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A PROGRAM FOR THE KINETIC EVALUATION OF THERMOANALYTICAL CURVES OBTAINED BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The kinetic investigation of thermoanalytical curves of complex chemical reactions requires tedious calculation and large arrays for data processing. A computer program (BASIC) has been developed with which the intricate thermoanalytical curves can be resolved into individual signals and the signals evaluated kinetically according to several mathematical expressions. A computed simulation of the thermoanalytical curves using the parameters of bulk reaction is carried out to verify the validity of the parameters. The method is suitable for determining the amount of isothermal conversion in dynamically observed curing reaction of epoxy resins.

INTRODUCTION

In differential scanning calorimetric (DSC) experiments, the temperature dependent heat flow for exothermic chemical reactions comprises implicitly all the kinetic data necessary to calculate the amount of conversion of an isothermally conducted reaction. In the development of reactive resins for high grade electrical insulations these quantities are required for optimizing the processing conditions since the exothermic curing reactions are mostly carried out in several temperature steps (ref. 1).

Mathematical expressions serve as a computation base in establishing a relationship between the general law of homogeneous kinetics and the Arrhenius equation. Bulk quantities are thus obtained corresponding to the order of reaction (n), the energy of activation (E) and the frequency factor (A) (ref. 2). With these operands the rate constants (k) and the enthalpy values (ΔH) proportional to the conversion are determined.

The calculation involved and the processing of large arrays can be handled rationally only with computers (ref.3). Commercially available programs in general operate with a fixed mathematical expression in a fixed range of the thermoanalytical curve and do not therefore permit either the mutual comparison of different known methods of evaluation or the concentrated localization of

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the range of evaluation. This paper describes a computer program in which four alternative methods of computation are used. It also contains a facility for resolving the intricate thermoanalytical curves, which result due to polymer reactions taking place either parallelly or successively, into individual signals and for investigating the signals separately. For evaluation of the kinetic aspects, intermediate results are plotted and the thermoanalytical curves simulated mathematically by using the calculated bulk quantities which correspond to the kinetic parameters. Only on adequate agreement of the thermoanalytical curve with the simulated one are the parameters used to calculate the amount of isothermal conversion of the reaction.

COMPUTATION BASE

a) Kinetic evaluation of the thermoanalytical curves

The total enthalpy of reaction (ΔH) is calculated after substracting the base line of the measurement peak from the equidistant original data:

$$\Delta H \approx \frac{c}{dT/dt} \cdot \Delta T \cdot \sum_{i=0}^{\infty} \frac{dH_i}{dt}$$

c = cell factor, dT/dt = heating rate, T = temperatur difference between two readings, dH/dt = heat flow, t = dimensionless term for the time with respect to the time unit. The partial enthalpy of reaction (H_j) up to the temperature (T_j) is given by

$$H_j \approx \Delta H \cdot \sum_{i=0}^{j} \frac{dH_i}{dt} \Big/ \sum_{i=0}^{\infty} \frac{dH_i}{dt}$$

Applying the mathematical expression due to Borchhardt and Daniels, the rate constant (k) for a fixed reaction order is calculated using the total enthalpy of reaction and the partial enthalpy and heat flow as a function of the temperature (T), these parameters being obtained from the thermoanalytical experiment (ref. 4):

$$k = \frac{1}{\Delta H} \cdot \frac{dH}{dt} \Big/ \left(1 - \frac{H}{\Delta H}\right)^n$$

ln k is plotted against 1/T, the Arrhenius straight line and the correlation with the straight line being calculated. The value of n leading to the best correlation is determined by scaling down the interval. In accordance with

$$\ln k = \ln A - \frac{E}{R} \cdot \frac{1}{T}$$

ln A is obtained as the axis intercept and -E/R as the slope of this straight line ($R = 8.31\ \mathrm{J\ mol^{-1}\ K^{-1}}$).

