

KINETIC ASPECTS ARISING DURING THE DIFFERENTIAL SCANNING CALORIMETRIC INVESTIGATION OF CURING EPOXY RESINS WITH ANHYDRIDES

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ABSTRACT

The activation energy, the frequency factor and the bulk reaction order were calculated from dynamic DSC experiments of curing epoxy resins with anhydrides, using different methods of kinetic evaluation and with a reaction conversion between 20 % and 60 %. Dynamic thermograms were simulated by fitting these kinetic data to estimate the relevancy of these values in calculating the reaction conversion under isothermal performance of the experiment, as is required in optimizing curing conditions for technical processes. In the range of conversion considered, there is a good agreement with the experiment. The simple kinetic expressions have to be extended for low and high reaction conversions.

INTRODUCTION

Epoxy resins cured with anhydrides are highgrade insulating materials in electrical technology. They are obtained by polyaddition of epoxy resins with dicarboxylic acid anhydrides in the presence of basic accelerators. Processing occurs at high temperatures and mostly in several successive temperature steps. Using differential scanning calorimetry (DSC), the reaction characteristics can rapidly be ascertained using dynamic control of the experiment (ref. 1-4). Thus, the method offers the prerequisite for establishing and optimizing the curing conditions. However, the activation parameters and the reaction order of the bulk reaction have to be calculated by kinetic analysis in order to determine subsequently the isothermal conversion at arbitrary temperatures (ref. 5,6).

EXPERIMENTAL

Bisphenol A-diglycidyl ether (BADGE, epoxy content 5,77 mol/kg) and hexahydrophthalic anhydride (HHPA) were mixed at a molar ratio of 1:1, treated with 1.5 % 1-ethyl imidazole (1-EI, with respect to epoxy resin) and cold welded in an aluminium micropan. Curing was carried out using a "thermal analyzer" 910/1090 (Du Pont) at heating rates of 5, 10 and 20 K/min. For the kinetic evaluation, the heat flow in steps of 1 K and the corresponding

partial enthalpy were derived from the thermograms. The data set was processed by a desktop computer (9836, Hewlett-Packard) with own programmes.

CALCULATIONS

In order to calculate the activation parameters and the reaction order of the bulk reaction, mathematical expressions were used which, without further corrections, combine the general law of homogeneous kinetics

$$d\alpha/dt = k (1-\alpha)^n$$

with the Arrhenius equation

$$k = A \exp (-E/RT)$$

The reaction conversion is expressed by the partial enthalpy of reaction (ref. 7). Thus, the resulting equations are:

according to Borchhardt and Daniels (ref.8)

$$\frac{1}{\Delta H} * \frac{dH}{dt} = A \left(1 - \frac{H}{\Delta H} \right)^n \exp (-E/RT) \quad (1)$$

according to Freeman and Carroll (ref. 9)

$$\frac{\ln \left(\frac{dH_2}{dt} * \frac{dt}{dH_1} \right)}{\ln \left(\frac{\Delta H - H_2}{\Delta H - H_1} \right)} = n - E * \frac{T_1 - T_2}{T_1 * T_2 * R * \ln \left(\frac{\Delta H - H_2}{\Delta H - H_1} \right)} \quad (2)$$

or

$$s = n - E \tilde{\tau}$$

(see Fig. 3)

and according to Fillerstein (refs. 10,11)

$$T^2 * \frac{d^2H/dT^2}{dH/dT} = \frac{E}{R} - \frac{n * T^2}{\Delta H - H} * \frac{dH}{dT} \quad (3)$$

or $\lambda = E/R - n \vartheta$ (see Figs. 4 and 6)

A	frequency factor	k	rate constant
$\alpha = H/\Delta H$	conversion of reaction	n	reaction order
E	Activation energy	R	8.31 J mol ⁻¹ K ⁻¹
ΔH	Total enthalpy of reaction	T	Temperature
H	Partial enthalpy of reaction	t	Time

In order to solve Borchardt-Daniels equation (1), the reaction order n was varied between 0 and 3 and the associated correlation factor was determined after linear regression from the semi-logarithmic plot of rate constant versus 1/T (see Fig. 1). Subsequently, the activation parameters were derived from the diagram, which corresponds to the reaction order with maximum correlation coefficient of the regression line (see Fig. 2).

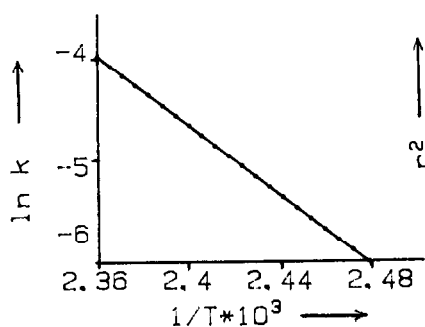


Fig. 1. Arrhenius plot from Borchardt-Daniels calculation of curing BADGE/HHPA with 1,5 % I-EI

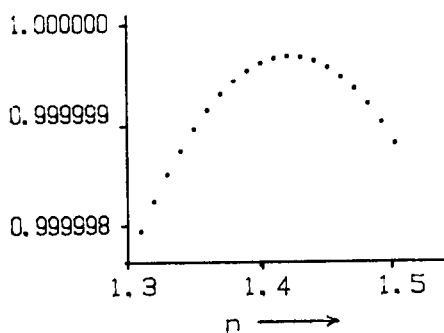


Fig. 2 Relationship between reaction order n and correlation coefficient r^2

According to equation (2), the activation energy was obtained from the slope and the reaction order from the axis intercept by plotting the complex terms against each other in an diagramm (see Fig. 3).

