Letters

Deterministic Approach to Obtain Autocatalytic Cure Kinetics Model Constants by Normal Equations of Least-Squares Method

Sukrut Prashant Phansalkar and Bongtae Han

***Abstract*— This letter proposes a novel method to determine the constants of the autocatalytic model using the differential scanning calorimetry (DSC) data. The proposed method is based on the normal equations, which is an analytical approach of the least-squares method. The method requires only two standard DSC dynamic scan data obtained at the linear heating rates of 5 and 10 °C/min but can obtain the four cure kinetics parameters of the autocatalytic model, including the activation energy, analytically but accurately without regression analyses. The method is implemented for a highly filled epoxy molding compound (EMC). Excellent agreements between the predicted cure extent and the test data corroborate the robustness and accuracy of the proposed method.**

***Index Terms*— Cure kinetics, differential scanning calorimetry (DSC), epoxy molding compounds (EMC), Kamal–Sourour (KS) model, normal equations.**

I. INTRODUCTION

The thermoset cure process is exothermic, and the amount of heat released can be directly measured by differential scanning calorimetry (DSC). The measured quantity provides the degree of cure, which can be used to investigate cure kinetics.

There are several methodologies and techniques available in the literature to determine the cure kinetics model constants. After the pioneering and original work by Borchardt and Daniels (B/D) [1], the American Society for Testing and Materials (ASTM) established a standard test method based on *linear* regression, through which the kinetic parameters of the well-known *n*th-order model are determined from a single temperature scanning DSC data at a linear heating rate (also known as dynamic heating scan measurement data) [2].

Numerous advanced thermosets, typically highly filled with silicas (50–90 wt.%), are used in the semiconductor packaging industry. Understanding the curing behavior of the filled thermosets is increasingly important to optimize the manufacturing processes, as the packages are becoming thinner and complex [3], [4].

The advanced thermosets typically follow the autocatalytic behavior, for which the autocatalytic kinetics model should be used to describe the curing behavior faithfully, especially at the beginning of cure. Several types of *nonlinear* regression algorithms have been implemented to determine the kinetic parameters of the autocatalytic model [5]. Due to the extreme nonlinear nature of the model, the nonlinear regression usually requires a large quantity of dynamic scan data obtained at three or more heating rates to ensure proper convergence during the regression, unless the initial values of the constants are selected carefully [5], [6].

This letter proposes a novel method to determine the constants of the autocatalytic model using the DSC data. The proposed method is based on the *normal* equations, which is an analytical approach of the least-squares method. The method requires only two standard DSC dynamic scan data obtained at the linear heating rates of 5 and 10 °C/min but can obtain the four cure kinetics parameters of the autocatalytic model, including the activation energy, analytically but accurately without regression analyses. The method is described in detail after briefly reviewing the autocatalytic cure kinetics model. The method is implemented for a highly filled epoxy molding compound (EMC). The experimental data and the predictions of cure extent are presented, and the robustness and accuracy of the method are discussed.

II. CURE KINETICS MODEL

The general form of reaction kinetics model is expressed as [7]

$$\frac{dp}{dt} = k(T, p) \cdot f(p) \tag{1}$$

where k is the rate constant; and $f(p)$ is the cure kinetics function that can take any mathematical form of p. The rate constant can be a function of both temperature (T) and cure extent (p). For most thermosets used in the semiconductor packaging industry, it has been known that the rate constant is independent (or a very weak function) of cure extent [8], [9], [10], and it can be expressed using the Arrhenius equation as

$$k(T) = A \exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

where A is the Arrhenius constant, E_a is the activation energy, and R is the ideal gas constant (8.314 $J\text{mol}^{-1}\text{K}^{-1}$).

Then, the modified autocatalytic model, known as Kamal–Sourour (KS) model, takes the following form [11]:

$$\frac{dp}{dt} = k(T) \cdot p^m (1-p)^n; \quad k(T) = A \exp\left(-\frac{E_a}{RT}\right) \tag{3}$$

where n and m are the reaction orders associated with the model.

III. PROPOSED DETERMINISTIC APPROACH

The proposed method is based on the normal equation, which is an analytical approach of the least-squares method [12]. The normal equation-based least-squares method was utilized successfully to determine the elastic constants using the experimental full-field displacement field [13]. A similar approach is adopted to determine the KS model constants.

