

Investigation of Cure Kinetics of Advanced Epoxy Molding Compound Using Dynamic Heating Scan: An Overlooked Second Reaction

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Abstract—Cure kinetics of epoxy molding compounds (EMCs) is a fundamental material property that affects the molding process of semiconductor chips and final package performance. However, due to measurement challenges related to the small polymer fraction, only the main reaction is considered in the current industry practice for EMC cure kinetics evaluation. In this work, we show that a second reaction exotherm is clearly identified in commercial multi-resin EMC systems upon dynamic heating scan using differential scanning calorimetry (DSC). The second reaction completes the overall reaction from about 0.8 to 1.0 fractional conversion, which is critical for designing cure schedules to achieve ultimate properties, especially the post-mold curing (PMC) procedure during manufacturing.

Keywords—advanced packaging, microelectronics encapsulation, semiconductors, epoxy molding compound, cure kinetics, thermosets, glass transition, filled polymers

I. INTRODUCTION

Epoxy molding compounds (EMCs) are highly formulated chemical products extensively used for microelectronics encapsulation since the 1970s [1]. They are highly-filled thermosetting polymers that typically contain more than ten [2] raw materials, including epoxy resins, hardener resins, accelerators, inorganic fillers, flame retardants, coupling agents, pigments, and other proprietary additives, to achieve desired performance and productivity. The types of epoxy and hardener resins determine the basic physical properties and moldability of an EMC. The most commonly used resin systems are cresol novolac, dicyclopentadiene type novolac, biphenyl epoxy, multi-aromatic epoxy, among others, cured with phenol novolac and multifunctional phenolic resins. More often than not, today's EMCs are formulated with two or more different resin systems [3] to meet ever-increasing stringent specifications as packaging technologies evolve towards miniaturization and 3D heterogeneous integration.

During the manufacturing process, the thermosetting epoxy resins are molded around semiconductor devices (via, e.g.,

transfer molding or compression molding) and cured at elevated temperatures. Curing involves chemical reactions of the low-viscosity monomers and oligomers that increase the molecular weight and form a cross-linked polymer network. The physical properties of a thermosetting polymer depend greatly on the degree of cure. Proper cure schedules (cure temperature, ramp rate, and cure time) need to be designed for the molding process of the EMC.

In addition, cure-dependent viscoelastic properties, i.e., the shear and bulk moduli, of the EMC are critical to predicting the evolution of warpage and stresses within the package during various steps of manufacturing [4]. Larger wafers, thinner layers, and more complex chip designs, such as in Fan-Out Wafer-Level Packaging (FOWLP) [5, 6] and Package-on-Package (PoP) [7, 8], are even more susceptible to warpage and reliability issues. Understanding the EMC cure characteristics is important because (1) it affects the process-dependent properties of the EMC and as a result, impacts the performance and thermo-mechanical reliability of the final package, and (2) it helps the industry optimize molding processes to increase current manufacturing productivity, as well as improve the numerical Design of Experiments (DoE) to accelerate R&D in developing future advanced packaging technologies.

Differential scanning calorimetry (DSC) provides a convenient and robust technique to measure the degree of cure for thermosetting polymers and investigate cure kinetics. The thermoset cure process is typically exothermic. The amount of heat released is directly measured by the DSC. When evaluating an unspecified, multi-component, highly-filled, commercial EMC, the first step is to measure the total heat of reaction on a completely unreacted sample. The easiest test method is by performing a dynamic heating scan where the temperature is ramped linearly with time. By integrating the exothermic peak in the DSC curve, the value of the heat of reaction (ΔH_{rxn}) can be obtained. As simple as it looks, there are a few technical considerations on experimental parameters for setting up a dynamic DSC measurement to evaluate the heat of reaction:

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A. Starting temperature

To minimize any amount of unrecorded reaction and ensure a reliable baseline for the integration, it is recommended to start the run at least 20 °C below the onset of the reaction. For better results, 40 °C below the onset of the reaction is recommended [9].

B. Heating rate

It is common practice to employ heating rates in the range of 5 °C/min to 20 °C/min for the initial investigation of a sample. Since the DSC sensitivity is directly proportional to the heating rate (and the sample mass), there is a tradeoff between sensitivity and allowing enough time for the reaction to go to completion. It usually takes a few runs to determine the optimum heating rate required to obtain an accurate heat of reaction.

C. Final temperature

The final temperature should provide a reasonable straight baseline at the end of the fully developed exothermic reaction peak to allow the reaction to complete without degradation. Depending on the EMC, a long nominally linear baseline may not be possible. For those cases, the final temperature can be decided in conjunction with selecting the proper heating rate.

