Monitoring extent of curing and thermal–mechanical property study of printed circuit board substrates

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Precise control of curing conversion for epoxy–based printed circuit board (PCB) substrates and clarification of curing–property relationship are critical for the performance and reliability assessment, and for the design optimization of electronic systems. In this article, various epoxy composites for PCB substrates were analyzed by infrared spectroscopy (IR), differential scanning calorimetry (DSC), rheometry, dynamic mechanical analysis (DMA), and scanning electron microscope (SEM). Compared with mid-IR and DSC, near-IR (NIR) is found to be a reliable method for the characterization of curing conversion process by detecting the consumption of epoxy groups. And DMA is a powerful method for measuring the conversion of PCB materials by testing glass transition temperatures (Tg) and viscoelastic properties. The curing behaviors of a variety of epoxy composites show distinct differences in both curing rate and activation energy, and the growth tendency of Tg with curing conversion also changed depending on the material compositions. Correlation of curing conversion versus thermal properties shows that the activation energy of curing at different stage by DSC resembles the tendency of Tg transitions tested by DMA. Mechanical properties of the composites show close relationship with the curing conversions. Peel strength, the indicator of adhesion strength between copper foil and epoxy composites, was tested on all the specimens of different curing conversions, and the results showed a maximum value at curing conversion between ca. 90 and 95%.

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1. Introduction

Laminates for printed circuit boards (PCBs) are composite materials, obtained by pressing layers of a resin-impregnated filler material under heat and pressure, the resin in which is mostly epoxy [1]. The curing procedure therefore has great effect on the performance of epoxy composites for PCB substrates, as well as their adhesion with copper foil. And the adhesion strength influences the stability and reliability of electronic systems. With the request of miniaturized designs and higher performance of semiconductor electronic devices, PCB materials are expected to perform even better than ever before [2,3].

Ordinarily, the epoxy composites for PCB substrates are composed of glass fiber, fillers, and a variety of epoxy resins and hardeners, like amines, phenolic resins, or imidazoles, as well as modifiers such as rubbers, thermoplastics and other materials. Consequently, a much more complicated procedure is requested for the characterization and optimization of curing conversion of these materials rather than that of neat resin systems. Therefore, from the view of both theoretical research and industrial applications, to characterize the conversion of epoxy composites precisely after processing, and to establish a relationship between curing conversion, structure, and property for different epoxy composites for PCB substrates become an urgent and tough task.

For neat thermosetting resins without modification or blending, it has been revealed previously in numerous systems that there is a quantitative relationship between the curing conversion of the thermoset and its glass transition temperature (Tg) value, independent of the time–temperature cure history [4–9]. The equation derived by DiBenedetto [10] for predicting the glass transition temperature of a polymer based on the crosslink density of the network was generally used as a starting point.

\[
\frac{T_g - T_{g0}}{T_{g0}} = \frac{X_c(\frac{F_c}{F_m} - \frac{F_{c0}}{F_{m0}})}{1 - X_c(1 - \frac{F_{c0}}{F_{m0}})}
\]  

(1)

In this equation, \(X_c\) is the mole fraction of segments that are crosslinked, \(T_{g0}\) is the glass transition temperature of the uncrosslinked polymer, \(F\) represents the lattice energy, \(F_c\) is the segmental mobility, and the subscripts \(x\) and \(m\) refer to the fully crosslinked and uncrosslinked polymers respectively.

For most polymers, the mobility of crosslinked units is essentially zero, so \(F_c/F_m\) can be set equal to zero [11]. Rearranging Eq. (1), one can obtain:
where $K$ contains the lattice energy terms. A plot of $T_g$ as a function of $X_c/[(1 - X_c)]$ should result in a straight line. Although experimental results always have some deviations from theoretical prediction, this can still be useful during application, since $T_g$ is often a simpler and more sensitive measurement than conversion itself.

DSC is always used to characterize the curing conversion of neat epoxy resins by testing the $T_g$ at different stage. However, this method has great limitations when multi exothermic peaks appear during resin curing or several glass transitions evolve in multi-component systems.

As a substitution, Infrared spectroscopy (IR) is also widely applied for curing conversion testing by observing the area change of functional groups relative to that of the internal standard groups [12]. However, in our previous work, it has been found in Mid-IR (MIR) that the bands of epoxy group at 916 and/or 851 cm$^{-1}$ may be overlapping other peaks, which hampers the conversion calculation of epoxy group by MIR method [13].

Whereas, Near-IR (NIR) has been successfully applied in various fields, including curing monitoring [14], resin and volatile-content quality control [15], storage characterization of prepregs, etc. While optical-fiber-connected NIR can also be used for in situ test of various reactions [16,17], however, no report has been published on the characterization of PCB materials by NIR till now.

