Kinetic analysis of epoxy-based composite curing

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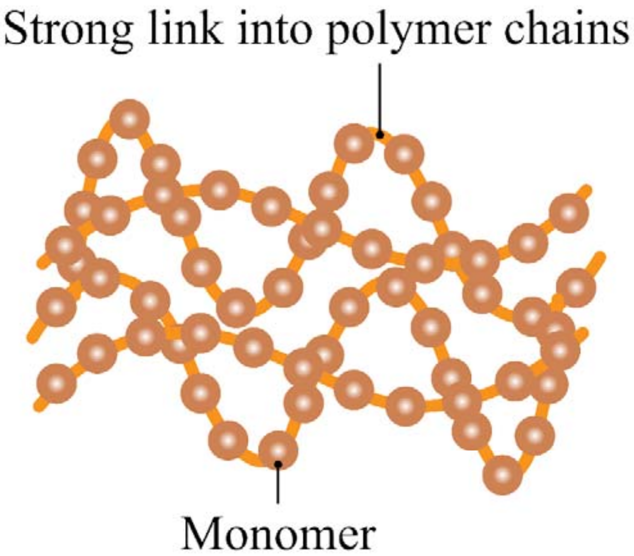
OUTLINE

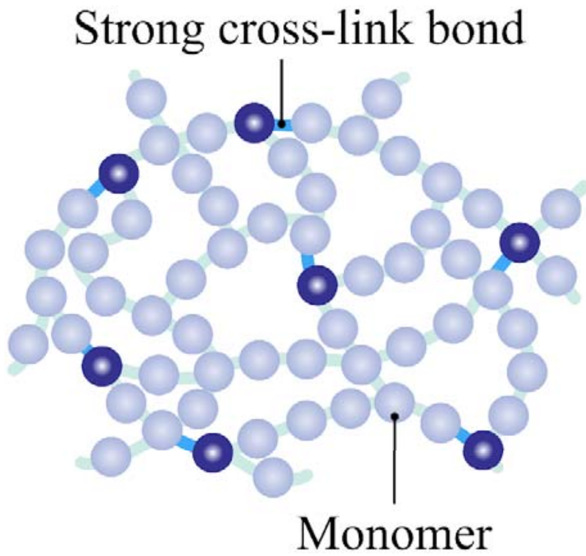
Resin curing

thermoplastic



- Weak intermolecular forces between polymer chains
- No cross-links between chains
- Softens when heated

thermoset



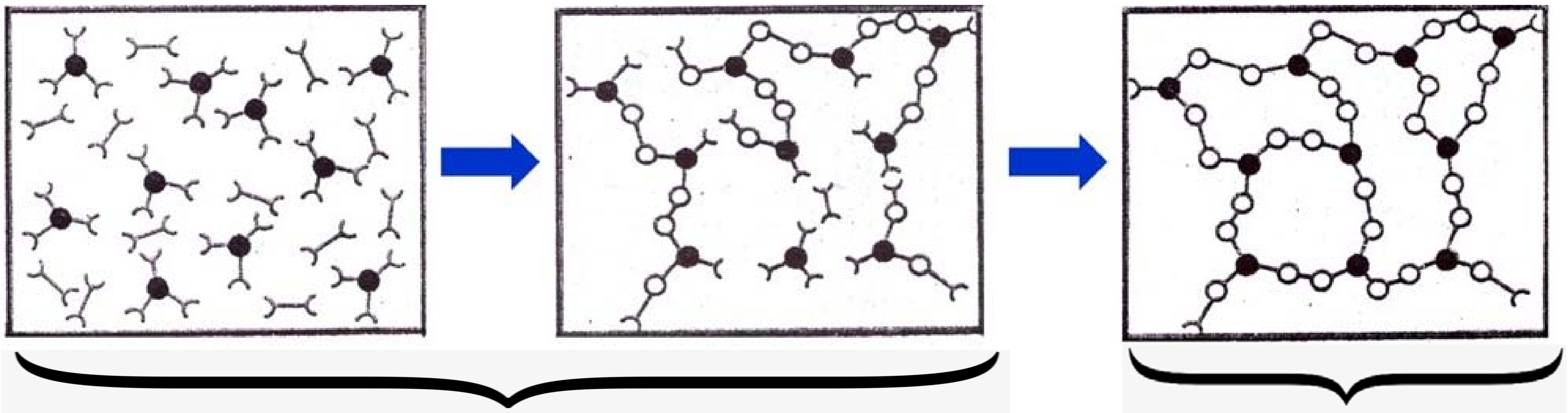
- Strong covalent bonds between polymer chains
- Remains hard when heated

Resin curing: formation of three-dimensional cross-linked thermoset structure

Resin curing

Stages:

- **chain extension:** primary amine reaction.
- **crosslinking**: secondary amine reaction



