



AMADE DAYS

Universitat de Girona
Grup de Recerca en Materials
i Termodinàmica

Modeling the Cure Kinetics of Epoxy Resins

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Introduction

Kinetic models for the chemical reaction

Numerical analysis without diffusion

Numerical analysis with diffusion

Experimental analysis

Kinetics of the chemical reaction

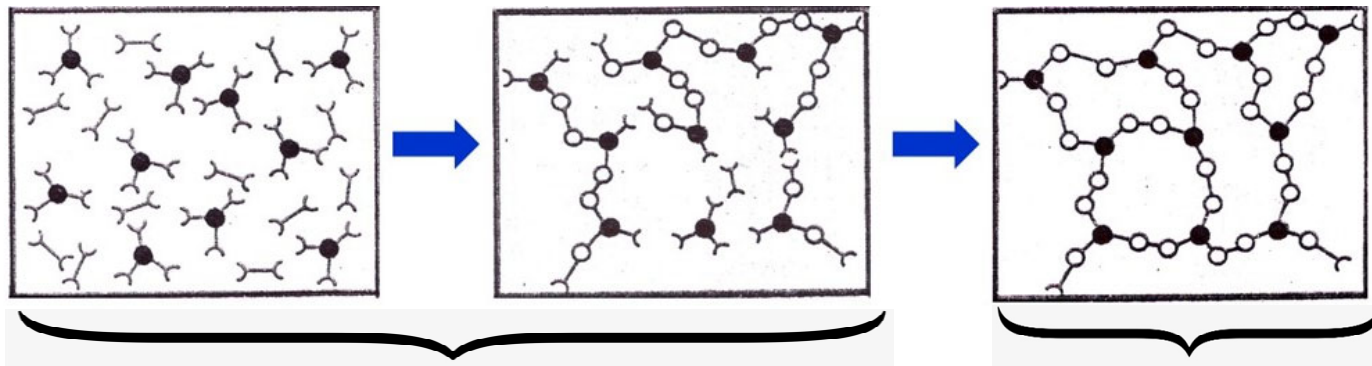
Diffusion kinetics

Conclusions

Introduction

Curing reaction of DGEBA with a diamine involves two major steps

- chain extension due to the primary amine reaction
- crosslinking associated with the secondary amine



liquid composed of comonomers and just formed
oligomers

rubbery or
glassy solid

Molecular weight
viscosity
glass transition temperature



time
molecular mobility



Modeling the Cure Kinetics of Epoxy Resins

Phenomenological models

✓ n^{th} 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: $\frac{d\alpha}{dt} = k_1(1 - \alpha)^{n_1} + k_2(1 - \alpha)^{n_2}\alpha^m$

✓ Reaction rate: $k(T) = Ae^{-E/(RT)}$

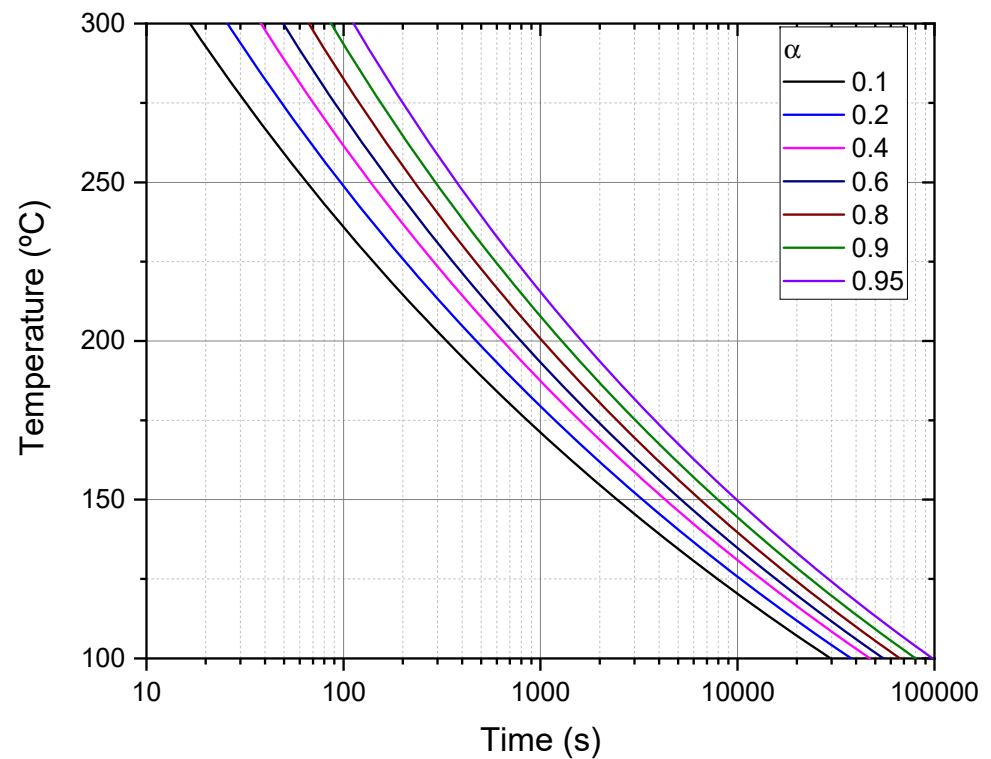
Model free methods (Isoconversional model)

$$\frac{d\alpha}{dt} = A_{\alpha}e^{-\frac{E_{\alpha}}{RT}} \quad \ln \left[\left(\frac{d\alpha}{dt} \right)_{T_{\alpha,i}} \right] = \ln[A_{\alpha}] - \frac{E_{\alpha}}{RT_{\alpha,i}}$$

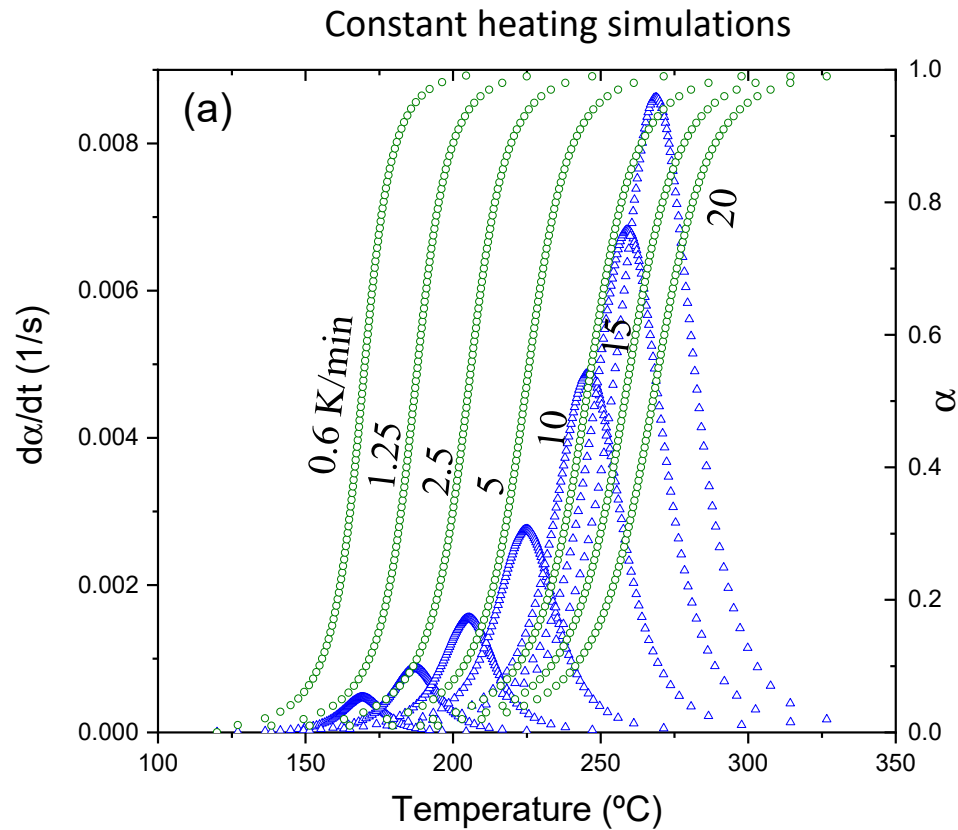
Modeling the Cure Kinetics of Epoxy Resins

Kinetics of RTM6 resin, Kamal and Sourour model **without Diffusion**:

A_1 (s ⁻¹)	19,000
A_2 (s ⁻¹)	22,080
E_1 (kJmol ⁻¹)	72.900
E_2 (kJmol ⁻¹)	57.820
n_1	1.97
n_2	1.53
m	1.29

