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# 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 by isothermal differential scanning calorimetry (DSC) measurements between 150 and 190°C, as relevant curing temperatures for the PCB industry. The extent of cure was calculated by integration of the exothermic peak and normalization by the total heat of reaction (obtained by nonisothermal DSC). Although the cross-linking was completed above 180°C, the kinetic profiles show two regimes: one fast and one slow. The kinetic parameters have been elucidated using an isoconversional model-free kinetic method, with the exact method of Friedman, to give to the PCB manufacturers a road map to predict curing behavior of base material. 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 within the fast regimen of reaction (i.e., without vitrification). Finally, we discuss how these kinetic measurements and models can be completed and optimized.**

***Keywords*—PCB, epoxy, composite, curing, kinetics, isothermal DSC**

## Introduction

Epoxy resins, reinforced by $SiO_2$ fibers or spherical filler particles [1,2], are composite materials of key interest to answer the increasing demand of miniaturization and performance in advanced microelectronics [3,4]. Their thermomechanical, adhesive, flame retardance, and dielectric properties make them being the perfect candidates as insulating build-up films (so-called semiadditive process [SAP]) in multilayer printed-circuit boards (PCB) and integrated-circuit substrates manufacturing [5-11].

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The epoxy resins are thermosets which are cross-linked during the reaction of curing, forming a 3-dimensional network of polymer chains [12,13]. From b-stage films (gelified matrix) to the final insulating layers, the hardening of the resin matrix is typically achieved by thermally induced oligomers cross-linking reactions. The degree of curing, $\alpha$, (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, a buildup with partially cured composite sheets has been found improving composite/Cu adherence [13-16], in SAP technology. The degree of curing, dictating the hardness and attackability of the material [17,18], is a key parameter when preparing the material for copper plating by desmear [19]. Therefore, the degree of conversion should be precisely known before any thermomechanical [13] and chemical treatment [17]. A lack of quantitative data for a mass-production epoxy composite motivated us to carry out an in-depth study of the curing kinetics.

For the investigation of curing behavior, most authors propose kinetic studies using differential scanning calorimetry (DSC), under either nonisothermal (i.e., dynamic, at a constant heating rate) [14,20,21] or more rarely isothermal conditions [20,22]. Isothermal DSC experiments are inherently more challenging than nonisothermal investigations, due to time-lagged measurement during the transition from ambient to target temperature. For this reason, most kinetic studies by DSC are made nonisothermally. However, two reasons motivated us to prefer isothermal methods: (1) industrially relevant curing schemes mostly comprise isothermal treatments [22] and (2) kinetic studies are more accurate because side reactions are avoided and the necessary computations are easier [23].

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.

## Theoretical Background

Vyazovkin et al. proposed a precise road map to follow to perform kinetic analyses [23]. Basically, it includes the determination of the kinetic triplet: the activation energy ($E_\alpha$), the pre-exponential factor ($A_\alpha$), and the degree of curing ($\alpha$).

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These key parameters are linked by the general kinetic eq. (1):

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

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

To elucidate the kinetic behavior of a reaction, two main approaches can be considered: model-free kinetic methods (MFK) [24] 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 [25]. This approximation is often reasonable, but its validity needs to be checked (i.e., no strong variation of $E_\alpha$ with the degree of conversion). 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 to elucidate the activation energy from any reaction [23], isoconversional MFK methods seemed to be 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, $\alpha$, 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 eq. (1) leads to the equation of Friedman (2):

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

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

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

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

## Materials and Methods

### 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 good thermomechanical behavior of the fully cured ABF GX-T31R [26] (see Table I) justifies why it is extensively used in mass production.

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).

Table I
Thermomechanical Properties of ABF GX-T31R [26]

| Parameters | ABF GX-T31R |
|---|---|
| CTE x-y (25-150°C, $10^{-6}$/°C) | 23 |
| CTE x-y (150-240°C, $10^{-6}$/°C) | 78 |
| $T_g$ (TMA °C) | 154 |
| Young's modulus (GPa) | 7.5 |
| Tensile strength (MPa) | 104 |
| Elongation (%) | 2.4 |

The incorporated fillers are silica spheres (~63 wt.%) with a diameter between few tens of nanometer and few microns.

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 × 2 min, 100°C, $P$ = 6 kg/cm$^2$, 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-sectional fracture, showing neither blistering nor inhomogeneities (Fig. 2).