liquid composed of comonomers and just formed oligomers

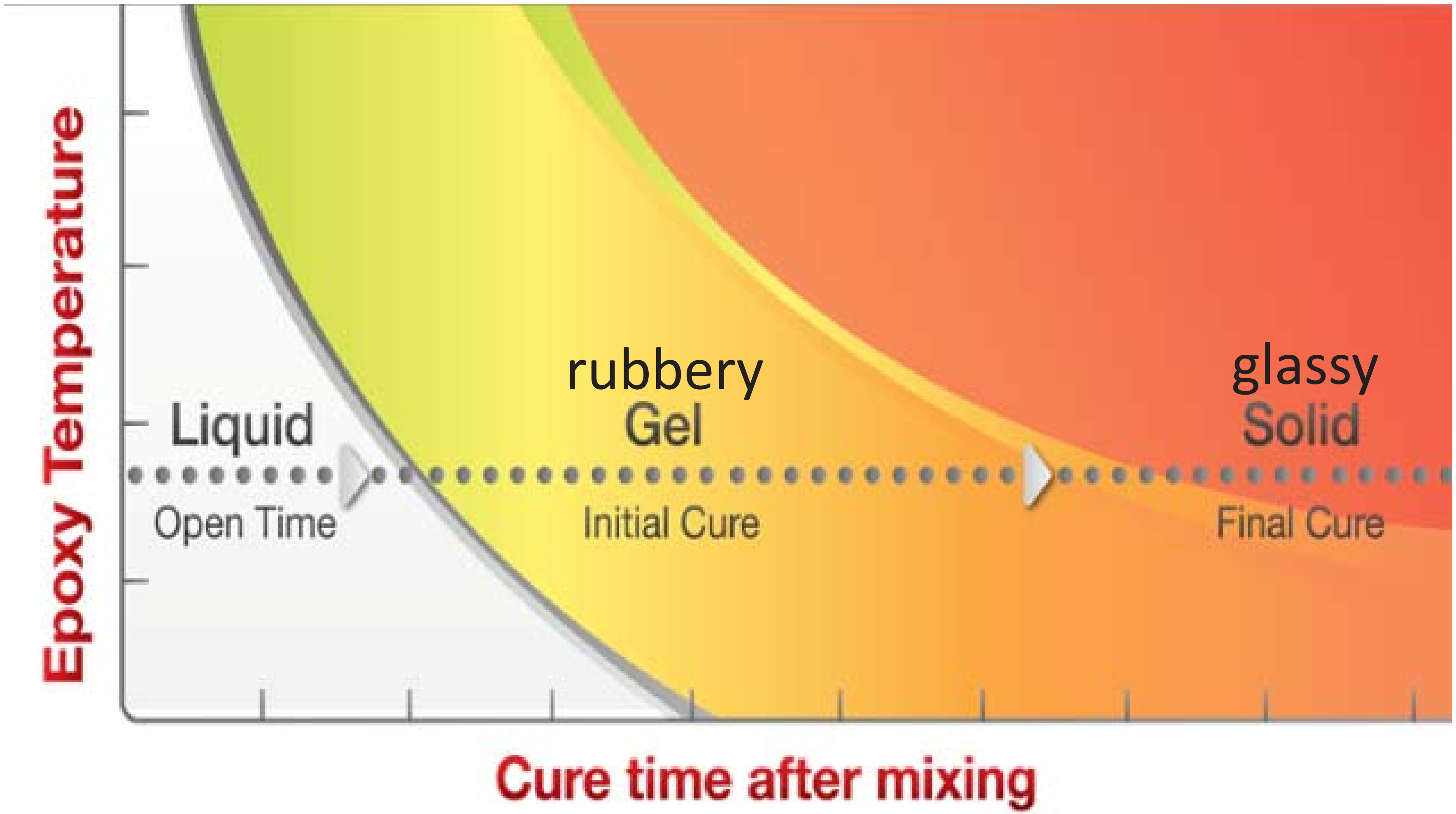
rubbery or glassy solid

time →

Molecular weight
viscosity
glass transition temperature ↑

molecular mobility ↓

Resin curing



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Resin curing

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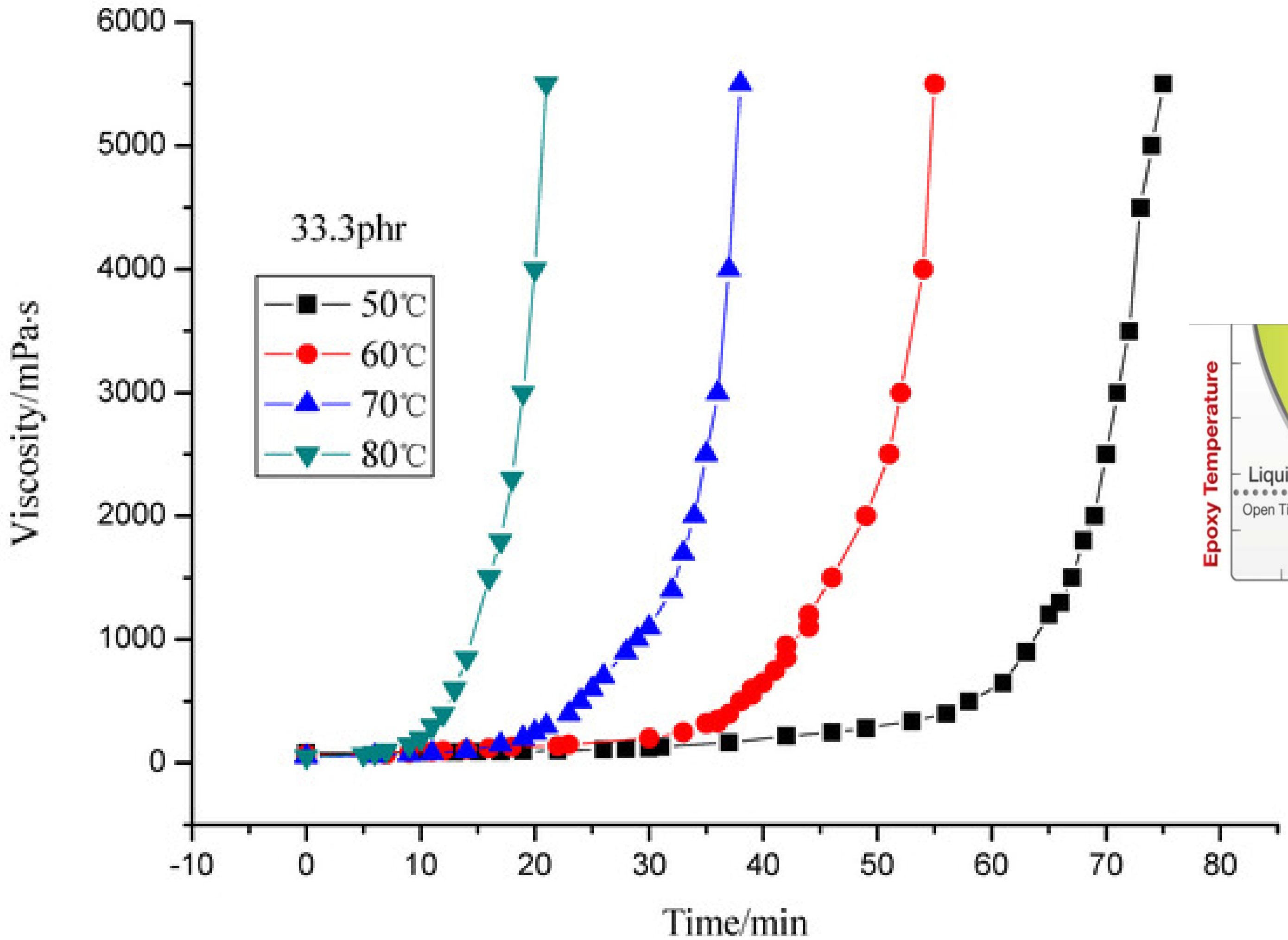
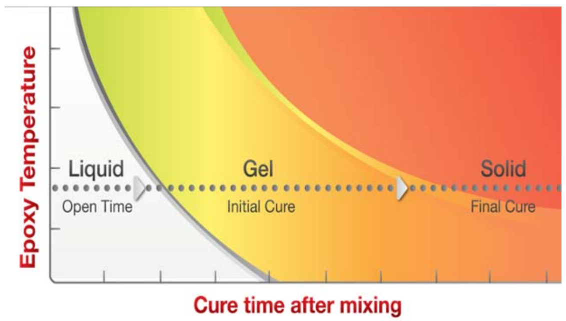
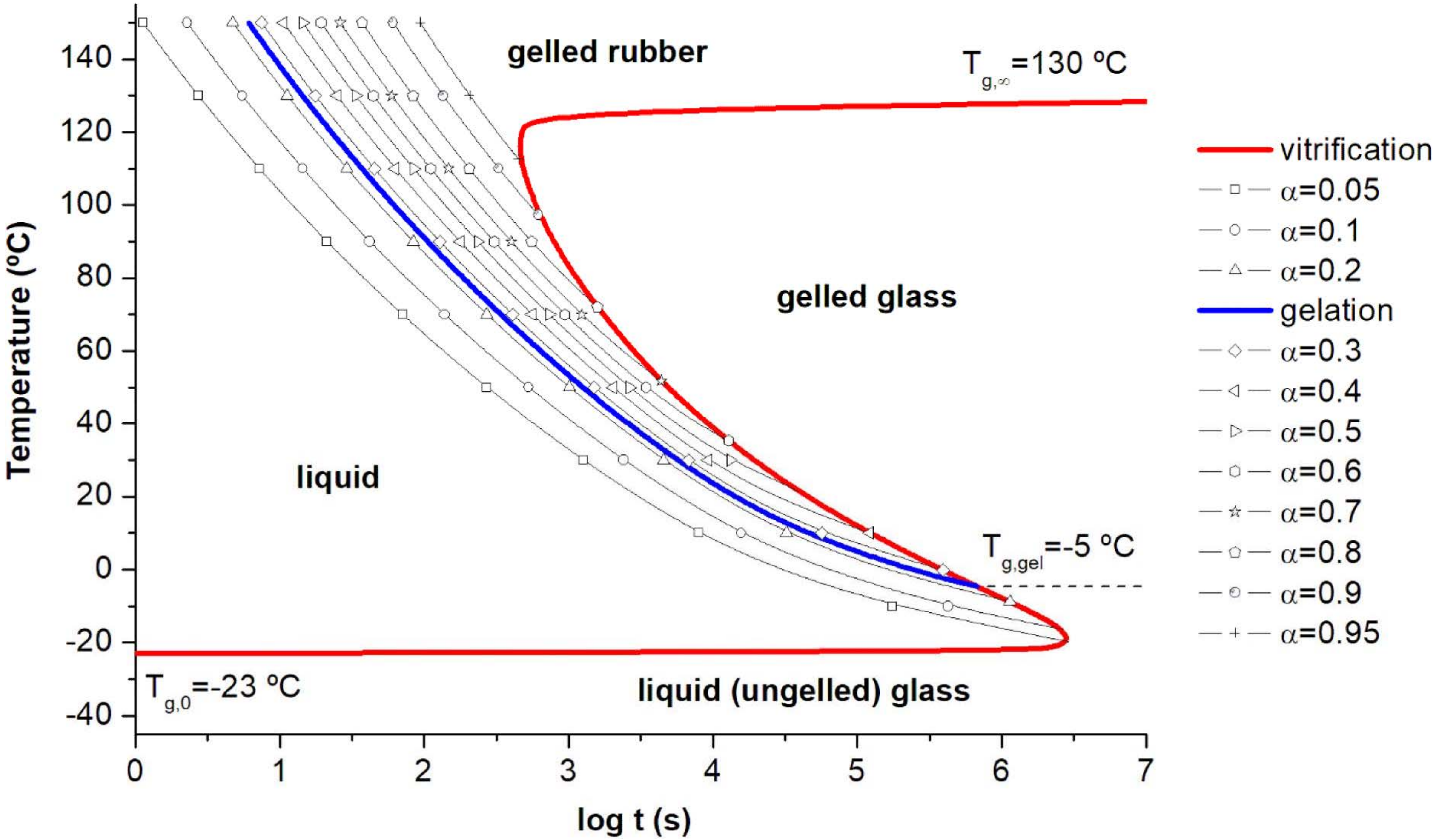


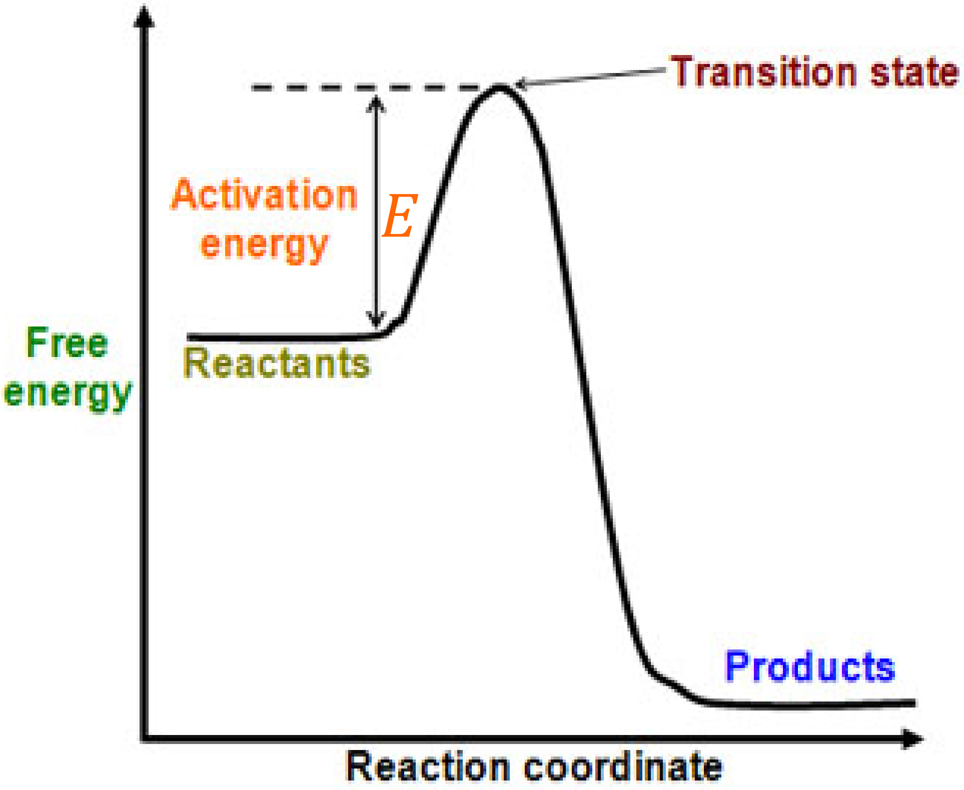


Resin curing

Time-temperature-transformation diagram of a thermosetting system



Thermally activated process



Degree of cure (0-1): α

Curing rate (s^{-1}):

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

Rate constant (s^{-1}):

$$k(T) = Ae^{-E/RT}$$

Activation energy (kJ/mol): E

Phenomenological models

- nth order reaction:

$$\frac{d\alpha}{dt} = k(T)(1-\alpha)^n$$

- Sestak-Berggren (autocatalytic behavior)

$$\frac{d\alpha}{dt} = k(T)\alpha^m(1-\alpha)^n$$

- Kamal model (k_1(T) non-catalyzed and k_2(T) catalyzed reaction).

$$\frac{d\alpha}{dt} = k_1(T)(1-\alpha)^n + k_2(T)\alpha^m(1-\alpha)^n$$

Phenomenological models (diffusion limitations)

$$\frac{d\alpha}{dt} = k(T)\left(\frac{\alpha}{\alpha_{max}(T)}\right)^m \left(1 - \frac{\alpha}{\alpha_{max}(T)}\right)^n$$

maximum fractional conversion at the specific temperature, α_{max}:

$$\alpha_{max}(T) = \frac{T_{g0}T_{g\infty}}{(T_{g0} - T_{g\infty})T} - \frac{T_{g\infty}}{(T_{g0} - T_{g\infty})}$$

A second approach assumes a serial combination of chemical reaction and diffusion

