# NUMERIC SIMULATION OF EPOXY CURE IN MOLDS
## Kinetic parameters from microcalorimetry

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Thermodynamic and kinetic parameters have been determined suitable for the numerical simulation of the curing reaction of the epoxy/anhydride based casting resin system Araldite CY 225/HY 225/filler. In particular, the decisive role of the heating rate on the evaluation of the kinetic parameters from dynamic DSC-experiments is discussed.

## Introduction

During recent years, the use of Computer Aided Design (CAD) and Manufacturing (CAM) penetrated into the plastics processing industries. Whereas computer programs and many material specific data are available for thermoplasts, little work has been accomplished on thermosetting polymer systems. This is mainly due to the often complex polymerization and crosslinking reactions which are specific for each thermoset, and the difficulties in conjunction with the numerical description of the kinetic and thermal parameters necessary for an adequate simulation of the cure process.

The reaction kinetics of the crosslinking reaction of epoxy resins is usually described using the general equation for a reaction of $n$-th order

$$-\mathrm{d}\alpha / \mathrm{d}t = k\,\alpha^n \qquad (1)$$

with $\alpha$ representing the conversion factor (varying from 1 to 0, e.g. the relative concentration of the reactive species). The temperature dependence of the rate constant $k$ may be described by the Arrhenius equation

$$k = k_o \exp(-E_a / RT) \qquad (2)$$

with the thermal activation energy of the reaction $E_a$, the gas constant $R$, and the absolute temperature $T$. Combination of Eqs (1) and (2) result in

$$-\mathrm{d}\alpha / \mathrm{d}t = k_o \ \alpha^n \ \exp\left(-E_a / RT\right) \qquad\qquad (3)$$

The three parameters in Eq. (3) may be fitted to experimental kinetic data from isothermal or temperature dynamic thermoanalytical experiments. Typical results from fitting algorithms such as proposed by Daniels and Borchardt [1] or others applied to dynamic Differential Scanning Calorimetry (DSC) data of thermoset cure reactions are discussed by R. B. Prime [2]. Usually, appropriate software for the evaluation of DSC-data according to Eq. (3) or similar kinetic models is available from the manufacturers of thermoanalytical instruments.

In previously published work on computer modelling of thermosetting polymers usually one set of parameters obtained from a single dynamic DSC experiments was utilized [3], thus neglecting the influence of the heating rate on the results.

In this paper, we report on thermodynamic and kinetic parameters necessary for the simulation of the cure process of an epoxy system. The kinetic parameters have been evaluated considering the influence of the heating rate on the reactions kinetic.

Experimental data are reported for a commercially available epoxy/anhydride based system (Araldite(R) CY 225/HY 225) which is widely used for the fabrication of high voltage insulators and sizeable power switching housings.

## Experimental

The Ciba-Geigy Araldite(R) casting resin system CY 225, a bisphenol-A based epoxy resin, hardener HY 225, a modified anhydride, and quartz powder W 12 (Quartzwerke GmbH, Frechen, BRD) was used in the mixing ratio (by weight) 100:80:270 [4]. For the microcalorimetric measurements two different instruments were used, a Mettler TA 3000 with the standard DSC-cell and a Perkin-Elmer DSC-7.

Although there are several highly sophisticated Finite Element Method computer programs commercially available, for heuristic purposes we have developed a rather simple software taking advantage of an idealized cylinder geometry. With this assumption, the description of the cylinder may be reduced to a one-dimensional problem if the height of the cylinder is assumed to be rather large compared to the diameter. In a first order approximation, this geometry may well represent the body of a high voltage insulator. For the

specific examples in the text, we have assumed the radius of this cylinder to be 30 mm. We employed the explicit finite difference approximation for the solution of the general heat transfer equation as described in standard textbooks [5].

## Results and discussion

For the determination of the kinetic parameters of the reactive epoxy system CY 225/HY 225/silica, the reaction exotherm was measured using dynamic DSC. Figure 1 shows the exotherm for the reactive mixture at a heating rate of 10 K/min, a typical rate for such experiments. In a second DSC-run of the same sample, a glass transition temperature ($T_g$) with a range of 95 to 108° was observed. This $T_g$-range is representative for the reactive system under investigation, and the same glass transition was also observed after the recommended cure cycle 5 h 80° + 16 h 130° [4].

