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# Optimization of cure kinetics model parameters from DSC-data

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## Abstract

A program for parameter optimization has been used to derive kinetic models for a vinylester and an epoxy resin. Data from isothermal DSC experiments were used to obtain a quantitative measure of both the heat and rate of reaction The models are based on a few measurements and have been derived with little effort by the use of the optimization program. The importance of the experimental procedure for DSC measurements such as the choice of load temperature is discussed.

## 1. Introduction

Process simulation can be an efficient tool for optimization of complex processes such as the cure of thermoset resins. It has become clear that simple geltime experiments and resin reactivity measurements are not sufficient as a base for cure optimization. The cure process is dependent on several process conditions and material properties which can not be taken into account only from resin cure characteristics

Process models for different manufacturing processes have been developed recently [1-3] which rest on submodels for chemical kinetics of thermoset resins. This means that a correct cure model with a set of accurate parameters is a prerequisite to gain useful results from a process model. Both empirical and fundamentally based rate equations for the cure of thermosets can be found in the literature [4,5]. However, empirical equations dominates in process modelling studies.

This paper presents kinetic models for an epoxy resin and a vinylester resin. The models are based on data from Differential Scanning Calorimetry measurements. The model parameters have been chosen from a best fit with a non-linear least squares optimization technique described in [3].

## 2. Theory

The cure of thermoset resins involves the transformation of a liquid resin into a hard solid by a crosslinking reaction. The reaction mechanism can vary significantly between different resin systems and do most often involve copolymerization Several thermoset resins such as unsaturated polyester and vinylester resins are cured by free radical reactions[6] The theory for radical reactions is well known and has been used to obtain kinetic models for thermosets[5]

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However, these models which are based on a mechanistic approach are complex and the effort to investigate cure mechanisms and to determine model parameters may not be motivated for industrial use.

Empirical and semiempirical models are often based on the assumption that the overall rate of cure can be described as:

$$d\alpha/dt = k\, f(\alpha) \qquad (1)$$

where k is the rate constant and $\alpha$ is the degree of cure. The temperature dependence is assumed to reside in the rate constant, k, and is then expressed as an Arrhenius relation:

$$k = A \exp(E/RT) \qquad (2)$$

where A is the preexponential rate constant, E is the activation energy, R is the gas constant and T is the temperature. A rate function which have been extensively used and shown to predict the cure of several thermoset resins accurately is[4]

$$f(\alpha) = k\, \alpha^m (1-\alpha)^n \qquad (3)$$

This rate function can describe autocatalytic behavior which is often shown by thermosets.

The optimization of the kinetic parameters is done by a minimization of the sum of squares of the weighted difference between the experimental reaction rate and the model prediction. The numerical method with which the minimization is done progresses in an iterative fashion and follows the Levenberg-Maquardt algorithm.

## 3. Experimental

A vinylester resin (1) and an epoxy resin (2) have been used in the present study. A resin formulation for room temperature cure was used for resin 1 whereas resin 2 had practically no reactivity at low temperatures. Both resins are commercial resins used in several composite applications. All resin materials were used as delivered without any purification

A Perkin Elmer DSC-7 was used for the calorimetric measurements. All measurements have been conducted in isothermal conditions at 20,40 and 60°C for resin 1 and at 90,110,120,125 and 130°C for resin 2. The samples, 5 - 25 mg of resin, were weighed (with an accuarcy of +/- 0.01 mg) and sealed in aluminum sample pans. The load temperature in the DSC cell was chosen to equal to the isothermal test temperature for resin 1 and to 30°C independent of isothermal test temperature for resin 2. The heating rate from load temperature to the isothermal temperature was chosen to 40 °C/minute for resin 2. The choices of instrumental conditions are based on several tests to minimize the time period from loading the sample to a stable instrument signal is obtained, see section 5.

## 4. Results

Examples of isothermal DSC plots for resin 1 and 2 are shown in figure 1 and 2. The curing characteristics for resin 1 is more complex than for resin 2 which can be seen in the DSC plots. The degree of cure and the rate of reaction was calculated from the experimental data at all measured temperatures based on the usual assumption that the rate of reaction is proportional to the heat generation. The total heat of reaction from isothermal measurement at 60 °C for resin 1 and at 130 °C for resin 2 was used as ultimate values for the heat of reaction.

