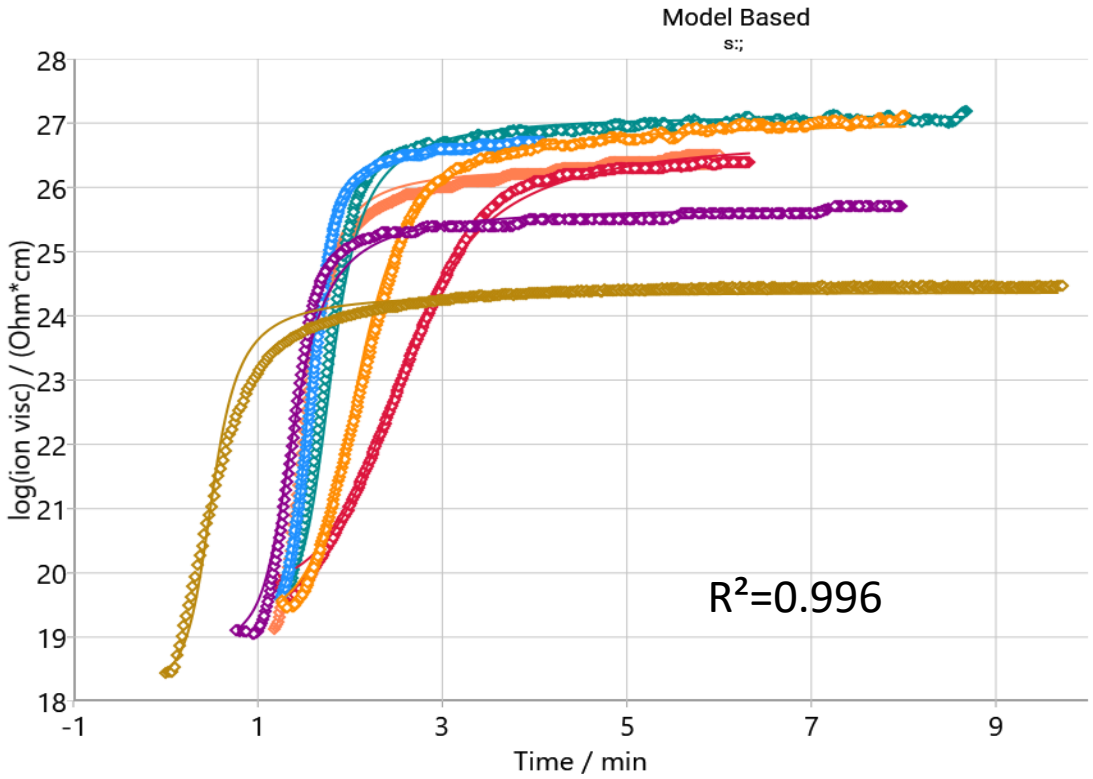
Isothermal DEA measurements at 30°C, 90°C, 150°C for light exposure at 75mW/cm²



Isothermal DEA measurements at 30°C for light exposure at different intensities from 75mW/cm² to 150mW/cm²

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



Temperatures

- 30°C
- 90°C
- 150°C

UV Intensities

- 36mW/cm²
- 75mW/cm²
- 150mW/cm²
- 300mW/cm²

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

5 Conclusion

Agenda

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1. Classical methods of kinetic analysis for curing processes

   Introduction,
   Approaches

2. Actual problems of kinetic analysis:

   Autocatalysis, diffusion control, influence of additional parameter

3. Dependence of two-component curing on mass ratio of reactants

4. Dependence of photocuring on intensity of UV light

5. Conclusion

Unique: Kinetics Analysis must fulfils ICTAC kinetics recommendations

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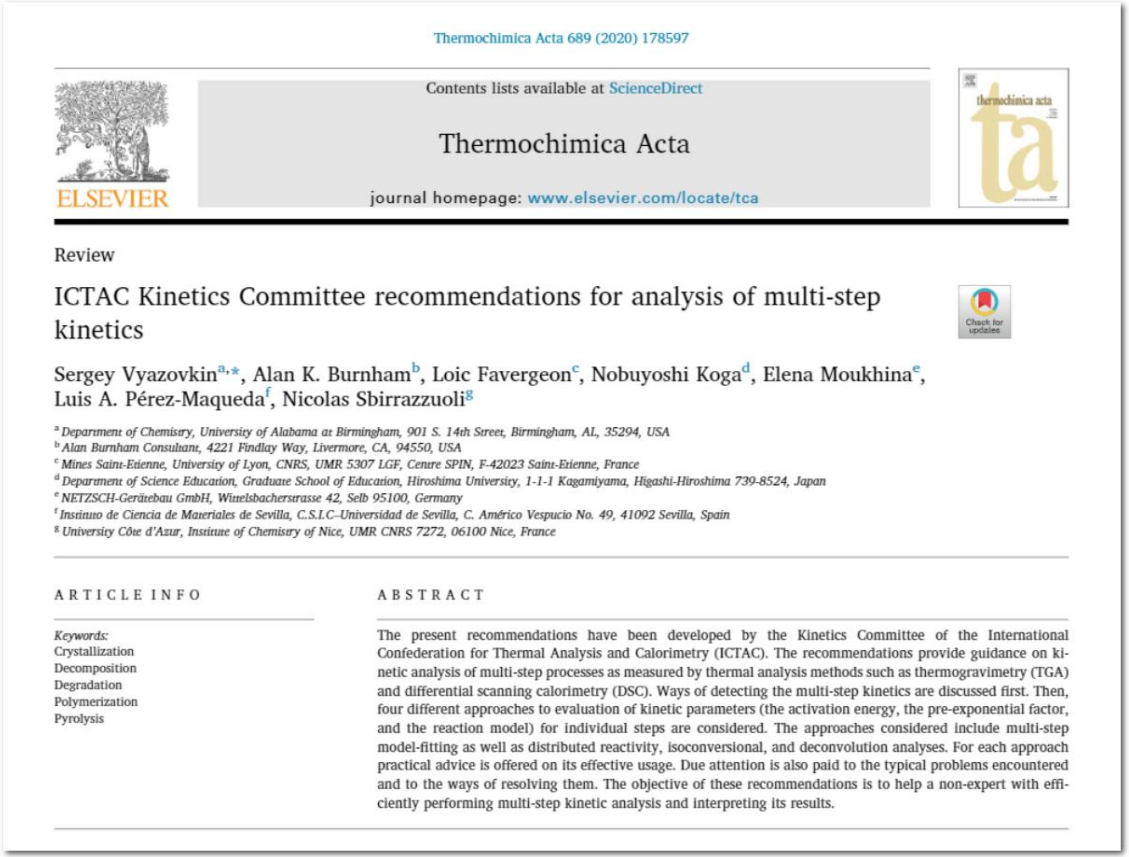
International Confederation for Thermal Analysis and Calorimetry