Meanwhile, the influence of curing conversion on structure-property relationships is somehow inconsistent and limited in scope for neat epoxy resins. For example:

(1) The maxima of the flexural or tensile modulus and impact resistance appeared well below full conversion and depended on the number-average functionality of the curing system [18].

(2) The tensile modulus decreases whereas the fracture toughness increases with postcuring [19].

(3) The room temperature modulus decreased with increasing extent of conversion [20].

(4) Tensile modulus decreased at the conversion range of 75–90%, while a minimum value was found in the fracture toughness at ~90% conversion [21]. The fracture toughness increased up to nearly fully cured [22].

Whereas, considering the complexity of multi-component PCB materials, one can easily anticipate that the functional relationship between $T_g$ and curing conversion cannot be applied into these systems, while the change of property with conversion should also be re-explored for optimization of the PCB performance.

At the present time, it is imperative for the PCB industry that a feasible method can be applied for precisely testing the curing conversion of epoxy composites for processing control, and a curing-property relationship could be established for optimization of PCB performance. In this work, we compared various instruments for the characterization of curing conversion of epoxy composites, and demonstrated that NIR and DMA are powerful instruments for both judgment of curing conversion and viscoelastic analysis of materials at different curing stage. Moreover, the curing behavior, conversion, and thermo-mechanical properties were correlated with each other for PCB materials.

2. Experimental methods and theory

2.1. Materials

The fresh roll of epoxy prepregs from Panasonic (Japan) and Elite Material Co. (Taiwan, China) were used for the study. The prepregs for PCB are generally composed of epoxy/phenolic resin or epoxy/dicyandiamide as specified by the manufactory. We random selected three samples EMC-285 (Elite Material Co.), R-1551v, and R-1570 (Panasonic) as representatives, and herein denote them as Sample a, Sample b, and Sample c.

Two kinds of samples for investigation were prepared by using either epoxy prepregs directly, or resin components of prepregs with glass fiber removed.

2.2. Experimental methods

2.2.1. Infrared spectroscopy monitoring

Mid-infrared (MIR) spectroscopy was performed with a Thermo Nicolet Nexus 440 spectrometer, and near-infrared (NIR) spectroscopy was performed with a Nicolet NEXUS 470 FTIR spectrometer. For the in situ NIR study, fresh prepregs were placed in the compartment and monitored in situ in the near-infrared region (11000–4000 cm$^{-1}$) at different temperatures.

2.2.2. Rheological test

The melt viscosity variations of resin components without glass-fiber were recorded on an ARES-9A rheometry instrument. All the samples were tested under a parallel plate mode with a controlled strain of 1% and frequency of 1 Hz. The resin components, which were from the fresh prepregs with glass-fiber removed, were sandwiched between the two round fixtures (diameter 25 mm), then the plate distance was adjusted to 1.0 mm quickly at the test temperature. As the standard industry processing temperature of the PCB prepregs is 171°C, the test temperature was fixed at this value in order to provide the most useful information for researchers in this area.

2.2.3. Dynamic mechanical analyses (DMA)

The dynamic mechanical properties were collected with a Netzsch DMA 242 operating in the tensile mode at multi oscillation frequencies of 1, 2, 5, and 10 Hz. The specimens were prepared in the form of cuboid bars with dimension of 15 × 50 mm$^2$, the thickness of the sample from one layer of cured epoxy prepregs was measured each time. The data were collected from 0°C to 260°C at a scanning rate of 3°C/min.

2.2.4. Mechanical test

The T-peel adhesion strengths between copper foil and epoxy composites were determined using an Instron Model 5565 universal tester at a constant temperature. Each test reported was the average of at least five sample measurements. Tensile strength of epoxy composites was tested according to China State Standard GB 1040-79, while peel strength was tested according to IPC-650-650 standard.

2.2.5. Scanning electron microscope (SEM)

The structure of samples after peeling test were observed under a SEM (Tescan TS 5163MM). All samples were coated with gold and mounted on copper mounts.

2.2.6. Different scanning calorimetry (DSC)

Calorimetric analyses were carried out on a Mettler DSC-823e thermal analyzer. Samples of approximately 5 mg in weight were cured in aluminium pans in a nitrogen atmosphere. The calorimeter was calibrated using indium standard (heat flow calibration) and an indium–lead–zinc standard (temperature calibration).