Similarly, equation (3) represents a straight-line equation, by analogous plotting however, the reaction order is derived from the slope and the activation energy from the axis intercept (see Fig. 4). The frequency factor was calculated by using equation (1).

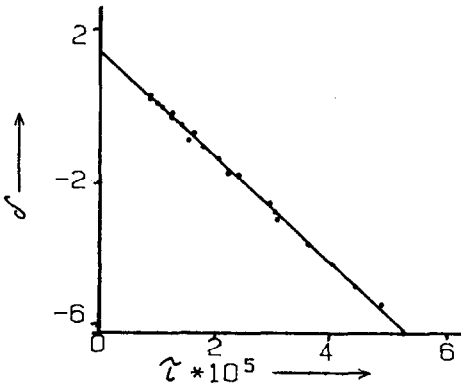


Fig. 3. Freeman-Carroll plot of curing BADGE/HHPA with 1,5 % I-EI

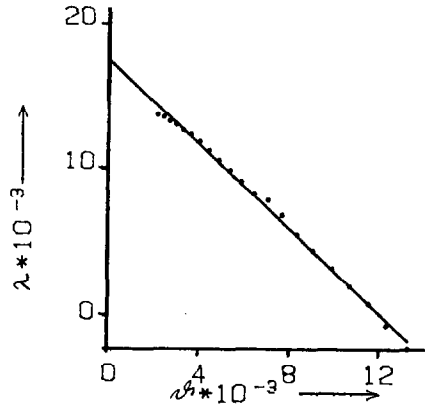


Fig. 4. Ellerstein plot of curing BADGE/HHPA with 1,5 % I-EI

Dynamic thermograms were simulated using these calculated kinetic parameters. This was done under the assumption that the rate constant of the reaction is constant in a temperature range of $\Delta T = 0.1$ K. Thus, the reaction time is specified while taking the heating rate into account. The heat flow dH/dt results from the isothermal enthalpy increment in this time interval. The dynamic thermogram is subsequently obtained by joining together the differential isothermal reaction steps.

RESULTS AND DISCUSSION

The kinetic evaluation method according to Borchardt-Daniels, Freeman-Carroll and Ellerstein was applied to the dynamic thermograms attained for curing bisphenol A-diglycidyl ether and hexahydrophthalic anhydride using imidazole accelerator. This application shows that the values measured between 20 % and 60 % conversion agree well with kinetic evaluations. The activation parameters and the reaction order thus calculated for the bulk reaction are shown in table 1.

TABLE 1

Kinetic analysis of DSC curing of BADGE and HHPA accelerated by 1-EI between 20 % and 60 % of the conversion

Evaluation	Heating rate K/min	E KJ/mol	n	ln A
Borchardt, Daniels	5	140	1.51	36.6
Freeman, Carroll	5	138	1.46	35.7
Ellerstein	5	141	1.51	36.9
Borchardt, Daniels	10	144	1.42	36.8
Freeman, Carroll	10	142	1.40	36.4
Ellerstein	10	146	1.42	37.6
Borchardt, Daniels	20	147	1.37	37.1
Freeman, Carroll	20	145	1.33	36.5
Ellerstein	20	156	1.42	39.7
		144	1.43	37.0

At the investigated heating rates only small differences in the kinetic parameters were obtained. This signifies that no change occurs in the reaction mechanism. This is also evident from the total reaction enthalpy (403 + 10) J/g which is independent of the heating rate. However, distinct changes occur if the evaluated range of conversion is extended. A comparison of the original thermograms with the ones simulated by using the calculated kinetic parameters (see Fig. 5) permits a valuation of the results regarding an assessment of the isothermal curing of epoxy resins. The curves coincide at a conversion between 20 % and 60 %. However, the calculated kinetic parameters yield reaction time which are too long at lower temperatures and too short at higher temperatures. Above the temperature of the reaction maximum the curves are not interpretable since the rise in viscosity during the curing reaction had so far been unconsidered in the method of kinetic analysis.

The method of valuation is confirmed by the Ellerstein plot of the simulated thermogram. An ideal straight line is displayed over the entire temperature range between 50°C and 200°C from which the identical kinetic parameters were derived (see Fig. 6). Thus, a method has been pointed out verifying the influence of corrections in mathematical expressions for the kinetic analysis of dynamic thermograms and thus of describing exactly the experimental.

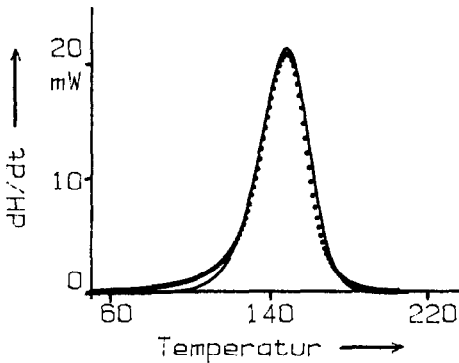


Fig. 5. Original thermogram (•) and simulated thermogram (-) of curing BABBGE/HHPA with 1,5 % I-EI

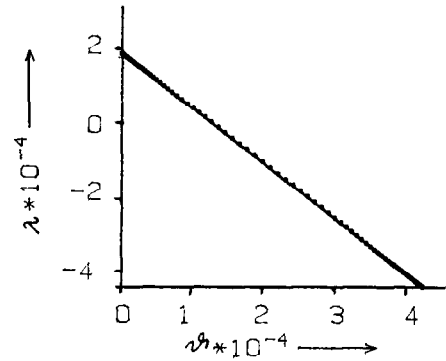


Fig. 6. Ellerstein plot of the simulated thermogram at reaction conversion between 0 and 100 %

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