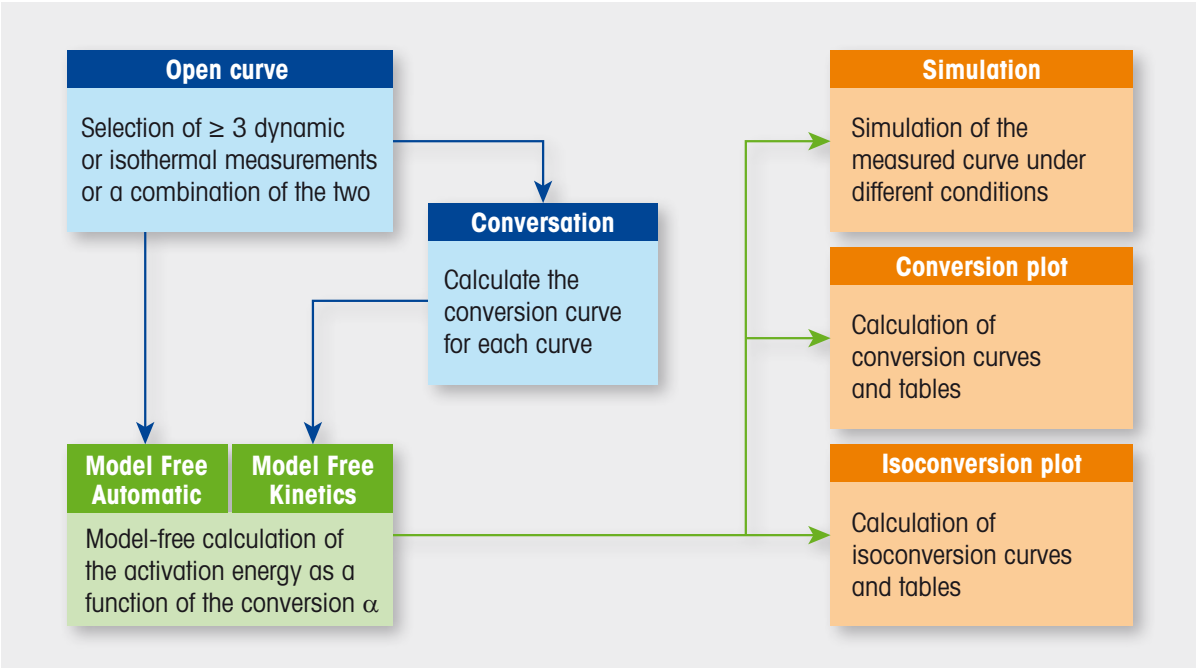
Thermal Analysis Option

Advanced Model Free Kinetics

Predictions for Process Optimization

STAR^{e} software's Advanced Model Free Kinetics (Advanced MFK) program helps in the investigation and optimization of a process. It allows the prediction of 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 experiments, or mathematical modelling.



The possibilities offered by advanced MFK are ideal for the iterative improvement of predictions on the course of reactions if one wants to extrapolate over a large temperature range. Advanced MFK also allows the predictions of materials' long-term behavior to be significantly improved.

Features and benefits

- **Model Free kinetics** – simulate chemical reactions based on dynamic or isothermal measurements to predict reaction behavior under different conditions
- **No reaction modelling** – allows complex chemical reactions to be analyzed without making any assumptions about a particular reaction model

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Theory and Evaluation Procedure
Vyazovkin and Wight's Model-Free Approach

The Advanced MFK software package extends the possibilities of MFK in that it can use any dynamic or isothermal temperature program or a combination of the two. The Advanced Model Free Kinetics program also includes advanced mathematical procedures.