The KS model can be expressed in the following form by taking natural logarithm of (3) as:

$$\ln\left(\frac{dp}{dt}\right) = \ln A + n\ln(1-p) + m\ln(p) - \frac{E_a}{RT}. \tag{4}$$

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The objective function (S) defined by the sum of square error (SSE) between the model prediction and the DSC data can be expressed as

$$\begin{aligned} S &= \sum_{i=1}^{N}\left[\ln\left(\frac{dp}{dt}\right)_{i,\text{model}} - \ln\left(\frac{dp}{dt}\right)_{i,\text{model}}\right]^2 \\ &= \sum_{i=1}^{N}\left[\ln A - \frac{E_a}{RT} + n\ln(1-p) + m\ln(p) - \ln\left(\frac{dp}{dt}\right)_{i,\text{model}}\right]^2. \end{aligned} \tag{5}$$

The least-squares criterion for the four independent variables (i.e., the first-order condition of the least-squares minimization) requires

$$\frac{\partial S}{\partial(\ln A)} = \frac{\partial S}{\partial E_a} = \frac{\partial S}{\partial m} = \frac{\partial S}{\partial n} = 0. \tag{6}$$

The above criterion produces a system of equations, known as the *normal* equations. The results can be expressed in a matrix form as

$$\{X\} = [C]^{-1}\{B\} \tag{7}$$

where $\{X\} = \begin{Bmatrix} \ln A \\ E_a \\ n \\ m \end{Bmatrix}$; $\{B\} = \sum_{i=1}^{N} \begin{Bmatrix} \ln\left(\frac{dp}{dt}\right)_i \\ -\frac{1000}{RT_i}\ln\left(\frac{dp}{dt}\right)_i \\ \ln(1-p_i)\ln\left(\frac{dp}{dt}\right)_i \\ \ln(p_i)\ln\left(\frac{dp}{dt}\right)_i \end{Bmatrix}$

$$[C\} = \sum_{i=1}^{N}\cdots$$

$$\begin{bmatrix} 1 & -\frac{1000}{RT_i} & \ln(1-p_i) & \ln(p_i) \\ -\frac{1000}{RT_i} & \frac{1000^2}{R^2T_i^2} & -\frac{1000}{RT_i}\ln(1-p_i) & -\frac{1000}{RT_i}\ln(p_i) \\ \ln(1-p_i) & -\frac{1000\ln(1-p_i)}{RT_i} & (\ln(1-p_i))^2 & \ln(1-p_i)\ln(p_i) \\ \ln(p_i) & -\frac{1000}{RT_i}\ln(p_i) & \ln(1-p_i)\ln(p_i) & (\ln(p_i))^2 \end{bmatrix}.$$

The values of dp/dt and p are directly obtained from DSC tests. In the above equations, "N" is the number of data points obtained from the DSC measurements. If there are no differences between the model predictions and the DSC data, the four constants in the above equation ($A, E_a, n,$ and m) can be determined using only four arbitrary points in the DSC data. In practice, discrepancies attributed to experimental uncertainties are always present, and this is the rationale of the over deterministic approach, where N is much larger than the number of constants to be determined [11]. It is also important to recall that the normal equation is a closed-form solution that minimizes the value of SSE. The solution is always unique (global minima) as long as $[C]^{-1}$ is determinable [12], [13], [14].

A. Data Required to Handle Nonlinearity of KS Model

The KS model poses a new regression analysis challenge due to its extreme nonlinearity, more specifically, dual power terms of cure extent. As explained clearly in the ASTM standard [3], the simpler nth-order model in a logarithm form can be expressed as a linear function with two independent variables (x, y), repeated here

$$z(x, y) = a + bx + cy \tag{8}$$

where $z \equiv \ln(dp/dt)$, $a \equiv \ln A$, $b \equiv n$, $x \equiv \ln(1-p)$, $c \equiv E_a/R$, and $y \equiv 1/T$. It is worth noting that the first independent variable, x, is a function of cure extent, p; and the second independent variable, y, is a function of temperature, T.

Equation (8) defines a plane for a given set of three parameters ($A, n,$ and E_a) in the (x, y) domain. This is graphically illustrated in Fig. 1. A line produced by a single dynamic scan data is also shown in Fig. 1. It is important to note that the line lies in the plane, but it is curved due to the nonlinear relationship between the x and y variables. Therefore, the solution obtained from the normal equations using a single dynamic scan data can define the plane uniquely; and thus, the three parameters ($A, E_a,$ and n) can be obtained by the normal equations using a single dynamic scan data.

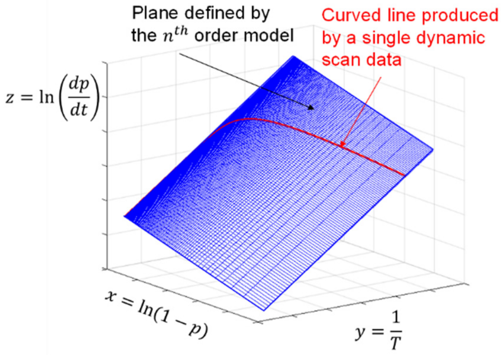

Fig. 1. Plane defined by the nth-order model (8) and a line produced by a single dynamic scan data.

