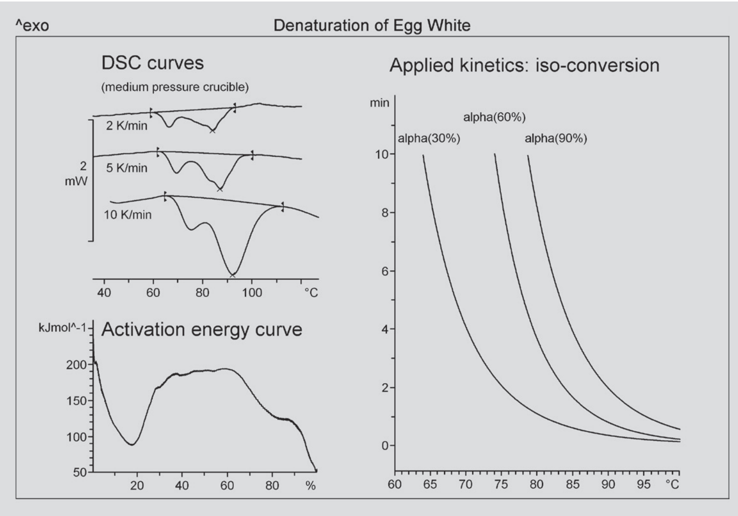
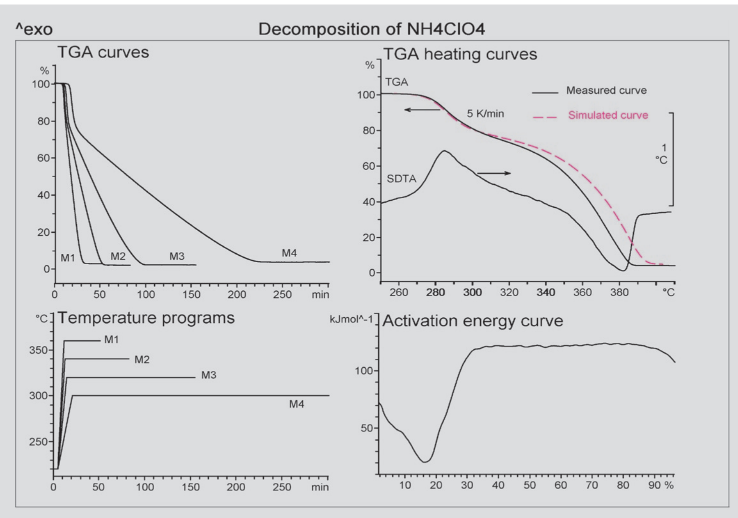
Denaturation of egg white



Egg white proteins are major functional ingredients in many baked food products. They contribute to texture formation through their ability to foam and gel at elevated temperatures, e.g. a good cake is characterized by the formation of a structural framework that is viscous enough to trap gas bubbles, and strong enough to be self-supporting when removed from the oven. This in fact requires a certain degree of egg white denaturation (described as conversion) to be achieved during the cooking or baking process.

Two main peaks at about 70 ° and 90 °C are observed in the DSC curves in the figure. The first peak corresponds to the denaturation of the conalbumin fraction and the second peak to the denaturation of the ovalbumin fraction. The denaturation of the proteins can be predicted for example from the iso-conversion plots. If a medium cooked egg is assumed to be 60% denatured, one can estimate from the iso-conversion plots that the corresponding cooking time is 3 min at 80 °C and 1 min at 90 °C. This prediction is in reasonable agreement with daily cooking practice.

Decomposition of a propellant



An understanding of the decomposition kinetics of materials such as explosives, propellants and other hazardous materials under different conditions is critical for estimating their stability, storage and shelf life times. Advanced MFK has proven to be a powerful tool for studying the decomposition kinetics of these types of material.

A typical TGA curve of ammonium perchlorate (AP) measured at 5 K/min, together with the SDTA™ curve, is shown in the figure. The decomposition reaction consists of two overlapping steps: exothermic decomposition to porous AP with the formation of gaseous products and endothermic dissociative sublimation of AP to ammonia and perchloric acid.