The fit of the heat flow curve in Fig. 1 to Eq. (3) results in the parameter set #5 (see Table 1 caption). The simulation of the dynamic DSC experiment on the basis of this parameter set shows a very good agreement with the experimental curve, as is indicated in Fig. 1.
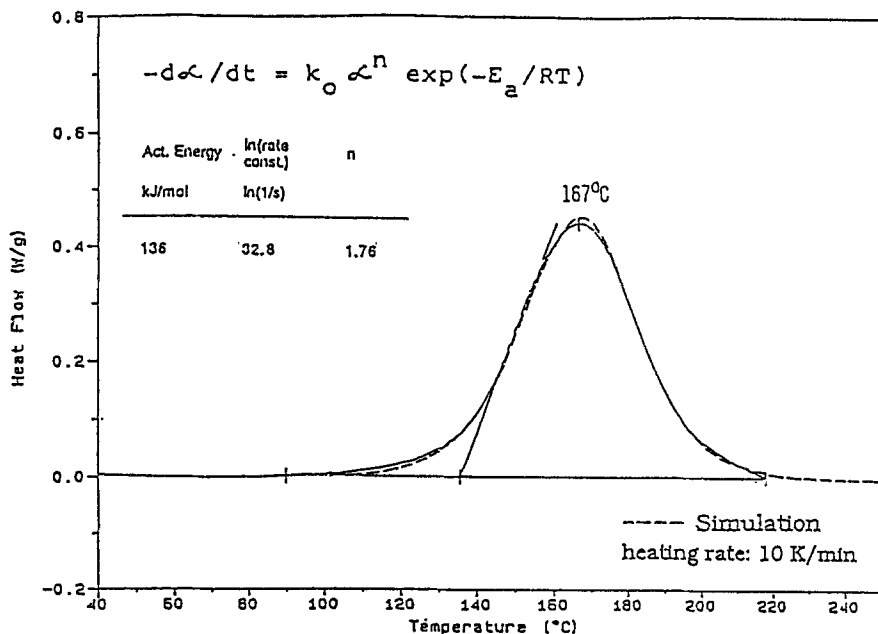


Fig. 1 Dynamic DSC scan of the reactive epoxy system at 10 K/min heating rate; comparison to simulated curve with parameter set #5 from Table 1

Table 1 Kinetic parameters for the Cure of the Filled Epoxy System CY 225, HY 225, quartz powder (100 : 80 : 270)

| Data set | Instrument {1} | Heating rate K/min | $T$(R-max) {2} °C | $E_a$ kJ/mol | ln $(k_o)$ ln (1/s) | $n$ |
|------|------|------|------|------|------|------|
| #1 | 1 | 2 | 139 | 166 | 42.9 | 1.87 |
| #2 | 2 | 2 | 141 | 155 | 39.2 | 2.41 |
| #3 | 1 | 5 | 154 | 153 | 38.4 | 1.74 |
| #4 | 2 | 5 | 156 | 147 | 36.2 | 1.61 |
| #5 | 1 | 10 | 167 | 136 | 32.8 | 1.76 |
| #6 | 2 | 10 | 170 | 124 | 29.1 | 1.41 |
| #7 | 1 | 20 | 182 | 127 | 29.9 | 1.62 |
| #8 | 2 | 20 | 183 | 120 | 27.5 | 1.50 |
| #9 | simple model | all | | 80 | 16.9 | 1.0 |
| | e.g. | 10 | 168 | | | |

{1}Instruments used: 1: Mettler TA 3000; 2: Perkin-Elmer DSC-7.
{2} Temperature at maximum of exothermal flow.

On the basis of these kinetic parameters and other properties of the epoxy system under study (cf. Table 2), a numerical simulation of the curing process in a cylindrical mold was performed. The temperature of the mold was assumed to be 160°, the initial temperature of the injected reactive mixture was set to 80°, the time necessary to fill the mold was assumed to be very short. The main results of this simulation are depicted in Fig. 2.

Table 2 Values for the parameters used for the FEM-Simulations

| | | |
|------|------|------|
| Rate Constant $k_o$ | | {Table 1} |
| Activation Energy $E_a$ | | {Table 1} |
| Heat of Reaction | 110 J/g | {1} |
| Specific Heat | 1.32 J/gK | {2} |
| Thermal Conductivity | 0.7 W/mK | {3} |
| Specific Mass | 1.84 g/cm$^3$ | |

{1} from integration of the DSC-exotherm peak
{2} mean value of cured system above $T_g$
{3} from experiment using the thermal comparator method, mean value for
$T =$ 120....180°C [6]

During the initial phase heat flows from the mold into the reactive mixture which is shown by the temporal evolution of the temperature distribution.

Later on, due to the additional heat generated in the reacting resin and the limited thermal conductivity, the central region of the reactive mass is heated up to temperatures near 250°, considerably above that of the mold.

