

Polymer Cure Modeling for Microelectronics Applications

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Abstract: *A review of polymer cure models used in microelectronics packaging applications reveals no clear consensus of the chemical rate constants for the cure reactions, or even of an effective model. The problem lies in the contrast between the actual cure process, which involves a sequence of distinct chemical reactions, and the models, which typically assume only one, (or two with some restrictions on the independence of their characteristic constants.) The standard techniques to determine the model parameters are based on differential scanning calorimetry (DSC), which cannot distinguish between the reactions, and hence yields results useful only under the same conditions, which completely misses the point of modeling. The obvious solution is for manufacturers to provide the modeling parameters, but failing that, an alternative experimental technique is required to determine individual reaction parameters, e.g. Fourier transform infra-red spectroscopy (FTIR).*

1. INTRODUCTION

Thermally cured epoxies and other polymers are extensively used in electronics packaging, as encapsulants, underfills, and adhesives, etc. The project which prompted this study was the microwave cure of a carbon-loaded epoxy encapsulant [1]. The temperature rises more rapidly than in conventional isothermal or reflow oven curing systems, and the cure proceeds more uniformly within the material. Optimization of the microwave power level and application time cannot be readily accomplished experimentally, especially given the speed of the cure, so simulation is seen as the tool to sensible planning of the process development. A literature review was the obvious first step to establish the model, including the thermal dependences of the chemical reaction parameters. Prior experience had suggested that the basic first order model is effective in electrically conductive adhesive applications, based on rapid resistance decreases at the calculated 100% cure point, with model parameters relatively easily obtained by DSC measurements [2, 3]. However, the observation of such resistance decreases at barely 20% cure [4] calls this criterion into question.

2. PHENOMENOLOGICAL CURE MODELS

2.1. Mathematical Models

For α = degree of cure, the basic assumption of all models is that the reaction rate can be expressed in terms of the temperature dependent chemical rate constant, K , and a function, $f(\alpha)$, of reactant concentration at absolute temperature, T , as

$$\frac{d\alpha}{dt} = K \cdot f(\alpha) = A \cdot \exp\left[-\frac{E}{RT}\right] \cdot f(\alpha) \quad (1)$$

Reaction rate parameters A and activation energy E are assumed to be characteristic constants of the polymer, and $R=8.31\text{J/K.mole}$. Cure models vary in the assumed form of $f(\alpha)$, as listed below:

○ n^{th} order models: $f(\alpha) = (1 - \alpha)^n$ (2)

In these cases, one can find α analytically for constant T , (i.e. isothermal cure) as:

- 1st order: $d\alpha/dt = K(1 - \alpha)$, $\therefore \alpha = 1 - \exp(-Kt)$
- 2nd order: $d\alpha/dt = K(1 - \alpha)^2$, $\therefore \alpha = 1 - [1 + Kt]^{-1}$
- n^{th} order: $d\alpha/dt = K(1 - \alpha)^n$,
 $\therefore \alpha = 1 - [1 + (n - 1)Kt]^{-1/(n-1)}$

o Auto-catalyzed models:

▪ Single-step: $d\alpha/dt = K \alpha^m (1 - \alpha)^n$ (3)

▪ Double step (linear combination):
 $d\alpha/dt = (K_1 + K_2 \alpha^m)(1 - \alpha)^n$ (4)

▪ Modified double step:
 $d\alpha/dt = K(y_1 + y_2 \alpha^m)(1 - \alpha)^n$ where $y_1 + y_2 = 1$ (5)

2.2. Physical Basis

The n^{th} order model (equation 2) is based on the simple notion that the reaction rate is proportional to the un-reacted reagent mass available. There is a theoretical basis for the values of n below for the reaction modes quoted [5], but n varies much more widely in practice.

- $n=1/2$ Phase boundary reaction (area)
- $n=1/3$ Phase boundary reaction (volume)
- $n=2/3$ Nucleation sphere (volume growth)

A branching nucleation/growth model supports the single step autocatalytic model (equation 3), where the dependence on α suggests that the reaction proceeds at the boundary of reacted and un-reacted material, e.g. activated by an exothermic reaction. Note, however, that $d\alpha/dt=0$ for $\alpha=0$, which is non-physical and leads to “starting” problems.