Four TGA measurements were performed to study the isothermal decomposition kinetics. Dynamic segments were used before the isothermal segments so that the weight loss of the samples during initial heating of the furnace to the isothermal temperatures was included in the measurement. These heating segments are taken into account in the Advanced MFK evaluation.

The activation energy curve obtained can be used to simulate multistage decomposition reactions with different temperature programs. For example, the TGA curve at a heating rate of 5 K/min was simulated. The simulated curve agrees well with the measured curve considering the complexity of the reaction.

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Advanced Model Free Kinetics

Advanced Model Free Kinetics (Advanced MFK) is a powerful software program that helps you to optimize a process or investigate a reaction. It also allows you to predict the behavior of a sample outside of the practical measurement range. Information on aging, oxidative stability, product lifetime and process optimization can be obtained without the need for time-consuming measurements.

The advantages of Advanced Model Free Kinetics are:

- kinetic evaluations can be made without the previous selection of a reaction model,
- the method can be applied both to simple and complex reactions,
- simulation studies are possible, e.g. prediction of the reaction kinetics under other conditions.

Advanced MFK can evaluate curves measured with any desired temperature program.

This software option therefore allows you to analyze

- dynamic curves
- isothermal curves and
- curves measured with a combination of dynamic and isothermal segments

Advanced MFK has the advantage that it can also be used for isothermal measurements. It is well known that isothermal measurements offer a number of advantages:

1. The reaction of interest can be measured practically free of any disturbing influences. Side reactions and decomposition usually only occur at higher temperatures.
2. Changes in the heat capacity of the sample do not influence the DSC curve.
3. Interpretation of isothermal DSC curves is easy because at the end of the reaction, the heat flow asymptotically reaches a value of 0 mW.

A number of interesting applications are foreseen for this technique:

Industry	Effects that can be analyzed with Advanced MFK
Automobile and aerospace	Curing reactions, stability, decomposition
Chemical	Safety investigations, stability, shelf life, storage and process conditions,
Electronics	Curing reactions, stability, storage and process conditions
Paints	Curing reactions, stability
Rubber (elastomers)	Vulcanization, thermal stability
Plastics (thermosets, prepregs, coatings, films, adhesives, thermoplastics, packaging, cables)	Curing reactions, thermal and oxidative stability, decomposition, lifetime, stability, storage and process conditions, reaction kinetics, polymerization
Propellants and energetic materials	Stability, decomposition, reaction kinetics
Food industry	Thermal stability, denaturation, process conditions
Pharmaceuticals	Decomposition behavior, thermal stability, shelf life, storage and process conditions, reaction kinetics

$$I(E_\alpha) = \sum_{i=1}^{n}\sum_{j\neq i}^{n} \frac{J_1(E_\alpha, T_i(t_\alpha))}{J_2(E_\alpha, T_j(t_\alpha))}$$

where

$$J_1(E_\alpha, T_i(t_\alpha)) = \int_{t_\alpha - \Delta\alpha}^{t_\alpha} e^{\frac{E\alpha}{R \cdot Ti(t)}} dt$$

$$J_2(E_\alpha, T_j(t_\alpha)) = \int_{t_\alpha - \Delta\alpha}^{t_\alpha} e^{\frac{E\alpha}{R \cdot Tj(t)}} dt$$

Theory

The enhanced version of Model Free Kinetics (the Advanced MFK software option) uses a new evaluation algorithm that was originally developed by Prof. Dr. S. Vyazovkin and most recently improved by Prof. Dr. S. Vyazovkin and Prof. Dr. Ch. A. Wight.

