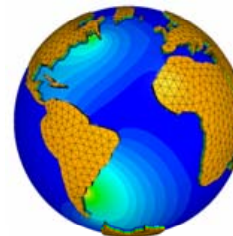




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ERFT
Composites

Engineering
Research and
Flow
Technology for Composites

Motivation

Industrial/research requirement for a simple characterization methodology to model resin cure kinetics from DSC measures

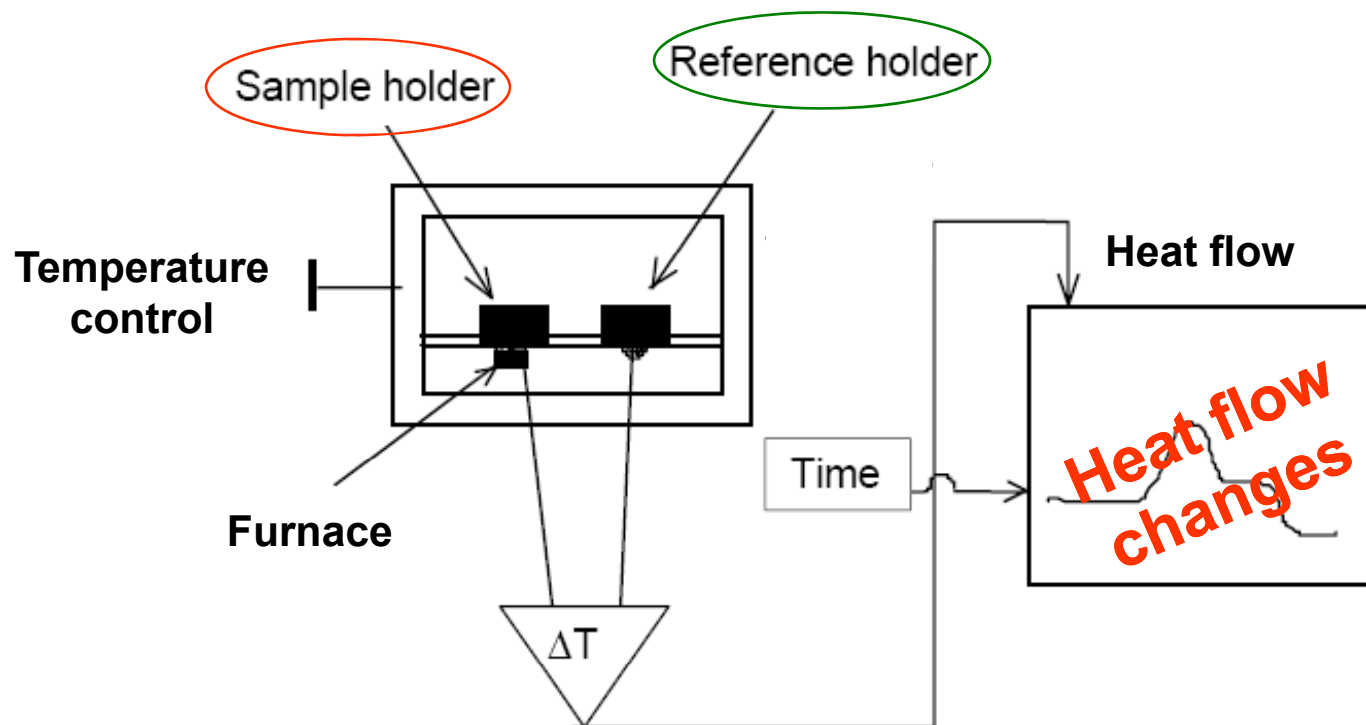
Software goals

1. Accurate numerical solutions for experimental data analysis taking into account trends accuracy and DSC sensitivity
2. Software package for cure kinetics modeling implementing standard models as well as user defined models
3. Creation of glass transition temperature, Inhibition time and gel time models
4. Generation of TTT diagrams
5. Prediction of cure evolution for a user defined temperature profile

Differential Scanning Calorimetry (DSC)

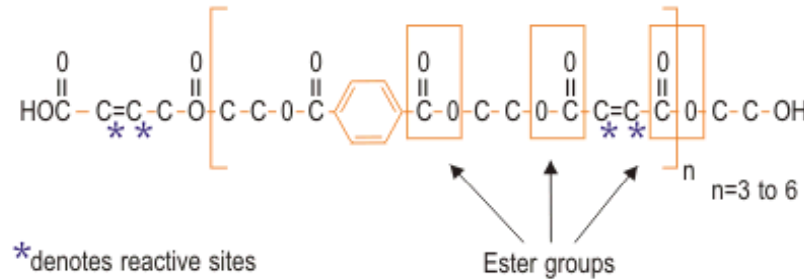
With a DSC instrument phase transitions or chemical reactions in a material can be analyzed when sample is heated, held at a constant temperature or cooled off