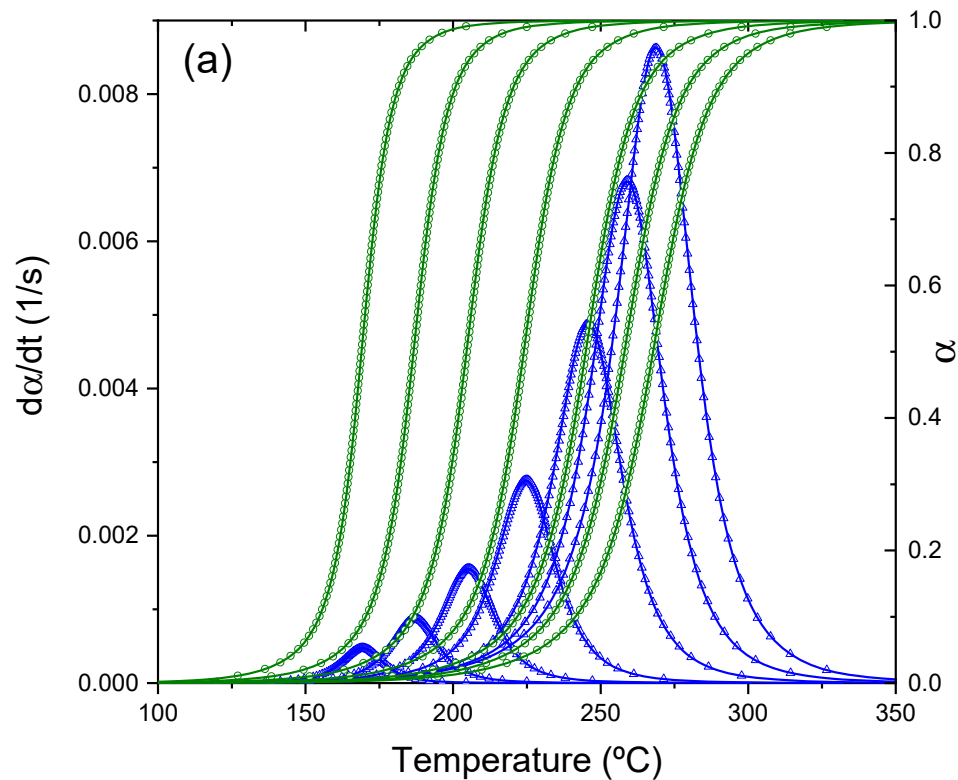


Modeling the Cure Kinetics of Epoxy Resins

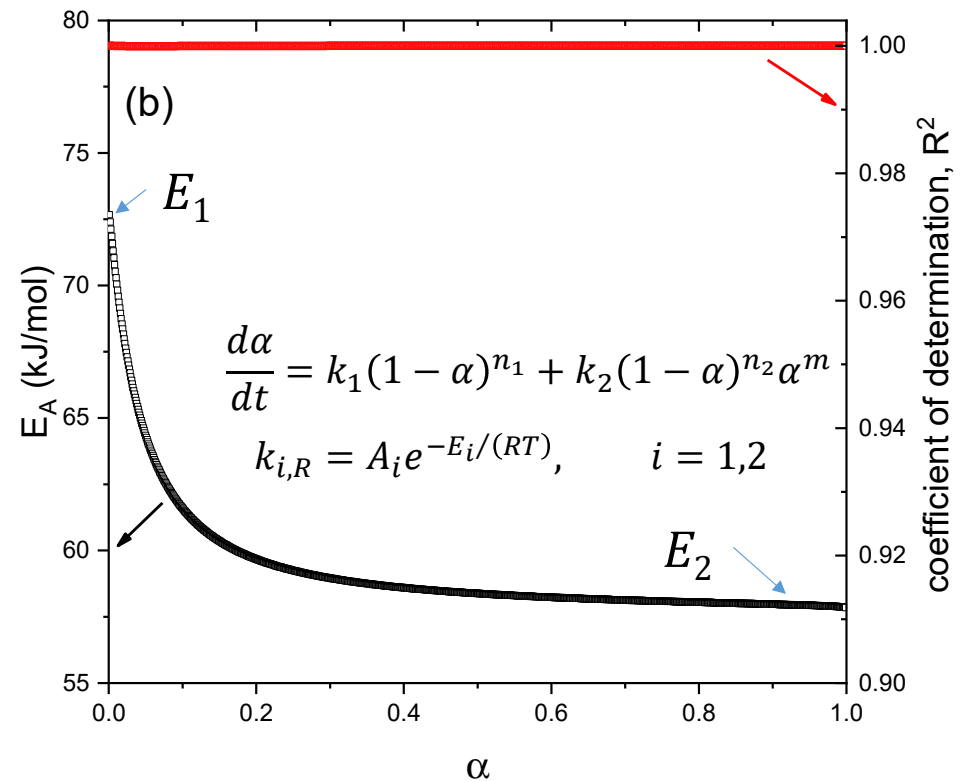


Modeling the Cure Kinetics of Epoxy Resins

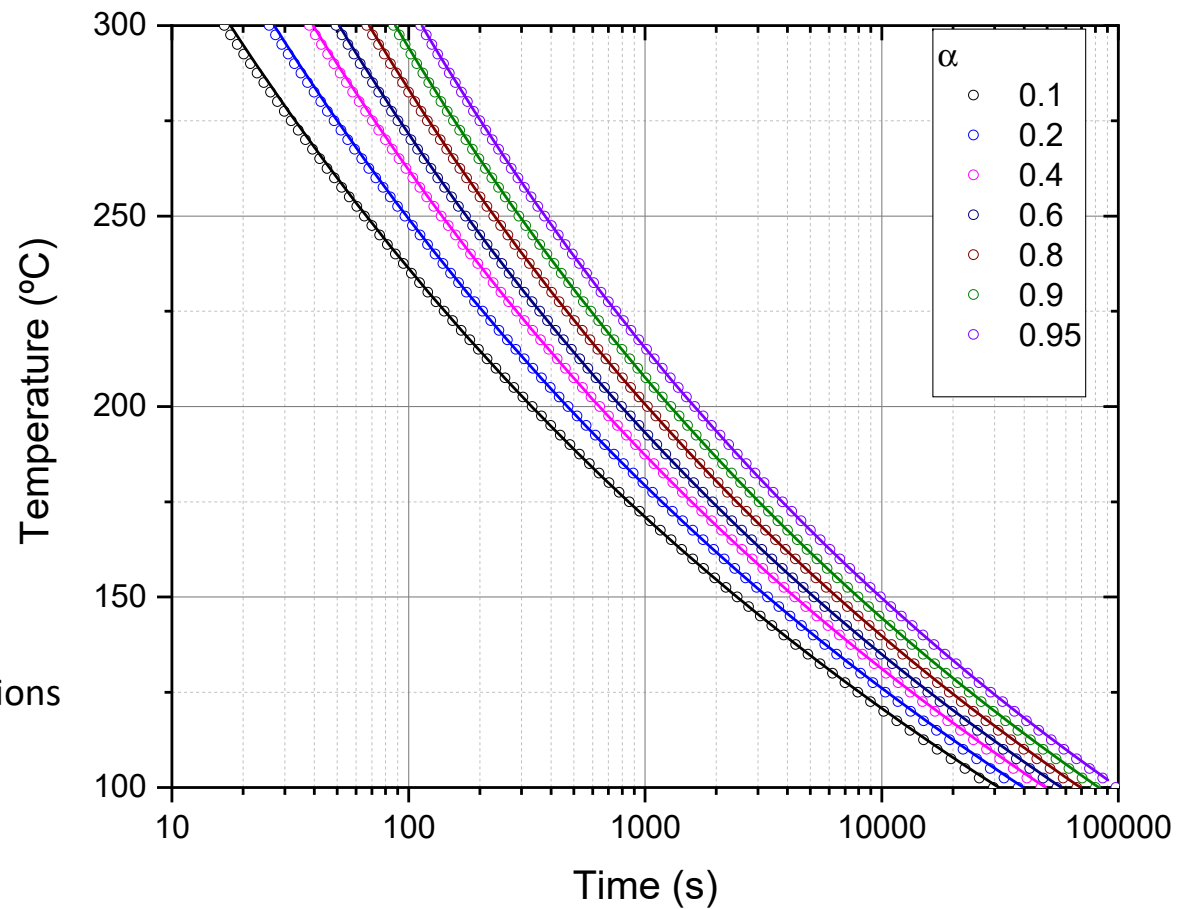
Constant heating simulations



Isoconversional analysis

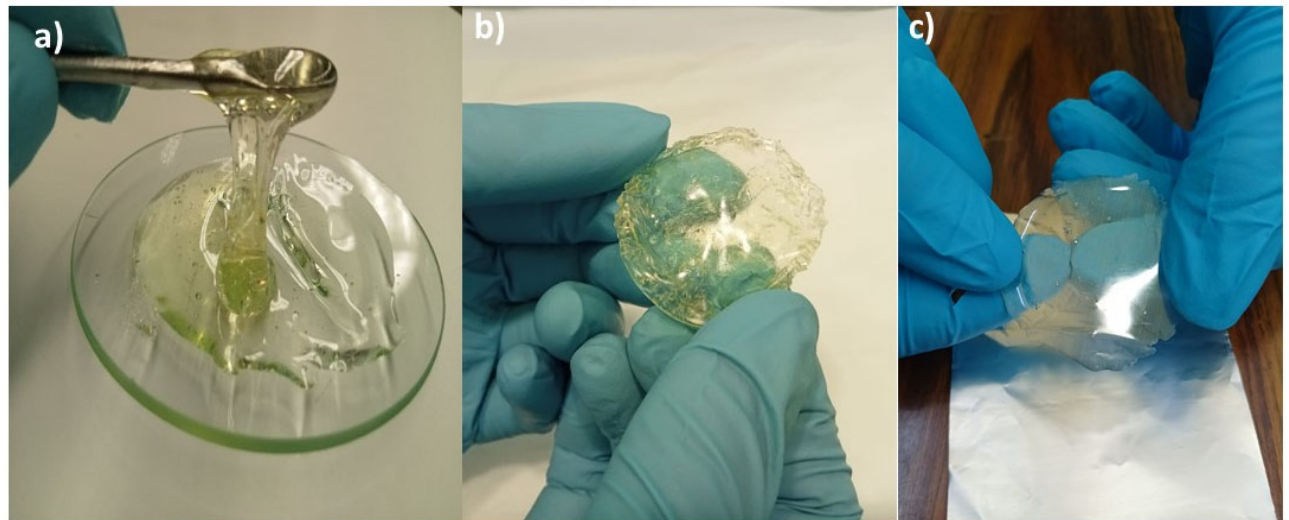
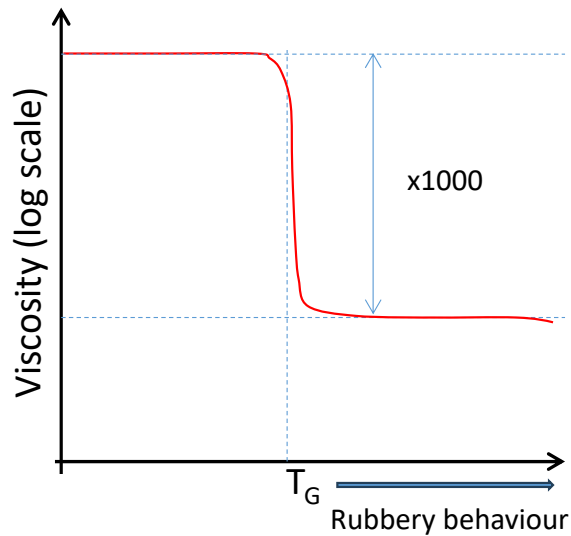


Modeling the Cure Kinetics of Epoxy Resins



Modeling the Cure Kinetics of Epoxy Resins

The glass transition temperature



Evolution of the rheological properties of the bio-based resin during the curing at 30 °C : (a) 2 h, b) 3 h and c) 24 h.

Modeling the Cure Kinetics of Epoxy Resins

How should diffusion be taken into account?