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

Kinetic analysis

- **Model-fitting (phenomenological models)**
- **Model free methods**

Isoconversional methods

$$\left[\frac{d\,ln(d\,\alpha/d\,t)}{dT^{-1}}\right]_{\alpha} = -\frac{E_{\alpha}}{R} \quad (1)$$

E_{α} is the apparent activation energy

Integration of (1) yields:

$$\frac{d\alpha}{dt} = Af(\alpha)e^{-E_{\alpha}/RT}$$

Kinetic analysis

- **Model-fitting (phenomenological models)**
- **Model free methods**

Isoconversional methods

$$\left[\frac{d\,ln(d\,\alpha/d\,t)}{dT^{-1}}\right]_{\alpha} = -\frac{E_{\alpha}}{R} \qquad (1)$$

E_{α} is the apparent activation energy

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

$$E_{\alpha} = \frac{A_{chem}\exp\left(-\frac{E_{chem}}{RT}\right)E_{diff} + A_{diff}\exp\left(-\frac{E_{diff}}{RT}\right)E_{chem}}{A_{chem}\exp\left(-\frac{E_{chem}}{RT}\right) + A_{diff}\exp\left(-\frac{E_{diff}}{RT}\right)}$$

Kinetic analysis

Monitoring methods:

- Rheological analysis (Rheometer, DMA)
- Thermal analysis (DSC)
- Spectroscopic analysis (FTIR, Raman, fluorescence)
- Ultrasonic analysis

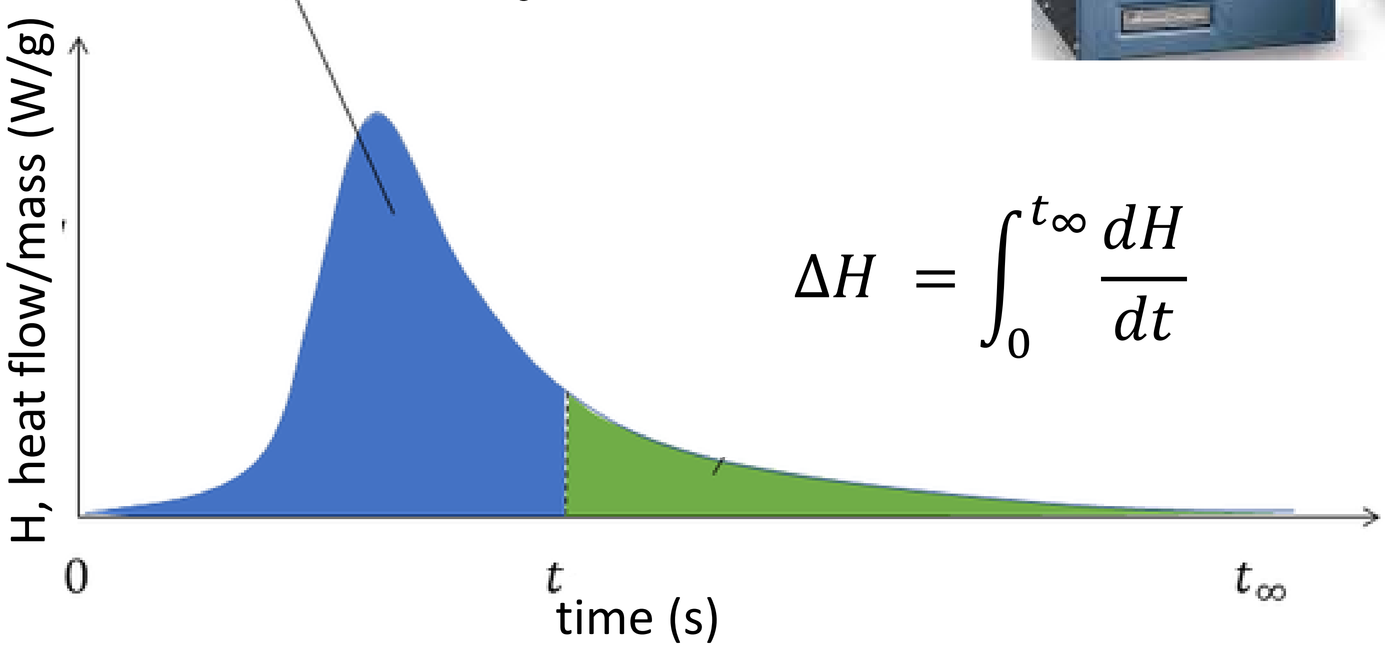
Kinetic analysis

- **Thermal analysis (DSC)**

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H}\frac{dH}{dt}$$

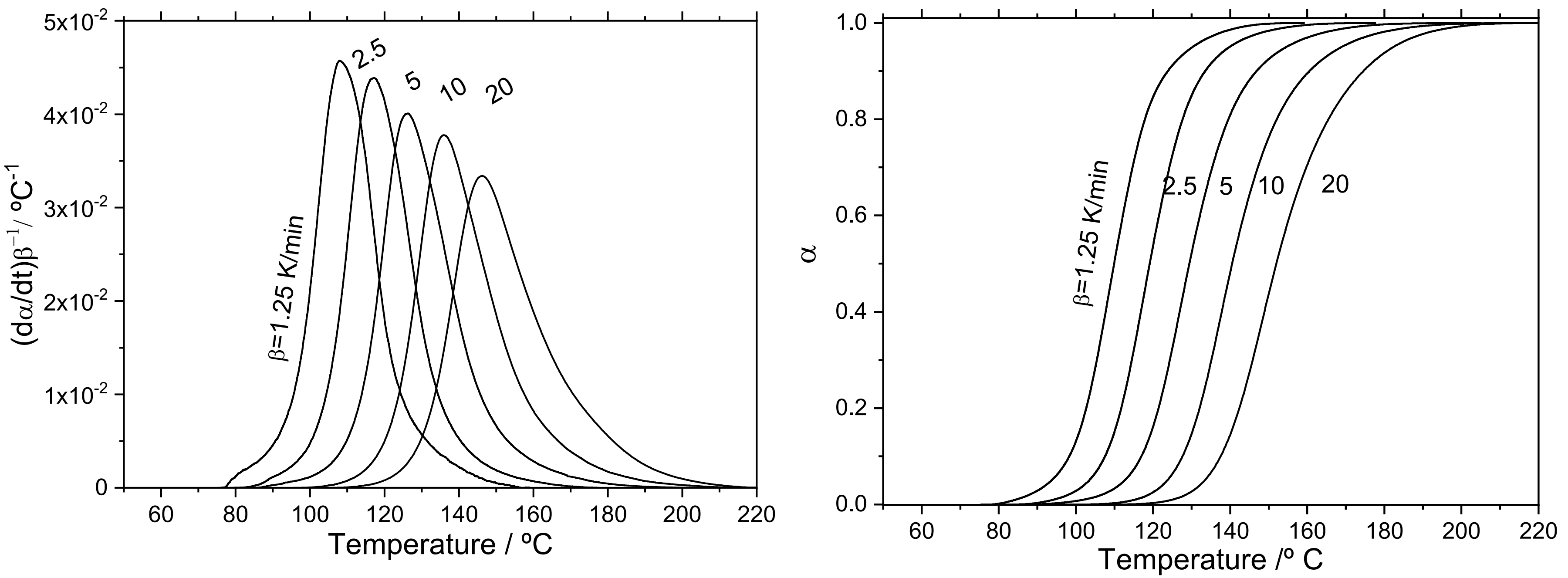
$$\alpha = \frac{1}{\Delta H}\int_0^t \frac{dH}{dt}dt$$

$$\Delta H = \int_0^{t_\infty} \frac{dH}{dt}$$



Temperature dependence?

- Isothermal experiments



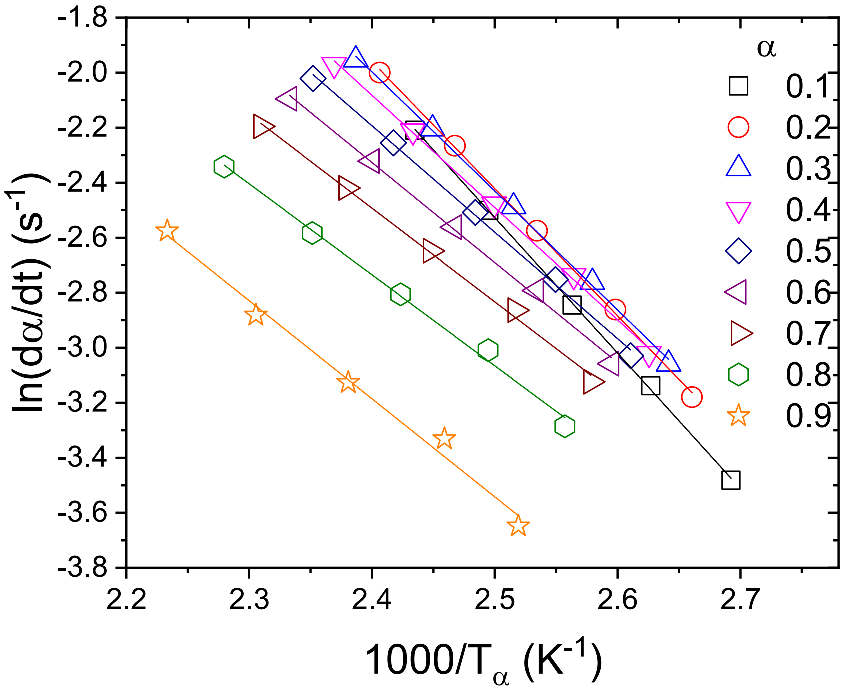
Kinetic analysis

For a given α linear relationship between $\frac{d\alpha}{dt}$ and $\frac{1}{T_\alpha}$

$$\ln\left(\frac{d\alpha}{dt}\right)_\alpha = -\frac{E_\alpha}{RT_\alpha} + \ln(Af(\alpha))$$

Friedman differential isoconversional method.

For each β_i, $d\alpha/dt|_{\alpha,i}$ and $T_{\alpha,i}$ are determined



$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = -\frac{E_\alpha}{RT_{\alpha,i}} + \ln(Af(\alpha))$$

Kinetic analysis

Vyazovkin's advanced integral isoconversional method, minimum of function $\Omega(E_\alpha)$:

$$\Omega(E_\alpha) = \sum_{i=1}^{n} \sum_{j=1, j\neq i}^{n} \frac{\beta_j \Delta p(x_{\alpha,i})}{\beta_i \Delta p(x_{\alpha,j})}$$

$$\Delta p(x_\alpha) \equiv p(x_\alpha) - p(x_{\alpha-\Delta\alpha}) = \int_{x_\alpha}^{x_{\alpha-\Delta\alpha}} \frac{e^{-u}}{u^2} du,\ u = \frac{E}{RT}$$

Once E_α and $Af(\alpha)$ have been determined, the evolution of the cure reaction can be obtained from

$$\frac{d\alpha}{dt} = Af(\alpha) e^{-E_\alpha/RT}$$

Kinetic analysis

Prediction for an arbitrary temperature program, $T(t)$.