Applying the multilinear regression to the operational equation due to Borchhardt and Daniels, a linear equation system is established using the formula

$$y_i = x_{i,1} \cdot \ln A + x_{i,2} \cdot n + x_{i,3} \cdot E$$

and the values calculated from an arbitrary number ($j > 3$) of equidistant points of the thermoanalytical curve (ref. 5):

$$y_i = \ln\left(\frac{1}{\Delta H} \cdot \frac{dH_i}{dt}\right) \qquad x_{1,i} = 1$$

$$x_{2,i} = \ln\left(1 - \frac{H_i}{\Delta H}\right) \qquad x_{3,i} = -\frac{1}{R \cdot T_i}$$

Written in matrix form we obtain:

$$\underbrace{\begin{pmatrix} y_1 \\ y_2 \\ \vdots \\ y_j \end{pmatrix}}_{Y} = \underbrace{\begin{pmatrix} x_{11} & x_{12} & x_{13} \\ x_{21} & x_{22} & x_{23} \\ \vdots & \vdots & \vdots \\ x_{j1} & x_{j2} & x_{j3} \end{pmatrix}}_{X} \underbrace{\begin{pmatrix} \ln A \\ n \\ E \\ \\ \end{pmatrix}}_{L}$$

The bulk quantities for ln A, n and E are calculated using the expression $L = (X^T \cdot X)^{-1} \cdot X^T \cdot Y$, where X^T signifies the transposed matrix of X (ref. 6). In this manner the thermoanalytical curve is investigated stepwise in the overlapping intervals of temperature.

For calculation using the expression due to Freeman and Carroll, the terms

$$x_i = (T_i - T_{i+1})/T_i \cdot T_{i+1} \cdot R \cdot \ln\left(\frac{\Delta H - H_{i+1}}{\Delta H - H_i}\right)$$

and

$$y_i = \ln\left(\frac{dH_{i+1}}{dt} \cdot \frac{dt}{dH_i}\right) \Big/ \ln\left(\frac{\Delta H - H_{i+1}}{\Delta H - H_i}\right)$$

are determined stepwise over the entire range of values for two successive pairs of values (i and i+1) (ref. 7). After plotting y against x, the bulk quantities for n and E are calculated from the axis intercept and from the slope of straight lines according to the straight line equation y = n - E . x. The mean of the two pairs of values which lie nearest to the straight line yields the bulk quantity for the frequency factor according to

$$\ln A = \ln\left(\frac{\overline{dH}}{dt} \cdot \frac{1}{\Delta H}\right) - n \cdot \ln\left(1 - \frac{\overline{H}}{\Delta H}\right) + \frac{E}{R \cdot \overline{T}}$$

Applying the equation due to Ellerstein, which can also be reduced to a straight line equation, the two neighbouring pairs of values (i - 1 and i + 1) in addition to the observed pair of values (i), and the heating rate (dT/dt) are taken into account in determining x_i and y_i (ref. 8) :

$$x_i = T_i^2 \cdot \frac{dH_2}{dt} \cdot \frac{dt}{dT} \Big/ (\Delta H - H_i)$$

$$y_i = T_2^2 \cdot \left(\frac{dH_{i+1}}{dt} - \frac{dH_{i-1}}{dt}\right) \Big/ (T_{i+1} - T_{i-1}) \frac{dH_i}{dt}$$

The bulk quantitaties for E and n result, according to y = E/R - n.x, from the axis intercept and the slope of the straight lines for y over x.
ln A is calculated for the pair of values which lies nearest to the straight line.

b) Mathematical simulation of the thermoanalytical curves

Starting from the partial enthalpy of reaction H = 0 and in recursive steps of 0.1 K the integral dependency H = f (T) is calculated from

$$H_i \approx H_{i-1} + \Delta H \cdot \left(1 - \frac{H_{i-1}}{\Delta H}\right)^n \cdot \exp\left(\ln A - \frac{E}{R \cdot T}\right) \cdot \frac{dt}{dT} \cdot \Delta T$$