The double-step auto-catalytic model (equation 4) is designed to solve this problem, but the single n -exponent does not suggest two independent reactions. However, it is the only model with more than a single chemical rate constant, i.e. all others implicitly assume a single chemical curing reaction, or at least a single rate controlling reaction across the full temperature range of interest. (The modified double-step (equation 5) provides two reaction rates, but with a single activation energy.)

3. PHYSICAL MODEL

3.1. Cure Reactions

In practice, the cure of bisphenol-A diglycidyl ether (BADGE), for example, a commonly employed epoxy in packaging applications, requires two steps, (with a third etherification reaction only occurring at high cure temperatures.) So the double step auto-catalyzed model is the only one of these with a realistic physical basis which can be expected to apply outside the conditions used to determine A, E.

The two reactions [6-8] can be written as:

- I. Primary amine + epoxide \rightarrow secondary amine
 - II. Secondary amine + epoxide \rightarrow tertiary amine
- where neither of these totally dominates rate control.

At temperatures below the glass transition temperature, T_g , (which increases with degree of cure,) the cure rate is controlled by reagent diffusion [9], (effectively stopping the reaction,) so in general the effective cure rate is given by

$$\frac{1}{K_{\text{effective}}} = \frac{1}{K_{\text{primary}}} + \frac{1}{K_{\text{secondary}}} + \frac{1}{K_{\text{etherification}}} + \frac{1}{K_{\text{diffusion}}} + \dots$$

$$\approx \frac{1}{K_{\text{primary}}} + \frac{1}{K_{\text{secondary}}} \text{ at low } T_{\text{cure}} > T_g \quad (6)$$

4. CURE PARAMETER DETERMINATION

To use the models, the rate parameters A and E must be determined, and to do so requires the assumption of the relevant model and the prior determination of the model parameters m and n , etc. There are mathematical techniques available to extract these from isothermal and/or dynamic DSC data, which are reviewed below.

4.1. Differential Scanning Calorimetry (DSC)

DSC monitors the heat flow into or out of the reaction chamber, i.e. the heat of reaction, as a function of time. For isothermal DSC, heat is provided or absorbed to maintain constant T . The sample size must be as small as possible to minimize thermal lag and the inevitable difference between sample and chamber temperatures during the reaction.

The instantaneous rate of heat flow from the chamber (for an exothermic cure reaction) corresponds to the instantaneous reaction rate, $d\alpha/dt$, and the area under the curve to the degree of cure, α , so both of these parameters are directly accessible [7, 10]. Normalization of the total area to $\alpha = 1$ is a usual first approximation, but can be improved by a second cure cycle which will indicate further curing and provide a second approximation (which can be further improved by successive cycles) of the first cycle’s degree of cure, $\alpha \leq 1$.

Iterative techniques have been used to develop multi-reaction models from DSC peak detail [11].

4.2. Isothermal DSC

For isothermal cure, there will be an initial period required to establish the constant cure temperature, T , which must exceed T_g .

n^{th} -order model: (Equation 2)

(A) Equation 2 may be re-written as [12]:

$$\ln(d\alpha/dt) = \ln K + n \ln(1 - \alpha) \quad (7)$$

For multiple isothermal DSC experiments at various values of T , $\ln(d\alpha/dt)$ is plotted vs. $\ln(1 - \alpha)$ for each T to find n and $K(T)$. (As a model check, n should be independent of T .) Then $\ln K(T)$ is plotted vs. $1/T$ (Arrhenius plot) to find E and A ; the plot should be linear for E , A to be independent of T , (i.e. for a single reaction.)

(B) Alternatively, equation 2 is written as:

$$\ln[(d\alpha/dt)/(1 - \alpha)^n] = \ln K(T) = -E/RT + \ln A \quad (8)$$

and $\ln[(d\alpha/dt)/(1 - \alpha)^n]$ is plotted vs. $1/T$ to yield E and A directly. However, this method requires one to assume a value of n , i.e. to vary n to obtain the linear Arrhenius plot for E and A independent of T .

