

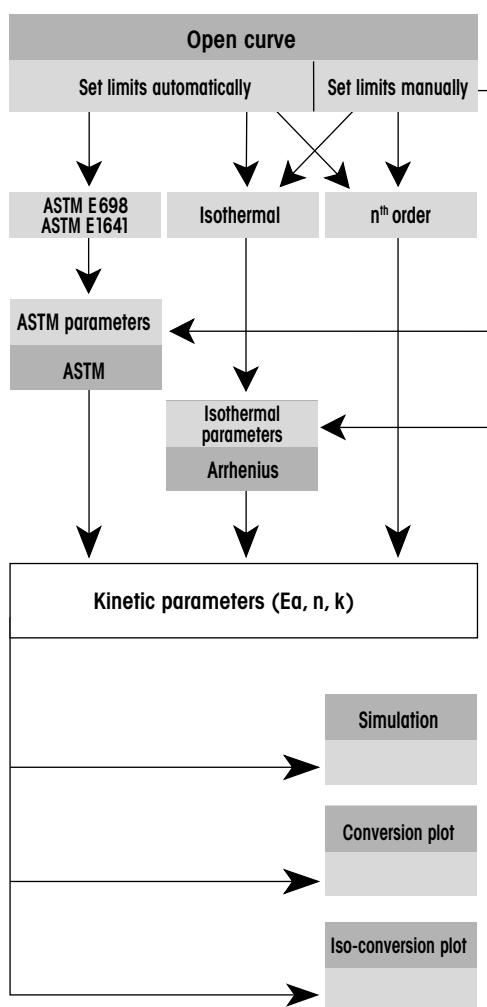
Kinetics, nth order

The kinetic models included with this option are suitable for the analysis and simulation of chemical reactions. On the basis of one or more measure-

ments with different heating rates (DSC or TGA), kinetic parameters can be calculated which allow a description of the reaction profile with time. This enables predictions of the reaction behavior in regard to conversion, time or temperature to be made.

This option includes the following applications:

- **nth order kinetics** (1 dynamic measurement) for simple chemical reactions
- **ASTM E698 Kinetics** (>2 dynamic DSC measurements)
- **ASTM E1641 Kinetics** (>3 dynamic TG measurements)
- **Isothermal nth order kinetics** (one or more isothermal measurements) for simple chemical reactions
- **Applied kinetics** (simulation, conversion plot and iso-conversion plot, each with table)



Theory

The general kinetic description of a reaction is based on the following assumptions:

1. The reaction rate, defined as the change in conversion per unit time, is a function of the conversion α .

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

2. The temperature dependence of the reaction rate constant, k , is described by the Arrhenius equation:

$$k(T) = k_0 \cdot \exp^{-E_a/RT}$$

3. Substituting k by the Arrhenius equation in the rate equation gives the following:

$$\frac{d\alpha}{dt} = k_0 \cdot \exp^{-E_a/RT} \cdot f(\alpha)$$

$$\frac{d\alpha}{dt} : \text{Reaction rate}$$

$k(T)$: Rate constant at temperature T

k_0 : Rate constant at infinite temperature (pre-exponential factor)

$f(\alpha)$: Reaction model

E_a : Activation energy

R : Universal gas constant

α : Conversion of the reaction

n : Reaction order

Simple processes can often be described with the nth order model

$f(\alpha) = (1-\alpha)^n$. This results in:

$$\frac{d\alpha}{dt} = k_0 \cdot \exp^{-E_a/RT} \cdot (1-\alpha)^n$$

Flexible result selection

From a single dynamic measurement, multiple linear regression can be used to calculate the desired parameters k_0 , E_a and n : The way in which $d\alpha/dt$ is determined depends on the type of measurement:

$$\text{DSC: } \frac{d\alpha}{dt} = \frac{dH}{dt} \cdot \frac{1}{\Delta H_{\text{tot}}}$$

$$\frac{dH}{dt} = \text{Heat flow above baseline}$$

$$\Delta H_{\text{tot}} = \text{Peak area of the reaction in mJ}$$

The reaction rate is proportional to the heat flow.

$$\text{TG: } \frac{d\alpha}{dt} = \frac{dm}{dt} \cdot \frac{1}{\Delta m_{\text{tot}}}$$

$$\frac{dm}{dt} = \text{Rate of the weight change, DTG}$$

$$\Delta m_{\text{tot}} = \text{Weight step of the reaction}$$

The reaction rate is proportional to the rate of the weight change.