✓ Diffusion:
$$\frac{1}{k} = \frac{1}{k_R} + \frac{1}{k_D}$$

Physical model

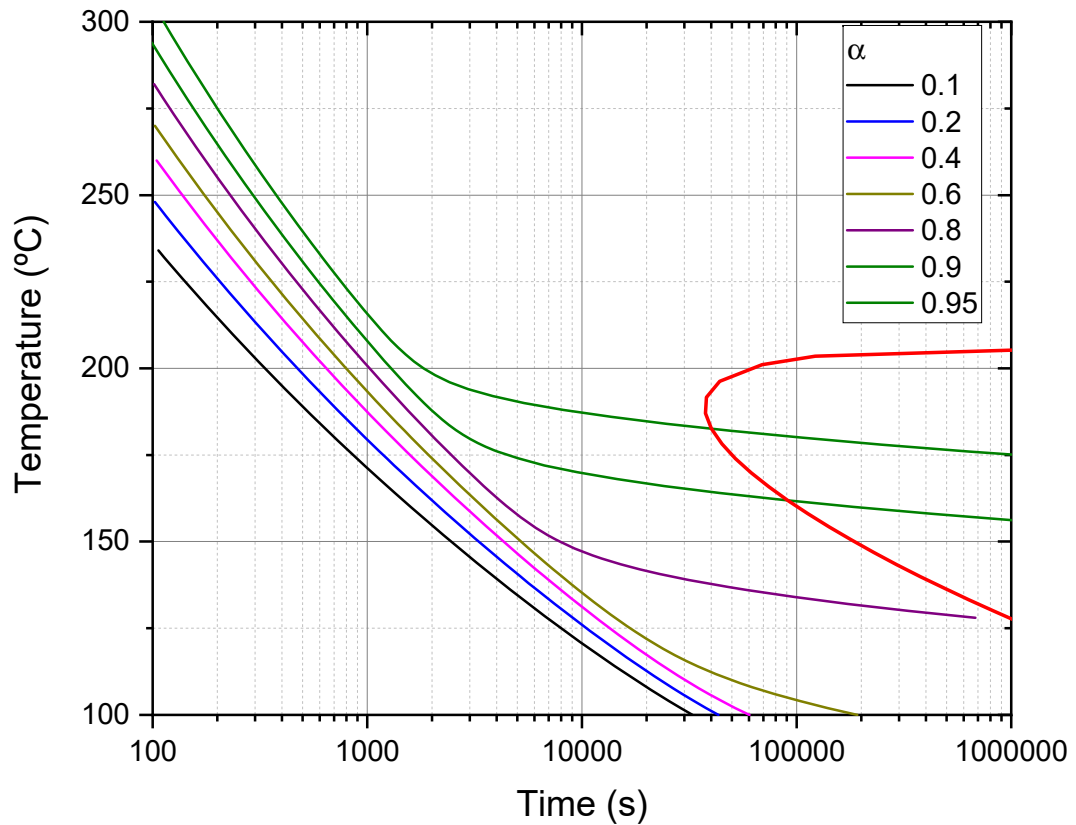
$$k_D = A_D e^{-E_D/(RT)} e^{-b/f}$$

$$f = 0.00048 (T - T_g) + 0.025$$

DiBenedetto equation:
$$\frac{(T_g - T_{g0})}{(T_{g\infty} - T_{g0})} = \frac{\lambda \alpha}{(1 - (1 - \lambda) \alpha)}$$

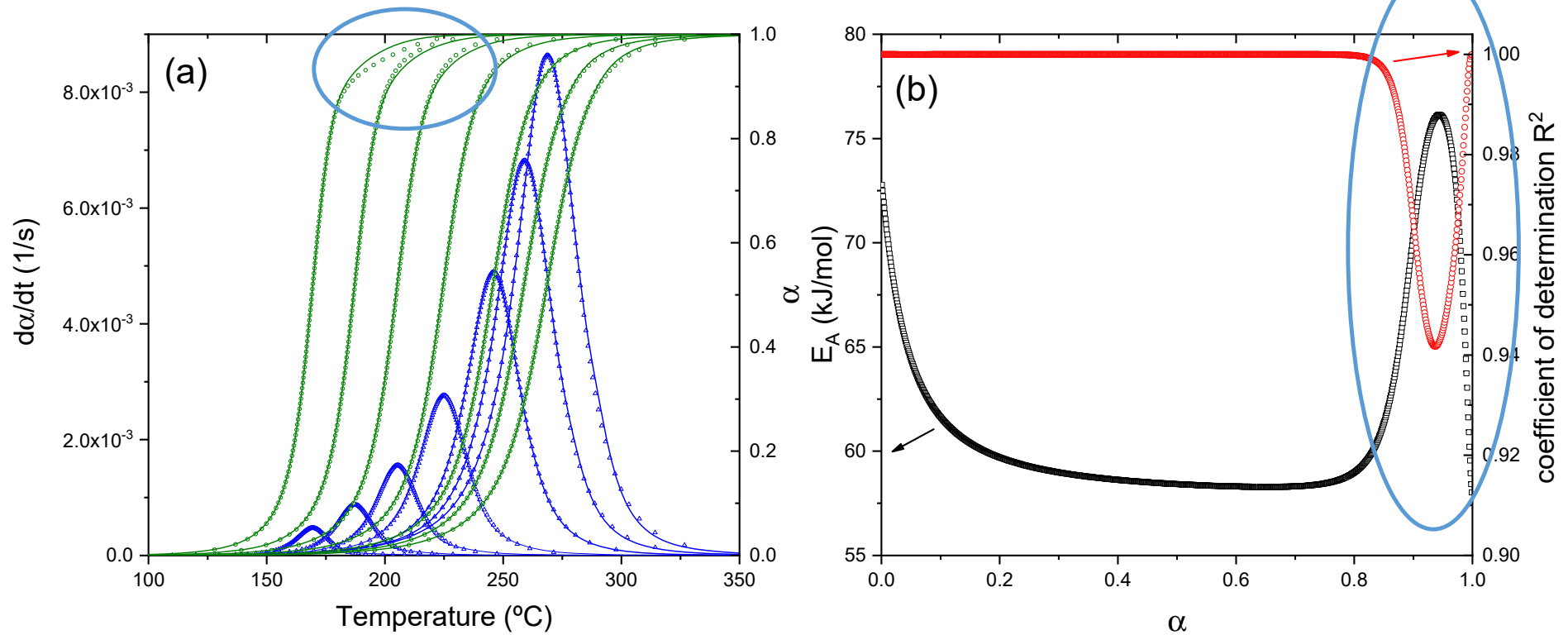
Kinetics of RTM6 resin, Kamal and Sourour model, **with Diffusion** :

A_1 (s ⁻¹)	19,000
A_2 (s ⁻¹)	22,080
E_1 (kJmol ⁻¹)	72.900
E_2 (kJmol ⁻¹)	57.820
n_1	1.97
n_2	1.53
m	1.29
A_D (s ⁻¹)	$6.76 \cdot 10^{18}$
E_D (kJmol ⁻¹)	138
b	0.452
T_{g0} (°C)	-11
$T_{g\infty}$ (°C)	206
λ	0.435