The KS model of (4) can be expressed using the similar notations as

$$z(x, y) = a + b_1x_1 + b_2x_2 + cy \tag{9}$$

where $z \equiv \ln(dp/dt)$, $a \equiv \ln A$, $b_1 \equiv n$, $x_1 \equiv \ln(1-p)$, $b_2 \equiv m$, $x_2 \equiv \ln p$, $c \equiv E_a/R$, and $y \equiv 1/T$.

The above equation contains two variables, (x_1, x_2), that are a function of p. They are related as $x_2 = \ln\left(1 - e^{x_1}\right)$. Thus, (9) can be rewritten as

$$z(x, y) = a + b_1x + b_2\ln\left(1 - e^{x}\right) + cy. \tag{10}$$

Equation (10) defines a curved surface for a given set of four parameters ($A, n, m,$ and E_a) in the (x, y) domain, which cannot be defined by a single curved line obtained from a single dynamic scan data; in other words, a curved plane cannot be defined uniquely by a single curved line. This implies that the closed-form solution obtained from (7) using a single dynamic scan data will not provide a unique set of the four parameters of the KS model. One more dynamic scan data (i.e., an additional curved line) is required to define the curved surface uniquely.

This can be expressed mathematically as

$$\begin{aligned} &[C]_1\{X\} + [C]_2\{X\} = \{B\}_1 + \{B\}_2 \\ &[C] = [C]_1 + [C]_2 \text{ and } \{B\} = \{B\}_1 + \{B\}_2 \end{aligned} \tag{11}$$

where $[C]_i$ and $\{B\}_i$ for $i = 1$ and 2 are the matrices obtained from two dynamic scan data.

IV. IMPLEMENTATION

A commercial EMC, which contains an epoxy-phenolic resin system, was used to determine the cure kinetics constants of the KS model. The EMC is filled with silica (SiO_2) particles with a content of 85–95 wt./wt.%. TA Discovery DSC 250 was used to obtain the dynamic scan data at the standard heating rates of $\beta =$ 5 and 10 °C/min. A preliminary test was conducted to determine the maximum temperature (200 °C) for DSC tests, beyond which no heat generation was observed. The heat flow data ($\dot{Q}$) obtained from DSC are shown as a function of temperature (°C) in Fig. 2, where the heat flow is scaled by the higher heating rate ($\beta_{\text{ref}} = 10$ °C/min).

The total enthalpy of the reaction (ΔH) was measured by subtracting the baseline determined using the start and the endpoint. The average enthalpy of the reaction obtained from both rates was 29.2 ± 0.16 J/g. The curing rate (dp/dt) as a function of temperature

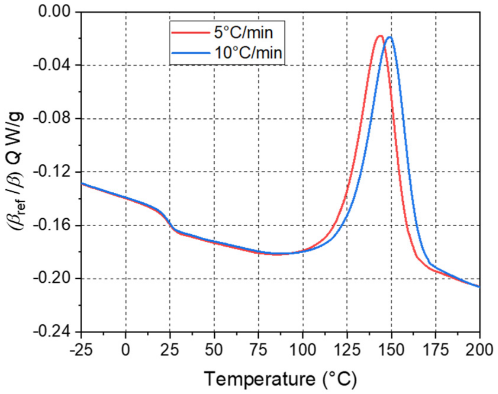

Fig. 2. DSC dynamic scan data at the standard heating rate of $\beta = 5$ and 10 °C/min.

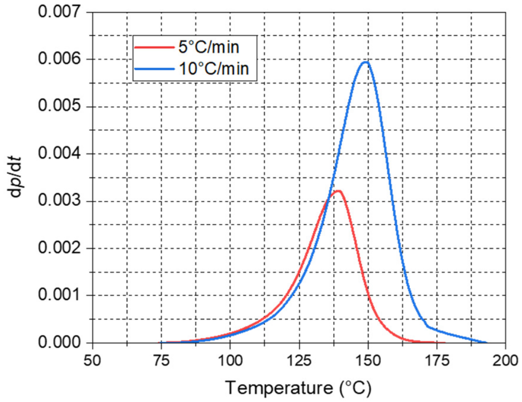

Fig. 3. Rate of reaction as a function of temperature, obtained from the data shown in Fig. 2.

was obtained by dividing the heat flow rate ($\dot{Q}$) by the total amount of heat released. The results are shown in Fig. 3.