A single isothermal measurement can be used to calculate k and n for the used temperature. If several isothermal measurements have been performed, k_0 , E_a and a mean n can be calculated.

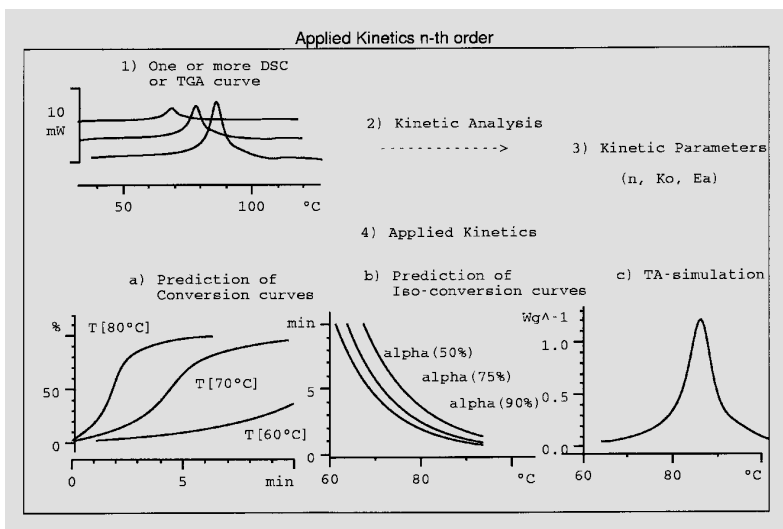
The evaluation following ASTM E698 is a preallocated algorithm for model-free determination of the activation energy E_a and k_0 from the peak temperatures of several dynamic DSC measurements. For the simulation and the predictions, the reaction order is set to 1 by definition.

ASTM E1641 allows the model-free determination of kinetic parameters from four or more thermogravimetric measurements. The evaluation of the sample measured at four different heating rates is done by determination of the temperature at which a given degree of decomposition, according to the standard between 5 and 20%, is found. For the simulation and the predictions, the reaction order is set to 1 by definition.

Applied kinetics

In addition to the analysis of the chemical reaction, which primarily supplies the kinetic parameters, these parameters can then be used to simulate the TA curves of the chemical reactions.

This is chiefly used to assess the quality of the parameter determination. The plots below show the possible procedure.



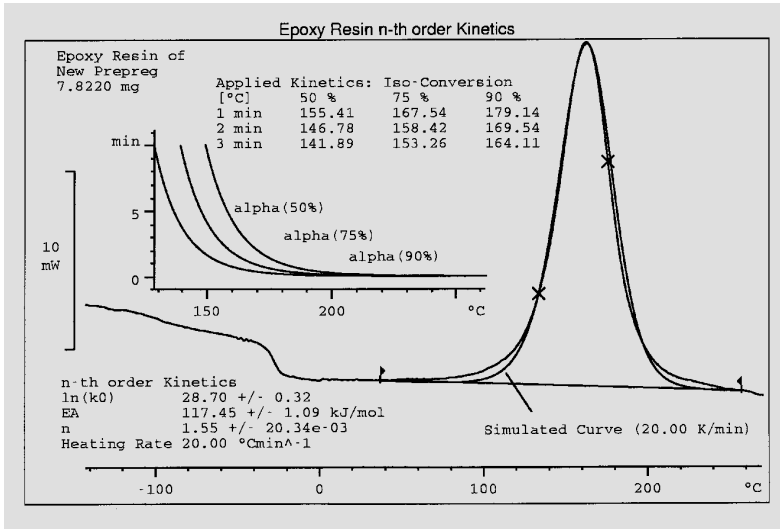
- 1 Performance of the required number of measurements. DSC or TGA, isothermally or dynamically.
- 2 Kinetic analysis of the measurements.
- 3 Determination of the kinetic parameters (n , k_0 , E_a).
- 4 Applied kinetics (graphically and/or in tabular form)
 - a) prediction of the conversion/time curve at selectable temperatures
 - b) prediction of the iso-conversion curve (time/temperature curve at selectable conversion α)
 - c) simulation of dynamic measurements (DSC, TGA, TMA).