The depency of heat flow on the temperature, which corresponds with the thermoanalytical curve, is obtained by approximating

$$dH_i / dt \approx (H_i - H_{i-1}) \cdot \frac{dT}{dt} \cdot \frac{1}{\Delta T}$$

c) Calculation of the amount of isothermal conversion of the reaction

From the thermodynamic measurement it is possible, applying the bulk quantities for n, E and A, to determine the rate constants at discrete temperatures (k_T) and the amount of isothermal conversion (α) of the reaction as a function of time according to Grentzer et al. (ref. 9):

$$\alpha = 1 - [(n - 1) \cdot k_T \cdot t + 1]^{1/(1-n)} \qquad n \neq 1$$

$$\alpha = 1 - \exp(- k_T \cdot t) \qquad n = 1$$

d) Separation of overlapped individual signals

A part of the thermoanalytical curve is fitted by superposition of m differential distribution functions. The resulting function has the form:

$$f(T) = \sum_{i=1}^{m} \frac{dH_i}{dt} \cdot \exp(- W_i \cdot (T - T_i^*)^2)$$

W = breadth of the distribution function
T* = temperature at maximum

For kinetic evaluation either the fitted function itself is taken into account or the function curve is deducted from the thermoanalytical curve before the evaluation. The pertinent enthalpy of reaction is obtained from the area under the curve to be evaluated with respect to the area of the total thermoanalytical curve.

EXPERIMENTAL

A mixture of bisphenol A-diglycidylether (epoxy content 5.77 mol/kg) and diisocyanato-diphenylmethane at a molar ratio of 1:2 was treated with 1 % dimethyl benzylamine (DMBA). An amount of roughly 10 mg of the reaction mixture was immediately cold welded in an aluminium micropan. The curing reaction was followed with a "thermal analyzer" 910/1090 (Du Pont) at a heating rate of 10 K/min and a sampling rate of 0.4 s/point in the temperature range of 10 to 328°C. The 4770 measured pairs of data dH/dt = f (T) were taken over on-line by a desktop computer HP 9836 (Hewlett Packard). The sample weight, the heating rate and the cell factor were fed in manually through the keyboard.

COMPUTER PROGRAM RUN

The computer program to evaluate the thermoanalytical curve is developed modularly in a so called softkey menu technique (Fig. 1). Owing to the size of the agreed arrays and the program range, only the sections necessary for the computation are called up from the mass storage unit. The program calls for constant dialogue. Intermediate results are plotted in each case.

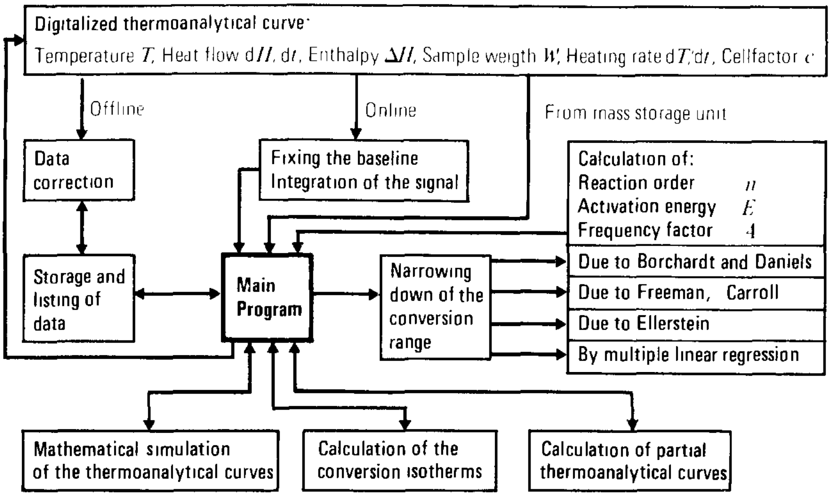

Figure 1: Program for the kinetic evaluation of thermoanalytical curves

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After on-line take over of the original data of measurement, the base line is calculated and deducted (Fig. 2). Up to 400 equidistant supporting points of the base-line-corrected thermoanalytical curve, the calculated partial enthalpy at each point, the total enthalpy of reaction, the sample weight and the heating rate are stored for further calculation. Complex thermoanalytical curves of superimposed reactions are resolved into individual signals, the signals evaluated over the entire range of values by the methods mentioned