Discretized at fixed time intervals $\Delta t, t_k = k \cdot \Delta t$: $T_k = T(t_k)$.

α_j at a given temperature T_j

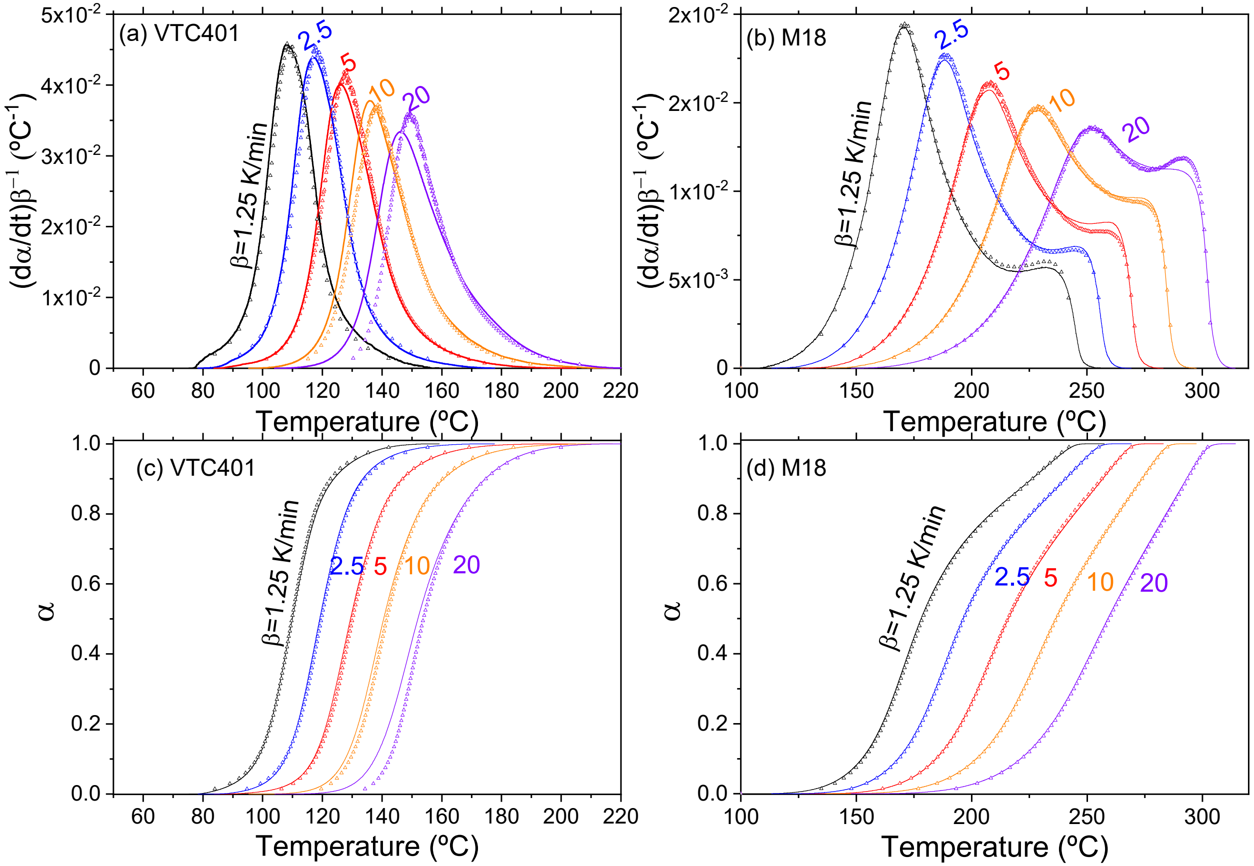
$$\alpha_{k+1} = \alpha_k + Af(\alpha)\Big|_k \cdot e^{-\frac{E_k}{RT_k}} \Delta t \quad , t_0 = 0 \text{ at } \alpha_0 = 0$$

t_j to reach α_j

$$t_j = t_{k_j} + \left\{\frac{1}{n_{exp}} \sum_{i=1}^{n_{exp}} \frac{E_j}{R\beta_i}\left[p\left(\frac{E_j}{RT_{j,i}}\right) - p\left(\frac{E_j}{RT_{j-1,i}}\right)\right] - \left[e^{-\frac{E_j}{RT_{k_{j-1}}}}\left(t_{k_{j-1}+1} - t_{j-1}\right) + \sum_{k=k_{j-1}+2}^{k_j} e^{-\frac{E_j}{RT_k}} \Delta t\right]\right\} e^{-\frac{E_j}{RT_k}}$$

Prediction of the evolution of two epoxy resin

DSC measurements



β (K/min)	ΔH (J/g)	
	VTC401	M18
1.25	687	688
2.5	684	683
5	662	667
10	641	695
20	647	677

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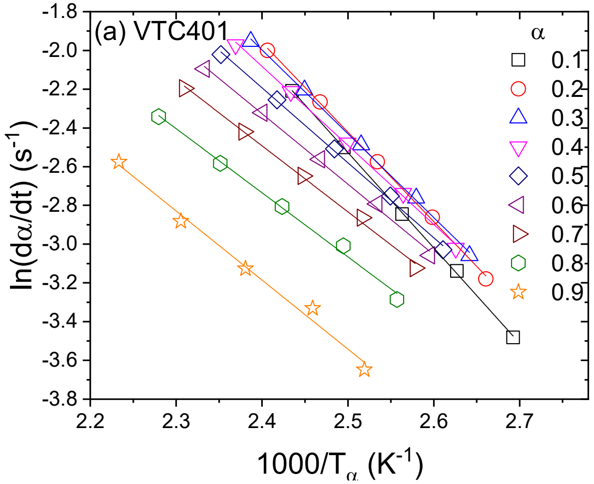
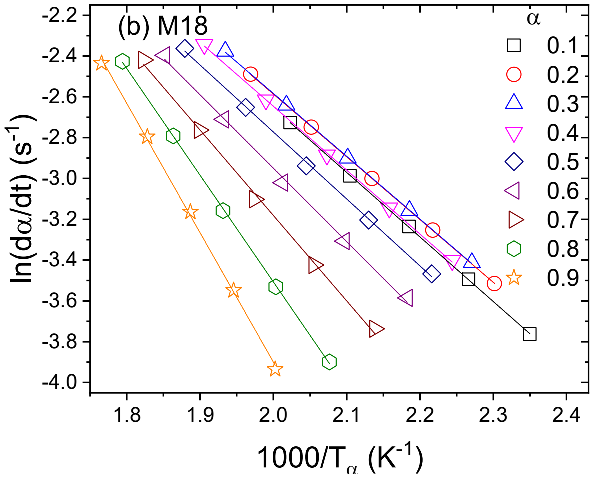
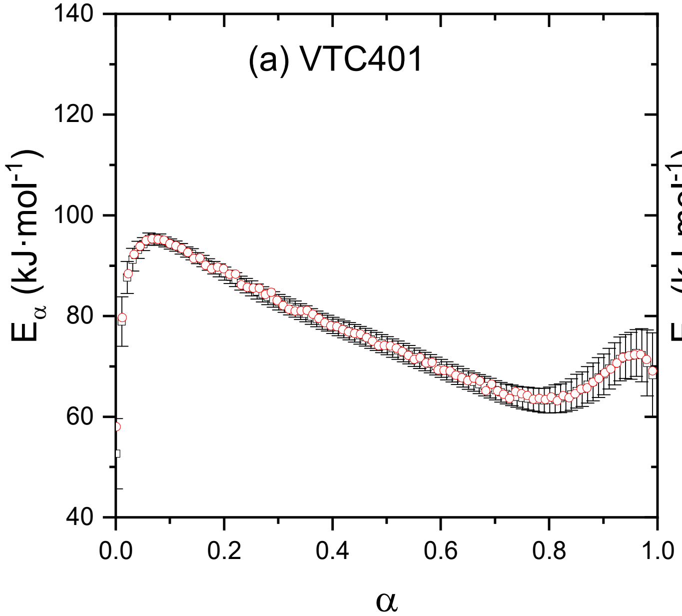
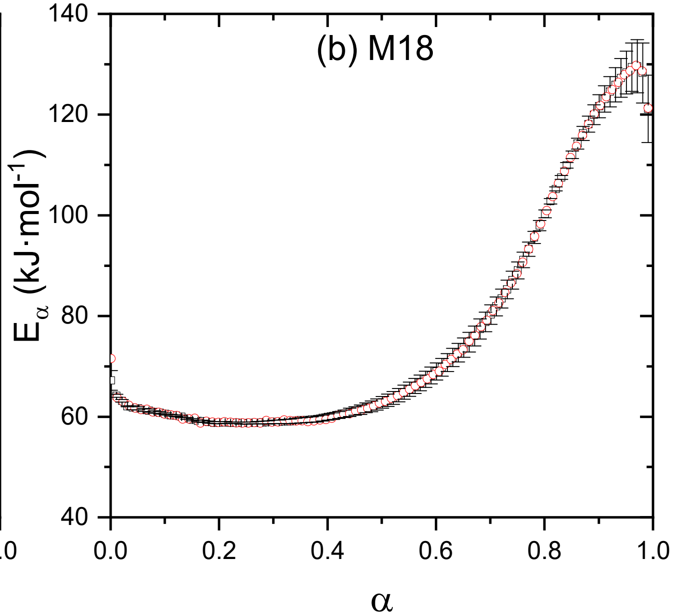
Friedman kinetic analysis