The glass transition temperature (T_g) can be measured by a dynamic DSC measurement. In calorimetric measurement of T_g , the specific heat capacity (C_p) of the material undergoes a step change (ΔC_p) from the glassy to the rubbery states. The value of ΔC_p at T_g is indicative of the amount of polymers that contribute to the mobility and configurational entropy of the network, which can be useful when assessing a filled composite [10] or a multiphase material [11]. The evolution of T_g as the reaction proceeds—where the EMC transforms from a viscous liquid to an elastic gel, then to a viscoelastic solid—is important because it is intimately related to reaction kinetics and to the ultimate degree of cure. In order to obtain a satisfactory extrapolated glass line for T_g determination, it is recommended that heating start at about 50 °C below the expected T_g [12].

Fig. 1 shows an example result of DSC dynamic heating scan from –40 °C to 200 °C at 5 °C/min for an uncured commercial EMC sample (EMC-1) which has been used for transfer molding. Also indicated in the figure are four important properties that will be used in the kinetics analyses in the Results section. General information of the EMC materials used in this work are listed in **Table 1**. Upon heating, the uncured EMC first exhibits a glass transition of uncured EMC, with T_{g0} , of = 24.3 °C (half height) and $\Delta C_p = 0.127$ J/(g °C), followed by a large exothermic reaction peak that corresponds to the curing of the thermosetting resin with peak temperature T_p of 144.4 °C and $\Delta H_{rxn} = 28.9$ J/g. The heat of reaction is obtained by drawing a baseline between the low and high-temperature ends of the reaction peak and calculating the area under the curve. **Fig. 1** represents a clean DSC heat flow response that can be analyzed without ambiguity. However, this is not always the case for advanced EMCs.

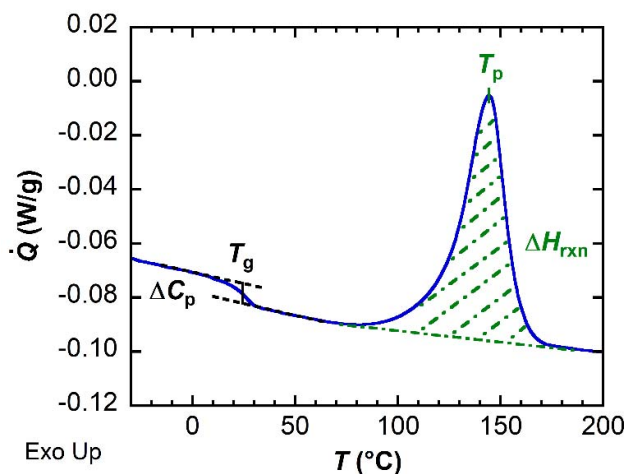


Fig. 1. DSC dynamic measurement at 5 °C/min for an uncured commercial EMC sample (EMC-1). Heat flow ($\dot{Q}$) is plotted as a function of temperature. The glass transition temperature (T_g) and the corresponding heat capacity change (ΔC_p) are indicated as black text. The peak temperature (T_p) and the total heat of reaction (ΔH_{rxn}) are indicated as green text. The black and green short vertical lines in the graph indicate the position of T_g and T_p , respectively. See text for details.

In the following section, we will show that for a commercial EMC with advanced formulation, two reaction exotherms are clearly identified upon dynamic measurements. The heating rates, along with the final temperature, need to be judiciously chosen, to reveal the second reaction exotherm. In the current industry practice for EMC cure kinetics evaluation, only the main reaction is considered. The information on the second reaction is critical for the design of post-mold curing (PMC) to achieve ultimate properties (e.g., high strength, chemical resistance, thermal stability, dimensional stability, etc.), for accurate prediction of stresses during the manufacturing process, and for thermo-mechanical reliability of the final package.

Furthermore, due to measurement challenges related to the small polymer fraction in EMCs, the determination of the ultimate glass transition temperature of the fully-cured EMC ($T_{g\infty}$) material is difficult. This is because of limits on the minimally resolved heat capacity change by DSC. As the crosslinking reaction proceeds, ΔC_p of the polymer decreases. For example, for a neat epoxy-novolac system [13], ΔC_p drops by a factor of 5 as conversion increases from 0 to 0.8 fractional conversion. For a highly-filled, highly crosslinked EMC, the detection of T_g by calorimetry is even more difficult, i.e., below the resolution of the DSC, classified as “undetectable”. The EMC suppliers usually choose to report the $T_{g\infty}$ values by other methods, most often by dynamic mechanical analyzer (DMA) or thermo-mechanical analyzer (TMA). In this work, we report the result of a second and higher $T_{g\infty}$, resulting from the formation of a secondary crosslinked network from the second reaction.