Advanced MFK requires at least three curves based on different temperature programs. The curves can be isothermal or dynamic or include a combination of both isothermal and dynamic segments. The curves are evaluated by calculating the minimum of the integral on the left, where

T:	temperature [K]	J_1,J_2:	subintegrals
t:	time [s]	E_α:	activation energy as a function of conversion
α:	conversion	R :	universal gas constant

METTLER TOLEDO

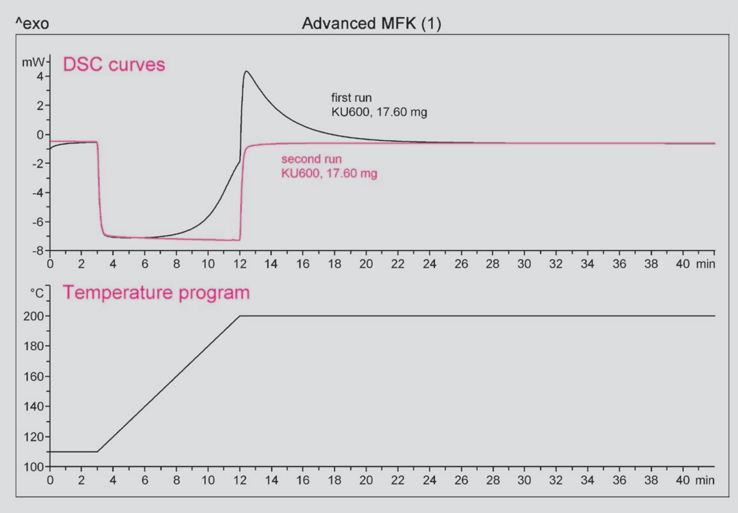


Fig. 1. The upper coordinate system displays the DSC curves of the curing of KU600 epoxy powder measured using a temperature program consisting of dynamic and isothermal segments. The second measurement serves as a "baseline". After this has been subtracted from the first curve, only the curve of the chemical reaction remains (see Fig. 2. below). The lower coordinate system shows the temperature program used for both measurements.

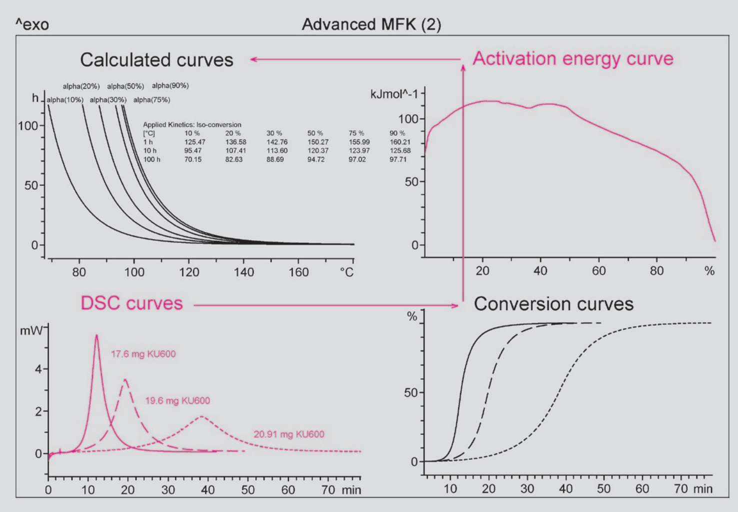
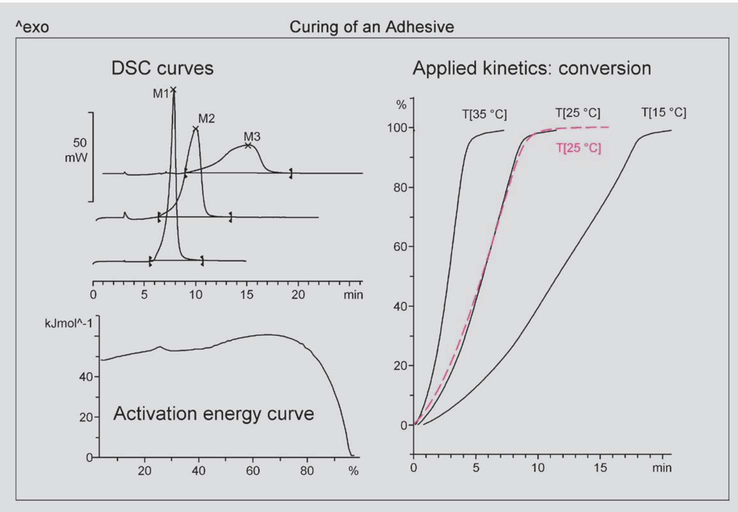