(C) Independent determination of n [13]: If the slopes at the leading and trailing saddle-points of the $d\alpha/dt$ curves are designated by a and b respectively, then it has been shown theoretically and experimentally that n can be determined for the n^{th} -order model only as

$$n = (a/0.63b)^{1/2} \quad (9)$$

Single-step autocatalytic: (Equation 3)

Equation 3 is re-written as:

$$\ln(d\alpha/dt) = \ln K + m \ln(\alpha) + n \ln(1 - \alpha) \quad (10)$$

(A) For multiple isothermal DSC experiments at various values of T , plots of:

- $\ln(d\alpha/dt)$ vs. $\ln(\alpha)$ for small $\alpha \ll 1$ give m , $K(T)$
- $\ln(d\alpha/dt)$ vs. $\ln(1 - \alpha)$ for large $\alpha \gg 0$ give n , $K(T)$

(Consistency of the $K(T)$ values for each plot pair at each T provides a model check.) Plotting $\ln K(T)$ vs. $1/T$ gives E and A as before, from a linear graph.

(B) If one assumes that $m+n=2$ [14], equation 3 becomes

$$d\alpha/dt = K \alpha^{2-n} (1 - \alpha)^n \quad (11)$$

and plots of $\ln[(d\alpha/dt)/\alpha^2]$ vs. $\ln(1/\alpha - 1)$ at each T give n (the slope) and $K(T)$. E and A are found from the Arrhenius plot, as before.

(C) One can also plot $(d\alpha/dt)/(1 - \alpha)^n$ vs. α^m directly at each T , varying n and m to obtain linear plots of slope $K(T)$, and hence E and A .

Double-step autocatalytic: (Equation 4)

(A) The double-step problem is that two independent temperature-dependent parameters must be found, a significant complication. The brute-force approach is to plot $d\alpha/dt$ vs. α for each isothermal T run, and to find the best fit, varying m , n , $K_1(T)$, and $K_2(T)$. Then plots of $\ln K_1(T)$, $\ln K_2(T)$, vs. $1/T$ give E_1 , E_2 , A_1 , A_2 . One set of results gave $m \sim 0.5-1$, $n \sim 2$ for $\alpha < 0.3-0.5$, while another yielded $m \sim 0.75$, $n \sim 1.5-2$.

(B) If one assumes $m=1$, $n=2$, (which experiment supports over a limited range in some cases,) a plot of $[(d\alpha/dt)/(1 - \alpha)^2]$ vs. α gives $K_1(T)$, and $K_2(T)$, and again the Arrhenius plots give E_1 , E_2 , A_1 , A_2 .

(C) One might reduce the added complexity by elimination of one of the variables, e.g. at the reaction peak α_p , where $d^2\alpha/dt^2 = 0$ gives:

$$K_1 = K_2 \alpha_p^{m-1} [(m/n) - \alpha_p^{1+m/n}], \text{ and hence}$$

$$(d\alpha/dt)_{\alpha_p} / [\alpha_p^m (1 - \alpha_p)^n] = K_2 (m/n) \cdot [\alpha_p^{-1} - 1]$$

which gives $K_2(T)$ and hence $K_1(T)$, although one must still find m and n by trial and error.

Modified double-step autocatalytic: (Equation 5)

(A) For the assumption that $m=n=1$ [15]:

$$Kt = \int_0^{\alpha} \frac{d\alpha}{(y_1 + y_2\alpha)(1 - \alpha)}$$

$$= \ln\left(\frac{1}{1 - \alpha}\right) + \ln\left(\alpha + \frac{y_1}{y_2}\right) - \ln\left(\frac{y_1}{y_2}\right)$$

At the peak α_p , (t_p) setting $d(d\alpha/dt)/d\alpha = 0$ gives

$$y_1/y_2 = 1 - 2\alpha_p$$

and (substituting back) gives: $Kt_p = -\ln(y_1/y_2)$, and hence: $\ln t_p = (E/R)/T + \ln[-A^{-1} \ln(y_1/y_2)]$.

