

Dynamic Cure Kinetics of Epoxy–Novolac Compounds as Studied by Differential Scanning Calorimetry

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ABSTRACT: The cure kinetics of epoxy–novolac compounds were studied by means of differential scanning calorimetry with a dynamic approach. On the basis of a modified version of our previously reported kinetic model, a procedure aiming at the phenomenological description of the cure kinetics was developed. The reactions were found to be autocatalytic in nature for both commercial epoxy–novolac molding compounds and silica-free imidaz-

ole-cured epoxy–novolac systems. The weak extent of autocatalysis in the epoxy–novolac molding compounds was likely due to their high content of silica fillers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2373–2377, 2009

Key words: curing of polymers; differential scanning calorimetry (DSC); thermosets

INTRODUCTION

As a current practice in the electronics industry, integrated circuits are often encapsulated with epoxy–novolac molding compounds by means of a transfer molding process.^{1–3} Despite the extensive use of the epoxy–novolac molding compounds over the last decade, only very limited information is available in the literature concerning the cure kinetics or the change in properties of these molding compounds during the cure process.^{4–6}

In general, the encapsulating resins are mainly composed of the silica filler (ca. 70 wt %), an epoxy cresol novolac prepolymer (CNE), and a phenol novolac (PN) or cresol novolac hardener. The average degree of polymerization of the oligomeric components is typically around 5.⁷ The molar ratio between the epoxide and the phenolic hydroxyl groups is commonly in the vicinity of 2.^{1,8} A small amount of catalyst (typically, a Lewis base such as imidazole derivates) is necessary to accelerate the reaction between the epoxide and the hydroxyl groups.^{7,9–11} Structures of the component prepolymers and the main reactions involved are given in

both Figures 1 and 2. In a previous study,¹² we examined the cure kinetics of a commercial molding compound (Nitto HC-10-2-8) using the dynamic differential scanning calorimetry (DSC) method. Following a modified Friedman method, we obtained an empirical kinetic expression:

$$d\alpha/dt = Af(\alpha) \exp(-E_a/RT) \quad (1)$$

where α is the conversion (or the extent of cure reaction) E_a is the activation energy, R is the gas constant at time t , A is the pre-exponential factor, $f(\alpha)$ is the differential conversion function, and T is the cure temperature.

$Af(\alpha) = 5.8 \times 10^6 (1 + 4.7\alpha - 6.5\alpha^2) s^{-1}$ and $E_a = 18.4$ kcal/mol were obtained by regression of the experimental data derived from DSC thermograms over a wide range of α 's (i.e., up to $\alpha = 0.8$) at quite different heating rates (ϕ 's = 40–0.5°C/min). In comparison with our isothermal DSC cure results, eq. (1) was valid for both the dynamic and the isothermal cases unless the effect of vitrification set in.¹³ In combination with dynamic DSC results, an empirical function relating conductivity to the temperature and α of HC-10-2-8 was successfully constructed. The strong maximum loss factor was found not to be directly related to the gelation or vitrification.¹⁴ Moreover, on the basis of a modified version of our previously reported kinetic model, an empirical Arrhenius-type expression relating the dynamic

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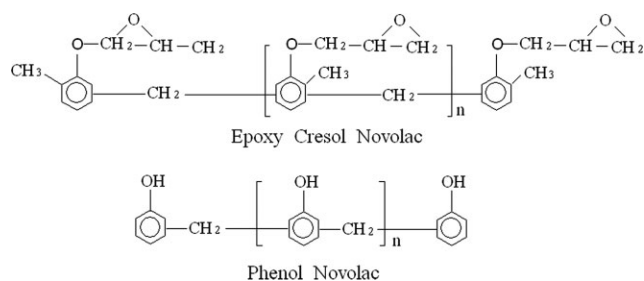


Figure 1 Structures of the compounds used in this study.

viscosity to temperature, frequency, and α of HC-10-2-8 was also successfully developed. At the gel point, dynamic viscosity showed a proportionality to the power of the frequency and varied with α . At low α 's ($\alpha < 0.05$), the system behaved approximately like a thermoplastic material. At high α 's, the rheological behavior of the system was dominated by the extent of curing.¹⁵

