# Isothermal DSC study of the curing kinetics of an epoxy/silica composite for microelectronics

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## Abstract

Curing kinetics of an industrially important printed-circuit board (PCB) base material (epoxy-phenol/glass fillers) were studied from isothermal differential scanning calorimetry (DSC) measurements between 150 and 190 °C. The extent of cure was calculated by integration of the exothermic peak and normalization by the total heat of reaction (obtained by non-isothermal DSC). The kinetic profiles show two regimes: one fast, and one slower. The completion was reached above 180 °C. The kinetic parameters have been elucidated using an isoconversional model-free kinetic method. The linearity of Arrhenius plots was satisfactory. The apparent activation energy of curing reaction has been found to increase with the degree of conversion. The elucidation of the kinetic parameters allows us to propose an accurate and predictive description of the curing kinetics of the composite until a degree of conversion of 50%. Finally, we discuss how these kinetic measurements and models can be completed and optimized.

## Key words
PCB, epoxy, composite, curing, kinetics, isothermal DSC

## I. Introduction

Epoxy resins, reinforced by $SiO_2$ fibers or spherical filler particles [1] are composite materials of key interest to answer the increasing demand of miniaturization and performance in advanced microelectronics [2]. Their thermo-mechanical, adhesive, flame retardance and dielectric properties make them the perfect candidates as insulating build up films (so-called semi-additive process, SAP) in multi-layer printed circuit boards (PCB) and integrated-circuit substrates manufacturing [3]–[9].

The epoxy resins are thermosets which are crosslinked during the reaction of curing, forming a 3-dimensional network of polymer chains [10], [11]. From b-stage films (gelified matrix) to the final insulating layers, the hardening of the resin matrix is typically achieved by thermally induced crosslinking reactions of the oligomers. The extent of cure α (i.e. degree of conversion) dictates the physical and chemical property of the workpiece in use. While fully-cured base materials were previously used for Cu plating in classic PCB manufacturing, the method of partially-cured composite sheets build-up has been found improving composite/Cu adherence [11], [12], in SAP technology. The state of curing, dictating the hardness and attackability of the material [13], [14] is a key-parameter when preparing the material for copper plating by desmear [15]. Therefore, the degree of conversion should be precisely known prior to any thermo-mechanical [11] and chemical treatment [13].

For the investigation of curing behavior, most authors propose kinetic studies using differential scanning calorimetry (DSC), under either non-isothermal (i.e. dynamic, at a constant heating rate) [16], or more rarely isothermal conditions [17]. Isothermal DSC experiments are inherently more challenging than non-isothermal investigations, due to measurement bias from the time-lag in the heating up period from ambient to target temperature. For this reason, most kinetic studies by DSC are made non-isothermally. However, two reasons motivated us to prefer isothermal methods: (i) industrially relevant curing schemes mostly comprise isothermal treatments [17], (ii) kinetic studies are more accurate because side reactions are avoided and the necessary computations are easier [18].

Herein, we present an isothermal DSC kinetic study of an industrially important SAP base material, for control and prediction of its state of curing, at any temperature of storage or processing.

## II. Theoretical background

Vyazovkin *et al.* proposed a precise roadmap to follow in order to perform kinetic analyses [18]. Basically it consists in the determination of the kinetic triplet: the activation energy ($E_\alpha$), the pre-exponential factor ($A_\alpha$) and the extent of cure (α). These key-parameters are linked by the general kinetic equation (1):

$$\frac{d\alpha}{dt} = A_\alpha \cdot e^{-\frac{E_\alpha}{RT}} f(\alpha) \tag{1}$$

wherein $f(\alpha)$ is a function modelling the reaction mechanisms, $T$ the temperature and $R$ the universal gas constant.

In order to elucidate the kinetic behavior of a reaction, two main approaches can be considered: model-free kinetic methods (MFK) [19] and model-fitting methods. They offer complementary results for the activation energy $E_\alpha$, and the model of reaction $f(\alpha)$. MFK analyses do not make any hypothesis about the exact reaction mechanisms other than assuming that the reaction consists of a single-step kinetic [20]. This approximation is often reasonable, but has to be checked for validity. Three categories of methods are known to the MFK analyses portfolio: isoconversional, Kissinger and invariant kinetic parameter methods. Having been reported as very powerful tools in order to elucidate the activation energy from any reaction [18], isoconversional MFK methods seemed the appropriate tools for our purposes.