(B) For the assumption that $m=1$, $n=2$:

$$Kt = \int_0^{\alpha} \frac{d\alpha}{(y_1 + y_2\alpha)(1 - \alpha)^2}$$

$$= \frac{-y_1}{1 - \alpha} + y_2 \left[\ln\left(\alpha + \frac{y_1}{y_2}\right) - \ln\left(\frac{y_1}{y_2}\right) - \ln(1 - \alpha)^2 \right]$$

At the peak α_p , setting $d(d\alpha/dt)/d\alpha = 0$ gives

$$y_1/y_2 = \frac{1}{2}(1 - 3\alpha_p)$$

and (substituting back) gives:

$$Kt = -\frac{1}{2}y_2 + y_2 \ln[(1 - y_1/y_2)/4 (y_1/y_2)^3]$$

and hence:

$$\ln t_p = (E/R)/T + \ln[y_2 A^{-1} \{ \ln(1 - y_1/y_2)/4 (y_1/y_2)^3 \}^{-1/2}]$$

In both cases, (A and B,) plotting $\ln t_p$ vs. $1/T$ for each isothermal T yields E and A .

4.3. Dynamic DSC

In dynamic DSC, the temperature is ramped linearly with time, t , so $T = \beta t$. Endothermic solvent evaporation and specific heat effects must both be removed by baseline correction, typically by a second run after cure. (There will be a specific heat discontinuity on this second run as T passes through T_g .) In addition, it is imperative that β be sufficient to maintain $T > T_g$ throughout the process as T_g increases with cure, or the reaction may slow if $T_g(t) \sim T(t)$ or stop while $T(t) < T_g(t)$.

n^{th} -order model: (Equation 2)

For two different heating rates $\beta_1 \neq \beta_2$ [9]:-

For the same degree of conversion $\alpha_1 = \alpha_2$ at T_1, T_2
 $\ln[(d\alpha/dt)_1 / (d\alpha/dt)_2] = -(E/R)[1/T_1 - 1/T_2]$ gives E

And, at the same temperature $T_1 = T_2$
 $\ln[(d\alpha/dt)_1 / (d\alpha/dt)_2] = n \ln[(1 - \alpha_1) / (1 - \alpha_2)]$ gives n

For the same rate of conversion $(d\alpha/dt)_1 = (d\alpha/dt)_2$
 $\ln[(1 - \alpha_1) / (1 - \alpha_2)] = (E/nR)[1/T_1 - 1/T_2]$ confirms E, n

Iso-conversion: (Equations 2 and 3)

For $d\alpha/dt = K f(\alpha)$, where $K = A \exp(-E/RT)$, $T = \beta t$:
 $d^2\alpha/dt^2 = [(E/R\beta^2) + A \cdot f'(\alpha) \cdot \exp(-E/R\beta t)](d\alpha/dt)$,
and at peak α_p where $d\alpha/dt$ is maximum,
 $d^2\alpha/dt^2 = 0$ when $E/R\beta t_p^2 = -A \cdot f'(\alpha_p) \cdot \exp(-E/R\beta t_p)$,
i.e. when $E\beta/R T_p^2 = -A \cdot f'(\alpha_p) \cdot \exp(-E/R T_p)$,
or when $\ln(E/R) + \ln(\beta/T_p^2) = \ln(-A \cdot f'(\alpha_p)) - E/R T_p$ [5],
so plotting $\ln(\beta/T_p^2)$ vs $1/T_p$ gives E from the slope,
i.e. $E = R \cdot [d \ln(\beta/T_p^2) / d(1/T_p)]$ [12, 13, 16].

This method yields E independent of the specific model $f(\alpha)$, which is still needed, however, to then find A . With E known,

$$A = - (R T_p^2 / E \beta \cdot f'(\alpha_p)) \exp(E/R T_p),$$

and for the n^{th} order model: $f'(\alpha_p) = n(1 - \alpha)^{n-1}$, which $\rightarrow 1$ for $n=1$. For the single step auto-catalytic model,
 $f'(\alpha_p) = f(\alpha) \cdot [(m/\alpha) + n/(1 - \alpha)]$.

Note: This method does not apply to the double-step auto-catalytic model, only for single-K models.