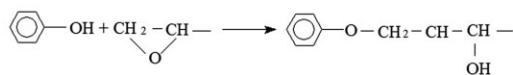
The dynamic kinetic approach can be used conveniently to monitor the real-time dielectric and chemrheology behavior of epoxy–novolac molding compounds.¹⁶ However, because of its strong phenomenological and empirical nature, eq. (1) does not properly capture the autocatalytic characteristics of the process; thus, it is unable to fully represent the mechanism of the cure reaction. Further modification is therefore needed. This article reports a modified kinetic model equation for the epoxy–novolac molding compound EME-1100D and silica-free imidazole-cured CNE/PN systems.

EXPERIMENTAL

Materials

The molding compounds studied were HC-10-2-8 and EME-1100D from Nitto Electric Industrial and Sumitomo Bakelite Co., Ltd. (Tokyo, Japan), respectively. These molding compounds were highly filled

Reaction of the epoxide with the phenlic hydroxyl



Reaction of the epoxide with secondary aliphatic hydroxyl :

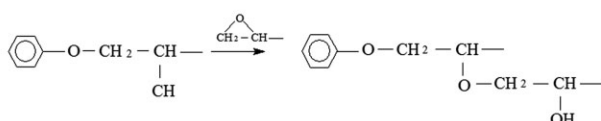


Figure 2 Typical cure reactions of the epoxy–novolac compounds.

(ca. 70 wt %) with silica and, according to the supplier, gelled within 20 to 24 s at 175°C.

ortho-CNE was used as a base epoxy resin, and PN was used as a curing agent. CNE and PN were received from Nippon Kayaku Co. (Tokyo, Japan) and Meiwa Kasei Co. (Tokyo, Japan), respectively.