### B. DSC Method

Calorimetric studies were performed with a DSC Q2000 from TA instrument, equipped with an autosampler. The Tzero™ central cell temperature sensor was calibrated with sapphires and the cell constant was determined with indium standards. The four-term heat flow (T4P) mode was used to correct the difference in shape of different pans. The composite 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, which is a typical temperature range of industrial isothermal curing.

Vyazovkin et al. reported that isothermal experiments are inherently much more difficult to perform than nonisothermal ones due to the isothermal curing introducing a bias during the heating-up time (thermal inertia) [27]. To obtain reliable results, this equilibration time must be negligible compared with the characteristic reaction time. Two techniques are proposed to shorten the equilibration time: a very fast nonisothermal 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

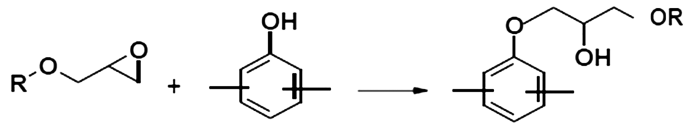


Fig. 1. Schematic curing reaction of ABF GX-series epoxy resin and phenolic hardener [26].

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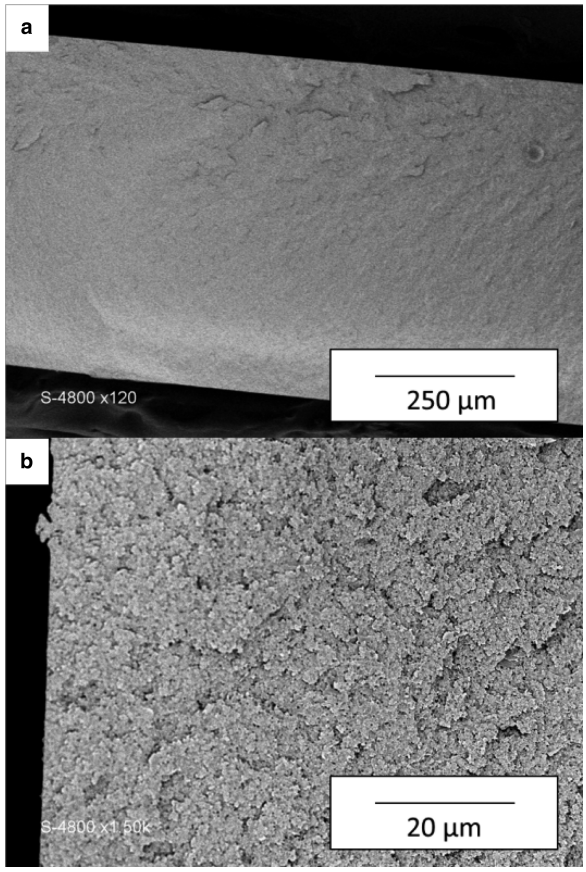


Fig. 2. Structural homogeneity of the 16-layer built-up composite as shown by SEM investigation (SE mode): (a) ×120 magnification and (b) ×1500 magnification.

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 with 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 preheated furnace with the help of the autosampler, resulting in an excellent accuracy and precision.

## 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 [28,29]—in other words, the heats of possible side reactions are negligible:

$$\alpha(t) = \int_0^t \frac{\Phi(t)}{\Delta H_{\mathrm{TOTAL}}} \times dt \qquad (4)$$

with $\Phi(t)$ being the specific heat flow and $\Delta H_{\mathrm{TOTAL}}$ the overall heat of reaction (i.e., realized heat until completion).

The overall heat of reaction $\Delta H_{\mathrm{TOTAL}}$ has been calculated from classical dynamic DSC analysis, to secure a complete reaction. The exothermic peak was numerically integrated between the curve and a straight line, with regard to the time. $\Delta H_{\mathrm{TOTAL}}$ has been evaluated being equal to 86.1 ± 2.8 J/g of composite (average of five repetitions, 95% of confidence). Because of the relatively large amount of 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 $\Delta H_{\mathrm{TOTAL}}$ = 232.7 J/g, which we found to be in fair agreement with other chemically similar epoxy/phenol–terminated systems (e.g., 206.3 J/g in [30]).

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.

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

As described by eq. (4), the degree of curing 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 degree of curing over the time, one obtains the kinetic profiles depicted in Fig. 4.