Temperature integral method [17]:

Re-writing equation 1 as:

$$\begin{aligned} g(\alpha) &= \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \\ &= -\frac{AE}{\beta R} \int_{x_0}^x \frac{\exp(-x)}{x^2} dx, \text{ where } x = \frac{E}{RT} \\ &\approx \frac{AE}{\beta R} \int_x^\infty \frac{\exp(-x)}{x^2} dx = \frac{AE}{\beta R} \cdot p(x) \\ &= \frac{AE}{\beta R} \int_1^\infty \frac{\exp(-zy)}{zy^2} dy = \frac{AE}{\beta R} \cdot \frac{E_2(z)}{z} \end{aligned} \quad (12)$$

for $T_0 \rightarrow 0$ and $x = zy$ so $y = 1 \rightarrow \infty$ as $x = x \rightarrow \infty$

(A) There are many possible solutions for the RHS: $p(x) = z^{-1} E_2(z)$, either by numerical integration by computer, or as series solutions [18]. Two of the most accurate approximations over appropriate ranges are:

$$\begin{aligned} p(x) &\approx \frac{e^{-x}}{x} \cdot \frac{1}{x + 1.8768} \text{ or} \\ p(x) &\approx \frac{e^{-x}}{x} \cdot \frac{x^3 + 18x^2 + 88x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \end{aligned}$$

The expression $\log[p(x)] \approx -2.315 - 0.4567E/RT$ (for $20 < E/RT < 60$) has been commonly used in the past [2,3] but is not as accurate. Rearranging equation 12: $g(\alpha) = (AE/\beta R)p(x) \rightarrow \ln \beta = \ln[AE/Rg(\alpha)] + \ln p(E/RT)$, which gives (Ozawa) $E = -(R/0.4567)[\Delta \log \beta / \Delta T_x^{-1}]$ where the same degree of cure α_x occurs at temperatures T_x as thermal ramp rate β is varied.

(B) Ideally, one needs a simple solution for:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{AE}{\beta R} p(x) \quad (13)$$

The RHS (thermal integral) is discussed above. Any expression for the LHS requires the assumption of a model $f(\alpha)$.

For $f(\alpha) = (1 - \alpha)$, $\alpha = 1 - \exp[-(AE/\beta R)p(x)]$, and for $f(\alpha) = (1 - \alpha)^n$, $\alpha = 1 - [1 - (n-1)(AE/\beta R)p(x)]^{-1/(n-1)}$.

For the auto-catalytic model $f(\alpha) = \alpha^m (1 - \alpha)^n$, the singularity at $\alpha=0$ means a generalized analytical integral \int_0 from zero is not possible, but indefinite integrals can be found for specific practical m and n values [19].

4.4 .Discussion

Only the isothermal DSC scan can yield K_1 , K_2 , m , and n , (a) by plotting $d\alpha/dt$ versus α and varying the four parameters for best fit, or (b) by plotting $d\alpha/dt$ versus $(1-\alpha)^2$ with the assumption of $m=1$, $n=2$, (which seems to be supported by some data), or (c) finding K_1 and K_2 independently from DSC peak values, but with m , n assumptions still required. Note the uncertainty such procedures would necessarily leave. (Note that there is no obvious reason why n should be the same for both reactions.) Arrhenius plots of K_1 , K_2 , then yield A_1 , A_2 , E_1 , and E_2 .

4.5. Near Infrared FTIR and HPLC

Fourier Transform Infrared (FTIR) Spectroscopy and High Performance Liquid Chromatography (HPLC) can both determine the concentrations of all the cure reagents directly at a given time, and as a function of temperature, which would provide direct tracking of all reactions involved in the cure process. The measurement time is a problem, since the measurements must be taken as a series of “snapshots” that are strung together to form a “movie.” These techniques have been shown to yield consistent measurements of α versus time [20-22].

5. EXPERIMENTAL RESULTS

Some measurement results for model and rate parameters from various sources in the literature are provided below for the various models above, applied to varied polymers [23] and BADGE [7]. It is impossible, however, to cover the diversity of assumed and measured model parameters fully.