Schematic picture of a DSC instrument

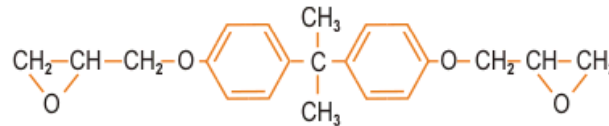


Polymerization reaction of thermosets

Unsaturated Polyester



Epoxy



The polymerization reaction is exothermic



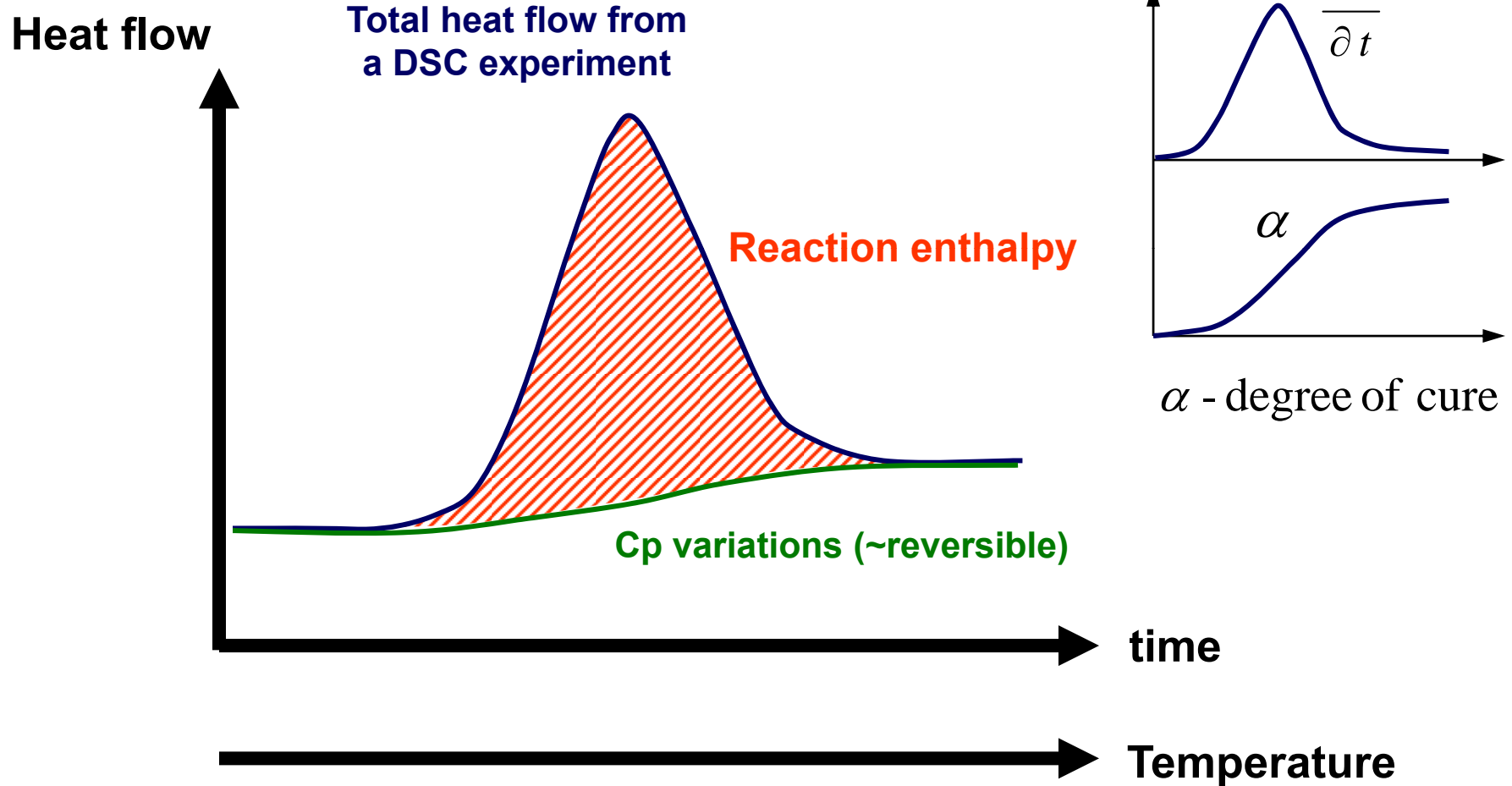
Exothermic reaction of unsaturated polyester

Differential calorimetry
DSC

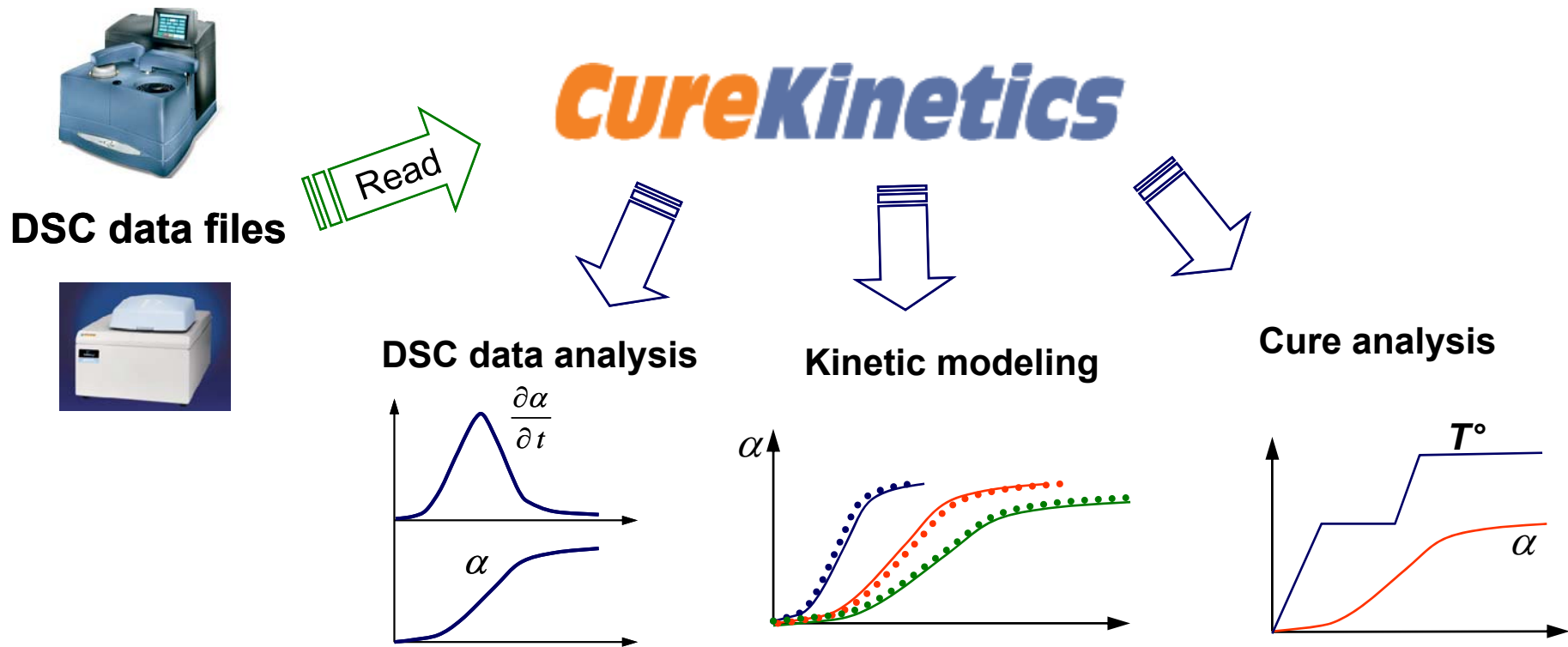
Cp variations;
(~reversible)

Polymerization reaction
(non-reversible)