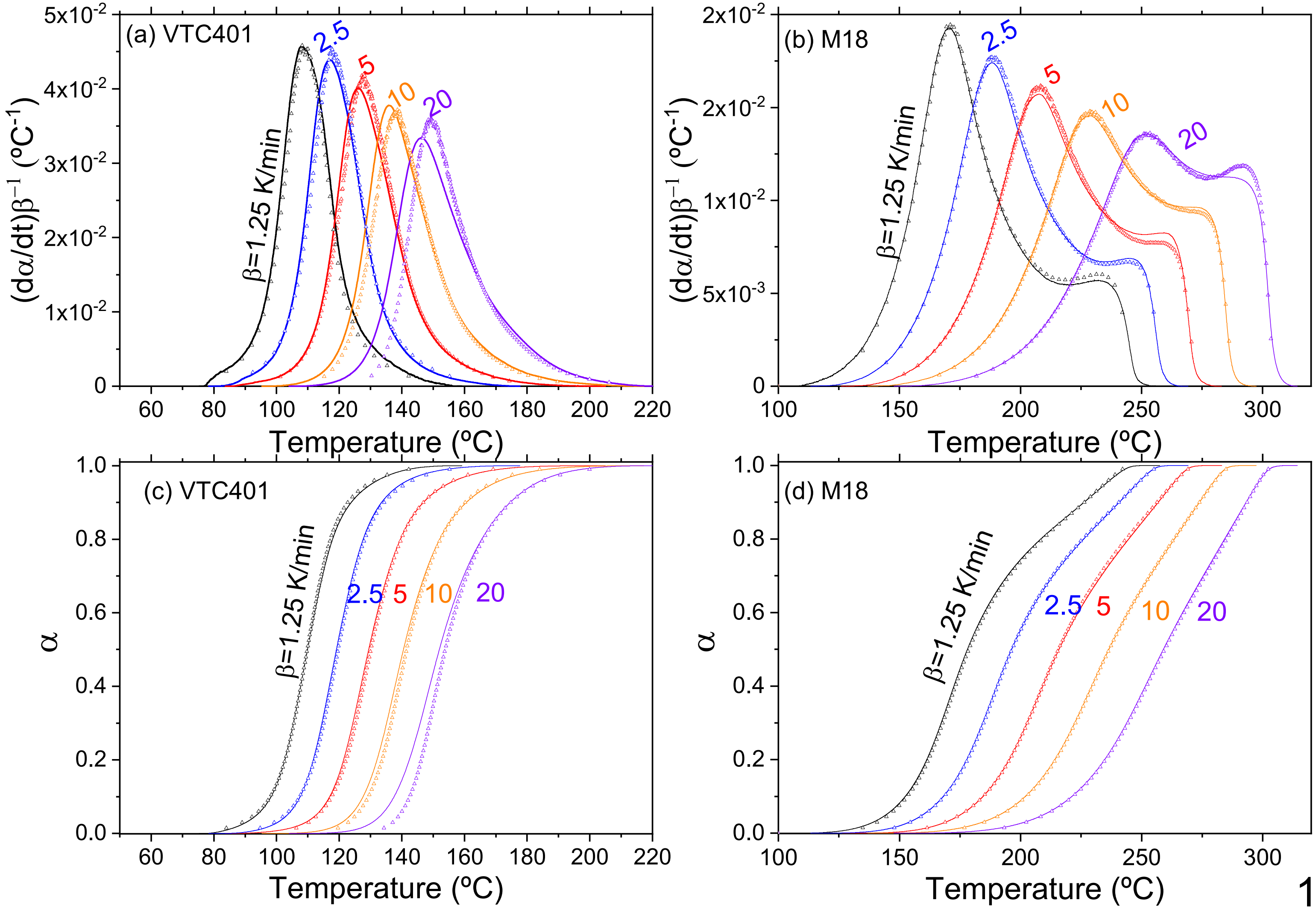






Prediction of the evolution of two epoxy resin

Self consistency test



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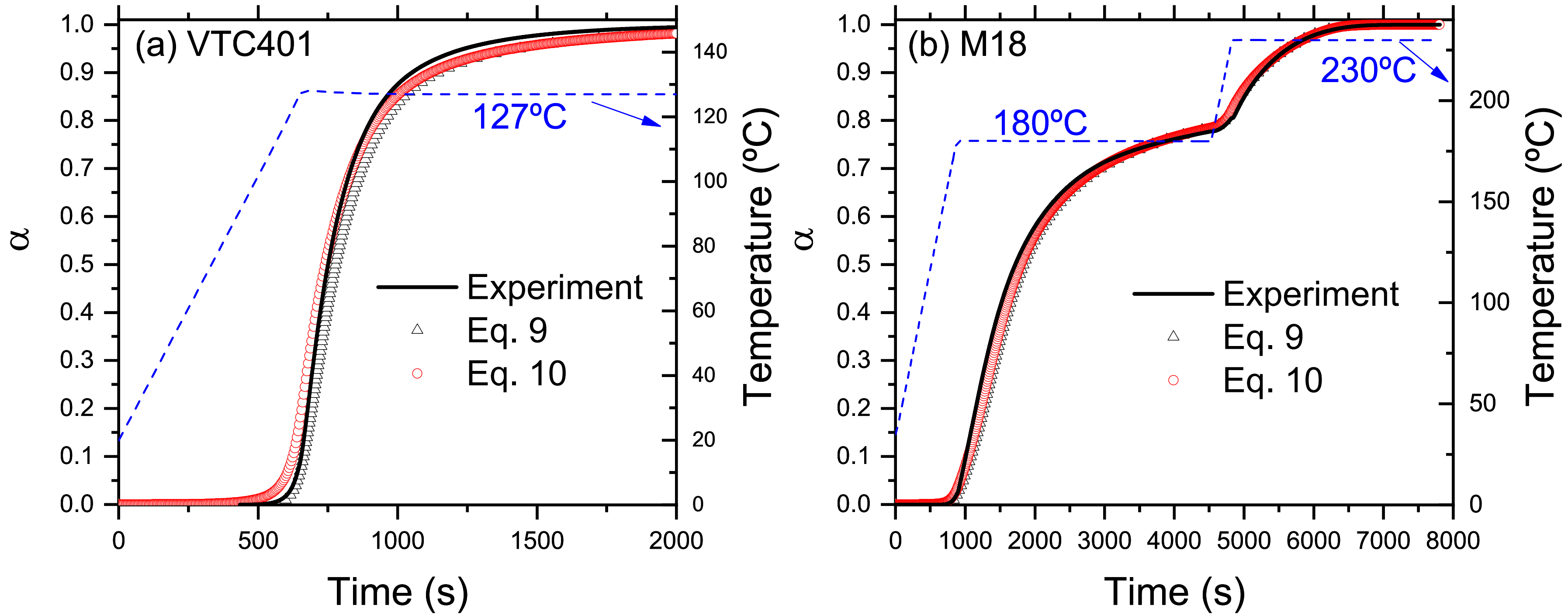
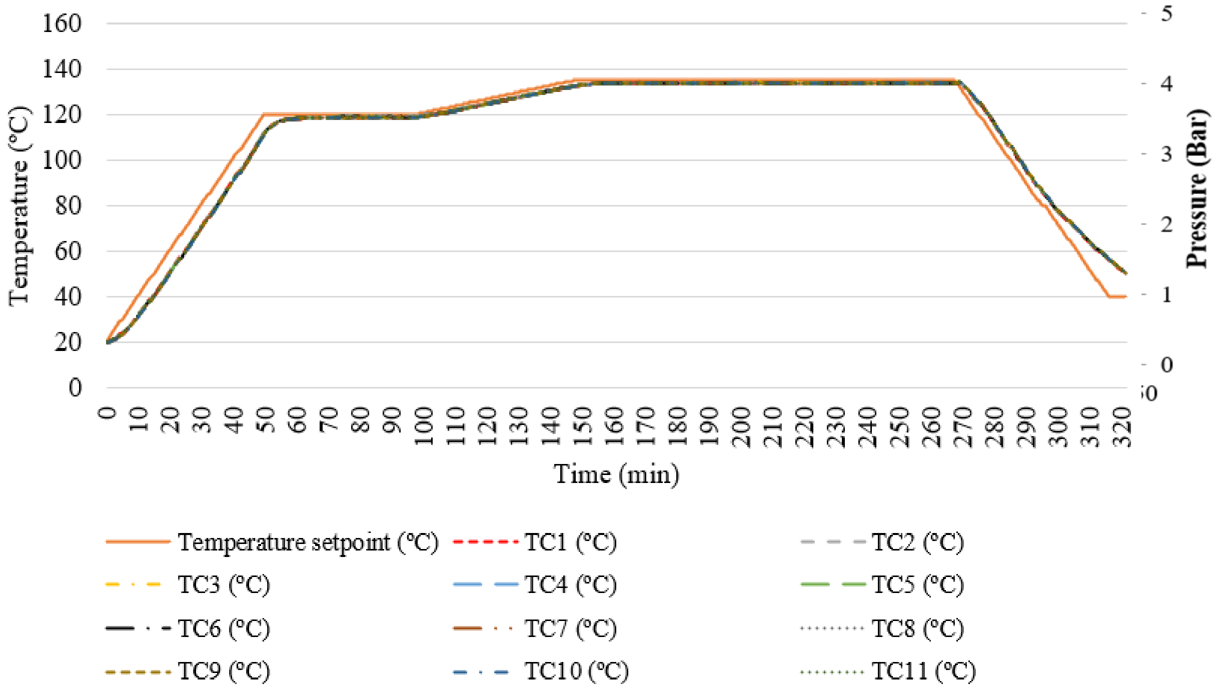
Prediction test



Prediction of the evolution of two epoxy resin

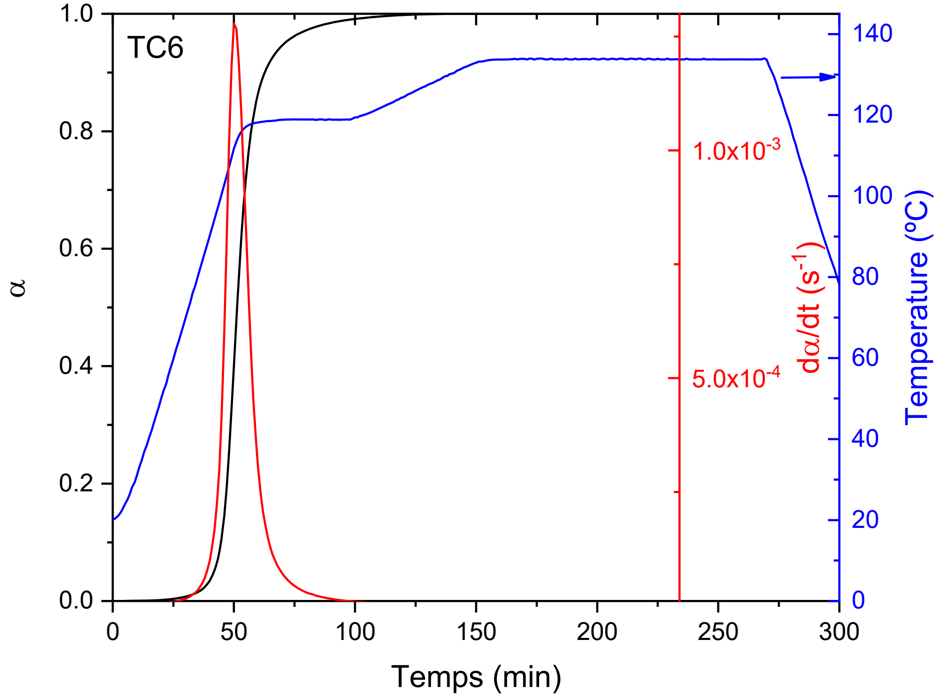
More than 5 hours, is it possible to reduce the time needed to fully cure the resin?