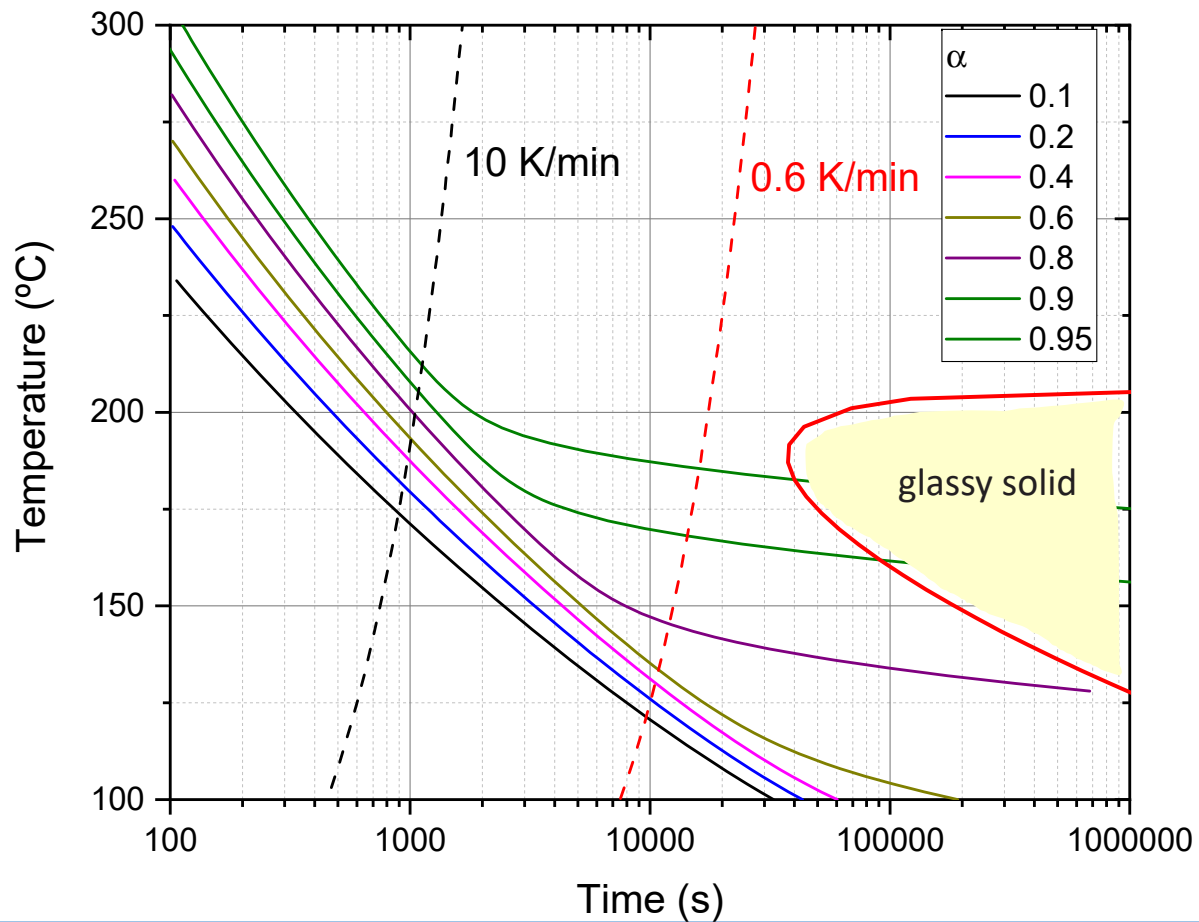


Modeling the Cure Kinetics of Epoxy Resins

Constant heating simulations



Modeling the Cure Kinetics of Epoxy Resins



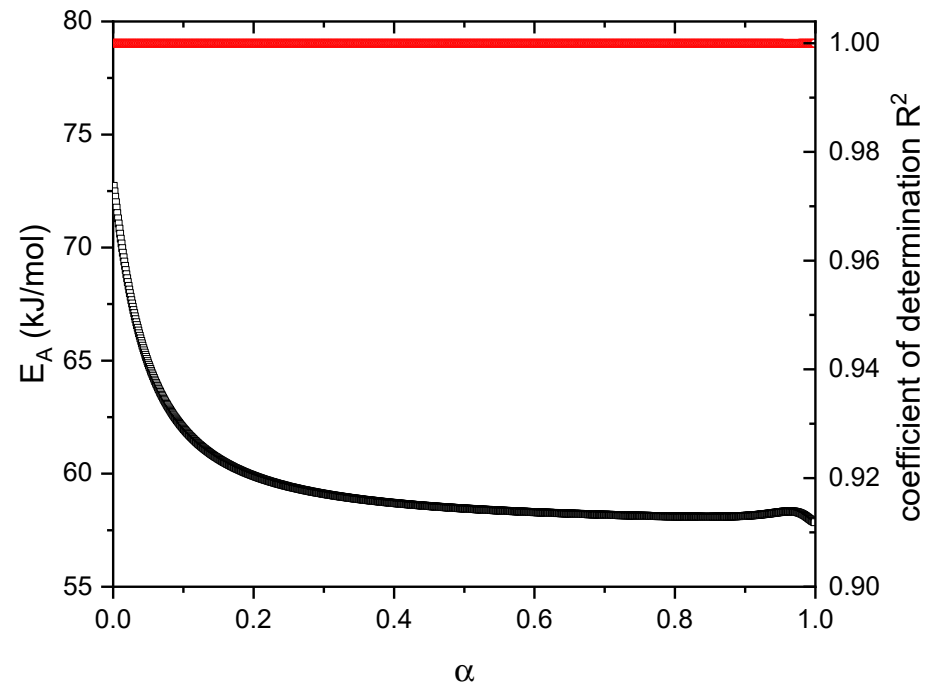
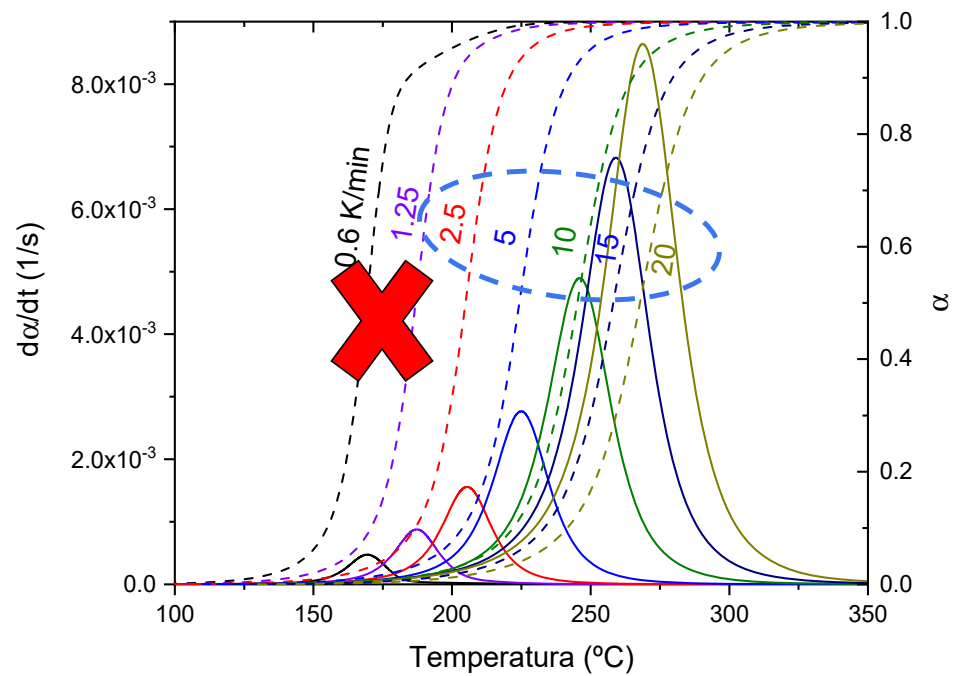
Modeling the Cure Kinetics of Epoxy Resins

To overcome the problem that the isoconversional approach does not **account for diffusion**, we have added the diffusion term, with the **addition of kinetic resistances** in series

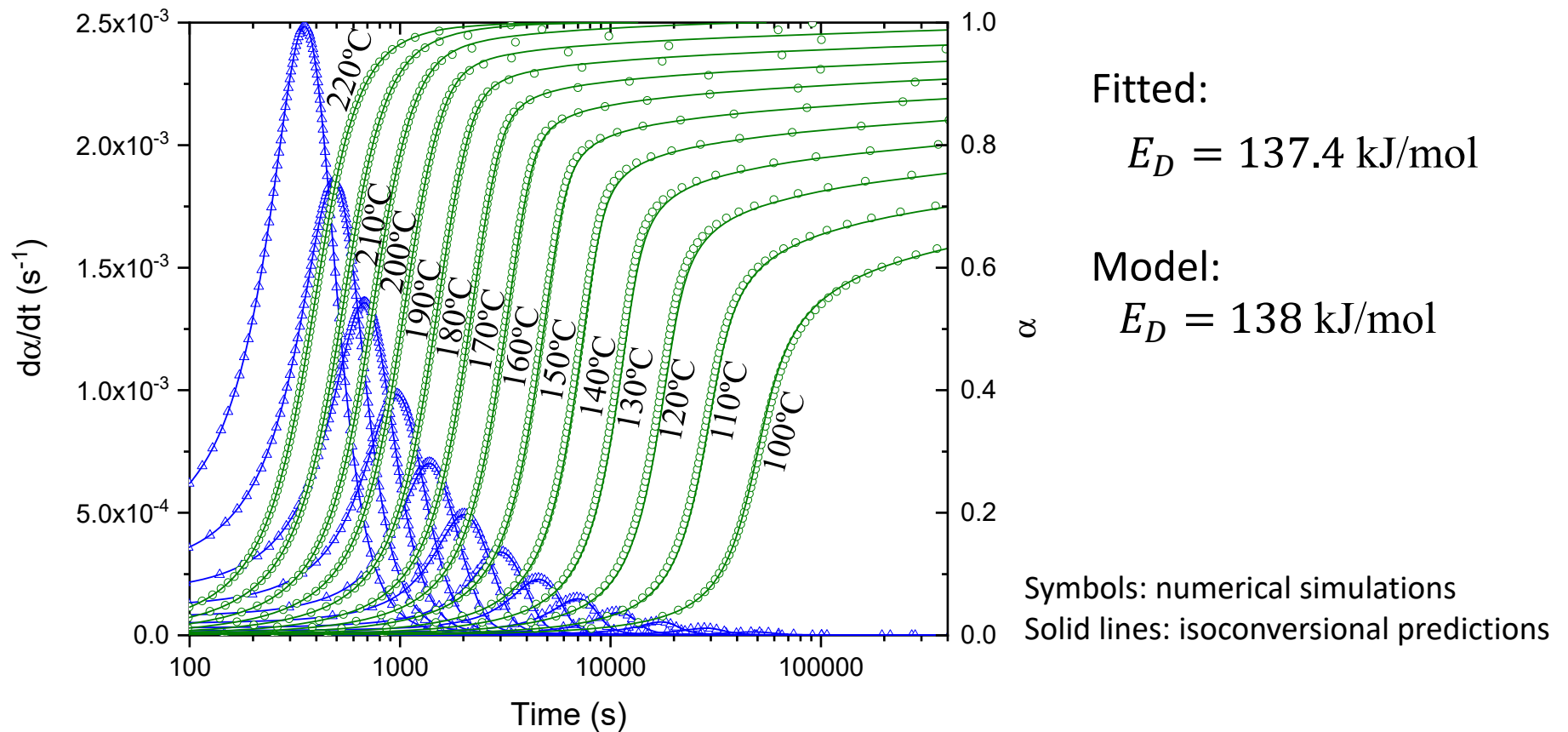
$$\frac{d\alpha}{dt} = \left[\frac{1}{k_{Iso}} + \frac{1}{k_D} \right]^{-1}$$

$$k_{Iso} = A_{\alpha} e^{-E_{\alpha}/(RT)}$$

$$k_D = A_D e^{-E_D/(RT)} e^{-b/f}$$



Modeling the Cure Kinetics of Epoxy Resins



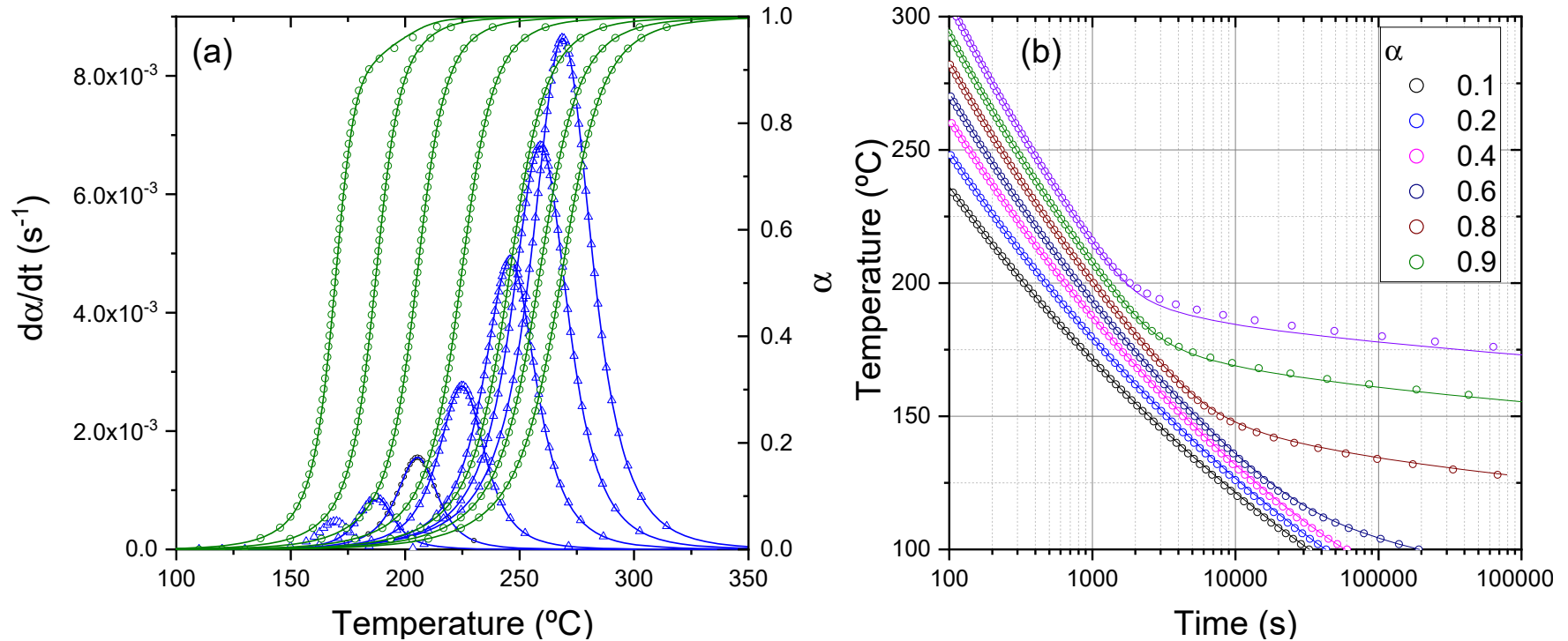
Fitted:

$$E_D = 137.4 \text{ kJ/mol}$$

Model:

$$E_D = 138 \text{ kJ/mol}$$

Modeling the Cure Kinetics of Epoxy Resins



Symbols: numerical simulations
Solid lines: isoconversional predictions

Thermal analysis: application to polymer characterisation

resin RTM6
(Hexcel Composites, Duxford, UK)

$T_g > 200^\circ\text{C}$

Enthalpy 450 J/g

- Thermal analysis (DSC)

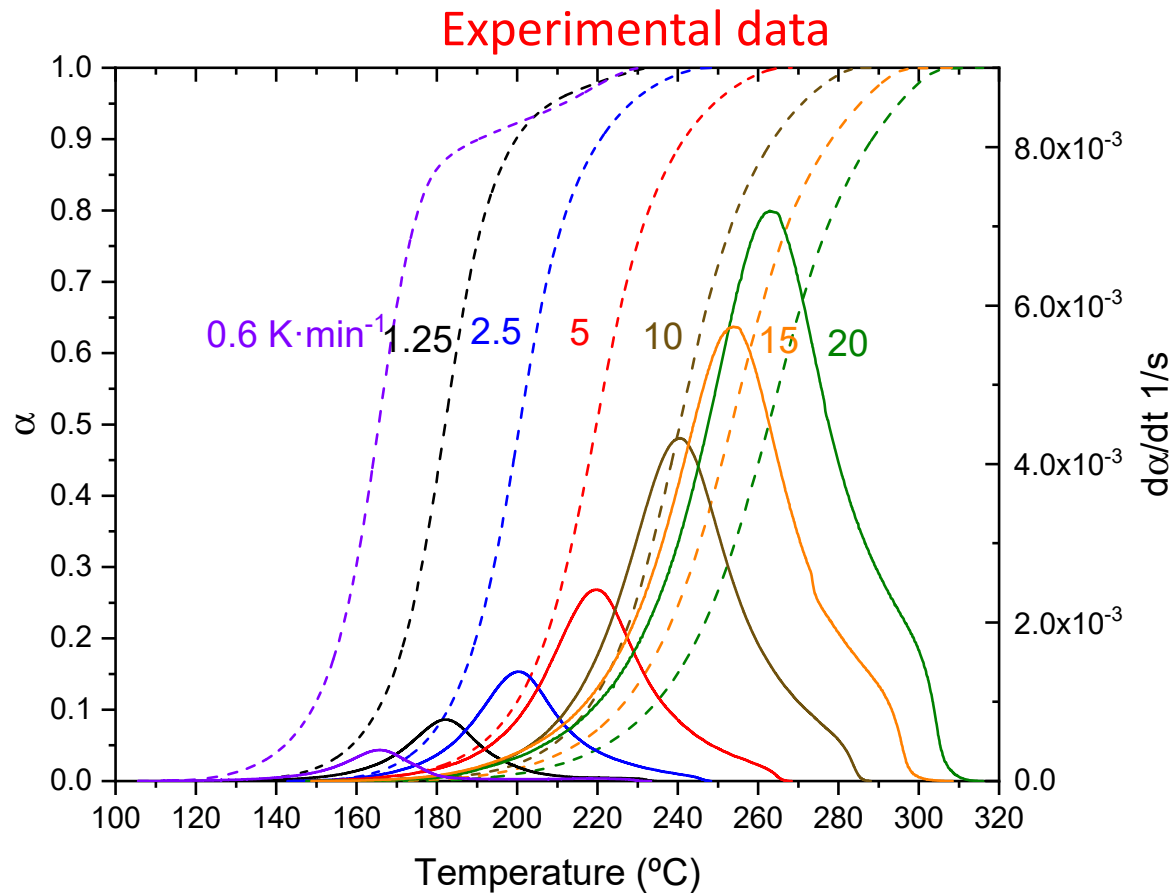
$$\frac{d\alpha}{dt} = \frac{1}{\Delta H} \frac{dH}{dt}$$

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

TA Instruments Q2000



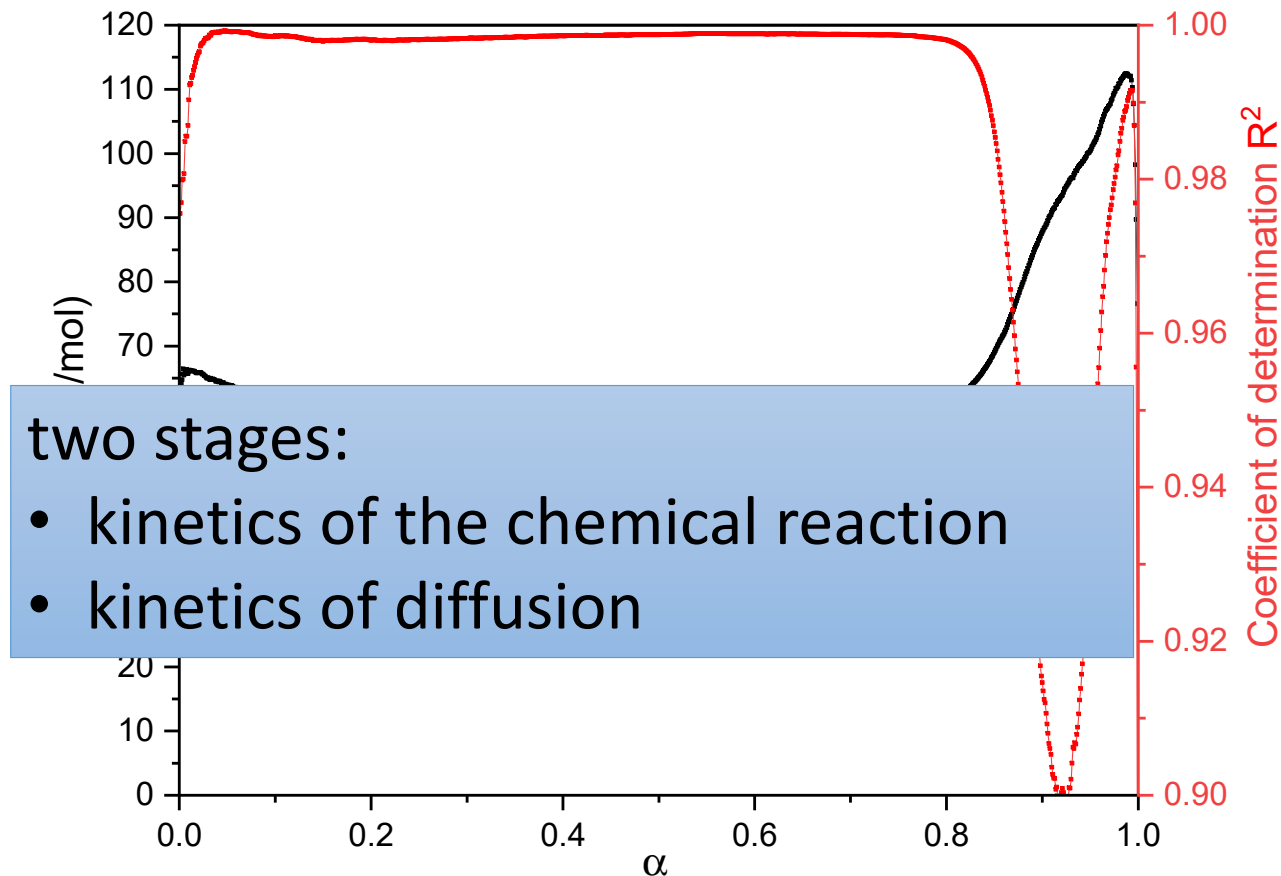
Modeling the Cure Kinetics of Epoxy Resins