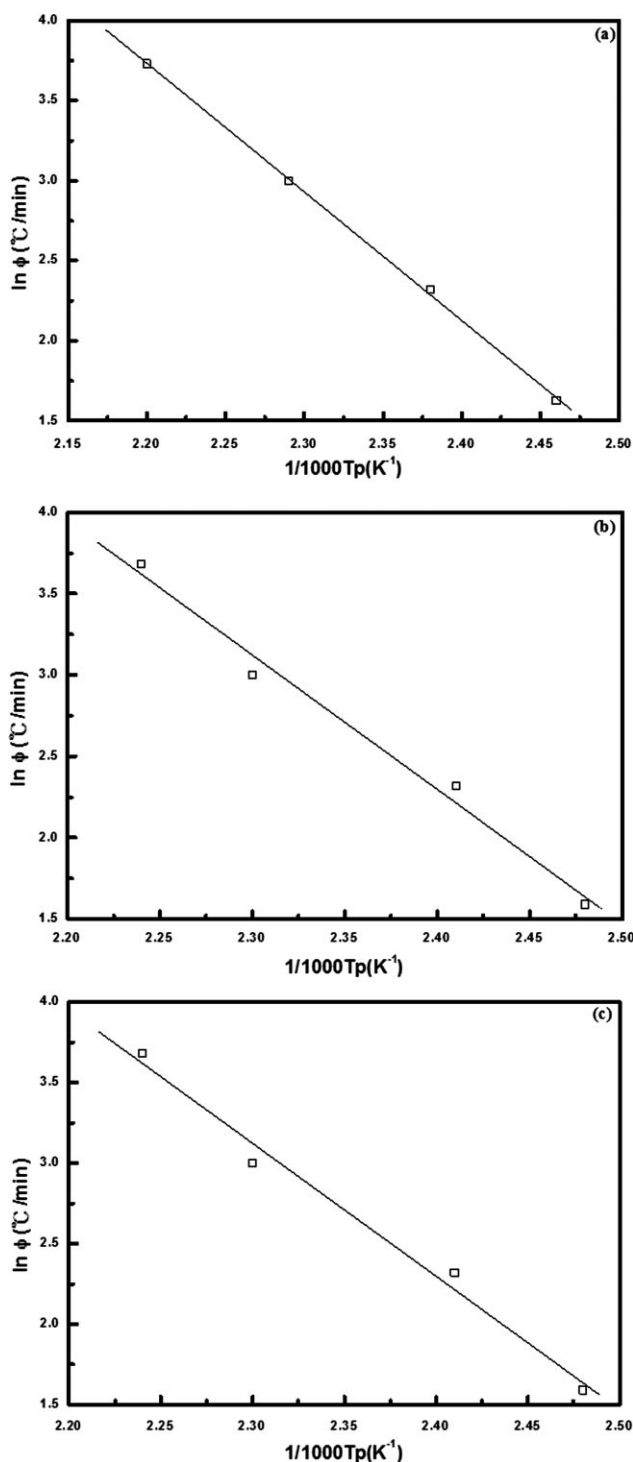


Figure 3 Linear relationship between $\ln \phi$ and the reciprocal T_p of the samples: (a) EME-1100D, (b) CNE/PN/EMI-1, and (c) CNE/PN/EMI-1.5.

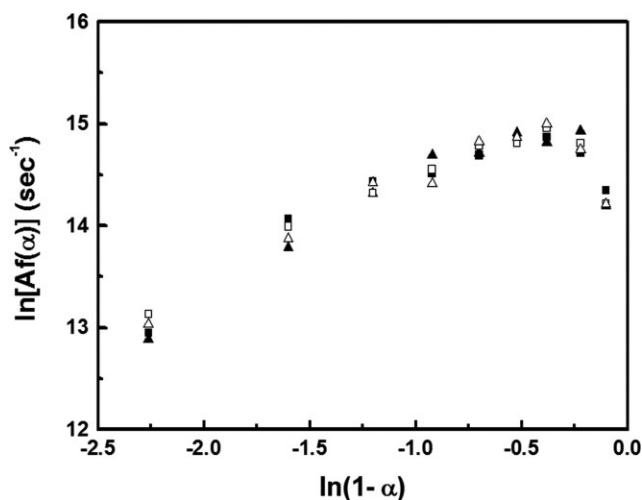


Figure 4 Variation of $\ln[Af(\alpha)]$ with $\ln(1 - \alpha)$ for EME-1100D at different ϕ 's: (Δ) 5, (\blacktriangle) 10, (\square) 20, and (\blacksquare) 40°C/min.

An epoxy equivalent weight of CNE was 192 g/mol, and the hydrogen equivalent weight of PN was 104 g/mol. 2-Ethyl-4-methyl imidazole (EMI), obtained from Wako Chemical Co. (Richmond, VA), was used as an accelerator.

CNE/PN/EMI compound preparation

We prepared the CNE/PN solution by dissolving CNE and PN at a molar ratio of 2 : 1 in spectrometric grade acetone, followed by the addition of various amount of EMI to the CNE/PN solution under rigorous stirring at room temperature and then the removal of acetone via evaporation *in vacuo* at 30°C

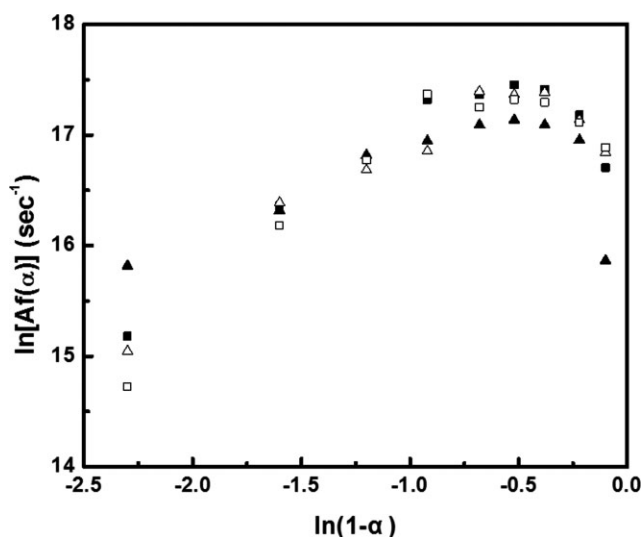


Figure 5 Variation of $\ln[Af(\alpha)]$ with $\ln(1 - \alpha)$ for the CNE/PN/EMI-1 compound at different ϕ 's: (Δ) 5, (\blacktriangle) 10, (\square) 20, and (\blacksquare) 40°C/min.

for 10 min. The resulting compound was immediately immersed in ice water to terminate the cure reaction before the kinetic studies.