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:

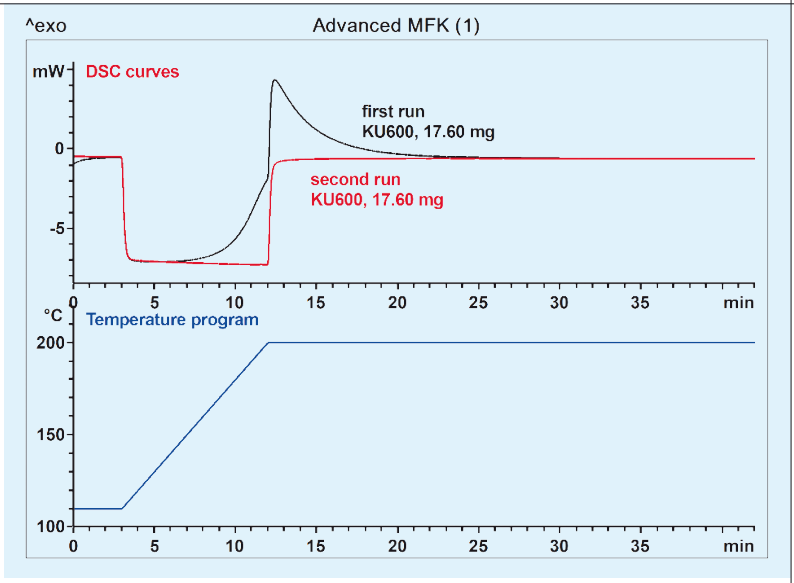
$$I(E_\alpha) = \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{J_1(E_\alpha, T_i(t_\alpha))}{J_2(E_\alpha, T_j(t_\alpha))}$$

where

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

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

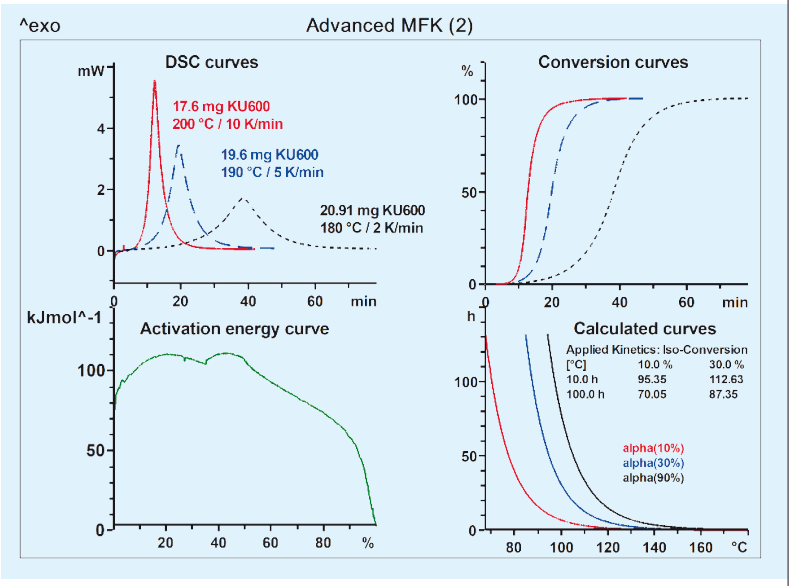
T: Temperature [K]
t: Time [s]
α: Conversion
J_1, J_2: Rate constan at infinite temperature
E_α: Reaction model
R: Universal gas constant



Advanced MFK

Plot 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.

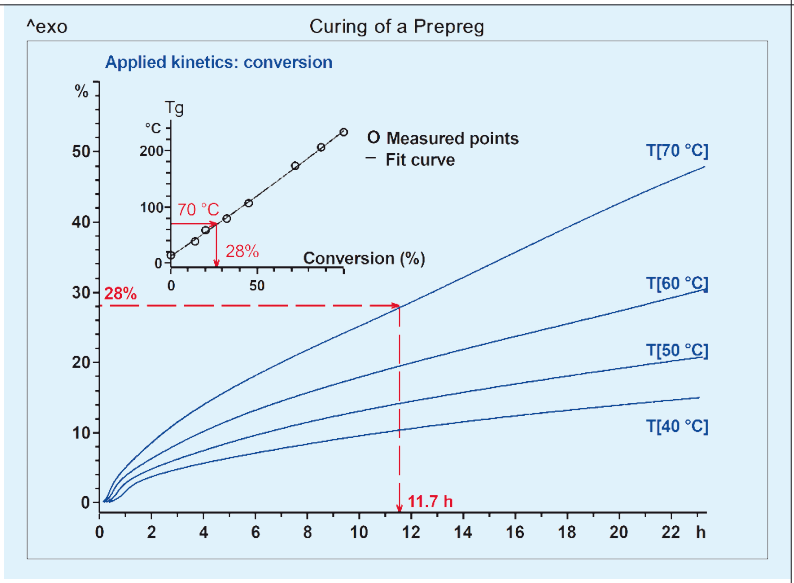
The lower coordinate system shows the temperature program used for both measurements.