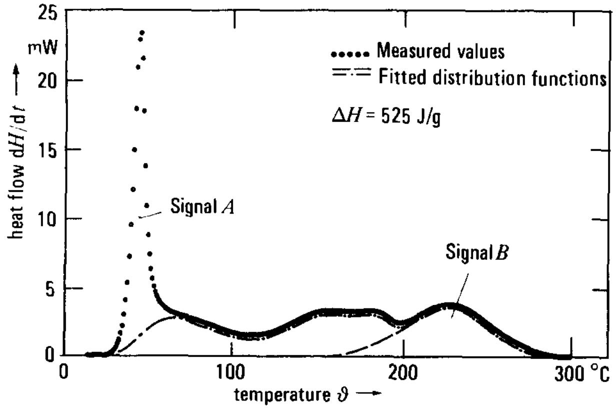

Figure 2: Thermoanalytical curve of a modified epoxy resin together with fitted distribution functions

in b) and the results plotted. Subsequently the evaluation range is narrowed down, the bulk quantities corresponding to the kinetic parameters recalculated and the signals thus simulated mathematically. As soon as there is adequate agreement between the measured and calculated data, the parameters are used to calculate the isothermal conversion curves.

RESULTS AND DISCUSSION

Following curing, the modified epoxy resin selected for the demonstration of the computer program yields a thermoanalytical curve having several maxima (Fig. 2). The total enthalpy of reaction amounts to 525 J/g. Without the resolution of this thermoanalytical curve into individual signals the bulk parameters cannot be calculated with any of the described mathematical expressions.As a result of the investigations of the chemical structure of partially cured epoxy resins, signal A is attributed to the exothermic trimerisation reaction of the modifying component and the signal B to the exothermic reaction of the residual epoxy groups.

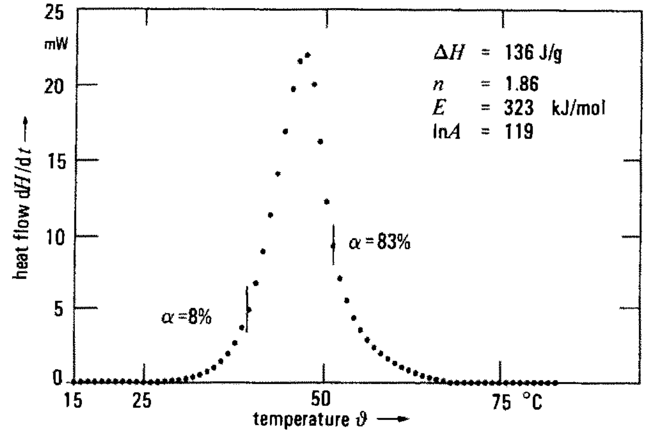

Figure 3: Calculation of the values corresponding to the bulk reaction parameters from signal *A*

Signal A, whose area corresponds to an enthalpy of reaction of 136 J/g, was separated by taking the difference between the thermoanalytical curve and the distribution function (drawn as a dash-dot line) and investigated by means of multiple regression in a narrowed range of 8 to 83 % of conversion using 13 supporting points in the dynamic experiment (Fig. 3). The signal

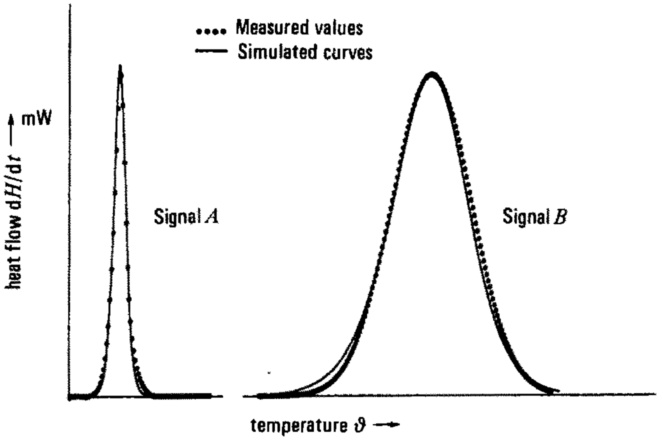

Figure 4: Mathematical simulation of thermoanalytical signals with the calculated values corresponding to the bulk reaction parameters

could be mathematically simulated in good approximation to the calculated values (Fig. 4). The conversion curves calculated with the same values at discrete temperatures show that the trimerisation reaction in this case is clearly detectable after 2 hours at 25°C. This reaction is practically completed after 10 min at 50°C (Fig. 5).