Application examples

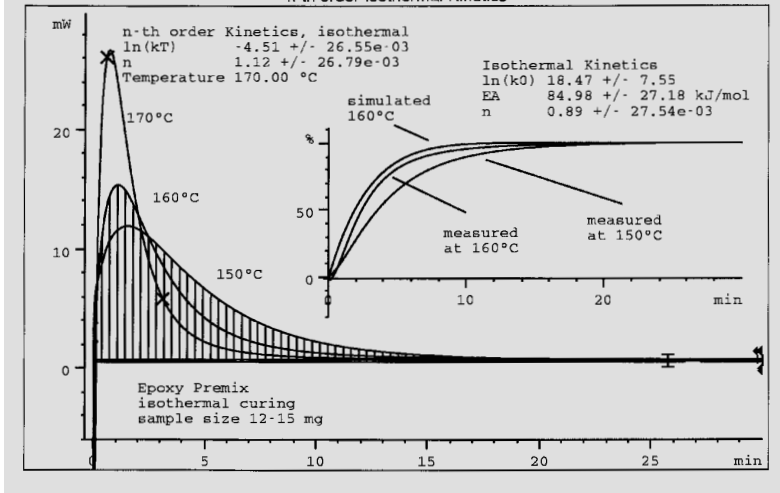
Dynamic curing of a thermosetting resins

The curing of an epoxy resin (prepeg) is used to illustrate the n^{th} order kinetics. The plot shows the DSC curve (with glass transition at -25°C and curing peak between 90 and 220°C) of a dynamic measurement recorded

at a heating rate of 20 K/min . The analysis of the exothermic reaction peak supplies the kinetic parameters shown opposite (n^{th} order kinetics). These can now be used to calculate the iso-conversion curves and tables. These describe the relation between individual conversions alpha and the temperature or time needed to attain these values. The temperature at which curing must be performed to obtain a specified conversion is immediately apparent. The DSC curve can also be simulated to check the kinetic parameters found and the model used. As can be seen here, the simulated curve shows good agreement with the measured DSC curve (Simulated curve).



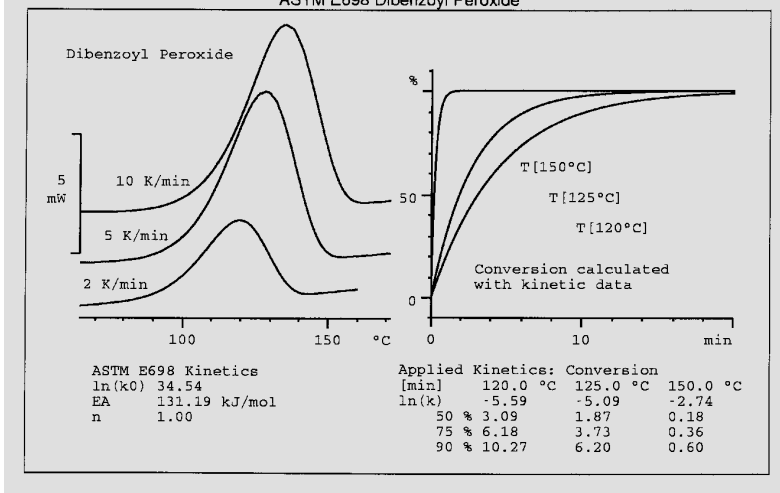
n-th order Isothermal Kinetics



Isothermal curing of resins

The curing behavior under isothermal conditions is very important in industrial practice. Of prime interest here is the degree of cure, which is a function of temperature and time. The plot shows three isothermal measurements recorded at 150 , 160 and 170°C . The analysis of a single measurement (n^{th} order kinetics, isothermal) provides n and $\ln(kT)$, the evaluation of several measurements (isothermal kinetics) allows the determination of n , $\ln(k_0)$ and E_a . The applied kinetics can again be used with these latter data to simulate the isothermal curing at other temperatures. This is yet another case where the simulated and experimental curves are in good agreement.