The general idea of isoconversional methods, applied to isothermal analysis, is to monitor how long the reaction takes to reach a certain degree of conversion α, at each individual temperature (index *i*). Based on the assumption that the progress of the reaction is only a function of temperature, the logarithmic differentiation of (1) leads to the equation of Friedman (2):

$$ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = ln[f(\alpha)A_\alpha] - \frac{E_\alpha}{RT_{\alpha,i}}. \tag{2}$$

If the temperature is independent of the time, i.e. in an isothermal treatment, introduction of $g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ yields one analytical solution for (2):

$$ln(t_{\alpha,i}) = ln\left[\frac{g(\alpha)}{A_\alpha}\right] - \frac{E_\alpha}{RT_i}. \tag{3}$$

Plotting $ln(t_{\alpha,i})$ over $1/RT_i$ for each given isoconversional α, the slope and ordinate intercept of the graphs reveal the activation energy and the natural logarithm of $g(\alpha)/A_\alpha$, respectively.

## III. Materials and method

*A. Material*

The studied material was ABF GX-T31R, a commercially available epoxy/silica composite by Ajinomoto Fine-Techno Co., Inc., supplied as b-stage films (gelified matrix) with a film thickness of 35 µm.

The exact details of the resin matrix remaining undisclosed, essentially it consists of epoxy terminated bisphenol oligomers, cross-linked by a phenol hardener. Its reaction of curing is an etherification, mainly involving the opening of the epoxide rings by nucleophilic attack of the phenol groups (Fig. 1). The incorporated fillers are silica spheres (~ 63 wt.%) with a diameter between few tens of nanometer and few microns.

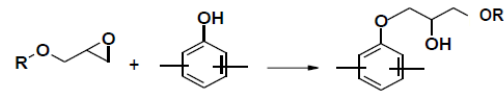


*Fig. 1 – Schematic curing reaction of the epoxy resin and the phenolic hardener*

Copper clad panels with ABF laminated on both sides (ABF/Cu/FR4/Cu/ABF), which are commonly used as test coupons in the PCB industry, did not provide enough DSC signal from the rather thin ABF layers. Thus, for experimental purposes model composites were built-up by cutting, stacking and laminating b-stage films (4 x 2 min, 100 °C, p = 6 kg/cm², high vacuum), until $2^4$ = 16 layers yielded a final thickness of ca. 0.56 mm. Structural uniformity of the obtained bulk material was verified by scanning electron microscopy (SEM), on a cross-section, showing neither blistering nor inhomogeneities (Fig. 2).

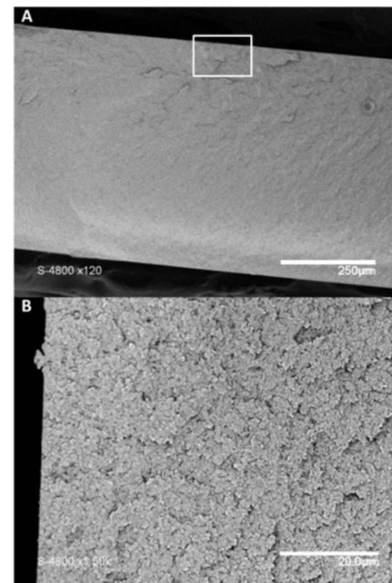


*Fig. 2 – Structural homogeneity of the 16 layers composite built-up as shown by SEM investigation (SE mode, magn(A) = 120x, magn(B) = 1500x)*



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### *B. DSC method*

Calorimetric studies were performed with a DSC Q2000 from TA instrument, equipped with an auto-sampler. The Tzero™ central cell temperature sensor was calibrated with sapphires and the cell constant was determined with indium standards. The T4P mode was used in order to correct the difference in shape of different pans. The samples were prepared as discs of 4 mm diameter and 0.56 mm thickness, weighing ca. 13.00 mg, the exact weight being measured on a $10^{-5}$ g precise analytical balance, before placement into pierced aluminum Tzero™ pans of 40 µL. The curing reaction was followed by monitoring the exothermic peak at the isothermal temperatures: 150, 160, 170, 180 and 190 °C.

Vyazovkin *et al.* reported that isothermal experiments are inherently much more difficult to perform than non-isothermal ones due to the isothermal curing introducing a bias during the heating-up time (thermal inertia) [21]. In order to obtain reliable results, this equilibration time must be negligible compared to the characteristic reaction time. Two techniques are proposed in order to shorten the equilibration time: a very fast non-isothermal ramp or a rapid sample insertion into a preheated furnace.