The calculated values of α and dα/dt from the isothermal measurements were used to obtain the parameters in equation(3) for both resin 1 and 2. Figure 3 and 4 show a comparison between the experimental results and the results for the model prediction at each isothermal temperature for the two resins. The model prediction for resin 2 is in good agreement with the experimental data. The model prediction for resin 1 is less accurate but fit the data fairly well.

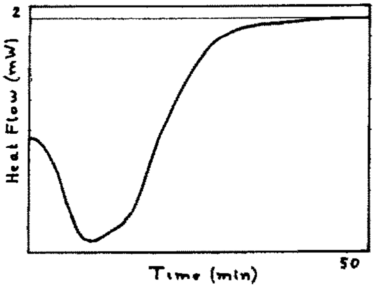

Figure 1. DSC plot for resin 1.
Isothermal temperature = 40 °C.

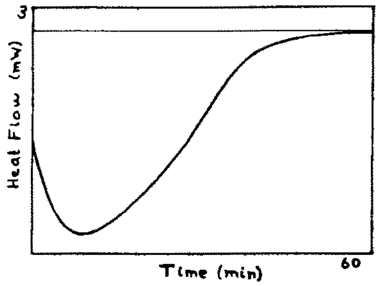

Figure 2. DSC plot for resin 2.
Isothermal temperature = 110 °C.

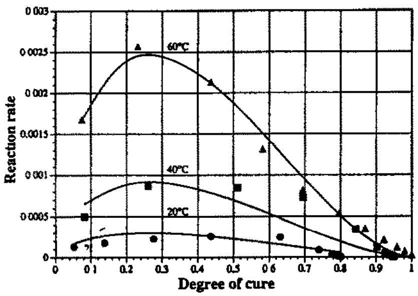

Figure 3. Reaction rate as a function of the degree of cure at different isothermal temperatures for resin 1. The points are experimental values and the lines are model predictions.

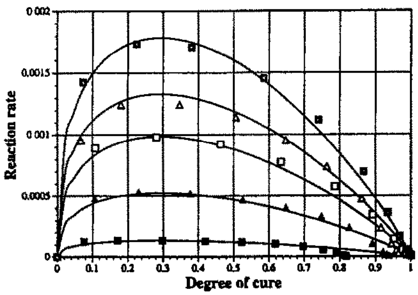

Figure 4. Reaction rate as a function of the degree of cure at different isothermal temperatures for resin 2. The points are experimantal values and the lines are model predictions.

## 5. Discussion

Kinetic models for thermoset resins can be obtained by DSC experiments and by the use of computer programs for optimization of model parameters. Therefore the use of simulation tools for the study of cure processes as well as optimization of process conditions can be made efficiently.

It is however important to obtain kinetic models which predict the cure process sufficiently well. Experimental measurements and choice of kinetic model are the two main and important parts in the development of a kinetic model since the numerical optimization of the parameters is usually no problem. The experimental part needs special attention since different resins have different material properties and reactivities and experiments with different resins can not be performed by a single standard procedure. DSC tests are easy to perform but measurements on reactive materials involves some special difficulties such as preparation of the sample in as short time as possible and to choose the instrumental conditions for minimization of the time to a stable instrumental signal

The choice of load temperature in the DSC cell can be a critical part to reach instrumental equilibrium in a short time. For resin 1 which reacts at room temperature with a short inhibition time the best choice of load temperature was to set it equal to the isothermal test temperature. On the other hand for resin 2 the best choice was a load temperature close to room temperature where the reaction rate can be neglected and furthermore to use a constant heating rate to the isothermal test temperature. In the last case the heat which evolves during heating the sample to the isothermal test temperature was negligible for resin 2 but can be obtained by a separate dynamic measurement.

It must be noted that this type of kinetic model which is described in equation 3 is of empirical nature and the use of such a model should be limited to close to the experimental temperature range from which it has been obtained. The model for resin 1 shows some deviations from the experimental values which is due to experimental errors but also because of the complex chemical kinetics for the vinylester which can not be described without the use of more fundamentally based models including effects such as changes in molecular mobility.

A disadvantage with empirical models is that a change in resin formulation requires a recharacterization. But simple models with few parameters can in several cases be sufficient for simulation purposes. Several practical problems in thermoset processing can therefore be solved by simulation with a minimum of effort The choice of extensive testing may be more time consuming and thus more costly.

## 6. References

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