Analyzing the local temperature/time dependence during the course of the reaction, the local heating rate vary between 0 (initial phase near the center of the mold) to about 80 K/min (840 s after injection, at maximum reaction rate at the center).

To check the validity of the kinetic parameter set for this rather broad range of heating rates, we measured the corresponding dynamic DSC-curves at heating rates of 2, 5, and 20 K/min. Further measurements at both lower and higher heating rates usually result in unreliable values, with lower heating rates due to the very small heat flux to or from the sample, with higher small sample volumes of the reaction mixtures employed in DSC measurements.

The parameters resulting from fitting Eq. (3) to the dynamic exotherms measured at different heating rates are also compiled in Table 1. For comparison, results obtained using two different DSC-instruments are listed. Considering the differences in construction, the measuring principles, and data evaluation procedures, the agreement is satisfactory.

Obviously enough, the kinetic parameters $k_0$, $E_a$ and $n$ vary considerably from 2 to 20 K/min, i.e. $k_0$ and $E_a$ continuously decrease, whereas $n$ is varying only slightly in case of the instrument 1 and rather drastically in case of the
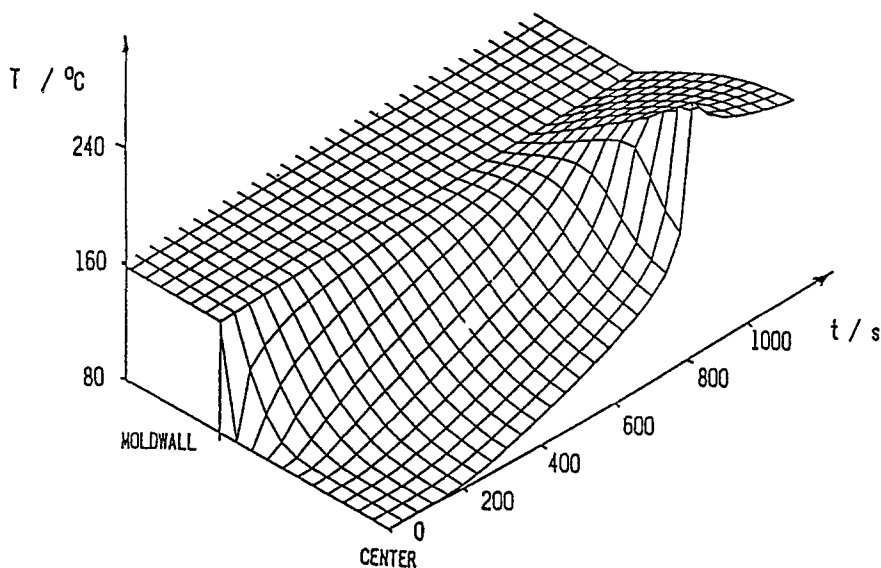