In this study, the CNE/PN/EMI compounds of different EMI contents were designated as CNE/PN/EMI-1 and CNE/PN/EMI-1.5, with the number indicating the weight percentage of EMI in the CNE/PN resin.

Kinetic analysis

A DuPont DSC 910 cell connected to a DuPont 9900 data station (TA Instruments Inc., New Castle, DE) was used in this study. Samples approximately 5–6 mg each were scanned in the calorimeter with ϕ values of 40, 20, 10, and 5°C/min over a range from 50 to 300°C. To examine the extrapolation ability of this kinetic model, additional runs were also made with ϕ values of 2, 1, and 0.5°C/min. Nitrogen gas was purged at a flow rate of about 10 mL/min. Calibration of the calorimeter was conducted at each ϕ by an indium standard.

RESULTS AND DISCUSSION

Various rate expressions have been proposed in the literature to capture the autocatalytic characteristics of the epoxy system, but perhaps the most successful one is the one by Kamal and Sourour:¹⁷

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (2)$$

where both k_1 and k_2 are the rate constants characterized by an Arrhenius temperature dependency and m and n represent the reaction orders. As a first

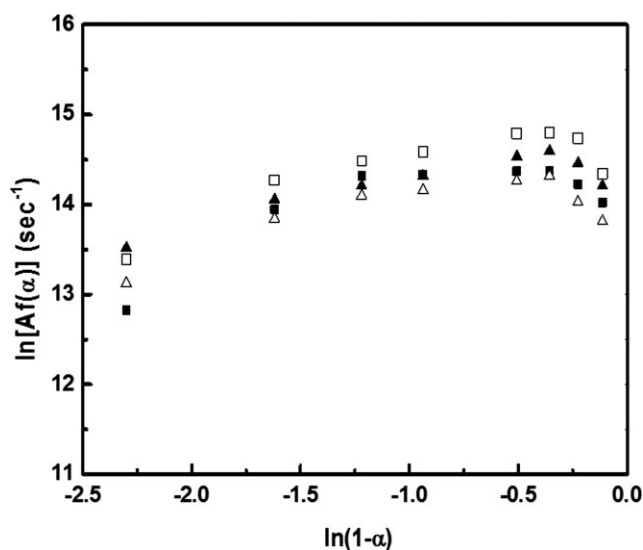


Figure 6 Variation of $\ln[Af(\alpha)]$ with $\ln(1 - \alpha)$ for the CNE/PN/EMI-1.5 compound at different ϕ 's: (Δ) 5, (\blacktriangle) 10, (\square) 20, and (\blacksquare) 40°C/min.

TABLE I
Kinetic Parameters of the Epoxy–Novolac Molding Compounds Obtained from the Dynamic DSC Results

| Compound | E_a (kcal/mol) | $A_1 \times 10^6$ (s ⁻¹) | $A_2 \times 10^7$ (s ⁻¹) | m | n | Correlation coefficient |
|-----------|------------------|--------------------------------------|--------------------------------------|-----|-----|-------------------------|
| HC-10-2-8 | 18.4 | 3.64 | 5.28 | 1.0 | 1.6 | 0.998 |
| EME-1100D | 17.6 | 2.50 | 4.30 | 1.1 | 1.6 | 0.999 |

TABLE II
Kinetic Parameters of the Imidazole-Cured Epoxy–Novolac Compounds Obtained from the Dynamic DSC Results

| Compound | E_a (kcal/mol) | $A_1 \times 10^7$ (s ⁻¹) | $A_2 \times 10^6$ (s ⁻¹) | m | n | Correlation coefficient |
|----------------|------------------|--------------------------------------|--------------------------------------|-----|-----|-------------------------|
| CNE/PN/EMI-1 | 16.1 | 0.02 | 9.0 | 1.4 | 1.6 | 0.994 |
| CNE/PN/EMI-1.5 | 15.9 | 0.13 | 8.2 | 1.6 | 1.4 | 0.993 |

approximation, we may assume that the E_a 's for the two rate constants are not too far apart so that the use of a single E_a is adequate.¹² The rate expression may, therefore, be rewritten as