In the Results and Discussion, we will first discuss methods for proper data representation with appropriate experimental parameters selection, to reveal the two distinct reaction exotherms for an advanced multi-resin EMC using dynamic DSC heating measurements. We perform a detailed kinetics analysis, first obtaining the activation energy by using the well-known Kissinger peak displacement method, and then fitting the experimental data to a modified autocatalytic model. We then show the experimental data and calculated results for the overall degree of cure, where a two-step cure process is evident. To be best of our knowledge, this is the first report of a two-step reaction profile for a commercial EMC. Finally, we present an example result for an additional EMC material, measured at the recommended heating rate of 5 °C/min to reveal the second reaction exotherm. We further discuss best practices for DSC measurements on cure kinetics evaluation of commercial EMCs.

TABLE I. THE EPOXY MOLDING COMPOUNDS (EMCs) INVESTIGATED IN THIS WORK

EMC	Application	Filler content (mass fraction, %) ^a
EMC-1	Transfer molding	87
EMC-2	Transfer molding	88
EMC-3	Compression molding	92

^a. Measured by thermal gravimetric analysis (TGA). The value of filler content is taken as the residual mass at the final temperature (1000 °C).

II. EXPERIMENTAL

A. Materials

The EMC materials investigated in this work are all from commercial sources. EMC-1 and EMC-2 were received in pressed pellet form and were pulverized into fine powders for measurements. EMC-3 was received in granular form and used as received. The EMCs were stored at 5 °C with desiccant for the duration of the study. General information for the EMCs is given in **Table 1**.

B. DSC Measurements

A dynamic scanning calorimeter (DSC) was used to study the cure kinetics of EMCs. It is equipped with a refrigerated cooling system and an integrated auto-sampler with nitrogen purge at a flow rate of 50 ml/min. The EMC samples were sealed in 40 µL hermetic aluminum pans for measurements. Dynamic DSC scans were performed on the uncured samples from -40 °C to 250 °C at different heating rates in the range of 1 °C/min to 30 °C/min. In a few cases, the final temperature used was higher than 250 °C as appropriate. The samples were then cooled to -40 °C at 10 °C/min and a second dynamic measurement to 250 °C at 10 °C/min was performed to obtain the glass transition temperature of fully cured EMC (T_{g0}). The standard uncertainties for temperature and heat flow are estimated to be ± 1 % and ± 3 %, respectively.

C. Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was performed under a nitrogen atmosphere. The EMC samples were placed in 100 µL high-temperature platinum pans for measurements. The samples were heated from 40 °C to 1000 °C at a heating rate of 10 °C/min. A standard uncertainty of ± 1 °C is assumed for temperature measurement.

III. RESULTS AND DISCUSSION

A. Proper data representation to discern the 2nd reaction

DSC heat flow responses for uncured EMC-2 at different heating rates are shown in **Fig. 2**. Two thermal transition events were observed. First, a characteristic step change in heat flow corresponding to the glass transition is observed for the uncured EMC (T_{g0}) at around 33 °C, followed by a “single” exothermic peak for the crosslinking polymerization. As expected, the reaction exotherm shifts to higher temperatures with increasing heating rate due to shorter reaction time at a given temperature. The values of the peak temperature, denoted as T_{p1} , are tabulated in **Table 2**. The final temperature of the dynamic scans, i.e., 250 °C, is a seemingly reasonable choice as it clearly allows resolution of the peak.

The plot of the normalized heat flow (W/g) as a function of temperature, as shown in **Fig. 2**, is a routine way of displaying the dynamic DSC curves for evaluation. However, it is often not the best way to interpret the data and identify all of the thermal events. The DSC signal sensitivity is directly proportional to the mass of the sample and the heating rate:

$$\dot{Q} = m \cdot C_p \cdot \beta \quad (1)$$

where $\dot{Q}$ is the heat flow, m is the sample mass, C_p is the specific heat capacity, and β is the heating rate. The more effective approach is to normalize the heat flow (i.e., the y-axis) by multiplying by (β_{ref}/β) , where β_{ref} can be taken as any reference heating rate of choice. In this way, the DSC curves, accounting for different heating rate effects, according to (1), are examined at the same sensitivity when comparing results.