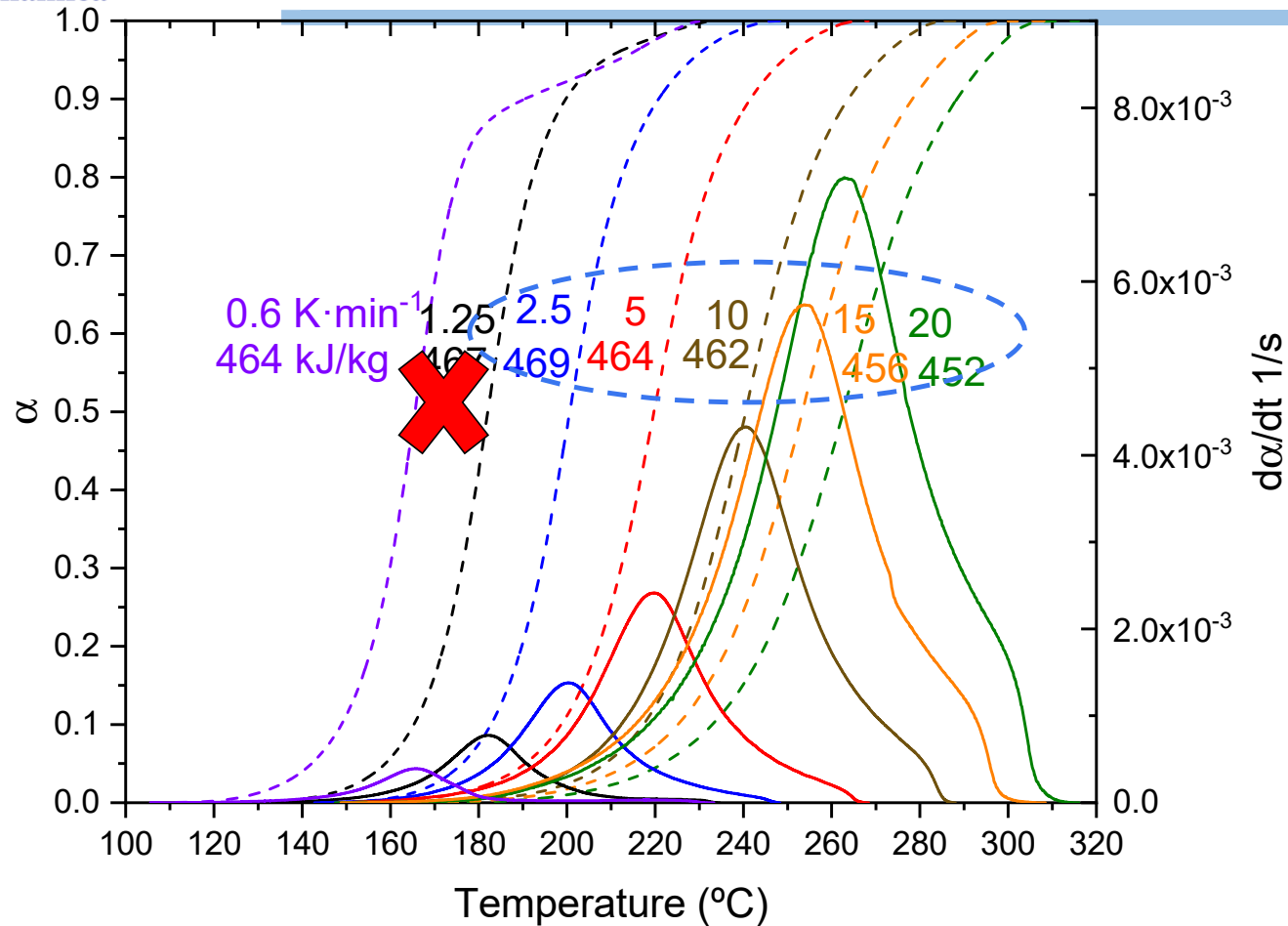


β K/min	Enthalpy (J/g)
0.6	464
1.25	467
2.5	469
5	464
10	462
15	456
20	452
	462±3

Modeling the Cure Kinetics of Epoxy Resins

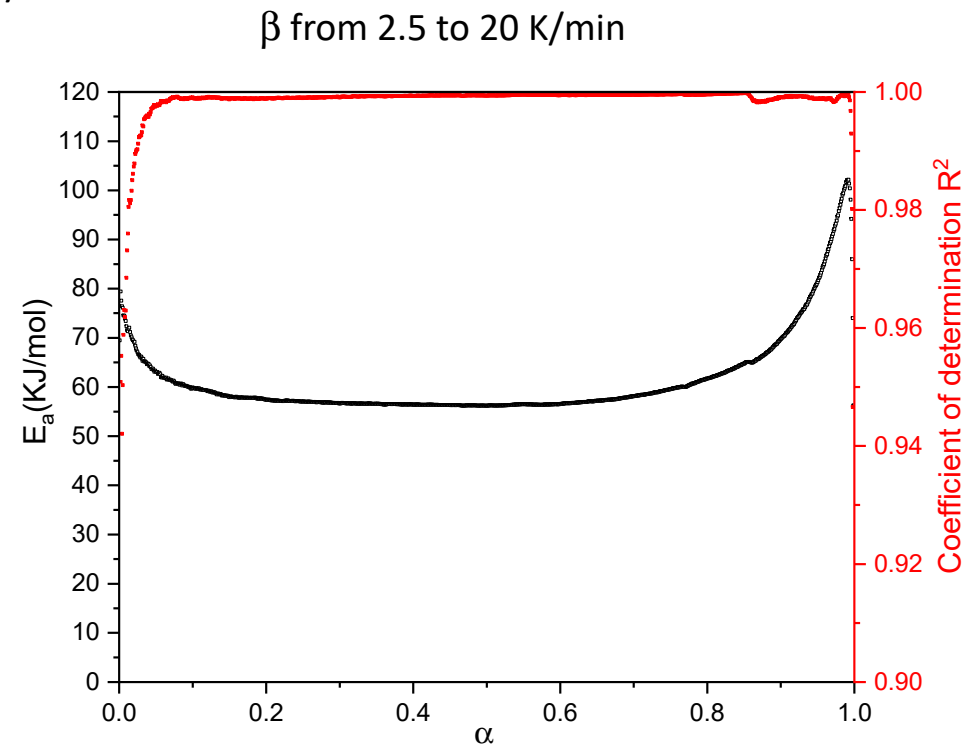
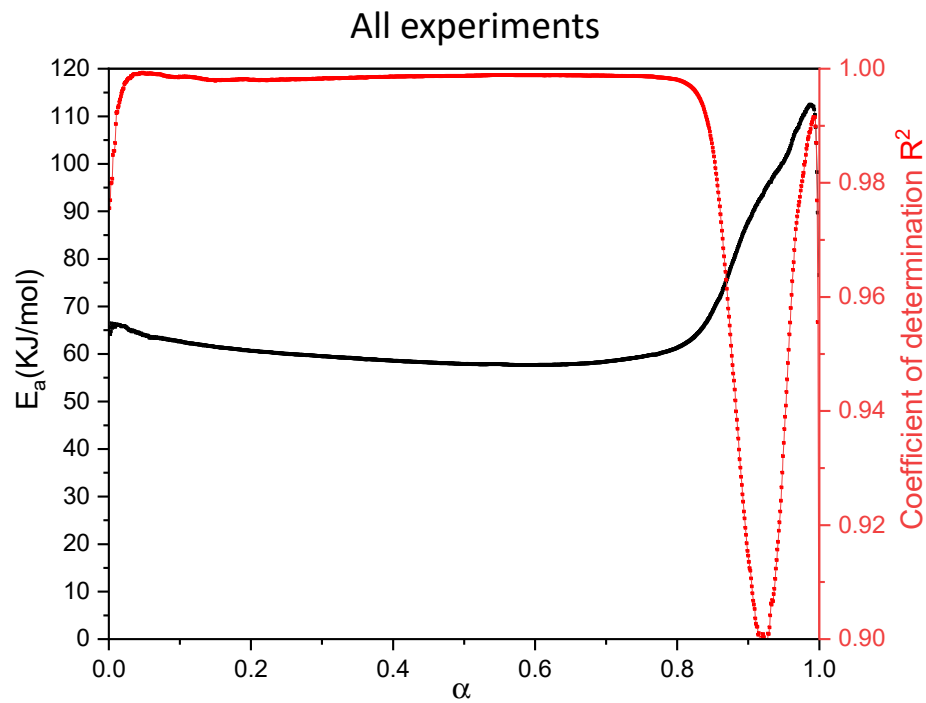
Isoconversional Friedman analysis



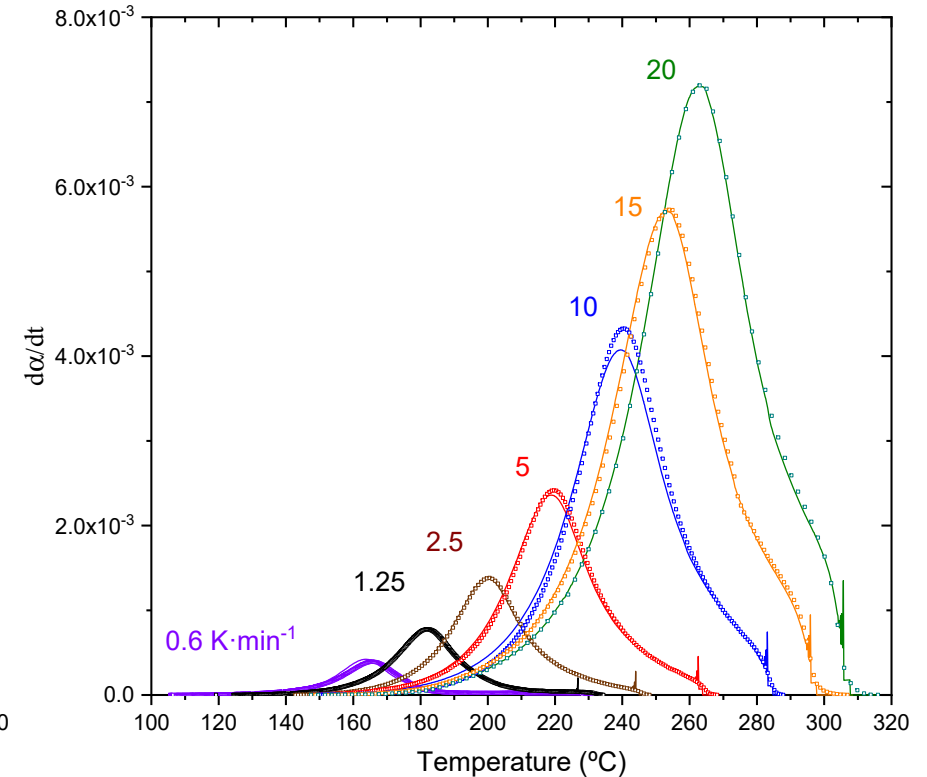
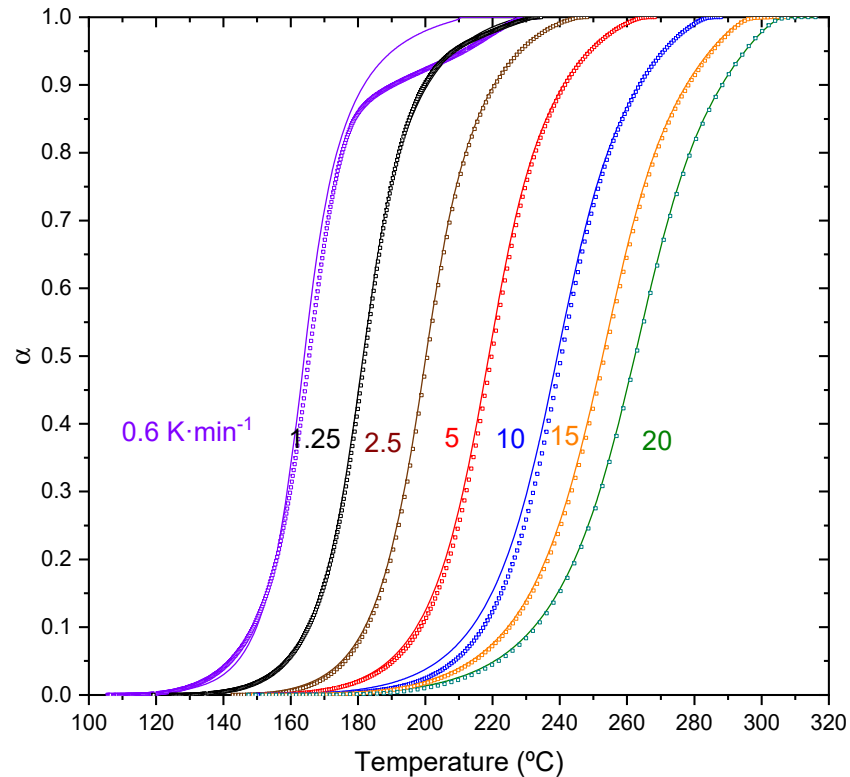