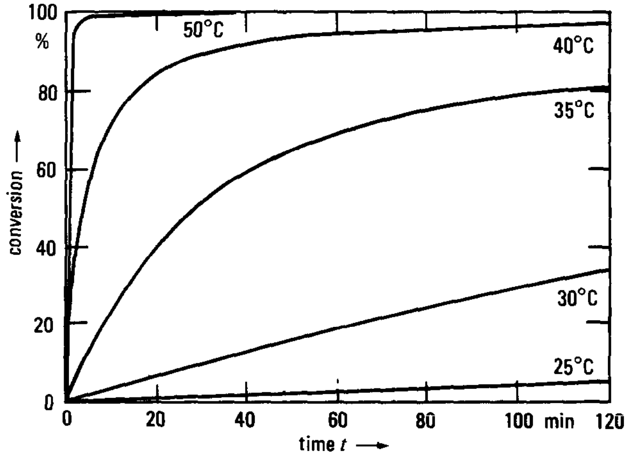

Figure 5: Percentage conversion with the trimerisation reaction of diphenylmethane diisocyanate in modified epoxy resin

Signal B, corresponding to a reaction enthalpy of 143 J/g, is represented by the distribution function drawn as a broken line (Fig.2). The calculation of the kinetic parameters was made according to Borchhardt and Daniels by confining the conversion to a range of 20 to 60 % in the dynamic experiment (Fig.6).

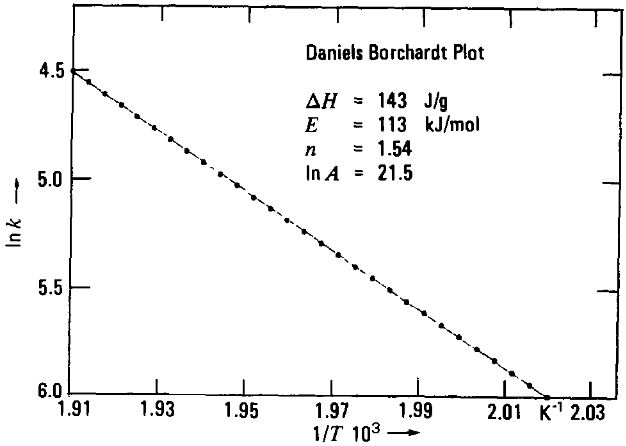

Figure 6: Calculation of the values corresponding to the bulk reaction parameters from signal B

The mathematical reconstruction leads equally to a good agreement (Fig.4). A temperature program was assumed for the reaction of residual epoxy groups to calculate the percentage of conversion. Almost complete conversion is achieved after a reaction time of 4 h in several temperature steps up to 140°C and subsequent tempering for 6 h at 150°C and a further 10 hours at 200°C (Fig. 7).

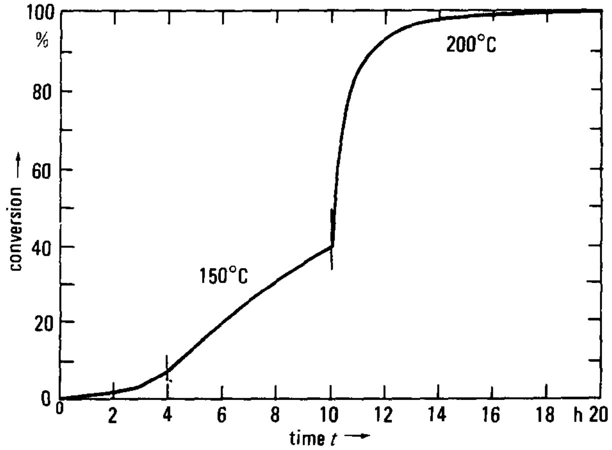

Figure 7: Percentage conversion of residual epoxy groups in modified epoxy resin

The results found are in good agreement with those for the determination of functional groups in partially cured moulding materials. The optional program steps that can be called up - resolving the thermoanalytical curve into individual signals, localization of the range of values, kinetic evaluation, mathematical simulation of the thermoanalytical curve for verification and calculation of the amount of isothermal conversion of the reaction - permit, for the first time, investigation of intricate thermoanalytical curves. Other analytical methods have to be employed for interpreting the thermoanalytical curves and the results.

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