$$d\alpha/dt = \exp(-E_a/RT)(A_1 + A_2\alpha^m)(1 - \alpha)^n \quad (3)$$

where both A_1 and A_2 are the pre-exponential factors. Equation (3) is equivalent to a simplified rate expression in the form of

$$d\alpha/dt = Af(\alpha) \exp(-E_a/RT) \quad (4)$$

with

$$Af(\alpha) = (A_1 + A_2\alpha^m)(1 - \alpha)^n \quad (5)$$

Dividing eq. (5) by $(1 - \alpha)^n$, we have

$$Af(\alpha)/(1 - \alpha)^n = (A_1 + A_2\alpha^m) \quad (6)$$

where the values of $Af(\alpha)$ can be obtained by the regression of the experimental data with a modified Friedman method as described in our earlier study.⁹

With the experimental errors taken into account, the average values of $Af(\alpha)$ at a given α 's from different ϕ 's were adopted here for the kinetic analysis. The kinetic parameters, including A_1 , A_2 , m , and n , were then determined by the performance of dynamic scans at various ϕ 's and the fitting of the rate-temperature data to eq. (6) via a nonlinear least-squares procedure. To further evaluate the modified kinetic model, EME-1100D, CNE/PN/EMI-1, and CNE/PN/EMI-1.5 were prepared as the test samples. For systems obeying eq. (4), Prime⁷ suggested that E_a could be estimated through the dependence of the peak temperature (T_p) on ϕ according to

$$E_a = -0.951R[d \ln \phi / d(1/T_p)] \quad (7)$$

As shown in Figure 3, a good linear relationship between $\ln \phi$ and the reciprocal of T_p was observed. With eq. (7), E_a values of the three tested systems were found to be 17.6, 16.1, and 15.9 kcal/mol, respectively.

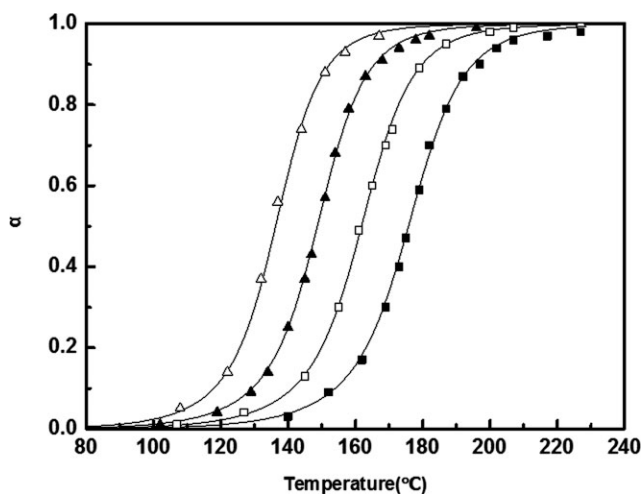


Figure 7 Comparison between the experimental and calculated α 's for the EME-1100D at different ϕ 's: (Δ) 5, (\blacktriangle) 10, (\square) 20, and (\blacksquare) 40°C/min. The solid lines are predictions from eq. (3).

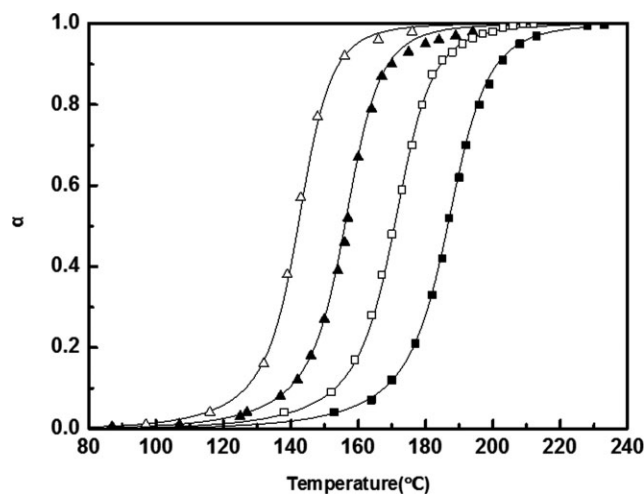


Figure 8 Comparison between the experimental and calculated α 's for the CNE/PN/EMI-1 compound at different ϕ 's: (Δ) 5, (\blacktriangle) 10, (\square) 20, and (\blacksquare) 40°C/min. The solid lines are predictions from eq. (3).