Fig. 3 shows the scaled dynamic DSC heating scan results. The same data as in **Fig. 2** are plotted, except that for the heating rates of 6 °C/min and 10 °C/min, the curves are continued to a higher final temperature of 300 °C. It becomes immediately evident that, for the slowest heating rates of 1 °C/min and 3 °C/min, two exothermic peaks are present. The second exotherm is broader and smaller, which appears immediately after the first large, sharp exotherm. The first exothermic peak is symmetric and similar in size for all heating rates. For the medium heating rates of 6 °C/min and 10 °C/min, the second exotherm is only observed at higher temperatures (250 °C to 300 °C), and is broad and asymmetric in shape, i.e., the peak position is skewed to the high-temperature side. The shape of the exotherm is informative—a symmetric exotherm suggests a relatively simple reaction, and an asymmetric peak means a more complex reaction mechanism and often with a non-constant activation energy [12]. Note that if the final temperature for the dynamic DSC measurement stops at 250 °C,

the second peak will not be accessed. Like the first reaction, the second exotherm shifts to a higher temperature as heating rate increases, because the material has a longer reaction time at slower heating rates. For the fast heating rates of 20 °C/min and 30 °C/min, only one large exotherm is observed in the measurement temperature range.

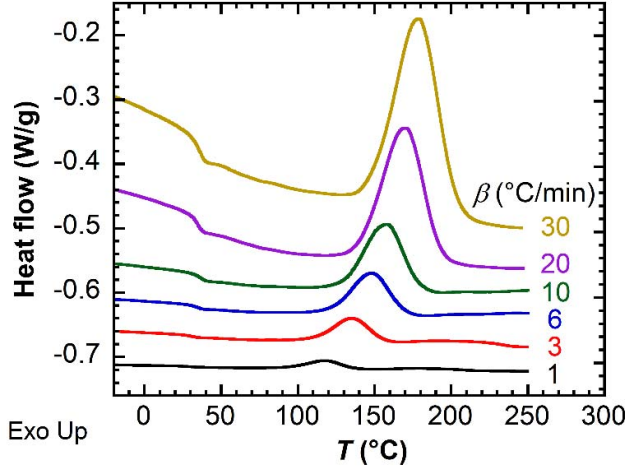


Fig. 2. Dynamic DSC scans of an uncured commercial EMC sample (EMC-2) as a function of temperature at different heating rates β . Heat flow curve responses are shown as a function of temperature.

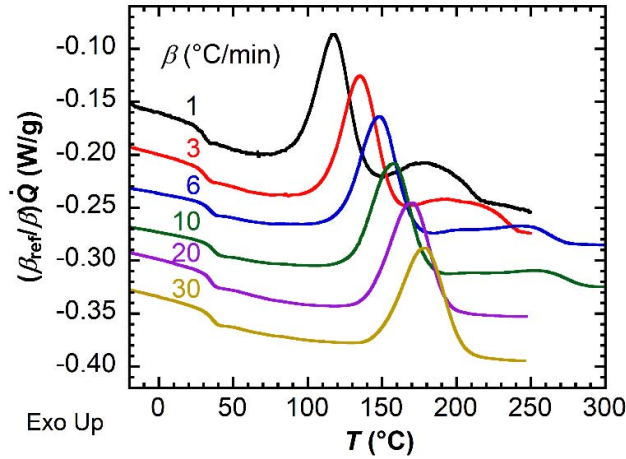


Fig. 3. Dynamic DSC heating scans at different heating rates β for EMC-2. Heat flow ($\dot{Q}$) is scaled by β_{ref}/β , where β_{ref} is taken to be 10 °C/min.

The values of the heat of reaction for the first reaction (ΔH_1), corresponding to the first exotherm are tabulated in **Table 2**, along with the values for the total heat of reaction, $\Delta H_T = \Delta H_1 + \Delta H_2$, where applicable, and the peak temperatures

for the first (T_{p1}) and second (T_{p2}) exotherms at different heating rates. The degree of cure or conversion can be expressed as:

$$\alpha(T) = \frac{\int_{T_0}^T \dot{Q} dT}{\beta \Delta H_T} \quad (2)$$

where α is the degree of cure and T_0 is a temperature below the onset of the reaction. The values of the conversion at the end of the first reaction, α_1 , are also listed in **Table 2**. The values of ΔH_1 are about the same, approximately 20.0 J/g for all heating rates. The total heat decreases slightly as the heating rate increases from 1 °C/min to 10 °C/min, due to a decrease in ΔH_2 for the second reaction. The dependence of ΔH_2 on heating rate suggests a complex reaction mechanism associated with the second reaction.