In the isothermal and dynamic curing process the degree of conversion by DSC ($\alpha_{DSC}$) was calculated as follows:

$$
\alpha_{DSC} = \frac{AH_c}{AH_{total}}
$$
where $\Delta H_r$ is the heat released up to a temperature $T$ obtained by integration of the calorimetric signal up to this temperature in the dynamic process, while for isothermal curing it corresponds to a curing time $t$, and $\Delta H_{\text{total}}$ is the total reaction heat associated with the complete conversion of all reactive groups.

2.3. Kinetic analysis

Integral non-isothermal kinetic analysis was used to determine the kinetic triplet. As the dependence of the rate constant on the temperature follows the Arrhenius equation, non-isothermal kinetic analysis may start with the kinetic equation:

$$\frac{d\alpha}{dt} = \beta \frac{dx}{dt} = A \exp \left( -\frac{E}{RT} \right) f(x)$$  \hspace{1cm} (4)

where $\beta$ is the heating rate, $dx/dt$ is the rate of conversion, $R$ is the universal gas constant, $T$ is the temperature and $f(x)$ is the differential conversion function, $A$ is a prefactor.

By using the Coats–Redfern [23] approximation to resolve the so-called temperature integral and considering that $2RT/E \ll 1$ may be written the Kissinger–Akahira–Sunose equation (KAS): [24]

$$\ln \frac{\beta}{T^2} = \ln \left( \frac{AR}{g(x)E} \right) - \frac{E}{RT}$$  \hspace{1cm} (5)

For each conversion degree, the $E$ and $\ln[AR/g(x)E]$ can be determined from the slope and the ordinate of the linear representation of $\ln[\beta/T^2]$ versus $T^{-1}$ in the origin. If the reaction model, $g(x)$, is known, for each conversion the corresponding pre-exponential factor can be calculated for every activation energy.

Integration of rate equation in isothermal conditions gives the isocoversional expression:

$$\ln t = \ln \left( \frac{g(x)}{A} \right) + \frac{E}{RT}$$  \hspace{1cm} (6)

where $t$ is the cure time. It can be observed how the isothermal constant $\ln[g(x)/A]$ (Eq. (6)) is directly related by $R/E$ for every value of $x$ to the constant $\ln[AR/g(x)E]$ of the non-isothermal adjustment (Eq. (5)). Thus, taking the non-isothermal data $\ln[AR/g(x)E]$ and $E$ from Eq. (5), we can determine the isothermal parameters of Eq. (5) and simulate isothermal curing without knowing $g(x)$.

3. Experimental results

3.1. In situ monitoring the curing by NIR

Detecting the exact curing conversion of composites is critical for property optimization and processing control. In previous works, although NIR has been applied for curing study of epoxy resins, most of them focused on either simple systems [16], or composites with quite low curing conversion [13,15]. Whereas, precise characterization of curing conversion of epoxy composites close to fully cured has barely been studied.

For conversion characterization by NIR, the primary work is to select suitable bands as internal standard for the calculation of epoxy variations with curing. To carry this point, in situ NIR isothermal study could be the most feasible way due to the easy comparison of different bands.

In the NIR spectra, the band at 4530 cm$^{-1}$ (Fig. 1a) is assigned to the combination vibrations of epoxy groups, which is always used to analyze the curing conversion [25–27]. In Fig. 1a, the NIR spectra of Sample b, as an example, represent the typical evolution of the relevant functional groups with isothermal curing. It is quite clear that the areas of all of the phenyl peaks near 4620 cm$^{-1}$ remain almost unchanged, whereas the consumption of the epoxy groups is evidently demonstrated by the decrease of the characteristic epoxy peak at 4530 cm$^{-1}$. The complete disappearance of the epoxy peak at 4530 cm$^{-1}$ is a common phenomenon for every fully cured prepregs.

As the integral intensity of the selected reference peak will be used to monitor epoxy conversion with curing, this peak must have a universal applicability for a broad range of commercial epoxy prepregs. To choose the right reference peak, we studied different types of epoxy prepregs from several companies and carefully analyzed the variations of different bands by in situ isothermal NIR spectroscopy.

As shown in Fig. 1b, the integral intensity of the epoxy peak and the band at 4613 cm$^{-1}$, which is assigned to the CH stretching of the benzene ring, were plotted as a function of isothermal curing time at 100 °C. Clearly, the integral intensity of the phenyl peak remains almost constant; the very slight fluctuations might come from either instrument deviation or sample flow, but these fluctuations have quite minimal effects on the calculation of the epoxy conversion. Therefore, we chose the phenyl peak at 4620 cm$^{-1}$ as the reference for further studying the curing conversion of different prepregs.