- n-th order model:
 - $f(\alpha) = (1 - \alpha)^n$ (Eqn. 2)
 - $n=0.2 \rightarrow 2$; typ. $n=1 \rightarrow 1.5$, or $n \approx 1$ or $n \approx 2$
- Single step auto-catalyzed model:
 - $d\alpha/dt = K f(\alpha) = K \alpha^m (1 - \alpha)^n$ (Eqn. 3)
 - Order $m+n=2$ [15] (or 3 [24, 25]); typically $m=n=1$, or $m \sim 0.5 \rightarrow 1$ & $n \sim 1.5$, with m , n temperature dependent [14, 26].
- Double step (linear combination):
 - $d\alpha/dt = (K_1 + K_2 \alpha^m)(1 - \alpha)^n$ (Eqn. 4)
 - $n \sim 2$, $m=1-2$; $n \approx 1.5$, $m \approx 0.75$; $m=1$, $n=2$ [27]; $m \sim 0.5-1$, $n \sim 2$ [28]

- $E_1=73$ & $E_2=60$; $E_1=44$ & $E_2=57$ (kJ/mole) and see [29].
- Modified double step:
 - $d\alpha/dt = K(y_1 + y_2 \alpha^m)(1 - \alpha)^n$ (Eqn. 5)
 - $E=240-243$ kJ/mole, $A=5 \times 10^{14}$, $y_1=0.0215$, $y_2=0.9785$ (PEEK) [15]

Overall, activation energies, E , range from 10 to 120 kJ/mole [7, 30], and both these “effective” E values and A are temperature and/or α -dependent [8, 31], indicative of multiple reactions. In general, these results differ for isothermal and dynamic DSC experiments [31], and vary with dynamic DSC ramp rates [12, 32]. Correlations between m , n , and between E , A , suggest numerical model problems [23].

6. CONCLUSIONS

The point of process modeling can be to verify theoretical understanding by matching to experiment, but here it is to predict process outcomes where experimental control is difficult. This study was conducted to assess the various cure models in use to determine the appropriate one for the microwave cure project. It is apparent, however, from a critical examination of these models in terms of the known chemical reactions that none is physically realistic. This view is supported by published model data for a variety of polymers where the single rate constant parameters, A and E , vary with temperature and/or degree of cure, making them applicable only within the range of measurement conditions, i.e. not useful as predictive tools.

The obvious solution is for manufacturers to provide full and accurate modeling parameters in their material data sheets, specifically the rate parameters for the individual reactions. However, in the meantime, FTIR studies of the cure process have been shown to be capable of distinguishing between the successive reactions. It is proposed that FTIR replace DSC in the determination of cure model parameters, based on equation 8.

6.1. Proposed Model

The double step auto-catalyzed model (equation 4) could conceivably then be modified as [11]:

$$d\alpha/dt = K_1(1-\alpha)^{n1} + K_2 \alpha^m (1 - \alpha)^{n2} \quad (14)$$

to separate the two reactions, with the α^m term in the second representing the secondary amine concentration, i.e. assuming that there is negligible conversion of secondary amines to tertiary. A more realistic model proposed for the two-step reaction is

$$d\alpha/dt = [K_1(1-\alpha_1)^{m_1} + K_2(\alpha_1-\alpha_2)^{m_2}] (1-\alpha)^n \quad (15)$$

where [27]

- α is re-defined as the fraction of reacted epoxide
- $(1-\alpha)$ is therefore the remaining fraction of unreacted epoxide
- α_1 is the fraction of reacted primary amines
- $(1-\alpha_1)$ is therefore the remaining fraction of unreacted primary amines
- α_2 is the fraction of tertiary amines, i.e. the fraction of reacted secondary amines, and
- $(\alpha_1-\alpha_2)$ is therefore the fraction of unreacted secondary amines

Note that the sum of primary, secondary, and tertiary amine fractions, $(1-\alpha_1) + (\alpha_1-\alpha_2) + \alpha_2 = 1$, and that furthermore

$$\alpha \cdot C_{\text{epoxide}} = (1+\alpha_2)\alpha_1 \cdot C_{\text{primary}} \quad (16)$$

where C_{epoxide} and C_{primary} are the original epoxide and primary amine concentrations, which simplifies to

$$\alpha = (1 + \alpha_2)\alpha_1 \quad (17)$$

for stoichiometric mixtures.

The added realism adds more parameters in m_1 and m_2 , α_1 and α_2 . There is arguably no reason why n should be the same for both reactions, as noted above, and two separate values, n_1 and n_2 , may be necessary, as in equation 7, at the cost of still greater complexity.

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