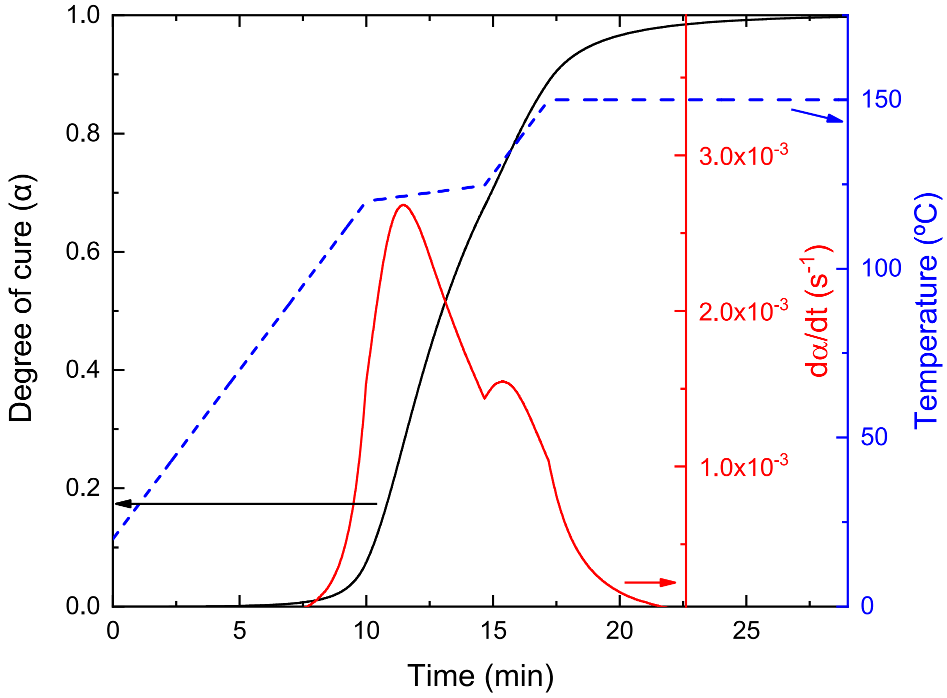
Manufacturer’s recommended cure cycle

Prediction of the evolution of two epoxy resin

Predicted evolution:



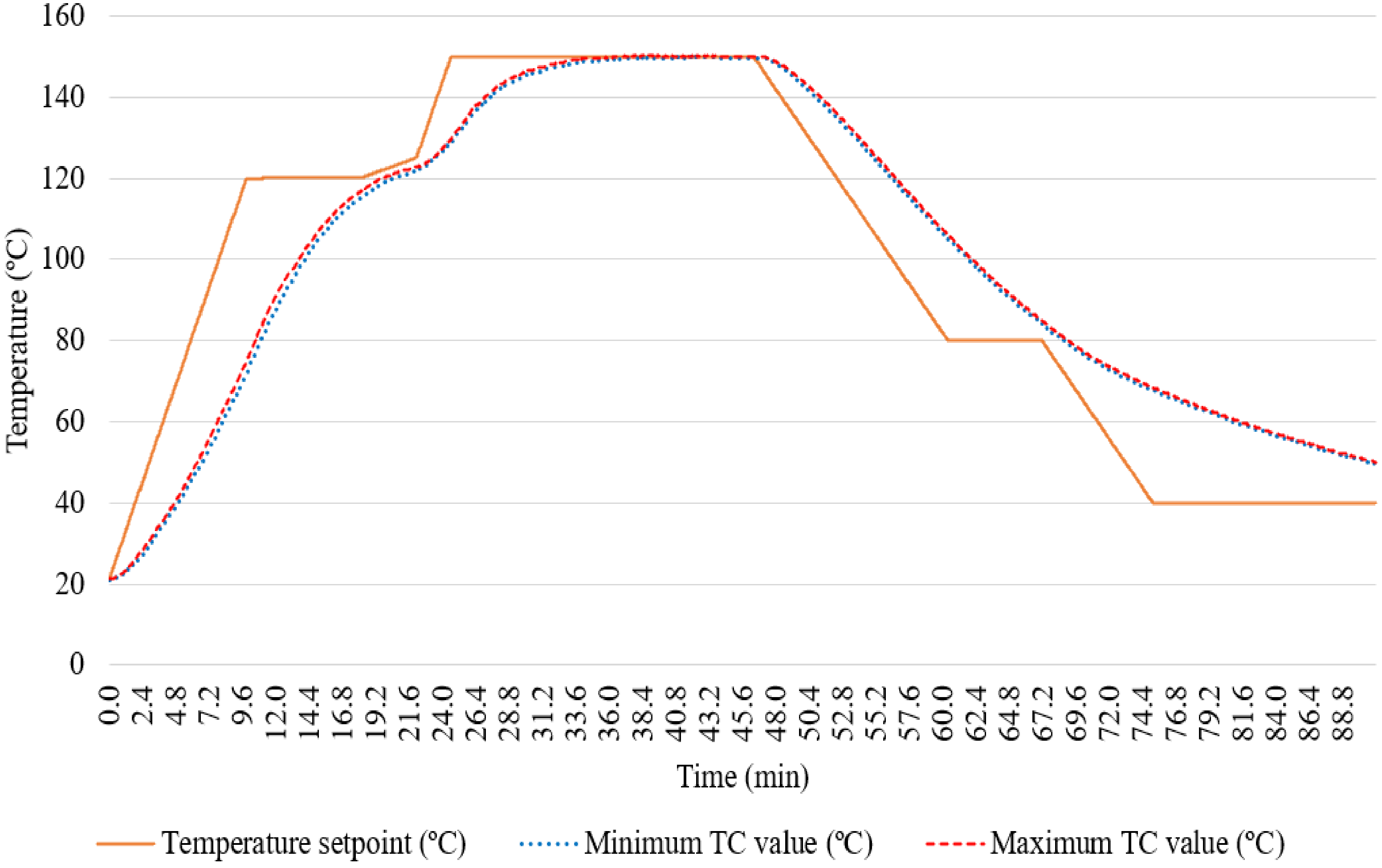
Manufacturer's recommended cure cycle



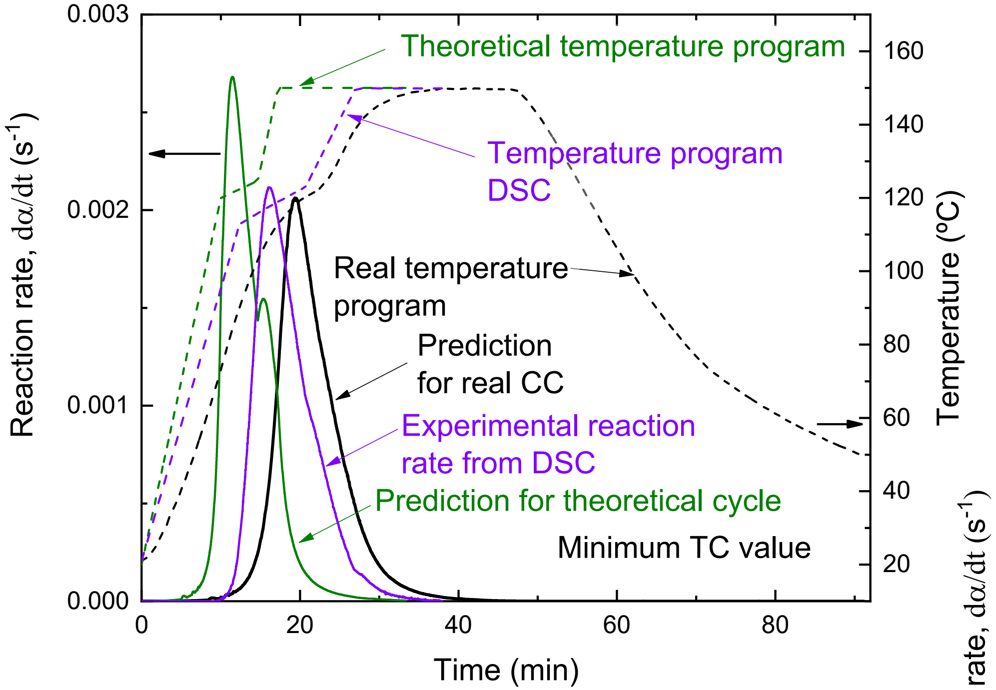
Optimized cure cycle

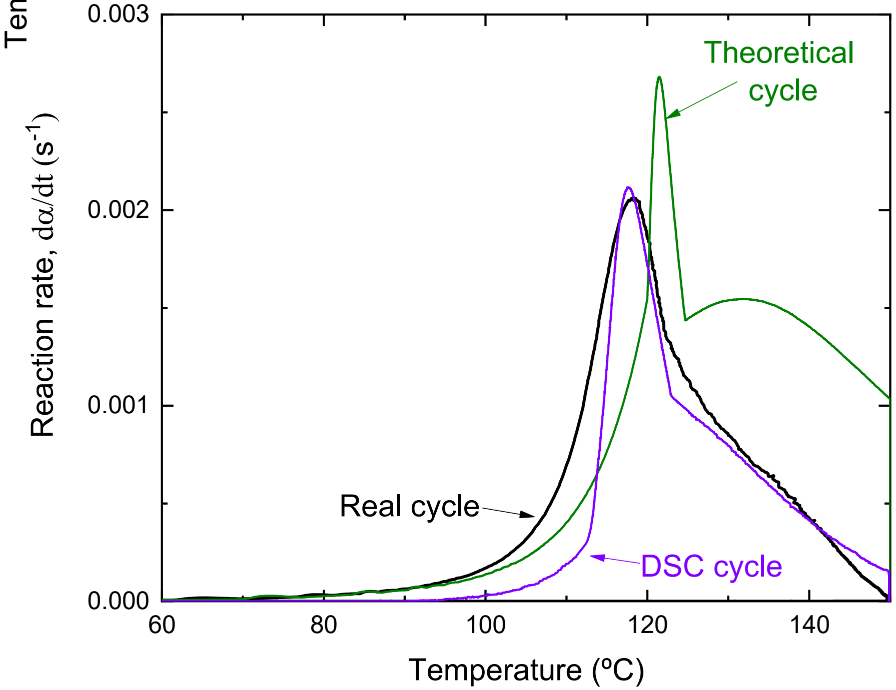
Prediction of the evolution of two epoxy resin