TABLE II. HEAT OF REACTION, DEGREE OF CURE, AND PEAK TEMPERATURES AT DIFFERENT HEATING RATES OF EMC-2

β (°C/min) ^a	ΔH_1 (J/g) ^b	ΔH_T (J/g)	α_1	T_{p1} (°C)	T_{p2} (°C)
1	20.2	25.9	0.78	118.2	185.5
3	20.0	24.9	0.80	135.0	211.4
6	19.8	24.4	0.82	147.9	247.4
10	20.0	23.9	0.84	158.1	257.3
20	20.1	N/A	N/A	170.9	N/A
30	20.1	N/A	N/A	179.4	N/A

^a. β , heating rate; ΔH_1 , heat of reaction for reaction 1; ΔH_T , total heat of reaction; α_1 , degree of cure at the end of reaction 1, i.e., $\alpha_1 = \Delta H_1/\Delta H_T$; T_{p1} , peak temperature of the first exotherm; T_{p2} , peak temperature of the second exotherm.

^b. Standard uncertainties u are $u(\Delta H) = 0.1$ J/g, $u(T) = 0.1$ °C

B. Activation energy determination from Kissinger's plot

From different dynamic DSC scans, one can conveniently estimate the activation energy from the Kissinger peak displacement method [14], which analyzes the variation of the peak temperature with the heating rate:

$$E_a = -R \frac{d \ln \left(\frac{\beta}{T_p^2} \right)}{dT_p^{-1}} \quad (3)$$

where E_a is the activation energy, R is the ideal gas constant (≈ 8.314 J mol⁻¹ K⁻¹). According to (3), the activation energy can be directly obtained from the slope of the Kissinger plot. As depicted in **Fig. 4**, the dashed line represents a linear fit to the data from the first reaction exotherm, which gives a value of $E_{a1} = 74.3 \pm 0.8$ kJ mol⁻¹ with $R^2 = 0.9993$. The linear fit to the second reaction exotherm yields an activation energy $E_{a2} = 53.4 \pm 5.6$ kJ mol⁻¹ with $R^2 = 0.9787$. A less confident fitting to the second reaction is due to the noticeable change in the second exotherm shape with the heating rate (**Fig. 3**) as discussed earlier.

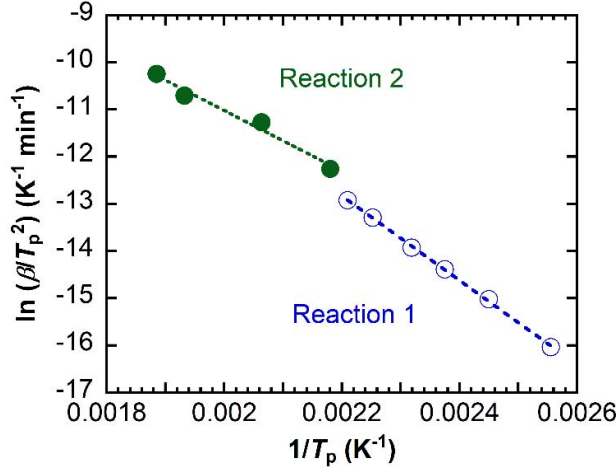


Fig. 4. Kissinger plot for the two reaction exotherms obtained from dynamic DSC scans for EMC-2. The dashed line is a linear fit to the data for reaction 1. The dotted line represents a linear fit to the data for reaction 2. The activation energy values for reaction 1 and reaction 2 are $74.3 \pm 0.8 \text{ kJ mol}^{-1}$ and $53.4 \pm 5.6 \text{ kJ mol}^{-1}$, respectively.

C. Kinetics modeling

A modified Kamal–Sourour [15] autocatalytic reaction model is adopted to describe the cure kinetics of the EMC:

$$\frac{d\alpha}{dt} = k(T)\alpha^m(1-\alpha)^n \quad (4)$$

where $k(T)$ is the rate constant that depends on temperature, and m and n are reaction orders for the autocatalytic reaction. The rate constant follows the Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

where A is the pre-exponential factor. By rearranging (4) and (5) and taking natural logarithm, the expression becomes:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln A + m \ln \alpha + n \ln(1-\alpha) - \frac{E_a}{RT} \quad (6)$$

The above equation is solved by multiple linear regression where the left-hand side of (6) is the dependent variable, and the independent variables are $\ln \alpha$, $\ln(1-\alpha)$, and $1/T$. Using the activation energy obtained from the Kissinger method (Fig. 4 and (3)), the values of A , m , and n can be obtained. The fitted results are shown Fig. 5 as dashed lines with $R^2 = 0.9925$ for reaction 1.