3.2. Curing conversion study by NIR spectroscopy

For the curing conversion study, the samples were either isothermal cured or multi-step cured with post-curing. With NIR,
the curing conversions of samples were calculated based on the following equation [28]:

\[ \alpha = \frac{A(e,t)/A(s,t)}{A(e,0)/A(s,0)} \]  

(7)

where \( \alpha \) is the curing conversion of epoxy prepregs; \( A(e,t) \) is the peak area of epoxy at a given curing time; \( A(s,t) \) is the peak area of internal standard (phenyl peak) at the same given time; \( A(e,0) \) is the origin peak area of epoxy without any conversion (B stage), while \( A(s,0) \) is the origin peak area of internal standard. However, for commercial reasons, it is almost impossible to obtain the IR spectra of initial uncured resin mixtures (in stage A). Therefore, the fresh epoxy prepregs from the manufacturers were used instead. As the research target of curing conversion for industry is to obtain a relationship between curing conversion and property of epoxy composites, a relative conversion has the same importance as the absolute value in this case.

An in situ isothermal study of curing by NIR was first performed to compare its accuracy with that from DSC study. Fig. 2a shows the curves of curing conversion at two isothermal curing temperatures tested by NIR and DSC (taking Sample b as an example). As the curing conversion of DSC is based on the total heat of reaction while NIR on the consumption of epoxy groups, one can observe from their comparison that the curves from DSC and NIR show quite similar tendency at the same temperature even though the data of conversion show a little difference, while the deviation may also result from the difference in heating stage temperature of the two methods. In other words, NIR provides conversion results comparable to those of DSC.

As NIR results are quite similar to those from DSC, samples after isothermal curing for different time (with known curing conversion from DSC) were quenched at liquid nitrogen to test the feasibility of NIR for conversion test. By using the method in our previous study, we can get an average value of the conversion from NIR by selecting at least 20 sites for the same sample to avoid deviations due to sample unevenness. Fig. 2b shows the test results of NIR as a comparison of those from DSC (Sample c cured at 170 °C as an example). As one can see, the NIR tests give quite good results, which correlated well to the careful controlled curing study by in situ DSC study.

From the study of different type of epoxy composites from several companies, including Hitachi and Shengyi (China), we found that NIR can be used successfully for the characterization of all kinds of prepregs. From this point, NIR spectroscopy was proved to be a reliable and convenient method for the curing conversion characterization of epoxy composites as it is a quick test method and provides accurate results under different conditions for a broad range of commercial products.

![Sample b](image1)

![Sample c](image2)

**Fig. 2.** Curing conversion compared by DSC and NIR measurements. (a) in situ cured Sample b at 160 °C and 190 °C and (b) NIR tested average values of Sample c as a comparison of that by DSC at 170 °C.

![Sample c](image3)

**Fig. 3.** DMA study of Sample c with different curing conversion.
3.3. Relationship between curing conversion and glass transition

Except spectrum characterization of consumption of epoxy group, the viscoelastic properties, such as glass transitions, are also closely related to conversion, which can be tested as a function of curing conversion [29]. Among all the test methods, DMA provides a relative straightforward result, including both thermo-transitions and viscoelastic properties, which has been applied in the characterization of epoxy molding compounds [30].

Fig. 4. Glass transition temperatures of different curing conversions tested by multi-frequency DMA scanning.

Fig. 5. Dynamic curing study of prepregs by DSC at different heating rate.
Epoxy composites cured from fresh prepregs by controlling iso-thermal time were re-proved by NIR to get the exact conversion value. The samples after long-time post-curing, as recommended by manufacturers, were denoted as 100% (fully-cured) for convenience (even though NIR spectrum still showed a little fluctuation). Fig. 3 shows the transition behavior of composites with different curing conversions (Sample c as an example). Although DMA gives a result of modulus not quite as accurate as that from tensile test, one can still observe that both modulus and tanδ increase with curing conversion. Glass transition temperatures can be identified by the sharp decrease of $E'$ or the corresponding peak of tanδ. In this study, the peak value of tanδ is adopted as glass transition temperature.

By using multi-frequency scanning method, we can obtain the glass transition temperatures of different conversion. Since the glass transition is inherently kinetic, it is strongly influenced by the rate or frequency of mechanical energy input. When the test frequency is increased, the relaxation associated with the glass transition has difficulty in keeping up with the mechanical strain input, and the polymer appears to be more rigid. The segmental motions associated with $T_g$ then can only occur at higher temperature, hence the $T_g$ increases with frequency. Fig. 4 shows the $T_g$ transitions at various frequency and corresponding conversion detected by DMA test of the prepregs. One can observe that $T_g$ increases with curing conversion at the same test frequency, while it is quite clear that the tendency of $T_g$ versus conversion cannot be described by the DiBenedetto equation (Eq. (1)) due to the multi-componential composition of these materials. Nevertheless, DMA could be a powerful method for the characterization of curing conversion through the test of glass transition temperature.