Real cure cicle



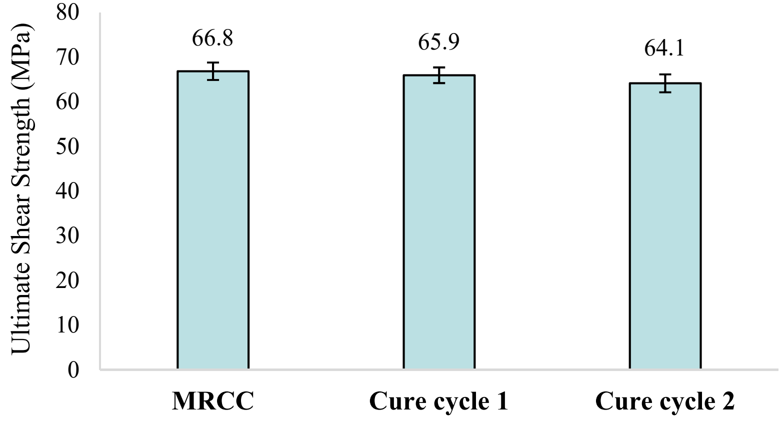
Prediction of the evolution of two epoxy resin



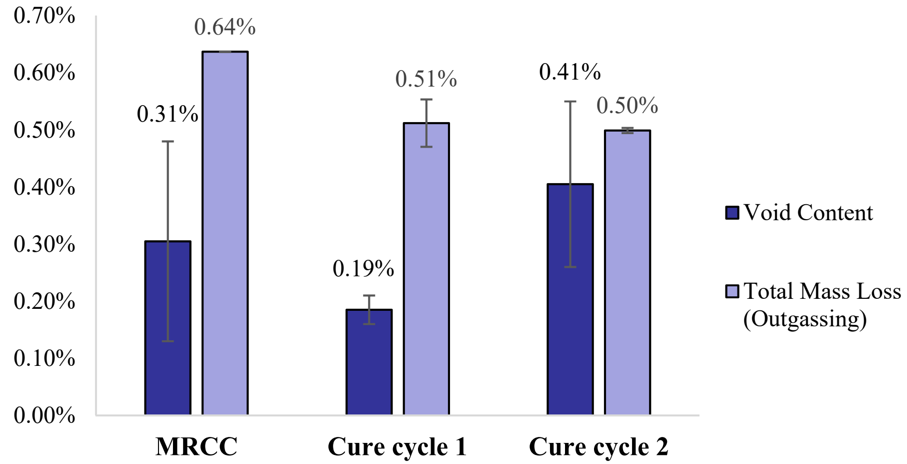


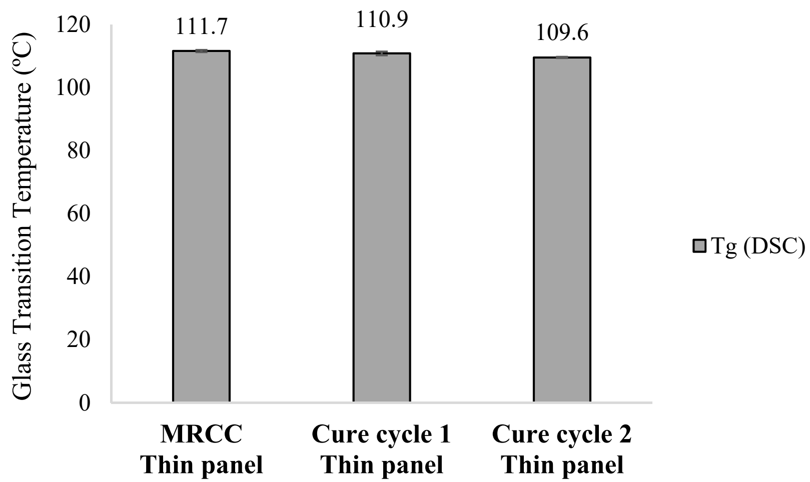
Prediction of the evolution of two epoxy resin