Fig. 2 Cure in a cylindrical mold: Temporal/spatial evolution of the temperature assuming parameter set #5, Table 1
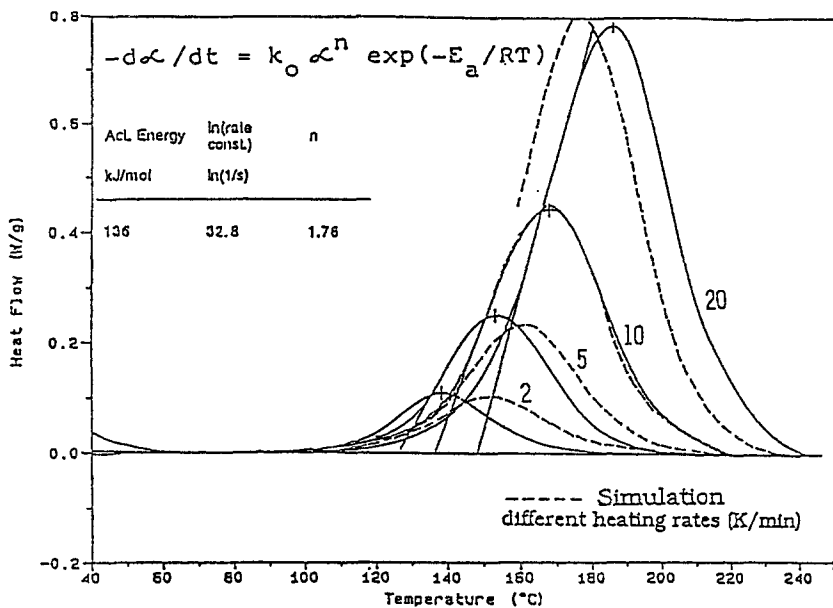
Fig. 3 DSC-experiment and simulation at different heating rates, parameter set #6, Table 1
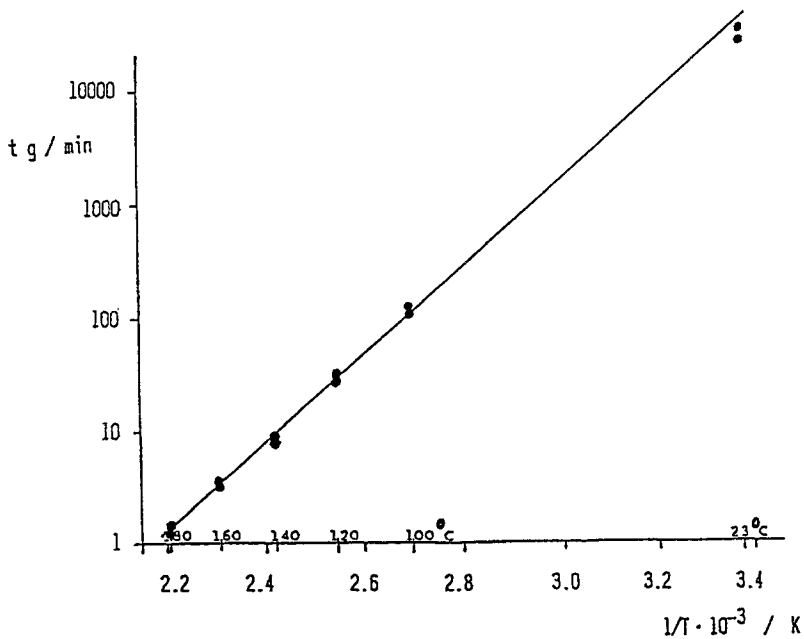


Fig. 4 Arrhenius plot of the gel times of the filled epoxy-system

instrument 2. The selection of the parameter set #5 in Table 1 (obtained from the 10 K/min experiment) to represent the reaction exotherms at other heating rates becomes obvious from Fig. 3, where the simulations of dynamic DSC heat flux curves for different heating rates are compared with the corresponding experimental ones. At low heating rates, the reaction rate predicted by the model is too slow, at the higher rate (20 K/min) it is too high, findings which could be predicted by the data sets of Table 1.

The sensitive dependence of the kinetic parameters on the heating rate could be an indication for the fact that there is not only one elementary chemical reaction responsible for the rate determining step. Instead, several parallel and consecutive reactions are in competition, forming a system far too complicated to be fully understood and modelled.
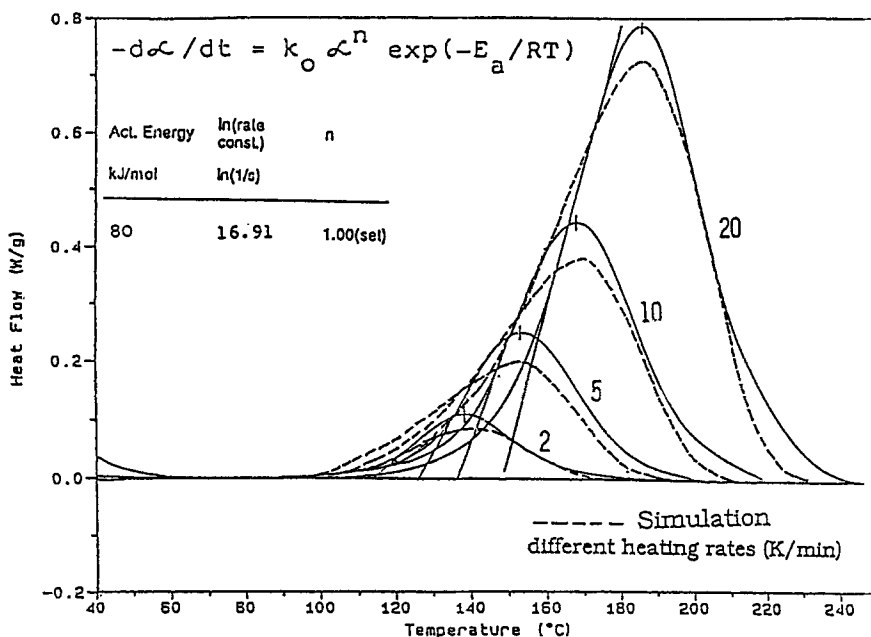