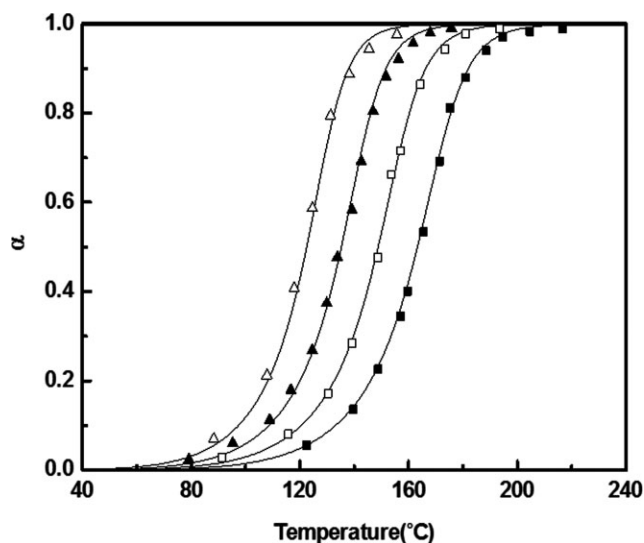


Figure 9 Comparison between the experimental and calculated α 's for the CNE/PN/EMI-1.5 compound at different ϕ 's: (Δ) 5, (\blacktriangle) 10, (\square) 20, and (\blacksquare) 40°C/min. The solid lines are predictions from eq. (3).

According to our previous studies on the modified kinetic analysis procedure, the corresponding $\ln Af(\alpha)$ at various α levels for the EME-1100D, CNE/PN/EMI-1, and CNE/PN/EMI-1.5 compounds are shown in Figures 4, 5, and 6, respectively. The results at different ϕ values also fell into a single master curve, which represented a ϕ independent expression, with clear maxima at $\alpha = 0.38$ and 0.41 (for the CNE/PN/EMI-1 and CNE/PN/EMI-1.5 compounds), respectively; this supported the conclusion that the cure reaction in each system was autocatalytic in nature. The kinetic parameters A_1 , A_2 , m , and n for the three systems were determined by the nonlinear least-squares curve-fitting method with eq. (6), with values thus obtained given in Tables I and II, respectively. Compared to Table I, in Table II, the HC-10-2-8 and EME-H1100D compounds are shown to have exhibited a significantly higher E_a than the CNE/PN/EMI compounds, likely because of the presence of nonreactive fillers. Moreover, the total reaction order ($m + n$) for both the HC-10-2-8 and EME-1100D molding compounds was about 2.7, which was lower than that of CNE/PN/EMI compounds (i.e., $m + n = 3.0$). This suggests that the CNE/PN/EMI compounds had a stronger tendency toward autocatalysis than the HC-10-2-8 and EME-H1100D molding compounds ($m = 1.4$ or 1.6 as compared to the case of HC-10-2-8 or EME-1100D, where

m is about 1.0), which was attributed to the presence of highly filled silica in these molding compounds.

The comparisons of the calculated and measured α data for the EME-1100D, CNE/PN/EMI-1, and CNE/PN/EMI-1.5 compounds are shown in Figures 7, 8, and 9, respectively. As shown, our modified kinetic model provided good agreement with the experimental data. The result also suggests that this method is simple to use and should be capable of representing the thermokinetics of thermosetting systems to monitor the cure reaction characteristics in a self-consistent manner.

CONCLUSIONS

We examined our earlier reported kinetic model equation and successfully developed a simple and effective procedure to study the cure kinetics of epoxy-novolac molding compounds or even silica-free imidazole-cured epoxy-novolac systems. The cure reactions were found to be autocatalytic in nature for both commercial epoxy-novolac molding compounds and silica-free imidazole-cured epoxy-novolac systems. The lower degree of autocatalysis in the epoxy-novolac molding compounds was likely due to their high content of silica fillers.

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