It is to be noted that for this particular EMC-2, the second reaction exotherm does not initiate before the first exotherm is fully developed and finished (Fig. 3). This is also evidenced by the invariant ΔH_1 (Table 2), the consistent shape of the first exothermic peak (Fig. 3), and the goodness of fit to a linear line in the Kissinger plot for the first reaction (Fig. 4).

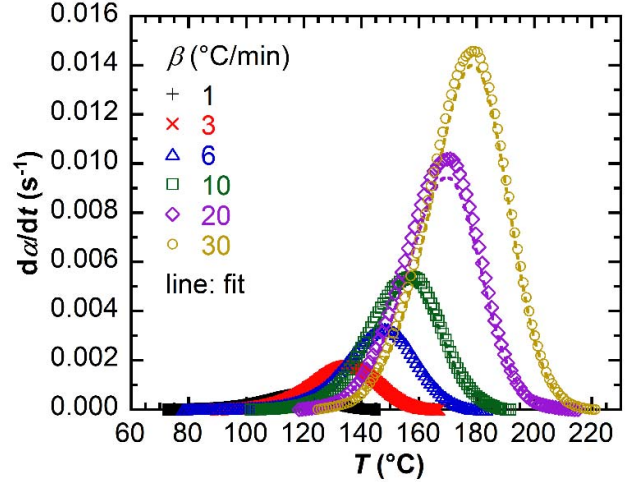


Fig. 5. Rate of reaction ($d\alpha/dt$) as a function of temperature at different heating rates (β) for reaction 1. The symbols are experimental data. The dashed lines are fits to the modified Kamal–Sourour autocatalytic equation (4) using the activation energy determined by the Kissinger method (Fig. 4). See text for details.

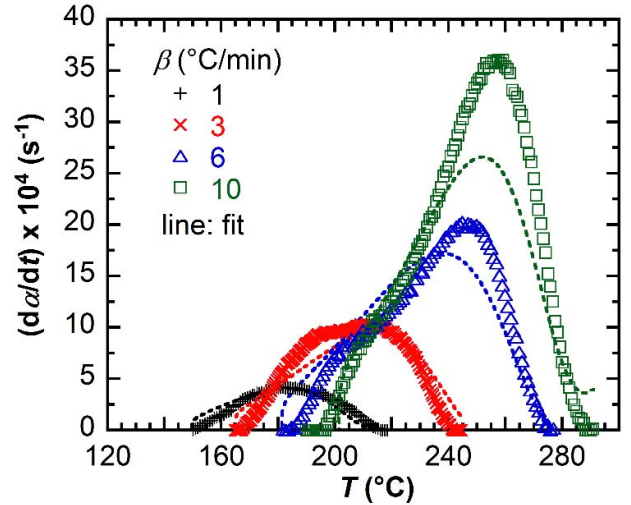


Fig. 6. Rate of reaction ($d\alpha/dt$) as a function of temperature at different heating rates (β) for reaction 2. The symbols are experimental data. The dashed lines are fits to the modified Kamal–Sourour autocatalytic equation (4) using the activation energy determined by the Kissinger method (Fig. 4). See text for details.

This non-overlapping, consecutive two-step reaction profile allows us to analyze the two reactions individually. As recommended by the International Confederation for Thermal Analysis and Calorimetry (ICTAC)— it is a good idea to separate the steps entirely when performing kinetics analysis for separated steps [16]. Following the same method as described above, the fitted results for reaction 2 are shown in Fig. 6. The dashed lines are fits to the model using the activation energy

from the Kissinger plot ($R^2 = 0.8106$). The rate of reaction for reaction 2 is slower than that of reaction 1. At heating rate of $10\text{ }^\circ\text{C/min}$, the maximum reaction rate is $36.1 \times 10^{-4}\text{ s}^{-1}$ for reaction 2, whereas the maximum rate for reaction 1 is higher at $52.0 \times 10^{-4}\text{ s}^{-1}$. Furthermore, the autocatalytic reaction model provides a less satisfactory fit to reaction 2 than the fitting to reaction 1, suggesting a more complicated mechanism is associated with the second exotherm observed in the dynamic DSC scan.

D. Overall degree of cure

The degree of cure for the overall reaction is shown in Fig. 7. The symbols are experimental data and the lines are fits to the autocatalytic reaction model (4). One remarkable finding from Fig. 7 is that, the overall cure of the EMC shows a two-step process. To the best of our knowledge, this is the first report of a two-step reaction profile for a commercial EMC. Upon the completion of the first reaction, the degree of cure reaches about 0.8, and the second reaction completes the overall reaction from about 0.8 to 1.0 fractional conversion. This information is critical for understanding the evolution of EMC properties during PMC, as well as for designing proper cure schedules to achieve ultimate properties while optimizing manufacturing productivity. As seen in Fig. 7, the model fits are in good agreement with the experimental data. For the second step, the autocatalytic model predicts a slightly accelerated reaction than the experimental results. This could be explained by the decreasing ΔH_T values as heating rate increases. As the crosslinking reaction progresses to such high conversion, the reactivity of functional groups is suppressed by topological constraints from the three-dimensional crosslinking network, resulting in a heterogeneous reaction mechanism. Additionally, the current reaction model is considered without diffusion kinetics which could also decelerate the reaction.