Fig. 5 DSC-experiment and simulation, parameter set #9, Table 1

One might try to employ a multidimensional regression procedure to fit the different data sets aiming at a more complicated function to express the dependence of the three kinetic parameters on the heating rate. But, due to the rather small data set, a regression to a higher order function will result in larger confidence limits. Instead, we concluded from the Arrhenius plot of the gel times (Fig. 4), that the reaction order is well represented by $n = 1$, since the experimental points follow rather well a straight line. Even the gel

time at room temperature (pot life) lies close to the interpolation line. Assuming $n = 1$, a two-parameter set valid for all heating rates can be deduced (#9, Table 1). The comparison between the simulations on basis of the simple model and the experimental DSC-curves is shown in Fig. 5, indicating a certain agreement of the calculated and experimental temperatures at the maxima of the corresponding heat flux curves at different heating rates. A systematic overestimation of the reaction rate can be stated on the low temperature side of the exotherm peak.

Based on the fact that the overall shape of all the curves, i.e. larger portions of the slopes and the positions of the maximum, are rather well represented by the simpler two-parameter model, we feel more confident with the extrapolation to higher heating rates than using either of the three-parameter sets.
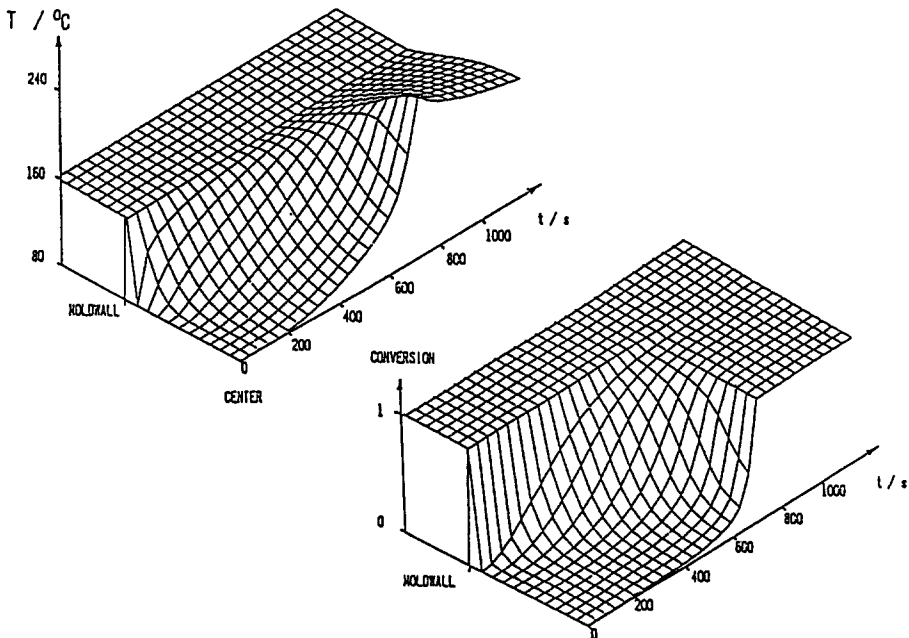


Fig. 6 Cure in a a cylindrical mold: Temporal/spacial evolution of the temperature and the conversion, respectively, assuming parameter set #9, Table 1

Results of a simulation of the thermal cure in a cylindrical mold using the two-parameter model is depicted in Fig. 6. Although the overall shape of the temperature/time evolution is similar to that of Fig. 3, maximum reaction rate is reached earlier and the peak temperature is somewhat lower (225°). The behaviour of the temperature in its temporal and spacial development can be

used, for example, to locate 'hot spot' formation, to predict the advancement of the gelation front, and to quantify the time dependence of the net heat flux through the mold walls. Variations of experimental parameters such as temperature(-program) of the mold, various geometries, other initial temperatures of the reaction mixture and even the different cure behaviour of the same reactive system with different filler load (considering the adequate changes in the thermal parameters) can be predicted almost instantly without consuming much more time and considerable amounts of the casting resin for test runs.

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## References

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**Zusammenfassung** — Mit Hilfe der Mikrokalorimetrie wurden thermodynamische (Reaktionsenthalpien) und kinetische (Arrhenius-Konstanten, Reaktionsordnung) Parameter eines gefüllten Epoxid/Anhydrid-Giessharz-Systems (Araldit CY 225/HY 225/Quarzmehl) bestimmt.

Die Eignung dieser Parameter zur praxisrelevanten Simulation der Härtungsreaktion in Giessformen wird demonstriert. Es zeigt sich, dass die Heizrate im dynamischen DSC-Experiment bei der Bestimmung der kinetischen Parameter eine entscheidende Rolle spielt.