Modeling the Cure Kinetics of Epoxy Resins

Isoconversional Friedman analysis

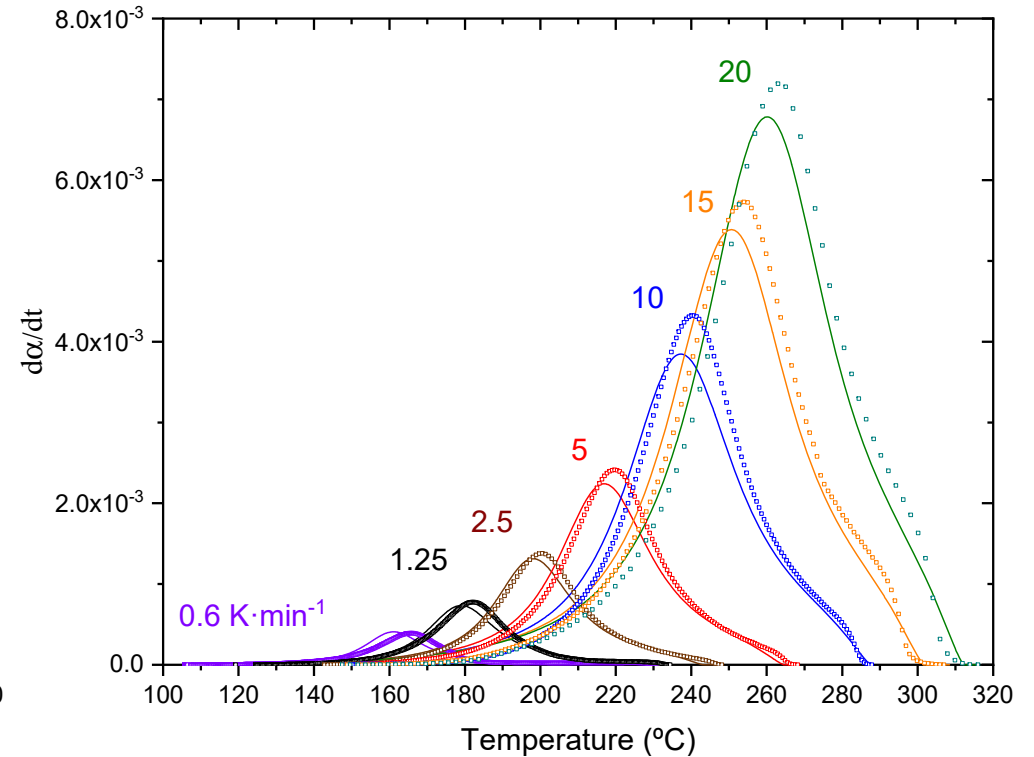
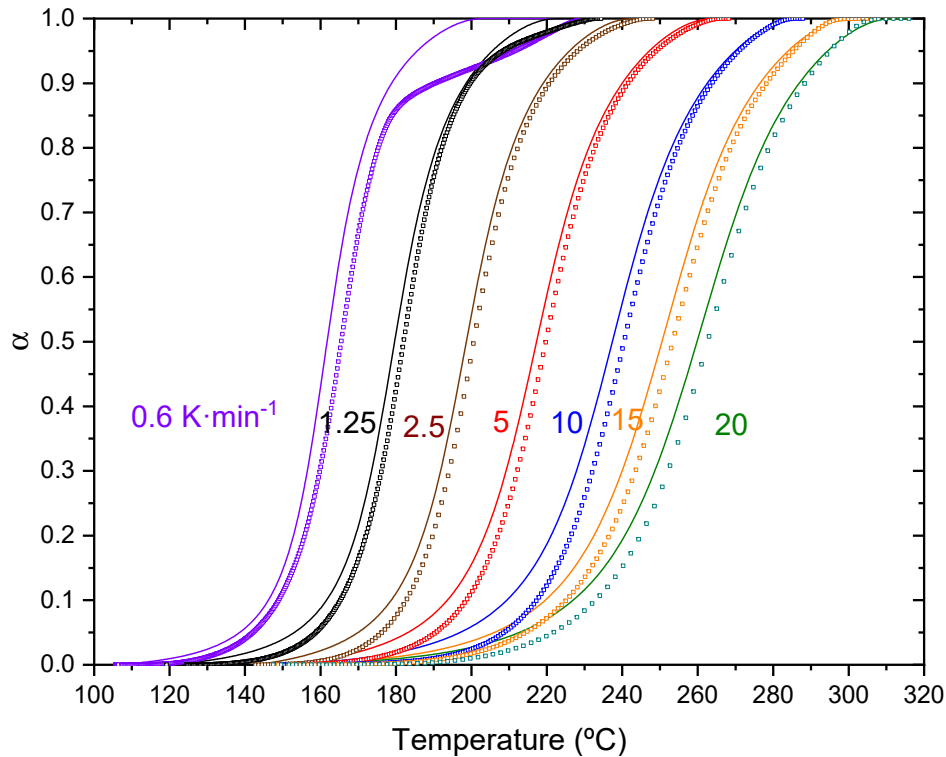


Modeling the Cure Kinetics of Epoxy Resins



Symbols: experimental data
Solid lines: isoconversional predictions

Modeling the Cure Kinetics of Epoxy Resins



Symbols: experimental data
Solid lines: fit to Kamal-Sourour model

Modeling the Cure Kinetics of Epoxy Resins

Fit of diffusion term

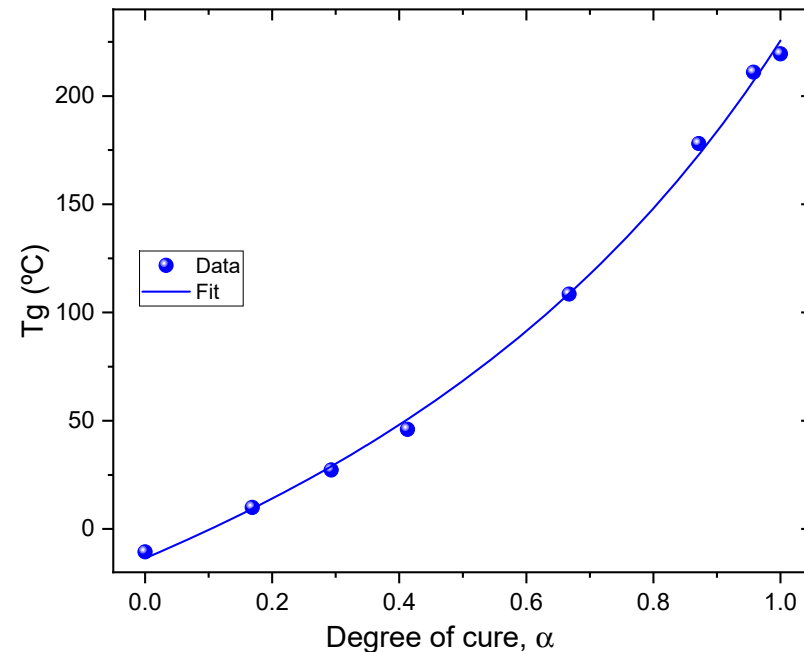
$$\frac{d\alpha}{dt} = \left[\frac{1}{k_{Iso}} + \frac{1}{k_D} \right]^{-1}$$

$$k_{Iso} = Ae^{-E_\alpha/(RT)} f(\alpha) \quad k_D = A_D e^{-E_D/(RT)} e^{-b/f}$$