E. Two $T_{g\infty}$ values of EMC-2

Fig. 8 shows the dynamic DSC measurement for the fully cured EMC-2. No residual heat was observed during the second heating scan, which confirmed the fully cured state of the EMC material. Two $T_{g\infty}$ values were observed; the first T_g is around $107\text{ }^\circ\text{C}$ (denoted as T_{g1}) and the second T_g is around $170\text{ }^\circ\text{C}$ (denoted as T_{g2}). This suggests that there are likely two resin systems in this EMC formulation, which was confirmed by the EMC supplier.

It is to be noted that T_g measurements can be challenging. As discussed in the Introduction, the corresponding ΔC_p at T_g reduces significantly as crosslink density increases, which has led many to erroneously conclude that a certain polymer “has no T_g ” [9]. The highly loaded fillers in EMC make the T_g detection more difficult because only mobile, disordered polymer chains in EMC contribute to ΔC_p at T_g . Upon careful examination of the DSC heat flow curve, as seen in Fig. 8, very subtle step changes from glassy to liquid states are identified with $\Delta C_{p1} = 0.06\text{ J g}^{-1}\text{ K}^{-1}$ and with $\Delta C_{p2} = 0.04\text{ J g}^{-1}\text{ K}^{-1}$, respectively, which are minimally resolved as compared to a typical T_g measurement for a neat polymer, for example, ΔC_p at $0.29\text{ J g}^{-1}\text{ K}^{-1}$ for polystyrene [10].

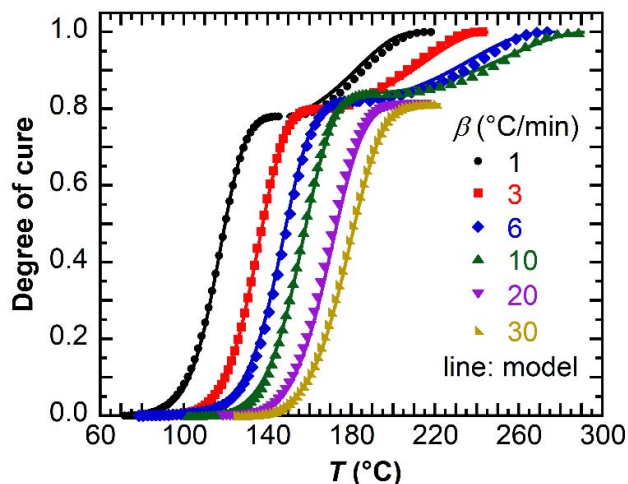


Fig. 7. Overall degree of cure (α) as a function of temperature at different heating rates β for EMC-2. The symbols are experimental data. The solid lines are fits to the modified Kamal-Sourour autocatalytic equation (4) by analyzing the two reactions independently.

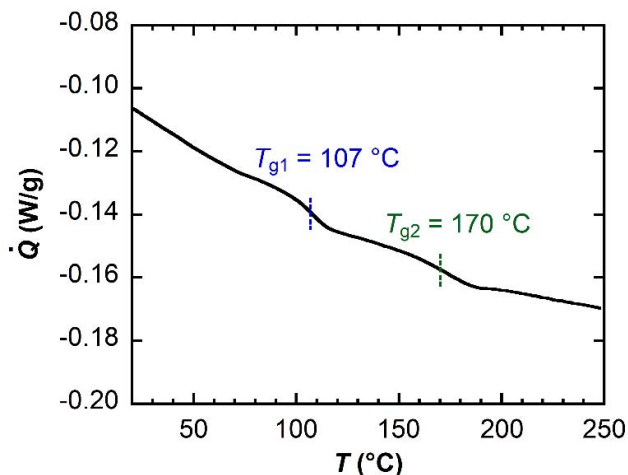


Fig. 8. DSC heat flow response on the second heating scan for a fully cured EMC-2. The vertical dotted lines indicate the glass transition temperatures.