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Review

ICTAC Kinetics Committee recommendations for analysis of multi-step kinetics

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ARTICLE INFO

Keywords:
Crystallization
Decomposition
Degradation
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)

KINETICS NEO

NETZSCH Kinetics Neo Web Site

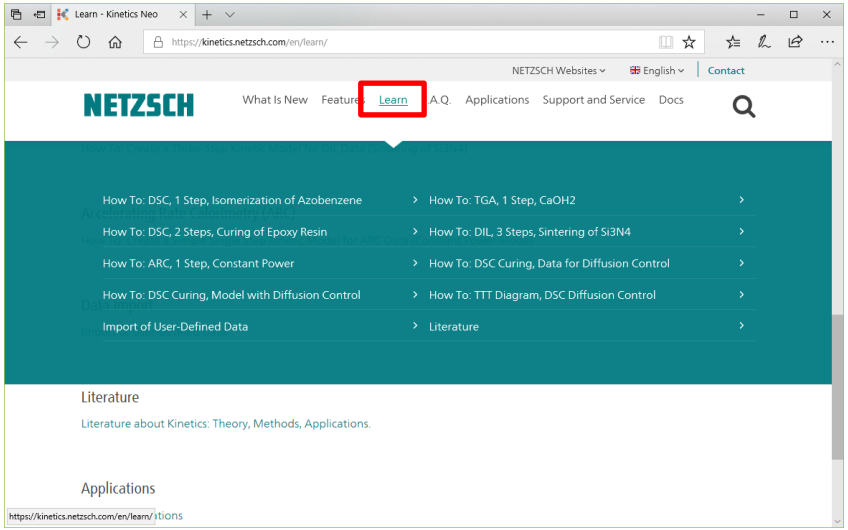
https://kinetics.netzsch.com

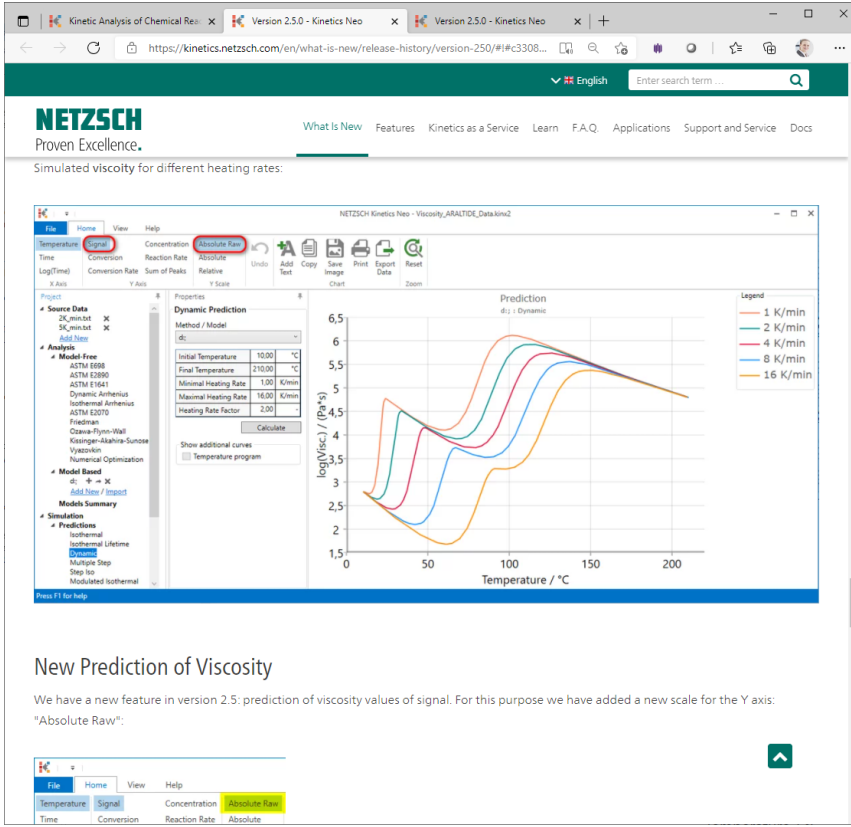
Users Guide, Training examples,

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





Curing reaction in solids: why stoichiometry does not work

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Dependence of two-component curing on mass ratio of reactants

Dependence of photocuring on intensity of UV light

- Morphological effects
  e.g particle shape
- Complex chemical mechanisms
  10 individual reactions are present, but only one peak is seen
- Presence of solvents or additives
- Impurities
- Exact molar masses of oligomers are unknown
- Exact molar concentrations of additives are unknown

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