Polymerization reaction of thermosets



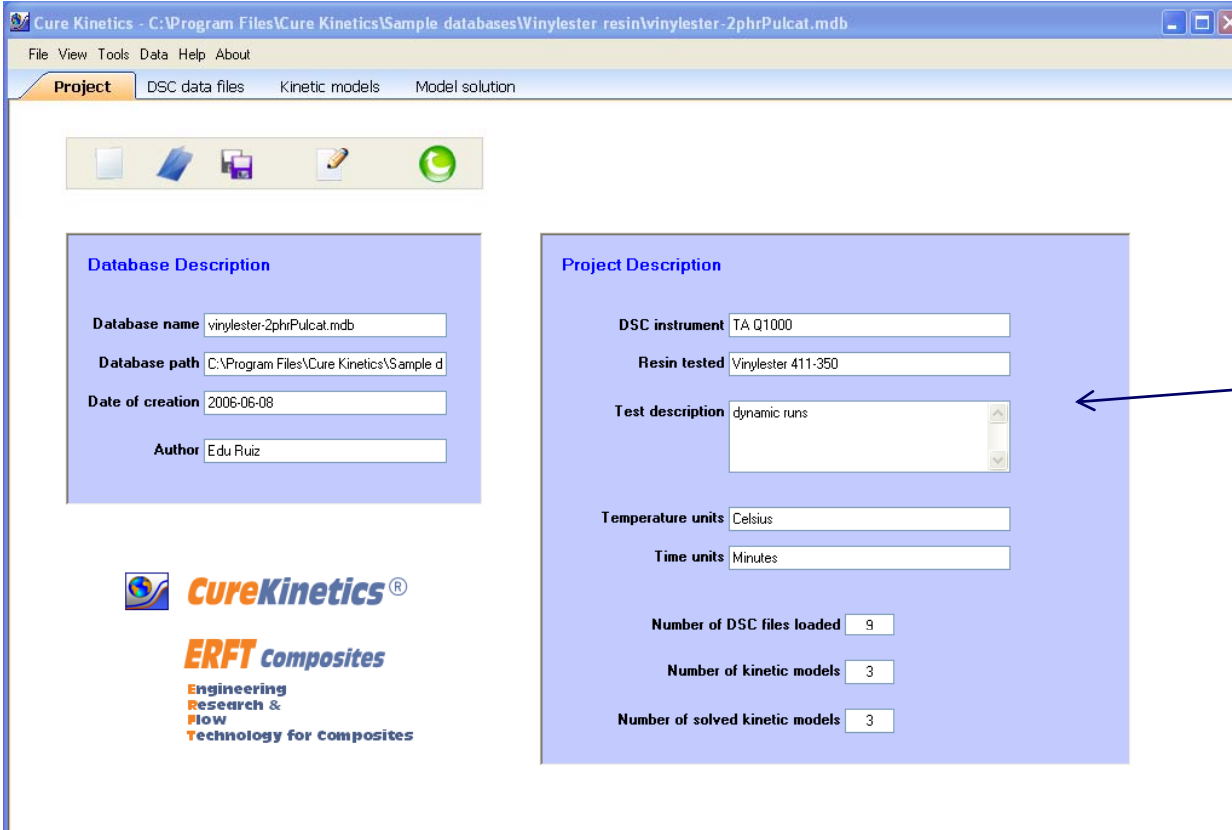
What *CureKinetics* does?



- Data are stored in a MS Access Database for easy user access
- Various kinetic models can be calculated for one set of DSC experiments
- Modeling reports can be generated in MS Word

How *CureKinetics* looks like?

Startup window



The screenshot shows the Cure Kinetics software interface. The title bar reads "Cure Kinetics - C:\Program Files\Cure Kinetics\Sample databases\Vinylester resin\vinylester-2phrPulcat.mdb". The menu bar includes "File", "View", "Tools", "Data", and "Help", with "About" also visible. Below the menu bar is a "Project" tab and a navigation bar with "DSC data files", "Kinetic models", and "Model solution". A toolbar with icons for file operations is located below the navigation bar. The main area is divided into two panels: "Database Description" and "Project Description".

Database Description

Database name	vinylester-2phrPulcat.mdb
Database path	C:\Program Files\Cure Kinetics\Sample d
Date of creation	2006-06-08
Author	Edu Ruiz

Project Description

DSC instrument	TA Q1000
Resin tested	Vinylester 411-350
Test description	dynamic runs
Temperature units	Celsius
Time units	Minutes
Number of DSC files loaded	9
Number of kinetic models	3
Number of solved kinetic models	3

At the bottom of the window, the CureKinetics logo and the ERFT Composites logo are displayed. The ERFT Composites logo includes the text "Engineering Research & Flow Technology for Composites".