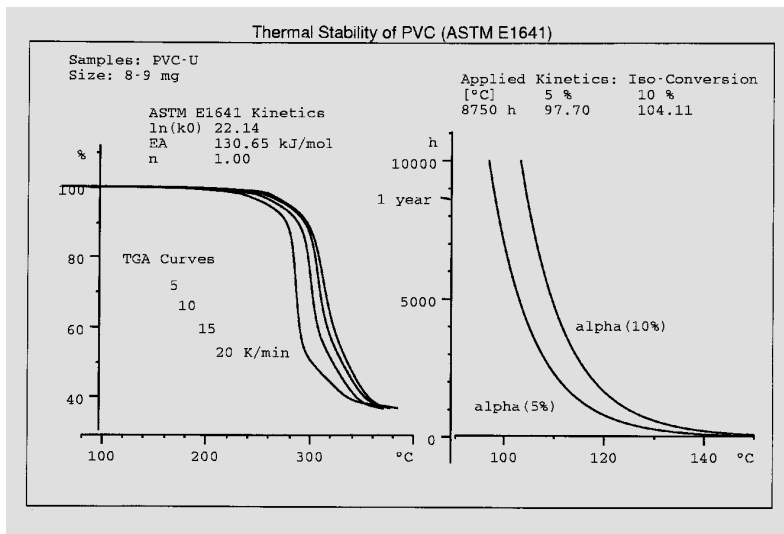
ASTM E698 Dibenzoyl Peroxide



ASTM E698 Thermal decomposition

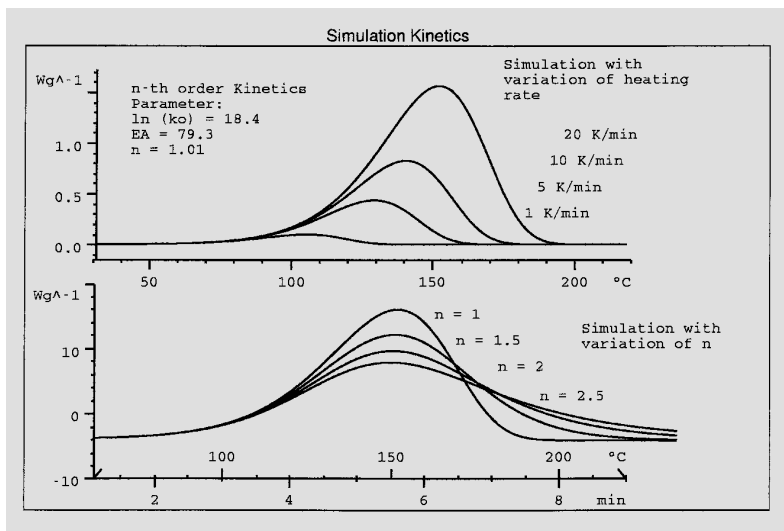
The example of the thermally induced decomposition reaction of benzoyl peroxide (dissolved in dibutyl phthalate) illustrates the ASTM E698 Kinetics. The three dynamic DSC measurements at different heating rates are used to calculate the kinetic data (ASTM E698 Kinetics). Again with the assumption of a reaction order of 1, the conversion can be simulated under isothermal conditions (Applied Kinetics: Conversion). This is shown in both tabular and graphical form for the temperatures 120 , 125 and 150°C .

Application examples



Thermal stability of PVC (ASTM E1641)

The pyrolysis of a rigid PVC sample was investigated thermogravimetrically at four different heating rates (5, 10, 15 and 20 K/min, at 20 ml N₂/min). The ASTM E1641 evaluation of the decomposition step caused by the separation of HCl provides the kinetic parameters shown in the diagram. These can in turn be used to predict the stability of the material with the aid of the iso-conversion curve, shown here for the conversions 5 and 10%.



Influence of the kinetic parameters on the TA curve

The example of a simple exothermic decomposition reaction of benzoyl peroxide is used to show how the applied kinetics can be employed to simulate the influences of parameters on a reaction sequence. The basis of the evaluations is the nth order kinetics, which furnish the parameters shown opposite for a measurement. The upper diagram shows how the reaction shifts under dynamic conditions to higher temperatures when the heating rate is raised.

The influence of the reaction order can also be studied as shown in the lower diagram. An increase in the reaction order keeping the other parameters constant leads to a broadening of the reaction peak.