The normal equation matrices [see (11)] obtain from each datasets are

$$\{X\} = \left([C]_{5\ ^\circ\mathrm{C/min}} + [C]_{10\ ^\circ\mathrm{C/min}}\right)^{-1} B. \tag{12}$$

This yields

$$\{X\} = \begin{Bmatrix} \ln A\ (s^{-1}) \\ E_a\ (kJ/mol) \\ n \\ m \end{Bmatrix} = \begin{Bmatrix} 17.556 \\ 75.44 \\ 1.13 \\ 0.62 \end{Bmatrix}. \tag{13}$$

The numerical values of matrices $-[C]$ and $\{B\}$ are available in the supplementary material. The values in Eq. (13) were used to predict the cure extent. The predicted cure extent is compared with the cure extent obtained from DSC data in Fig. 4. Two additional dynamic scan data obtained at the heating rates of $\beta = 2.5$ and 7.5 °C/min are also used for comparison. The predicted values and the experimental data show excellent agreements, not only at the two standard rates used to determine the parameters but also at the two additional rates.

V. DISCUSSION

As discussed earlier, the normal equation using a single dynamic scan data will not provide a unique set of the four parameters of the KS model. In order to examine this further, the four parameters were determined using the single dataset of 5 °C/min using (7). The results are

$$\{X\} = \begin{Bmatrix} \ln A\ (s^{-1}) \\ E_a\ (kJ/mol) \\ n \\ m \end{Bmatrix} = \begin{Bmatrix} -73.11 \\ -237.01 \\ 0.33 \\ 3.15 \end{Bmatrix}. \tag{14}$$

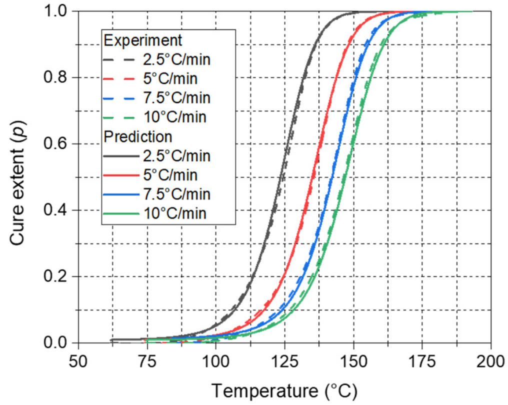

Fig. 4. Predicted cure extent compared with the DSC data. Only the data obtained from the standard rates of $\beta = 5$ and 10 °C/min are used to determine the model parameters, and the additional dynamic scan data ($\beta = 2.5$ and 7.5 °C/min) are used only for comparison.

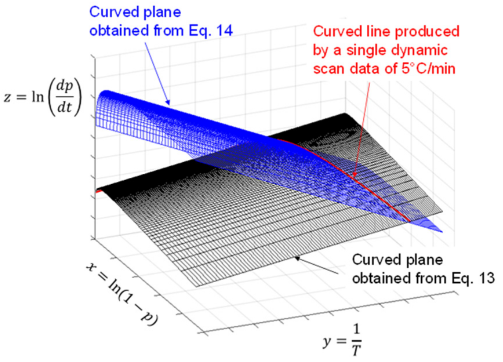

Fig. 5. Curved surface represented by (10), where black and blue planes are obtained from (13) and (14), respectively. The intersecting line (red) coincides with a curved line produced by the single dynamic scan data of 5 °C/min.

The values are significantly different from the values obtained from two dynamic scan data [see (13)].

This discrepancy is explained graphically in Fig. 5. The black plane shows the curved surface representing the true solution (13), while the blue plane shows the curved surface representing the solution obtained only using the single dynamic scan data of 5 °C/min [see (14)]. The intersecting line (red line) is identical to a curved line produced by the 5 °C/min dynamic scan data. It clearly shows that one additional curved line is required to define the black plane uniquely. Thus, the results confirm that more than one standard DSC dynamic scan data should be used to determine the model constants uniquely.

VI. CONCLUSION

An analytical approach based on the *normal* equations of the least-squares method was developed to determine the constants of the autocatalytic model, and it was implemented for a highly filled EMC. Only two standard DSC dynamic scan data ($\beta = 5$ and 10 °C/min) were required to uniquely obtain the four cure kinetics parameters of the autocatalytic model, including the activation energy. The predicted cure extent was compared with the cure extent obtained from DSC data. The predicted values and the experimental data showed excellent agreements, not only at the two standard rates used to determine the parameters but also at the two additional dynamic scan data obtained at the heating rates of $\beta = 2.5$ and 7.5 °C/min, which corroborated the robustness and the accuracy of the proposed method.

The method is "analytical" in nature and can be implemented by commercial spreadsheet application software. The method is efficient, but robust and accurate. More implementations using advanced thermosets in semiconductor packaging are expected.

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