Mechanical properties

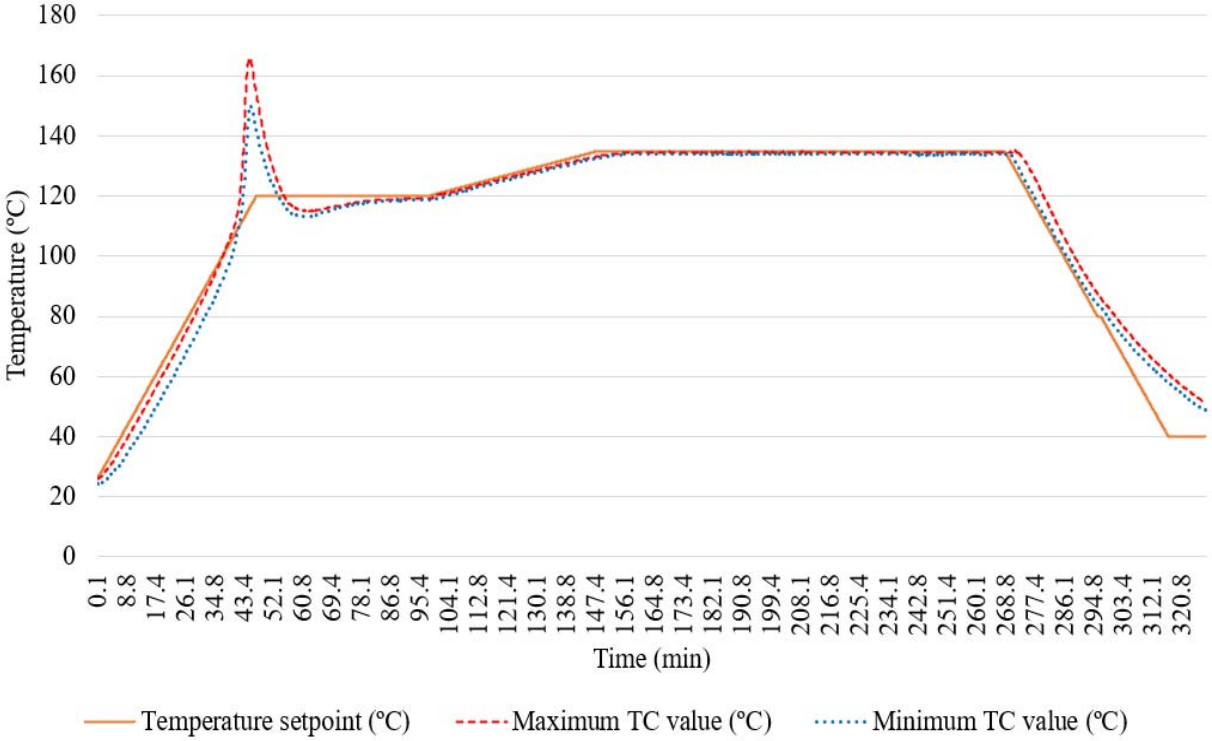


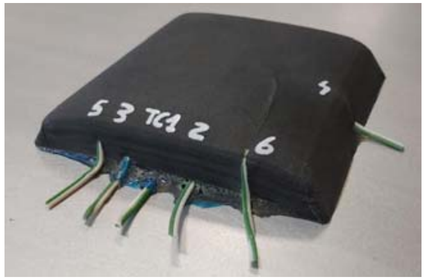
Physical properties





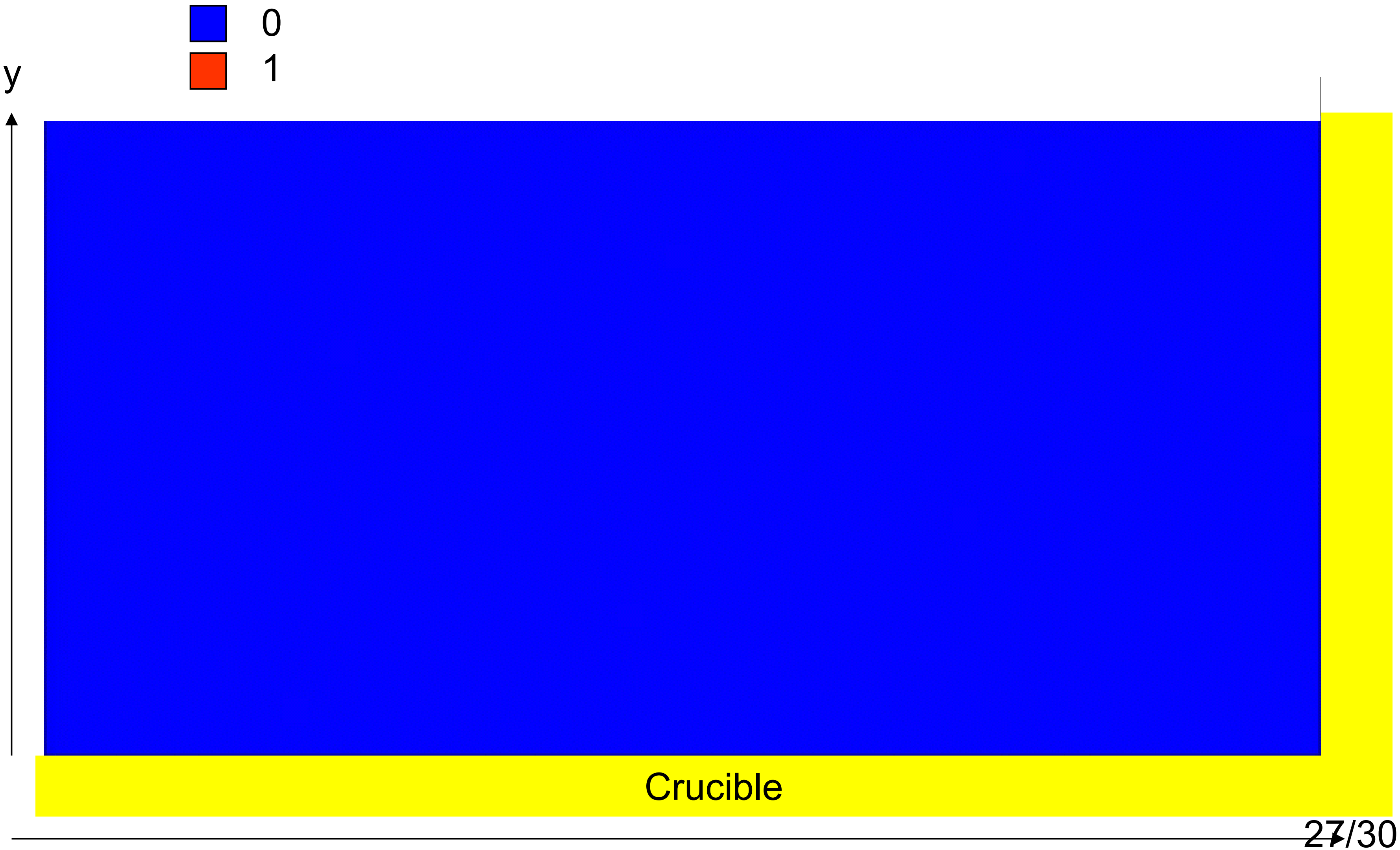
Overheating



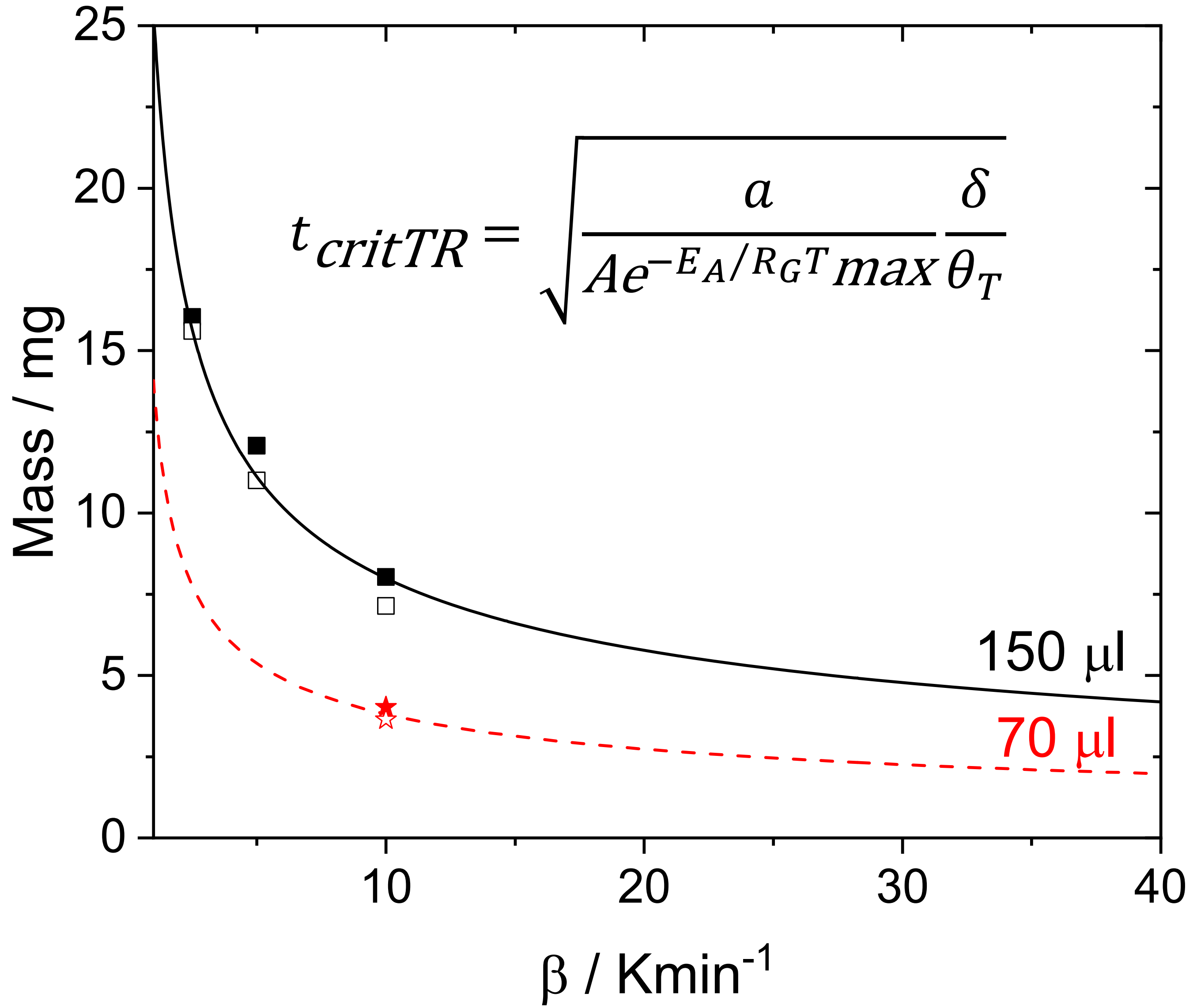


Overheating

Evolution of the transformed fraction (constant transformation rate):



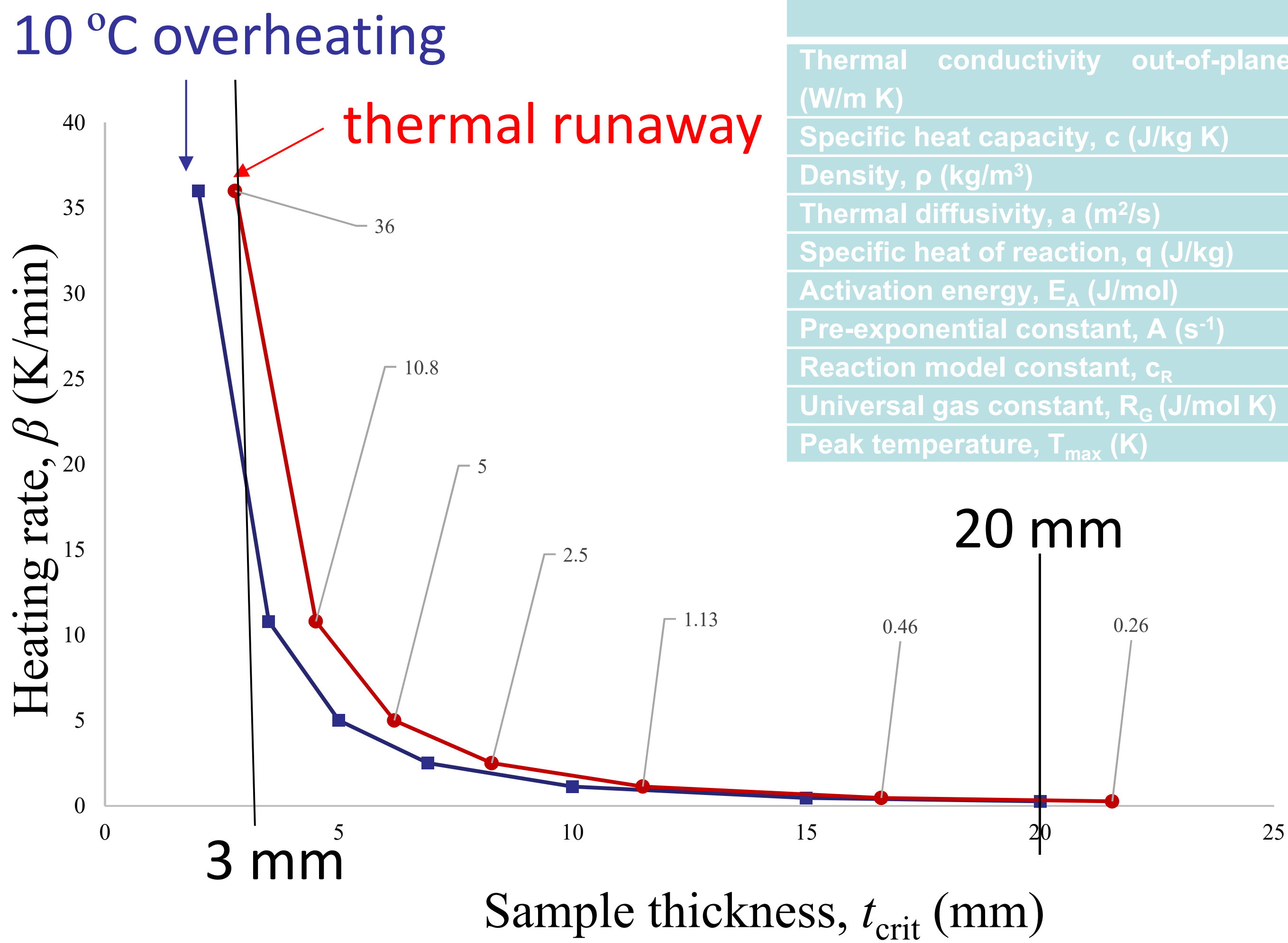
Overheating



Overheating

$$t_{crit} = 1.5\left(10^{-5}\Delta T\,\frac{caE_A}{R_G q}\,\frac{c_R}{Ae^{-E_A/R_G T_{max}}}\right)^{1/2}$$

Property	Value VTC401	Source
Thermal conductivity out-of-plane, λ (W/m K)	0.85	[29]*
Specific heat capacity, c (J/kg K)	1150	[29]*
Density, ρ (kg/m³)	1686	[13]
Thermal diffusivity, a (m²/s)	4.38×10^{-7}	[29]*
Specific heat of reaction, q (J/kg)	2.12×10^{5}	[13]
Activation energy, E_A (J/mol)	8.97×10^{4}	[13]
Pre-exponential constant, A (s^{-1})	3.0×10^{9}	[13]
Reaction model constant, c_R	2.4464	[18]
Universal gas constant, R_G (J/mol K)	8.314	[18]
Peak temperature, T_{max} (K)	390.2	[13]



Conclusions

- During the curing reaction there is a dramatic change of the physical properties of the material.
- The kinetics of the curing process is usually complex and involves more than one process. At the beginning is controlled by the chemical reaction but at the end diffusion is the kinetics limiting process.
- Isoconversional methods allow to fit the kinetics and predict the evolution.
- A total reduction in real time of up to 74 % has been achieved.
- It is possible to analytically determine the critical thickness for overheating.

Thermal decomposition of calcium propionate: films and powders

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