Plot 2: The three DSC curves of KU600 were measured at 2, 5 and 10 K/min. The temperature program consisted of dynamic measurements combined with isotherms at temperatures of 180, 190 and 200 °C.

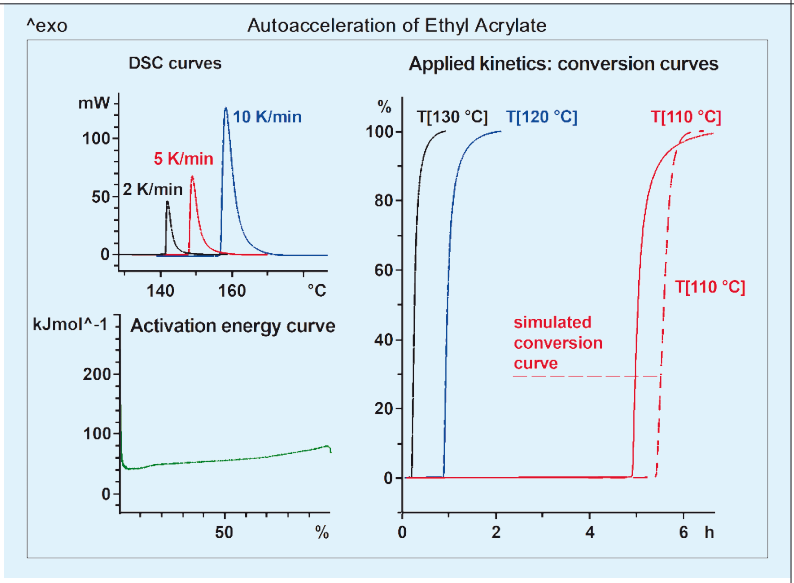
The conversion curves are obtained by integration of the DSC curves. The AMFK program then calculates the activation energy curve as a function of the conversion. Finally, predictions for conversions between 10 and 90% can be calculated. For example, at 160.2 °C, the sample would take one hour to cure to 90%.

Application Examples



Curing of prepreg

Advanced MFK was used to investigate the curing kinetics of a prepreg (a pre-cured material) and to estimate the shelf life at different temperatures. A series of dynamic DSC measurements was performed to determine the glass transition temperature (T_g) as a function of the conversion of the precured material. It can be seen that a Tg of 70 °C corresponds to a degree of conversion of 28%. The conversion plots were predicted from three dynamic DSC measurements using AMFK. It was found that 28% conversion is reached after 11.7 h at 70 °C. It can therefore be expected that the material vitrifies after 11.7 hours if it is stored at 70 °C. This was confirmed by additional experiments.



Safety analysis of a chemical

In safety investigations, information about whether a reaction exhibits autoacceleration behavior is of great importance. Ethyl acrylate quickly polymerizes without a stabilizer. The reaction is strongly exothermic and can lead to an explosion under adiabatic conditions.

The DSC curves show the behavior of the substance on heating. AMFK was used to calculate the activation energy curve and predict the isothermal reaction curves at different temperatures. For example, at 110 degrees, no reaction is observed until the inhibitor is completely used up after about 5 hours, whereupon the material suddenly polymerizes. The activation energy curve shows a low value that gradually increases. The predicted curve was verified by performing a suitable measurement. The resulting measured curve (red dashed curve) and the predicted curve (red continuous line) show good agreement.

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