Two regimes are visible: one fast regimen until approximately 70-80% of conversion, and a slower regimen in which the degree of conversion reaches a quasi-plateau (only 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, whereas lower temperatures conclude in a plateau with $\alpha < 1$. Note that at 180 and 190°C, the degree of curing slightly exceeds $\alpha = 1.0$. This behavior can be attributed to experimental (heating-up bias) and integral (baseline subtraction) errors. Nonetheless, the reproducibility was good, with errors below 5%. The kinetic profiles were therefore judged suitable for kinetic analysis.

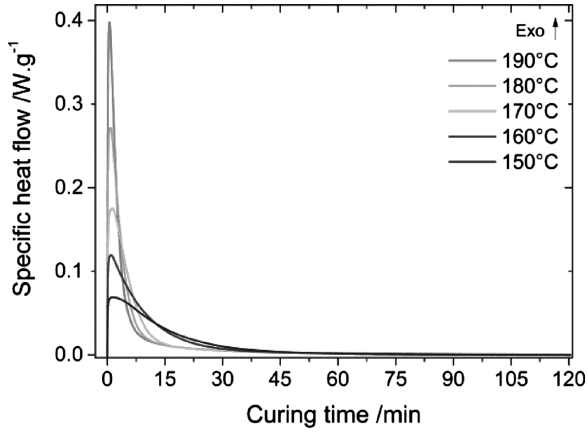


Fig. 3. Exothermic peaks of curing reaction, over 2 h, at the indicated isothermal temperatures.

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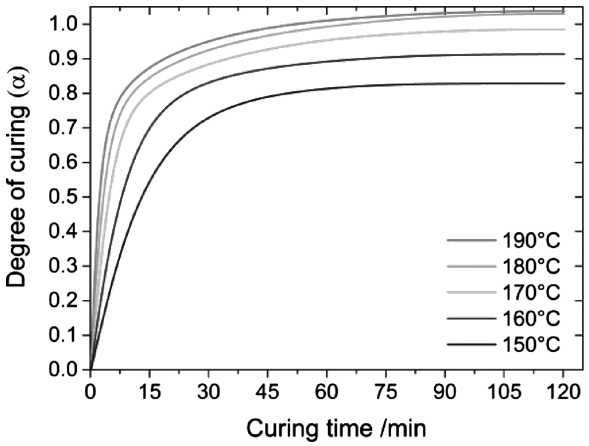


Fig. 4. Kinetic profiles suggest the accessible degree of conversion at each of the indicated isothermal temperatures.

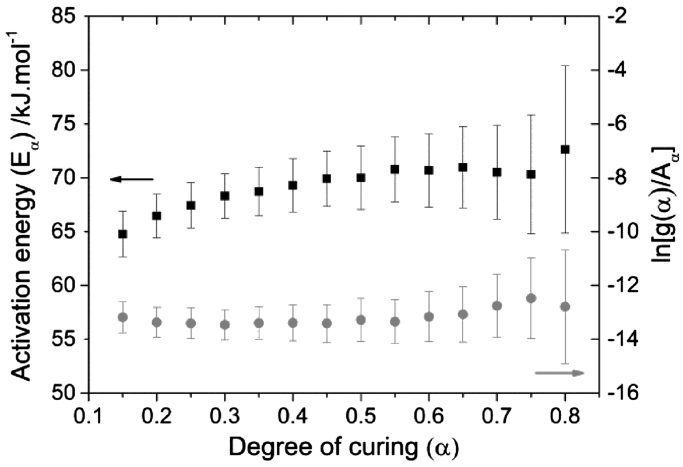


Fig. 6. Evolution of the kinetic parameters with the degree of curing.

### *B. Isoconversional Analysis*

The apparent activation energy was calculated by using MFK isoconversional methods as a function of the degree of curing. The method of Friedman eq. (3) was used to perform the isoconversional analysis. Fig. 5 shows corresponding Arrhenius plots for specific degrees of conversion $\alpha$ = 0.15-0.8 ($\Delta\alpha$ = 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 $\alpha \leq 0.6$).

As described earlier, slope and ordinate intercept of the Arrhenius plots provide the activation energy 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 $\alpha$ = 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 cross-links restraining and gradually freezing the molecular motion, thus adding a diffusion-attributed amount onto the activation energy. The system switched from reaction-controlled kinetics to diffusion-controlled kinetics [20,31]. The impact of this switch was even more pronounced when the glass transition temperature of the resin $T_g$, which increased gradually during the curing process, approached the isothermal curing temperature (e.g., 150 and 160°C in Fig. 4). In these cases, vitrification took place and the diffusion-induced part of the activation energy increased until finally the curing reaction came to a halt. Thus, the curing temperatures should be chosen significantly above the final $T_g$ of the resin to achieve fully cured materials.