← Project description

Loading DSC data files

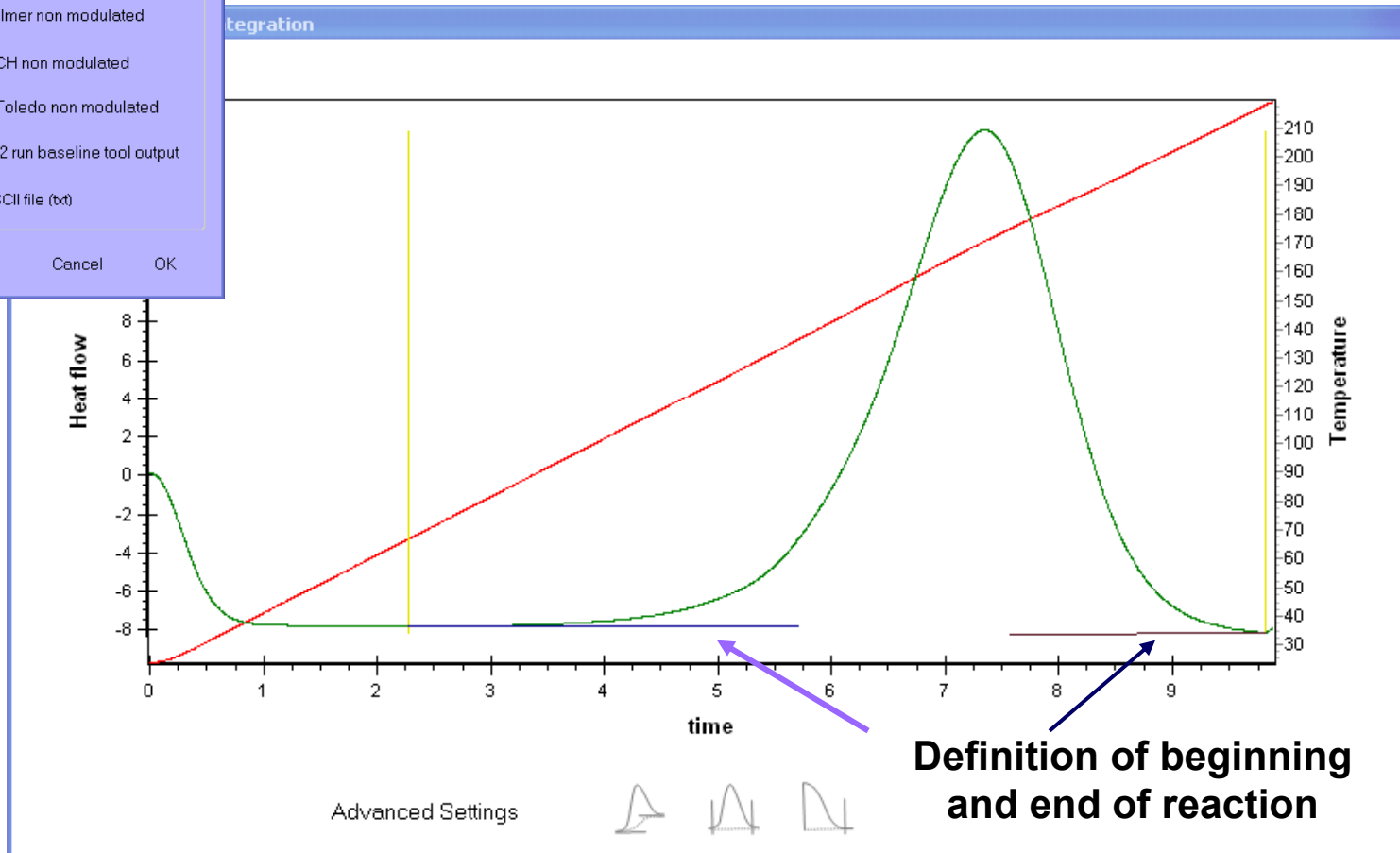
DSC files formats

Type of file selection

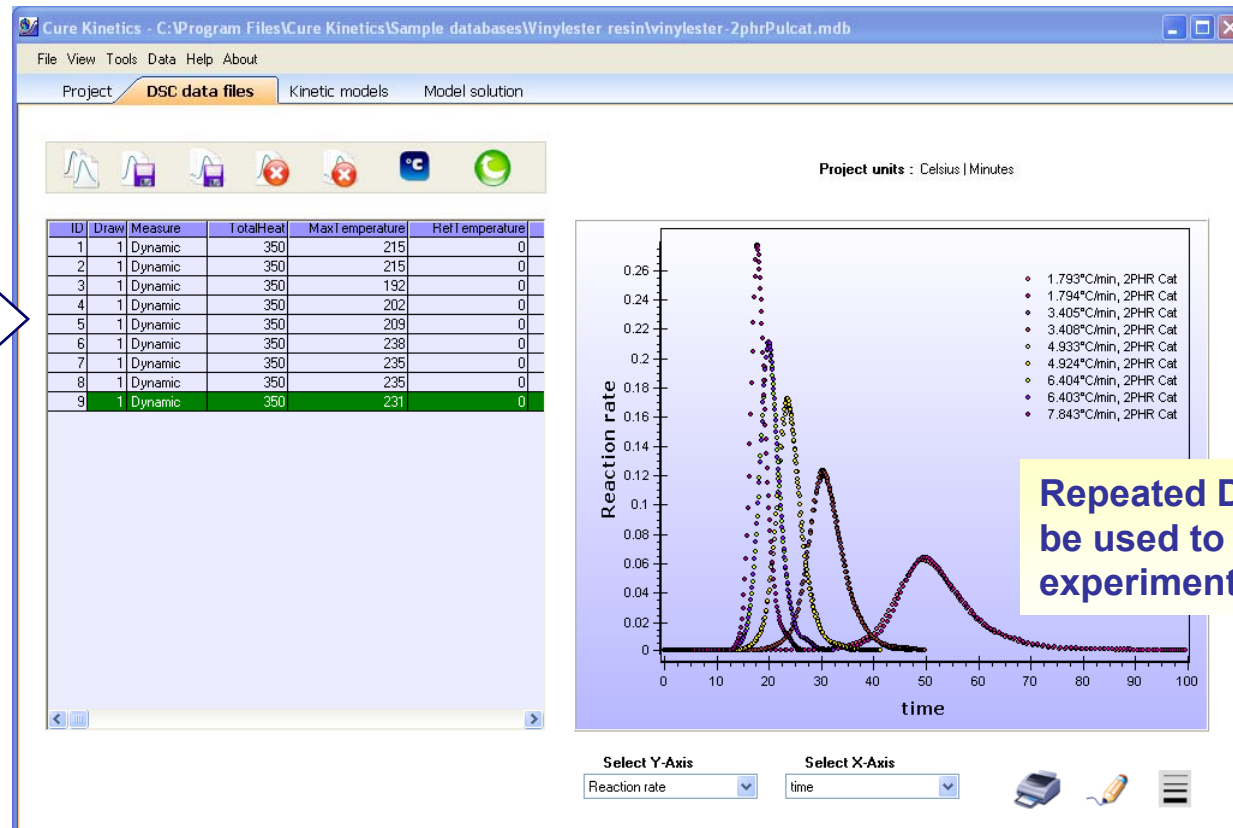
Select the corresponding type of DSC

- DSC TA Instruments (Q100, Q1000)
- DSC Perkin Elmer non modulated
- DSC NETZSCH non modulated
- DSC Mettler-Toledo non modulated
- DSC file from 2 run baseline tool output
- Formatted ASCII file (.txt)

Cancel OK



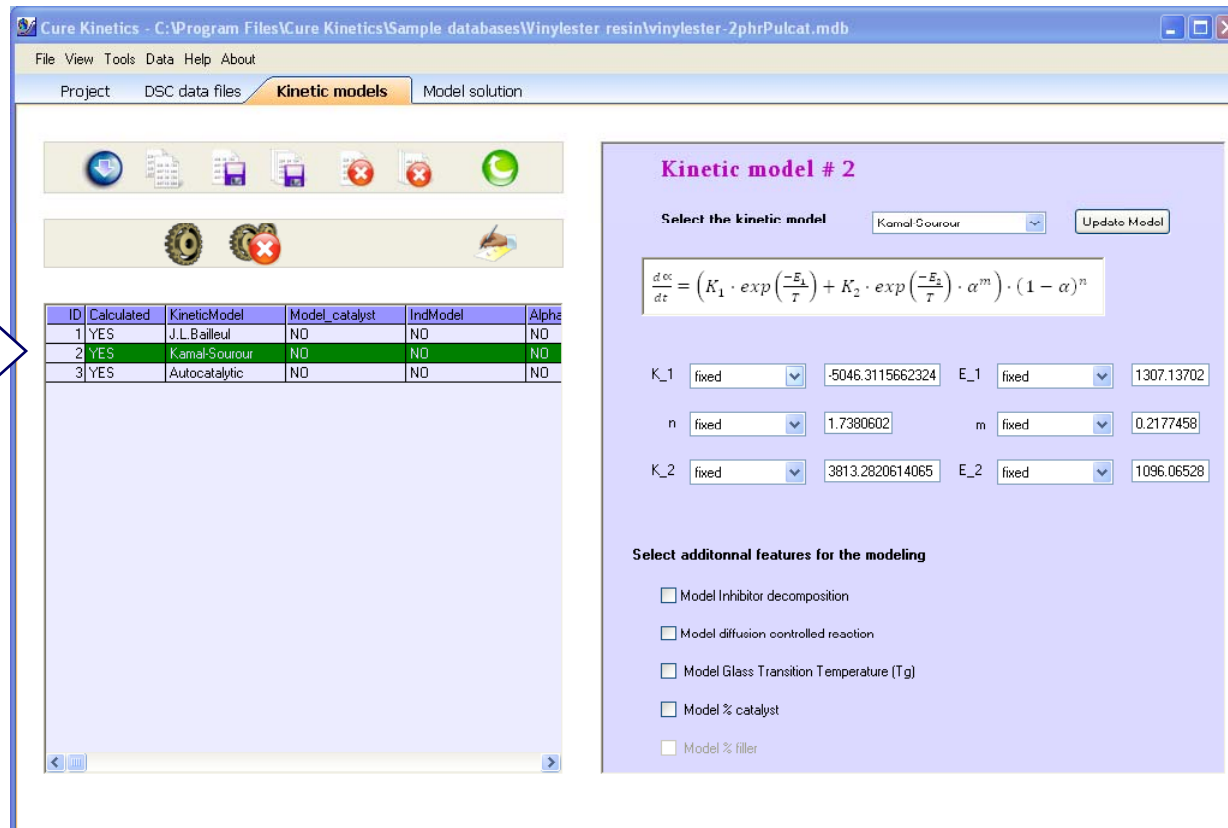
DSC data files loaded



Series of DSC runs

Repeated DSC tests can be used to consider experimental dispersion

Definition of kinetic models



The screenshot shows the 'Kinetic models' tab in the Cure Kinetics software. On the left, a table lists three models. Model 2, 'Kamal-Sourour', is highlighted. On the right, the 'Kinetic model # 2' configuration panel is shown, featuring a dropdown menu set to 'Kamal-Sourour', an 'Update Model' button, a mathematical equation for $\frac{d\alpha}{dt}$, and input fields for parameters K_1, E_1, n, m, K_2, and E_2. Below these are checkboxes for additional modeling features.