To minimize the described bias in the presented investigation, isothermal temperatures have been fixed being equal/or lower than the supplier's recommendation (adapted reaction rate regarding the equilibration time). Moreover, the equilibration time was found to be much shorter when inserting the samples into the preheated furnace (~ 20-30 s), as compared to the ability of the apparatus to process to a very fast temperature ramp without creating electronic artefacts (~ 2 min). Thus, the samples were inserted into the pre-heated furnace with the help of the auto-sampler, resulting in an excellent accuracy and reproducibility.

## IV. Results and discussion

### *A. Isothermal kinetic profiles*

The curing reaction of epoxy resins is an exothermic reaction, characterized by the release of heat. The general assumption with DSC kinetic analysis is that the instantaneous release of heat is directly proportional to the degree of conversion [22], [23] - in other words, the heats of possible side reactions are negligible:

$$\alpha(t) = \int_0^t \frac{\dot{q}}{\Delta H_{TOTAL}} \cdot dt \qquad (4)$$

with $\dot{q}$ being the specific heat flow and $\Delta H_{TOTAL}$ the overall heat of reaction (i.e. realised heat until completion).

The overall heat of reaction $\Delta H_{TOTAL}$ has been calculated from classical dynamic DSC analysis, in order to be sure to reach the completion of the reaction. The exothermic peak was numerically integrated between the curve and a straight line, with regards to the time. $\Delta H_{TOTAL}$ has been evaluated being equal to 86.1 ± 2.8 J/g of composite (average of 5 repetitions, 95% of confidence). Due to the relatively large amount of DSC inert $SiO_2$ fillers in the base material, the given value seemed very small, but after normalizing it with respect to the proportion of resin in the total mass used for the DSC investigation, we obtained a corrected $\Delta H_{TOTAL} = 232.7$ J/g, which we found to be in fair agreement with other epoxy/phenol systems (e.g. 206.3 J/g in [24]).

The thermograms in Fig. 3 monitor the specific heat flow over a curing time of 120 min, at the isothermal temperatures: 150, 160, 170, 180 and 190 °C. The average value of the specific heat flow measured during the latest minute of curing has been considered as the baseline, and thus has been subtracted.

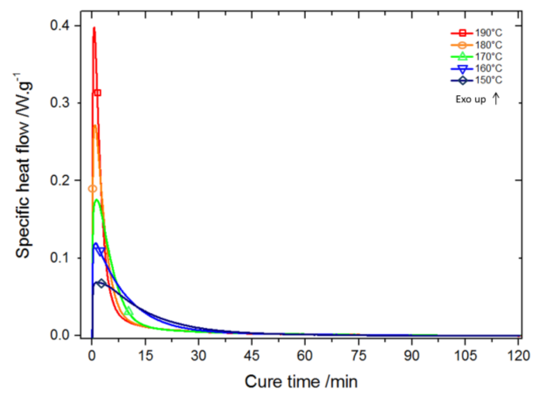


*Fig. 3 – Exothermic peaks of curing reactions, over two hours, at the indicated isothermal temperatures*

As expected, higher curing temperatures generate more intense and sharper exothermic peaks. The faster return to the baseline, as compared to lower temperatures indicates a quicker achievement of the curing reaction.

As described by (4), the extent of cure for each point in time is given by the cumulative area between the curve of the thermogram and the X-axis, with respect to the overall heat of reaction. By plotting the extent of cure over the time, one obtains the kinetic profiles depicted in Fig. 4.

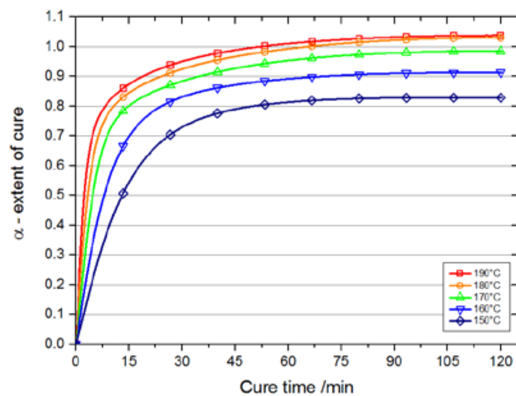


*Fig. 4 – Kinetic profiles suggest the accessible degree of conversion at each of the indicated isothermal temperatures*



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Two regimes are visible: one fast regime until approximately 70-80% of conversion, and a slower regime in which the degree of conversion reaches a quasi-plateau (only very slight increase remaining). Curing at an isothermal curing temperature significantly above the $T_g$ of the fully-cured base material (154 °C for the investigated ABF) yields a completely cured sample, while lower temperatures conclude in a plateau with $\alpha < 1$. Note that at 180 and 190 °C, the extent of cure slightly exceeds $\alpha = 1.0$. This behavior can be attributed to experimental (heating-up bias) and integral (baseline subtraction) errors. Nonetheless, the reproducibility was very good, with errors below 5%. The kinetic profiles were therefore judged suitable for kinetic analysis.