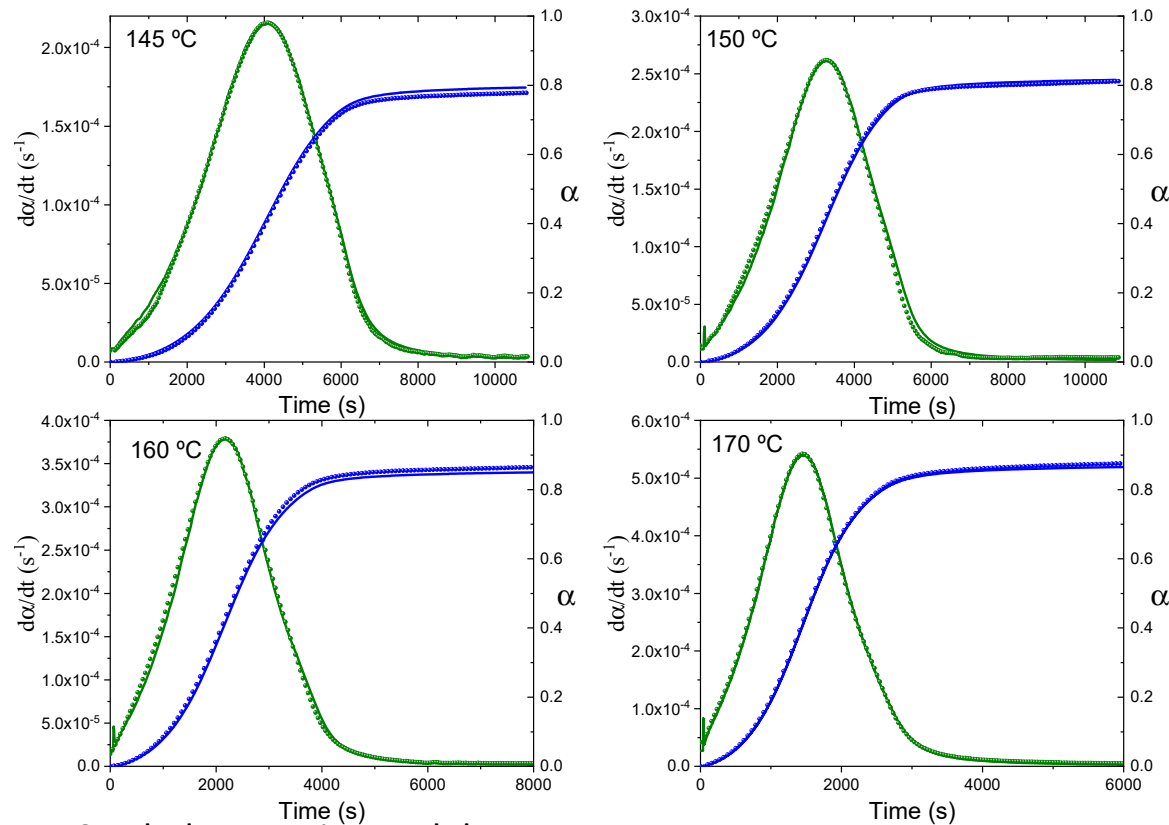
Fit of DiBenedetto's equation

$$\frac{(T_g - T_{g0})}{(T_{g\infty} - T_{g0})} = \frac{\lambda\alpha}{1 - (1 - \lambda)\alpha}$$

Parameter	fitted
T_{g0} (°C)	-13.5
$T_{g\infty}$ (°C)	225.6
λ	0.5212



Modeling the Cure Kinetics of Epoxy Resins



Symbols: experimental data

Solid lines: model fit (isoconversional + diffusion)

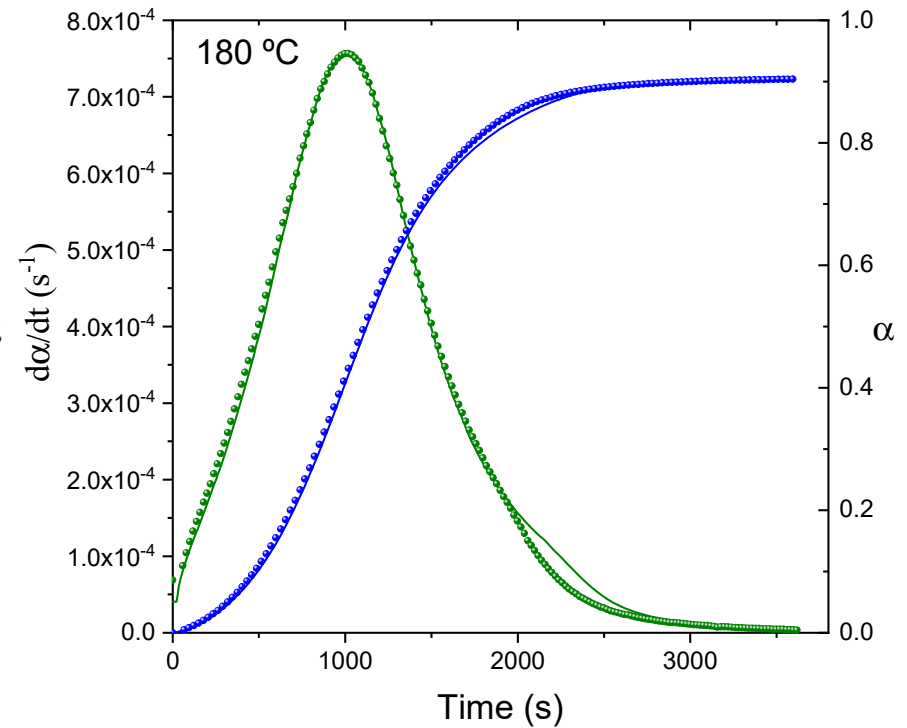
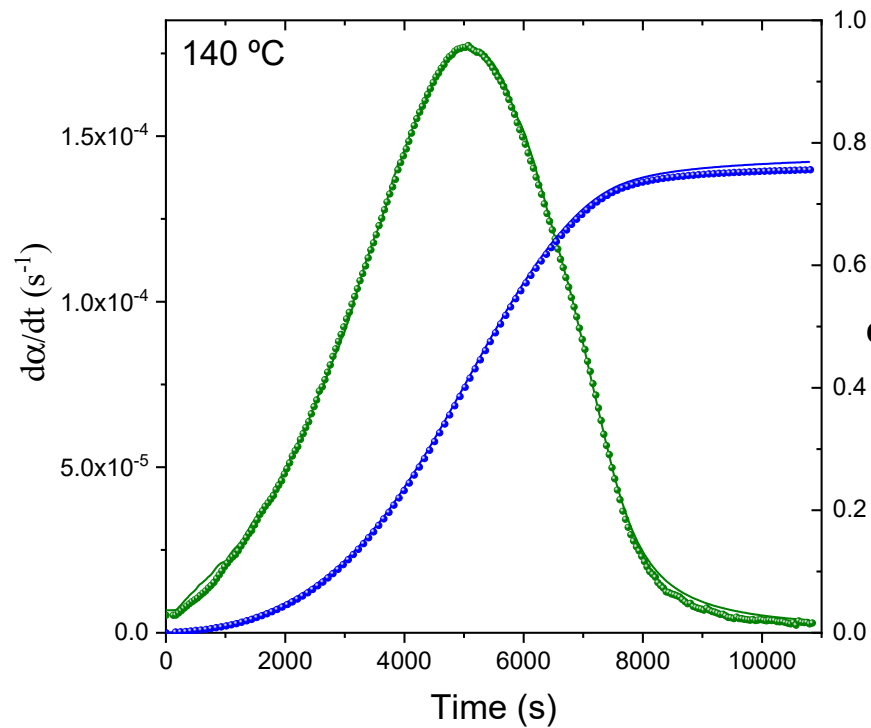
Fitted:

$$E_D = 143 \text{ kJ/mol}$$

Literature:

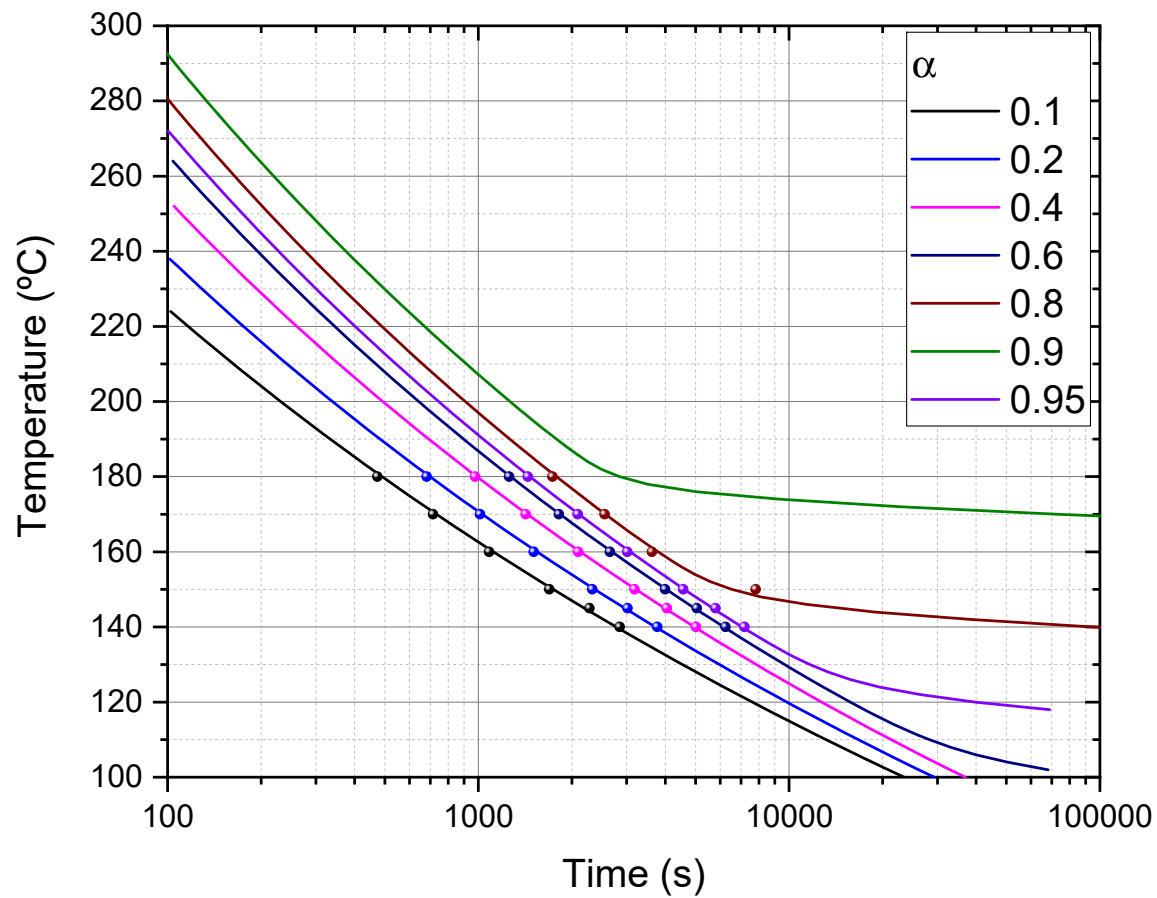
$$E_D = 138 \text{ kJ/mol}$$

Modeling the Cure Kinetics of Epoxy Resins



Symbols: experimental data
Solid lines: predictions

Modeling the Cure Kinetics of Epoxy Resins



Modeling the Cure Kinetics of Epoxy Resins

- Numerical simulations based on the Kamal-Sourour model demonstrated that isoconversional methods accurately reproduce the cure reaction kinetics
- To account for diffusion a novel two-step kinetic methodology has been developed.
- When applied to experimental data from RTM6 resin, this methodology revealed important insights. The isoconversional approach successfully captured the complexity of the real chemical reaction, while the Kamal-Sourour model failed to adequately describe the observed kinetics.
- We have been able to fit the diffusion term, the determined activation energy for diffusion is 143 kJ/mol, consistent with literature values for RTM6.



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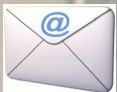
*Thank you
for your attention!!*



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