ID	Calculated	KineticModel	Model_catalyst	IndModel	Alpha
1	YES	J.L.Bailleul	NO	NO	NO
2	YES	Kamal-Sourour	NO	NO	NO
3	YES	Autocatalytic	NO	NO	NO

Kinetic model # 2

Select the kinetic model: Kamal-Sourour [Update Model]

$$\frac{d\alpha}{dt} = \left(K_1 \cdot \exp\left(\frac{-E_1}{T}\right) + K_2 \cdot \exp\left(\frac{-E_2}{T}\right) \cdot \alpha^m \right) \cdot (1 - \alpha)^n$$

K_1: fixed [0.50463115662324] E_1: fixed [1307.13702]
 n: fixed [1.7380602] m: fixed [0.2177458]
 K_2: fixed [3813.2820614065] E_2: fixed [1096.06528]

Select additional features for the modeling:

- Model Inhibitor decomposition
- Model diffusion controlled reaction
- Model Glass Transition Temperature (Tg)
- Model % catalyst
- Model % filler

Kinetics models

Model parameters

Available kinetic models

Autocatalytic $\frac{d\alpha}{dt} = K_1 \cdot \exp\left(\frac{-E_1}{T}\right) \cdot \alpha^m \cdot (\alpha_{max}(T) - \alpha)^n \cdot F(\alpha)$

Kamal-Sourour $\frac{d\alpha}{dt} = \left(K_1 \cdot \exp\left(\frac{-E_1}{T}\right) + K_2 \cdot \exp\left(\frac{-E_2}{T}\right) \cdot \alpha^m\right) \cdot (\alpha_{max}(T) - \alpha)^n \cdot F(\alpha)$

Ruiz $\frac{d\alpha}{dt} = K_1 \cdot \exp\left(-E_1 \left(\frac{T_{ref}}{T} - 1\right)\right) \cdot G(\alpha) \cdot (\alpha_{max}(T) - \alpha)^n \cdot F(\alpha)$

J.L. Bailleul $\frac{d\alpha}{dt} = K_1 \cdot \exp\left(-E_1 \left(\frac{T_{ref}}{T} - 1\right)\right) \cdot G(\alpha) \cdot F(\alpha)$

nth-order $\frac{d\alpha}{dt} = K_1 \cdot \exp\left(\frac{-E_1}{T}\right) \cdot (\alpha_{max}(T) - \alpha)^n \cdot F(\alpha)$

Mechanistic
$$\frac{d\alpha}{dt} = K_3 \exp\left(\frac{-E_3}{T}\right) \cdot I_0 \cdot (\alpha_{max}(T) - \alpha) \cdot \beta \cdot F(\alpha)$$

$$\frac{d\beta}{dt} = K_1 \exp\left(\frac{-E_1}{T}\right) - \left[K_1 \cdot \exp\left(\frac{-E_1}{T}\right) + K_2 \cdot \exp\left(\frac{-E_2}{T}\right)\right] \cdot \beta$$

Diffusion
$$F(\alpha) = \frac{1}{1 + \exp(E_1(\alpha - \alpha_c))}$$

User defined models

User Defined Kinetic Models

User Models

5) Modified K-Sourour model: ReactionKinetics : [a*exp(-b/x1)+c*exp(-d/x1)]*[

Kinetic Model Induction Model Alpha Max Model

Model name: Modified K-Sourour model

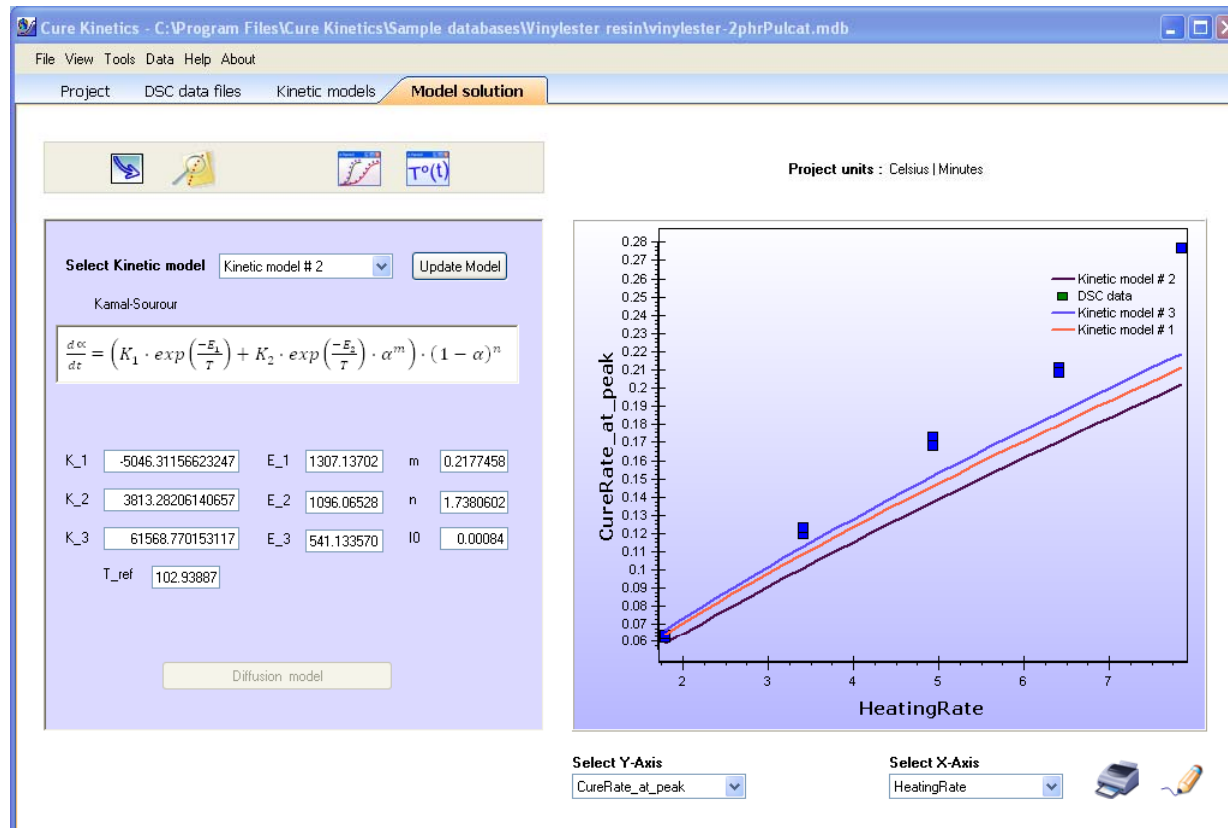
Nbr of independent variables: 6

List of parameters to be used: a,b,c,d,e,f

Write model here: [a*exp(-b/x1)+c*exp(-d/x1)]*(x2^e)*[abs([1-(1-0.4)]*(400-x

Delete Model Modify Model Add Model Close

Verification of kinetic parameters (rate at peak, cure at peak, etc)