### *B. Isoconversional analysis*

The apparent activation energy was calculated by using MFK isoconversional methods as a function of the extent of cure. The method of Friedman (3) was used to perform the isoconversional analysis. Fig. 5 shows corresponding Arrhenius plots for specific degrees of conversion $\alpha = 0.15$ to 0.8 ($\Delta\alpha = 0.05$). The maximum $\alpha = 0.8$ arises from the maximum degree of conversion reached by all isothermal runs, as shown in Fig. 4. Result quality was excellent as is obvious from the very linear Arrhenius plots ($R^2 > 0{,}96$ for all plots; $R^2 > 0.99$ for $\alpha \leq 0.6$).

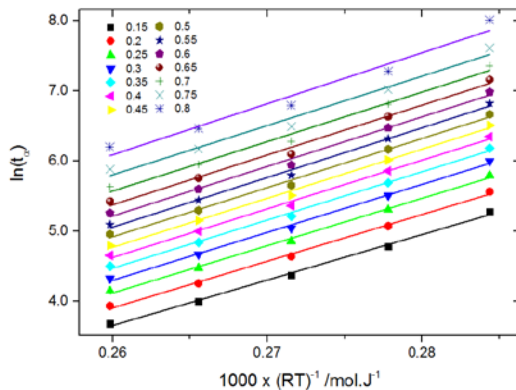


*Fig. 5 – Arrhenius plot based on Friedman's method. Each set of data corresponds to a given isoconversional α. Solid lines are linear regressions.*

As described above, slope and ordinate intercept of the Arrhenius plots provide the activation energy $E_\alpha$ and the logarithm of $g(\alpha)/A_\alpha$, combined as the kinetic triplets shown in Fig. 6. Inspection of the resulting graphs reveals that the apparent activation energy increases with the ongoing conversion, reaching a quasi-plateau at $\alpha \sim 0.5$-0.7, before starting to increase again at the latest observed degree of conversion. This last increase in activation energy can be attributed to the increasing numbers of crosslinks restraining and gradually freezing the molecular motion, thus adding a diffusion attributed amount onto the activation energy. The system switches from reaction-controlled kinetics to diffusion-controlled kinetics [20], [25]. The impact of this switch is even more pronounced when the glass transition temperature of the resin $T_g$, which increases gradually during the curing process, approaches the isothermal curing temperature (e.g. 150 and 160 °C in Fig. 4). In these cases vitrification takes place and the diffusion induced part of the activation energy increases until finally the curing reaction comes to a halt. For this reason curing temperatures should be chosen significantly above the final $T_g$ of the resin in order to achieve fully-cured materials.

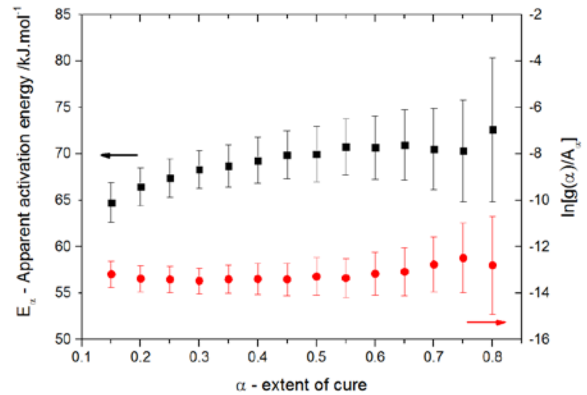


*Fig. 6 – Evolution of the kinetic parameters with the extent of cure*

The kinetic triplets in Fig. 6 show no strong fluctuation of the activation energy $E_\alpha$ until a degree of conversion $\alpha = 0.75$. This behavior strongly indicates a single-step reaction mechanism, at least until $\alpha = 0.75$, confirming the initial assumption of a single-step mechanism as prerequisite of MFK treatment. The second element of the kinetic triplets in Fig. 6 also shows a nearly stable behavior with $g(\alpha)/A_\alpha = 1.58 \pm 0.28\ 10^{-6}$ s. These values will be utilized in the next chapter for predicting the curing performance at an unknown temperature.

The increasing errors from linear regression for higher degrees of curing (*cf.* error bars in Fig. 6) are attributed to the smaller heat flow from the decelerating chemical reaction. Thus, as the DSC equipment approaches its limitations of measuring sensitivity, uncertainties increase, which are reflected by poorer linearity of the latest Arrhenius plots in Fig. 5.