The kinetic triplets in Fig. 6 show no strong fluctuation of the activation energy $E_\alpha$ = 69.0 ± 1.9 kJ/mol, 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, in line with [31], will be used in the next chapter for predicting the curing performance at arbitrary temperatures.

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.

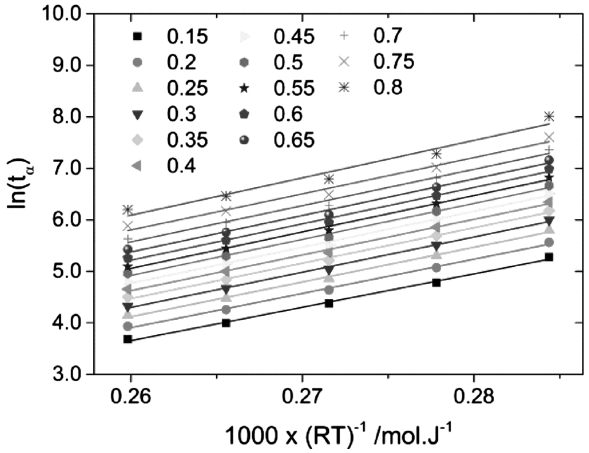


Fig. 5. Arrhenius plot based on Friedman's method. Each set of data corresponds to a given isoconversional $\alpha$. Solid lines are linear regressions.

### *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.

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

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

Predicted and measured values have been compared at arbitrary isothermal temperatures of 90, 110, 120, and 150°C, as shown in Fig. 7.

Within the fast regimen of reaction, the overall accordance between prediction and experiment is satisfactory. At 90 and 110°C, the slight deviations are assigned to measurement inaccuracies. The low curing temperatures provided a rather weak DSC signal, and caused subsequent baseline subtraction uncertainties. At 120°C, the accordance is excellent until a degree of conversion of $\alpha = 0.5$. Nevertheless, the prediction and experimental curve slopes show good accordance in all cases, within the fast regimen.

On the other hand, the predictions no longer match with experiment in the slow regimen of reaction, as observed for temperatures 110 and 120°C, in Fig. 7. As already described earlier, the systems vitrify when the increasing $T_g$ approaches the fixed curing temperature. The prediction is partly taking this into account for the temperature range used in the modeling: 150-190°C, which explains the very good accordance with 150°C. Nevertheless, the plateauing prediction differs more and more as the curing temperature is lower than this temperature range (e.g., slow regimen 110 and 120°C, the plateau is not reached for 90°C).

Future in-depth studies on network relaxations ($T_g$ and viscoelasticity) will permit to take into account the vitrification at any temperature, thus enhancing the curing predictions and will be reported elsewhere.

## Conclusions

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. Nontrivial 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 was in fair accordance with experimental data until critical conversion, at which vitrification phenomena start to increase the apparent activation energy (slow regimen). To enhance modeling 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 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 nondestructiveness, 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, to improve uniformity, repeatability, and overall performance of the final PCB.

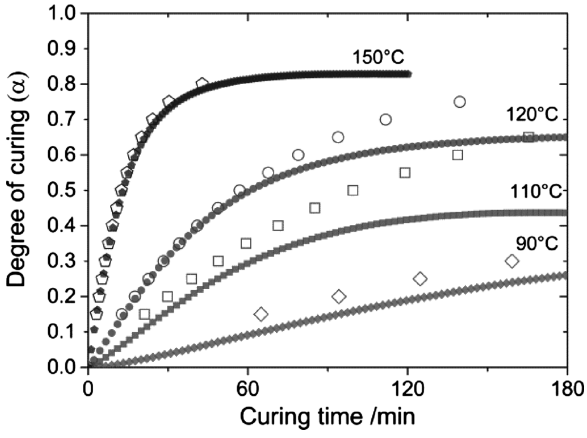


Fig. 7. Comparison of predicted and measured isothermal DSC kinetic profiles at the arbitrary temperatures of 90, 110, 120, and 150°C. Open symbols represent predictions and solid symbols represent measurement data.

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