Comparison of kinetic models and DSC data

Dynamic correction of model parameters

Dynamic parameters

Kinetic Model # 2

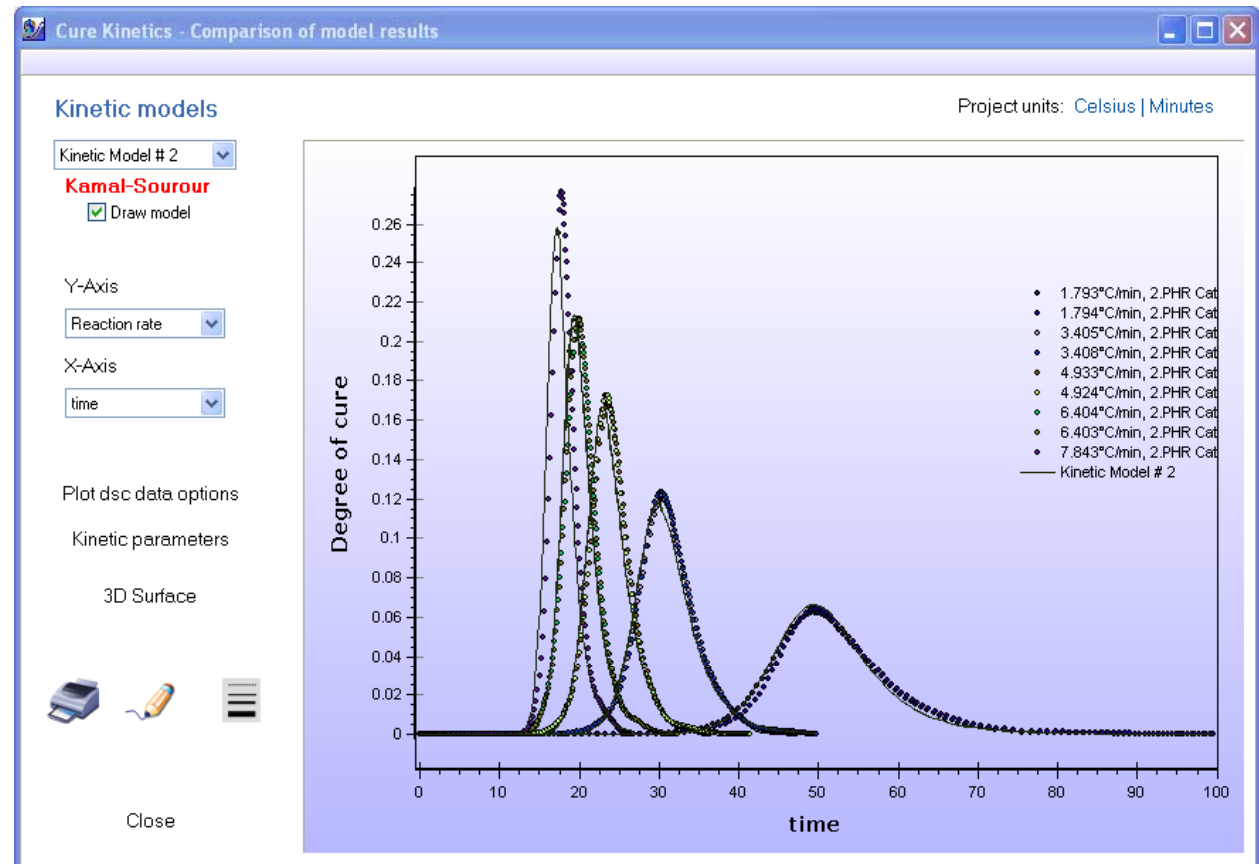
Select kinetic parameter

- K1
- K2
- E1
- E2
- M_A
- N_A
- Step

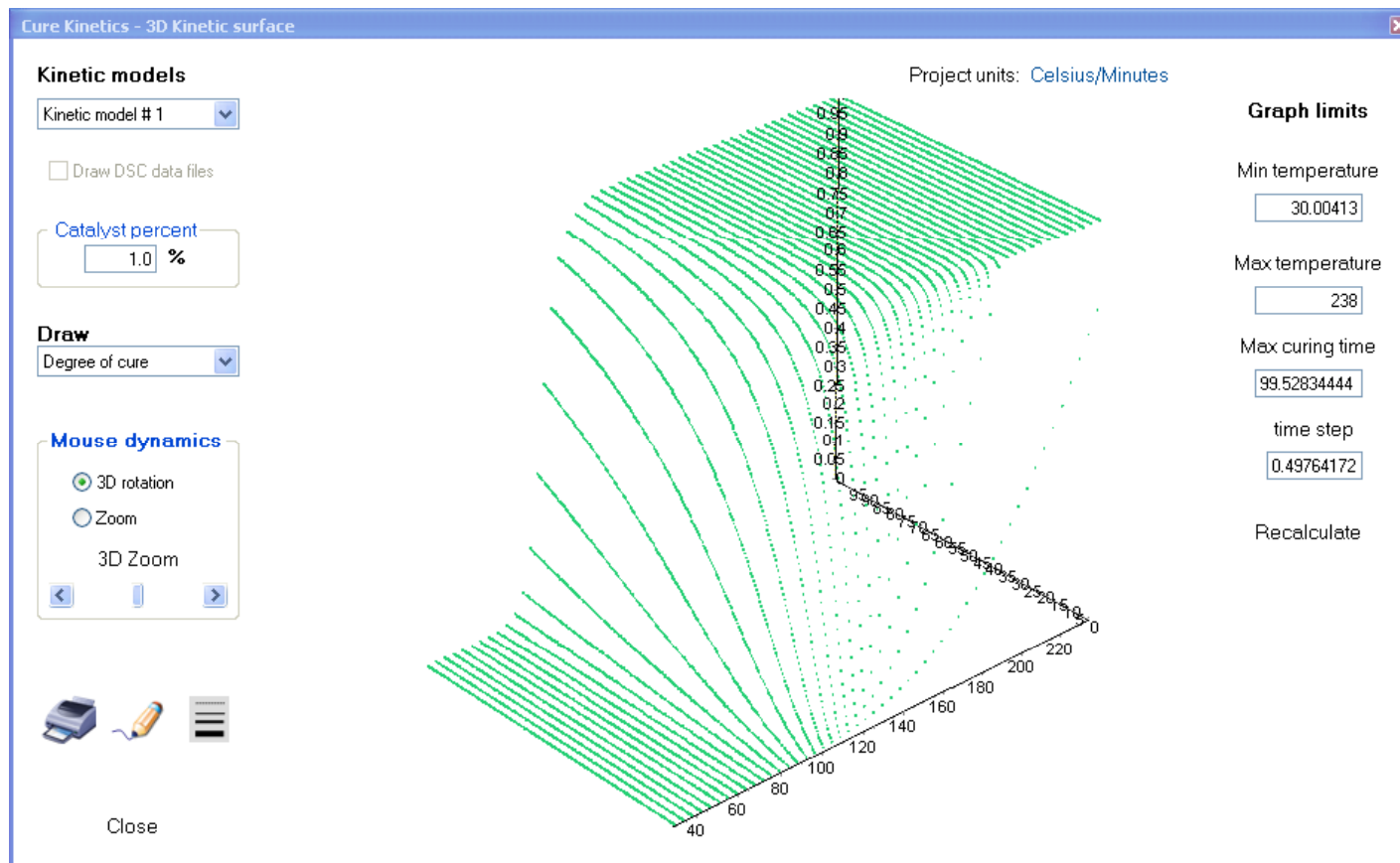
-50.4631156623247

Update model

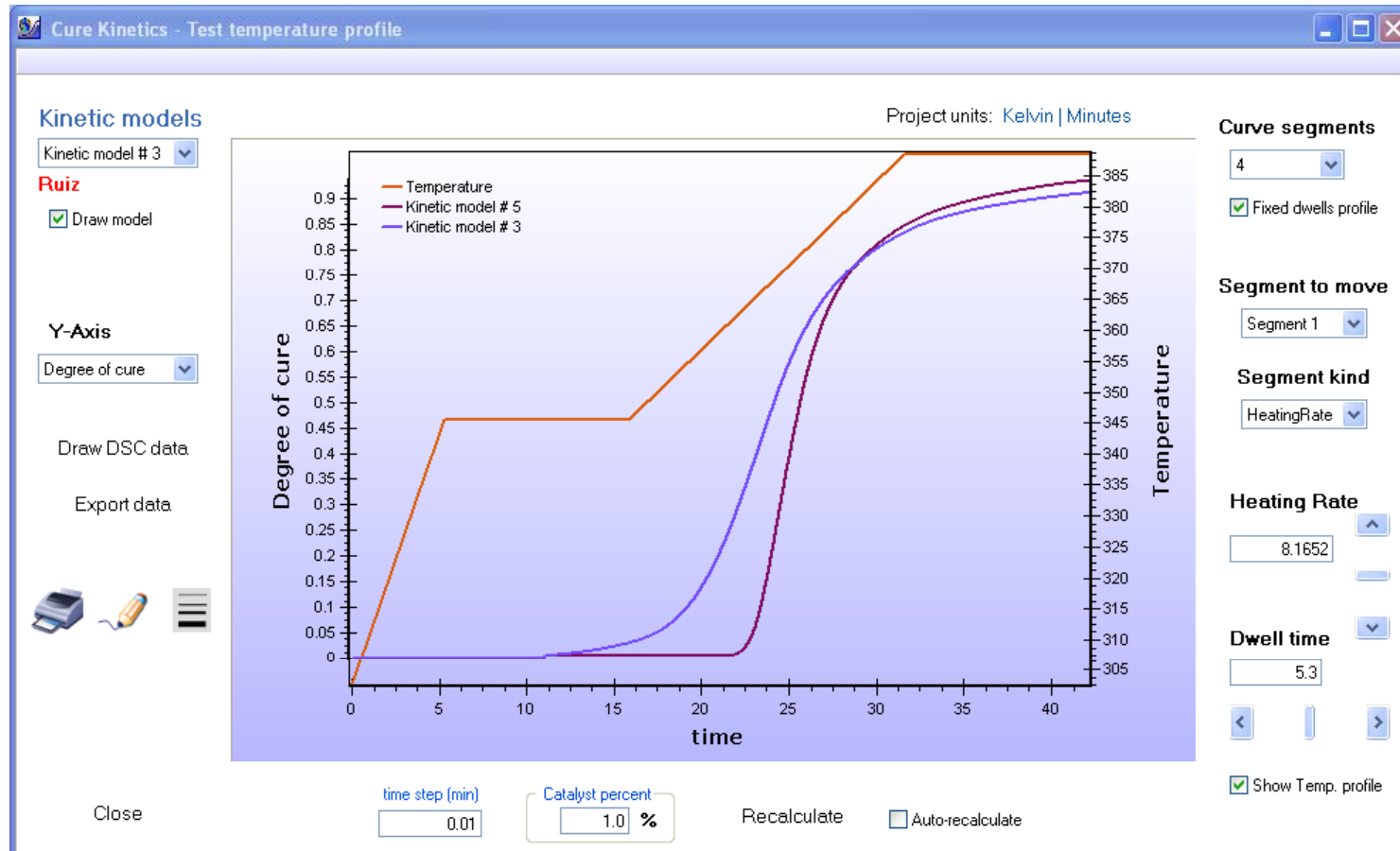
Close



3D graphs of kinetic models

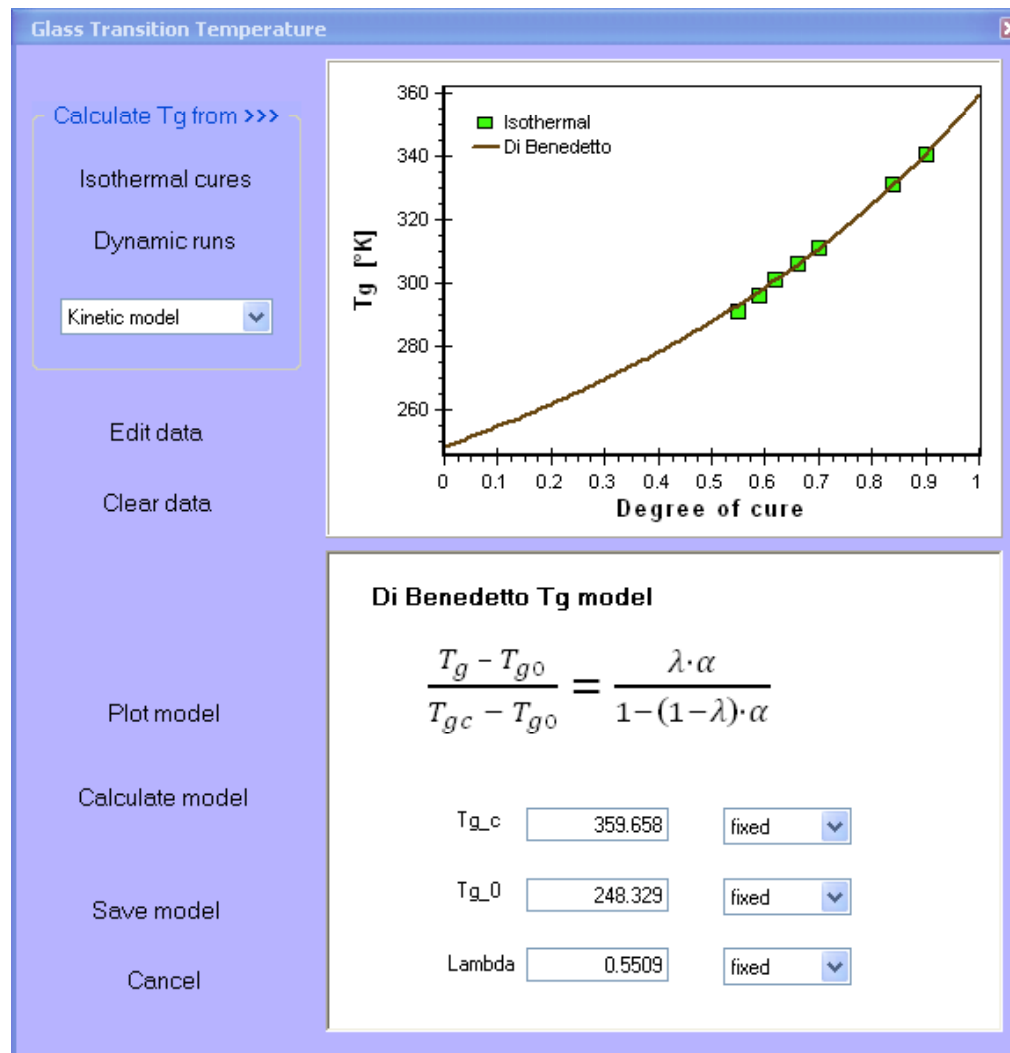


Model solution for a temperature profile





Glass transition temperature





Inhibition time model