### *C. A predictive model*

The ultimate goal of any kinetic study is to precisely predict the progress of the reaction and the condition of the observed system at random times and temperatures. Transferring this objective onto the curing reaction of PCB substrates within SAP application, this would allow to predict and thus control the state of the partially-cured composites after random exposition times at freely chosen temperatures (e.g. during storage, lamination or annealing), improving the general handling, as well as the reproducibility and reliability of PCB manufacturing.

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As the kinetic triplets have been elucidated for discrete isoconversions, the kinetics of the curing reaction can be determined by passing equation (3) to the exponential:

$$t_{\alpha,i} = \frac{g(\alpha)}{A_\alpha \exp(-\frac{E_\alpha}{RT_i})} . \quad (5)$$

Modeled values and measured values have been compared at an arbitrary isothermal temperature of 120 °C, over 150 minutes. The chosen temperature had to be different from the ones used in the kinetic analysis, and sufficiently high to avoid the measurement inaccuracies described above.

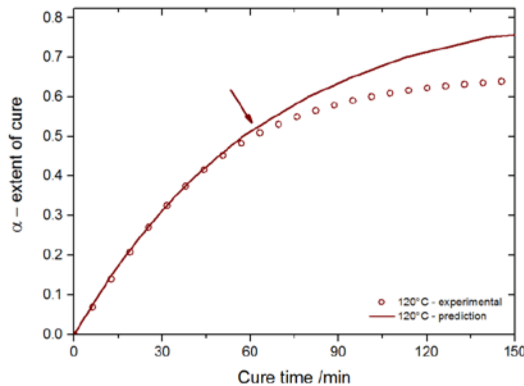


*Fig. 7 – Comparison of predicted and measured isothermal DSC kinetic profiles at an arbitrary temperature of 120 °C*

The predicted values accurately describe the measurements until a degree of conversion of α ~ 0.5 (see Fig. 7). The more the reaction progresses, the more it slows down as compared to the prediction. As already described above, due to the chosen curing temperature being lower than the $T_g$ of the fully cured material, vitrification is observed, which induces an increasing portion of the apparent activation energy. The prediction is partly taking this into account for the temperature range used to model the prediction (150-190 °C), but the prediction differs more and more as the used temperature deviates further from this range (e.g. 120 °C as in the experiment). The vitrification is depending on both temperature and degree of curing. Future in depth studies on network relaxations ($T_g$ and visco-elasticity) will permit to take into account the vitrification at any temperature, and thus enhance the curing predictions.

## V. Conclusion

Ongoing miniaturization and performance increase in advanced microelectronics lead to high performance processes such as SAP treatment, using partially-cured epoxy/silica composites materials, of which the curing state should be precisely controlled.

Thus, as a first part of our studies, the curing kinetics of a high performance base material have been elucidated by DSC. The b-stage sheets where stacked and laminated to form a bulk model composite suitable for calorimetric studies. During these investigations we have found that the high content of silica fillers does not interfere with the measurements. Non-trivial isothermal runs have been performed simulating the industrial processing of SAP base materials. Accuracy and reliability of the measurements were excellent, after fast robot-assisted insertion of specimens into the preheated furnace led to overcome the heating up bias, an inherent difficulty of isothermal DSC measurements.

The MFK isoconversional Friedman's method was used to compute the kinetic analysis, without making assumption on exact curing reaction mechanism. Activation energy has been found to increase, causing a slowing down of the reaction, assigned to the vitrification of the matrix. Prediction of curing reaction kinetics (at 120 °C) was very accurate until the critical conversion of α ~ 0.5, at which vitrification phenomena start to increase the apparent activation energy. In order to enhance modelling and predictions further investigations are ongoing and will be presented elsewhere. These include long term kinetic studies using alternative techniques as compensation for uncertainties linked to long term isothermal DSC experiments. Additionally, model fitting kinetics will take into account any vitrification effects

DSC has been found to be a powerful tool in order to elucidate the curing kinetics of industrially relevant epoxy/silica composites. The described protocol for isothermal DSC investigations can be transferred onto any bulk resin or composite, allowing PCB manufacturers to assess and classify new base materials. DSC as the reference method of thermoset curing kinetics will serve as a corner stone to back up future investigations with alternative techniques that are better suited to accept the challenges of industry applications, such as non-destructiveness, investigation of insulating composites/copper built-up composites and longer exposition times at lower temperatures.

Finally, one could imagine a fine tuning of the industrial processes with respect to the precisely known and controlled degree of conversion of any base material, in order to improve uniformity, repeatability and overall performance of the final PCB.

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