F. Other EMCs

To this end, we have shown that two commercial EMC materials, both used for transfer molding, present different characteristics upon dynamic DSC scan. EMC-1 displays a single exothermic reaction peak, while EMC-2 exhibits two consecutive exotherms. Here, we perform a dynamic DSC heating scan for another EMC sample, EMC-3, used for compression molding.

Fig. 9 shows the heat flow response measured at 5 °C/min for this granular EMC sample. The first exotherm, as shown by the blue-shaded region, is large ($\Delta H_1 = 23.6$ J/g), sharp, well-developed, and fully completed, before the second reaction begins. The second exotherm, as shown by the green-shaded region, is smaller ($\Delta H_2 = 2.7$ J/g), broader, and asymmetrical in shape. These are similar observations with those of EMC-2.

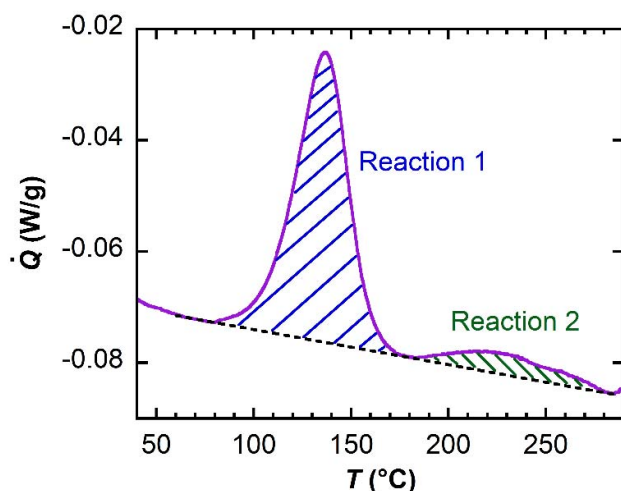


Fig. 9. Dynamic DSC measurement at 5 °C/min for an uncured commercial EMC sample (EMC-3). Two reaction exotherms are observed as shown by the blue and green shaded areas for the first and second reactions, respectively.

G. Recommendations for DSC measurements

In this study, we evaluated three different commercial EMCs and compared different reaction exotherms upon dynamic DSC scan. Experimental parameters needed to be carefully considered to obtain correct results for cure kinetics analysis. Therefore, we have the following recommendations for cure kinetics evaluation of a commercial EMC material using DSC:

- 1) Heating rate: The first test is to perform a dynamic DSC measurement at 5 °C/min.
- 2) Starting temperature: Start the run from about 40 °C below the expected onset of reaction for a better starting baseline. If measuring the uncured EMC T_{g0} is of interest, start the run at about 50 °C below the expected T_{g0} for a better glass line.
- 3) Final temperature: Use a final temperature to allow the reaction exotherm to fully develop without thermal degradation; it may take a few runs to select an appropriate heating rate together with the final temperature.
- 4) TGA is a useful tool to evaluate the onset of degradation.
- 5) Use a larger sample size (10 mg to 20 mg) for slower heating rates and for weak T_{g0} and T_{gz} detection.

IV. CONCLUSIONS

In this study, we reported a comprehensive cure kinetics study on commercial epoxy molding compounds (EMCs) used in the semiconductor packaging industry using dynamic DSC scans. We showed DSC data at certain heating rates, which were judiciously chosen, reveal two distinct reaction exotherms for multi-resin EMCs. The second exotherm, which was only discerned at appropriate heating rates with proper data representation methods, has been long, and conveniently, overlooked by the semiconductor community.

Upon evaluation of the two exotherms and a detailed cure kinetics analysis, we obtained the following conclusions:

- 1) The first reaction exhibits a symmetric exotherm with invariant heat of reaction at different heating rates.
- 2) A consecutive second reaction follows the first reaction at higher temperatures. The second reaction is more complex—as indicated by the asymmetric exotherm, and the changing shape with decreasing heat of reaction as heating rate increases.
- 3) The second reaction is slower than the first reaction, and has a lower activation energy.
- 4) Both reactions are well described by a modified autocatalytic model; the activation energy values were determined from the Kissinger method.
- 5) The second reaction completes the overall degree of cure from about 0.8 to 1.0, which is critical for the design of cure schedules, especially for the PMC.
- 6) For the fully-cured EMC, two glass transition temperatures (T_{gc}) are observed and attributed to the two network structures formed during the two-step cure of the EMC. It is to be noted that calorimetric T_g measurements of EMC can be challenging due to the small polymer fraction and high crosslink density.

DATA AVAILABILITY

All data associated with this paper are publicly available through the NIST Public Data Repository at <https://doi.org/10.18434/mds2-2948> [17].

DISCLAIMER

Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by NIST, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

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