Inhibition time model

Calculate $I(t,T)$ from :

- Isothermal cures
- Dynamic runs
- Kinetic model

Edit data

Clear graph

Plot model

Calculate model

Save model

Cancel

Integral time model

$$W(t,T) = t_{ref} - \int_0^{t_{ind}} \exp\left(-B \cdot \left(\frac{T_{ref}}{T} - 1\right)\right) \cdot dt$$

Degree of cure at inhibition :

Ref. Temperature :

Reference time :

B coef :



Gel time model

Gel time model

Calculate Gel time from

- Isothermal cures
- Dynamic runs
- Kinetic model

Edit data

Clear graph

Plot model

Calculate model

Save model

Cancel

Temperature [°K]	Gel time [Minutes]
300	150
310	100
320	60
330	35
340	20
360	10
380	5
400	2.5
420	1.2

Gel time model

$$t_{ref} = \int_0^{t_{Gel}} \exp\left(-B \cdot \left(\frac{T_{ref}}{T} - 1\right)\right) \cdot dt$$

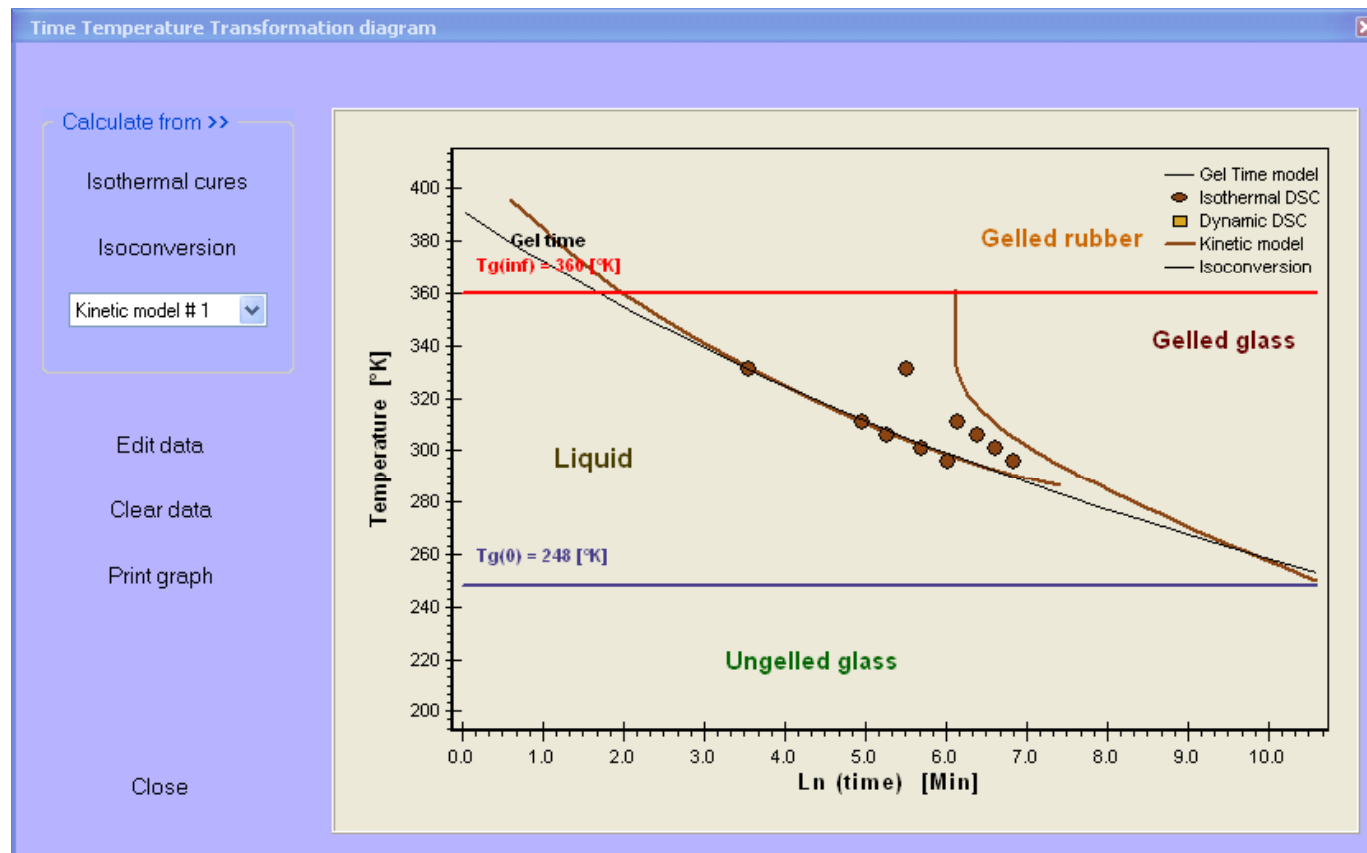
Degree of cure at Gel :

Ref. Temperature : fixed

Reference time : fixed

B coef : fixed

Time-Temperature-Transformation diagram

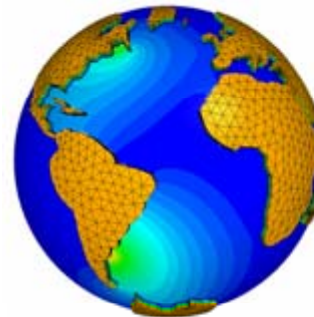




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