Fig. 2. Below left: This shows the three DSC curves obtained using different temperature programs consisting of dynamic and isothermal segments (in each case, the second run has been subtracted). The heating rates were 2, 5 and 10 K/min and the corresponding isothermal temperatures 180 °C, 190 °C and 200 °C.

Below right: The conversion curves are obtained by integration. From this data, the Advanced MFK program calculates the activation energy curve as a function of the conversion (above right). Finally, predictions for conversions between 10% and 90% (iso-conversion plots) are calculated (above left). From the table, one can for example see that, at 160.2 °C, the sample would cure to 90% in one hour (1 h).

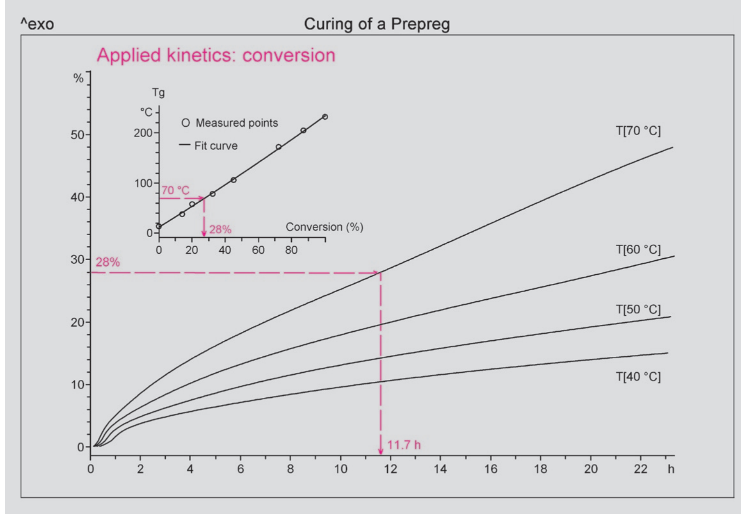
Curing behavior of an adhesive



The application field of adhesives is extremely wide, ranging from the electronics and automobile industries to the manufacture of cigarettes. Adhesives are expected to exhibit their adhesive properties under very different conditions, from freezing cold to tropical heat. Since the curing process is strongly temperature-dependent, it is important to know the curing time of an adhesive at different temperatures. Advanced MFK has proven to be extremely useful for these types of studies.

The figure shows three DSC curves measured with three different programs consisting of isothermal and heating segments. Predictions of the conversion as a function of time at typical application temperatures were made based on the activation energy curve. For comparison, the data obtained from an isothermal experiment at 25 °C (dashed line) was also plotted. Excellent agreement between the experimental data and the predictions was observed.

Curing of a prepreg

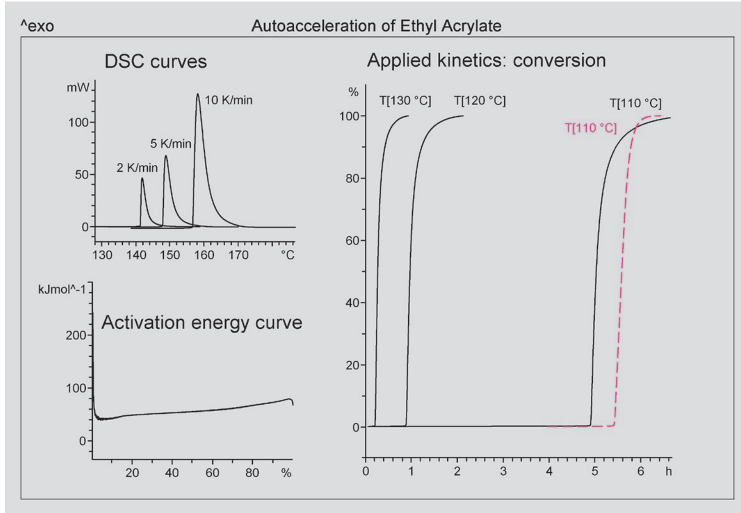


Prepregs are partially cured thermosetting materials. It is very important that the degree of cure does not change to any significant extent during storage: improper storage (i.e. storage at temperatures that are too high) would cause the glass transition temperature, T_g, to shift to higher temperature and have an adverse effect on later processing. Advanced MFK was used to investigate the curing kinetics of a prepreg and to estimate the storage time at different temperatures.

A series of dynamic DSC measurements was performed to determine T_g as a function of the conversion of the precured material. It can be seen that a T_g of 70 °C corresponds to a degree of conversion of 28% (upper diagram).

The conversion plots were predicted from three dynamic DSC measurements using Advanced MFK. It was found that 28% conversion is reached after 11.7 h at 70 °C (lower diagram). It can therefore be expected that the material vitrifies after 11.7 h if it is stored at 70 °C. This was confirmed by additional experiments.

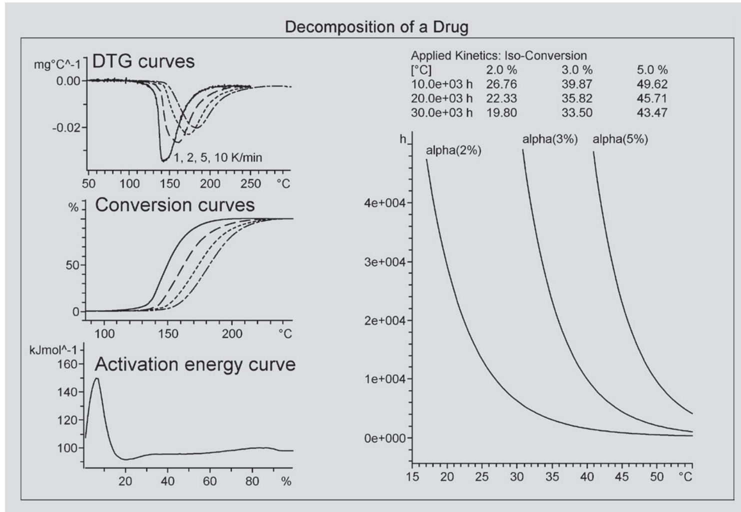
Safety analysis of a chemical



Reactions that exhibit autocatalytic behavior, i.e. where the onset of the main chemical reaction occurs after a certain induction period, are particularly important in safety investigations. Sometimes, the lack of knowledge of such behavior can lead to accidents or even explosions. Advanced MFK can be used to make predictions about the autoaccelerating behavior of chemicals. This information is a valuable guide for the time-consuming conventional isothermal measurements used for safety studies.

The figure shows three dynamic DSC curves of stabilized ethyl acrylate. The predicted conversion plots illustrate the autoaccelerating behavior observed in the polymerization of ethyl acrylate, e.g. when the material is held isothermally at 110 °C. The reaction begins after an induction period of about 4.9 h when the stabilizer has been used up. The prediction agrees well with an actual isothermal measurement (dashed line in the figure).

Shelf life of a drug



Active components of drugs are often very sensitive to temperature fluctuations. It is therefore important to know the shelf life of drugs, i.e. the period during which the drug remains effective. Shelf life can be estimated from the time it takes for the active component to reach a particular critical concentration on decomposition. Advanced MFK proves to be a fast and efficient method for the estimation of the shelf life of drugs.

Several dynamic TGA measurements of acetylsalicylic acid were performed. Since TGA curves do not terminate horizontally, the DTG curves were used to calculate the conversion curves. Conventionally, shelf life is defined as the time it takes for the material to reach 2%, 3% and 5% decomposition. The iso-conversion plots and the table show the estimated shelf life in the temperature range 20 … 50 °C. The predictions agree well with values of the measured shelf life reported in literature.