3.4. Change of viscoelasticity with curing conversion

Viscoelasticity of the materials is closely related to the chain mobility of crosslinked networks, which is a function of the curing conversion of epoxy. While the curing process is also controlled by chain diffusion after gelation, as a result, it would be expected that there might exist some kinds of relationship between curing behavior and viscoelasticity of materials at corresponding conversion.

DSC was used to investigate the evolution of the curing process for the prepregs (without glass fiber). Fig. 5 shows the calorimetric curves from 30 to 300 °C of the materials at different heating rate. From this figure, information about the nature of the curing reaction such as initial curing temperature, peak temperature, and the curing range of the resin at different scan rates can be derived. One can observe that as the heating rate increases, the exothermic peak shifts to higher temperatures. The shape of the exotherm changes dramatically with different prepregs. For example, Sample b shows two exothermic peaks with two maxima at 221 and 275 °C (with a heating rate of 10 °C/min) while Sample c also shows a shoulder at higher temperature, which definitely indicates a
multi-component composition of the epoxy resin matrix for the prepregs.

The total heat evolved in the curing of prepregs also varied as Sample a to be 101 J/g, Sample b 113 J/g, and Sample c 105 J/g (normalized by average of the four values of different heating rate). As the resin content in the resin/filler blends changes from ca. 70% to 85%, and the curing conversion of B-stage changes depending on the manufactures, a fluctuation in the enthalpy of curing is inevitable.

With the calorimetric signal in Fig. 5, the curing conversion of prepregs was calculated according to Eq. (3). The plots of conversion against temperature for the prepregs at various heating rates are shown in Fig. 6. The curing of epoxy in prepregs involves several different reactions. The relationship between the rates of these reactions and cure temperature is also in different ways. Thus, a change in the kind of prepreg and heating rate may change the order of reaction and vary the structure of the crosslinked network.

However, from another point of view, the control of curing reaction may be more complex. As one can see from the rheological study in Fig. 7 (Sample a as an example), before curing the epoxy is a medium viscosity blend with viscosity lower than 10 Pa s at 170 °C, while the loss modulus (G") is higher than storage modulus (G'), which indicates the state of viscous fluid at this stage. However, only after ca. 50 s, gelation takes place as the G’ crossovers G" and tanδ has a value of 1.0 at this point, whereas, the relative curing conversion as this point is below 10% from the isothermal DSC study of curing process. From then on, both G’ and G" increase quickly, and then the epoxy blends become an elastic body (with elastic modulus higher than 10^4 Pa s after 100 s of curing).

In other words, the curing reactions are diffusion controlled at the very beginning of curing reaction, i.e., the activation energy would increase due to the lower chain mobility with curing for...
neat epoxy resins, which contradicts what was observed in prepreg systems.

By using the iso-conversational approach via Kissinger–Akahira–Sunose equation, the activation energy was determined as a function of the extent of conversion and/or temperature. This dependence is determined without making any assumptions about the reaction model. Fig. 8 is activation energy calculated by the plot of \( \ln(\beta/\Delta T) \) versus \( T^{-1} \) for various values of \( n \) (\( n = 0.05, 0.1, 0.2, \ldots, 0.95 \)) covering the experimental range.

From Fig. 8 it can be observed that the prepregs may follow different kinds of curing mechanism. While for a single prepreg, it may follow several kinetic models at different curing stage. Take sample a as an example, from the point of view of kinetics in neat epoxy resins, initially, the activation energy increases, which may correspond to the kinetics reaction obeys \( n \) order, and then, it decreases due to autocatalysis reaction, at last, sharp ascending of \( E_a \) is observed due to high crosslinking.

As this kind of relaxation is closely related to the chain mobility at specific curing conversion, one would wonder: Is there any relationship between the curing process and glass transition at same level of conversion?

As thermo-transitions of epoxy materials, like glass transition process, correspond to relaxation process of polymer chain segments, the apparent activation energy of the relaxation process can be determined by multi-frequency test from the following equation [31]:

\[
\omega \tau = 2\pi f \tau_0 e^{E_a/k_B T} = 1
\]

where \( \omega \) is angular frequency, \( \tau \) relaxation time, \( f \) the frequency, \( T_p \) is the peak temperature of transition, \( E_a \) the apparent activation energy for the relaxation process and \( k_B \) the Boltzmann constant. Thus the natural logarithm of frequency is plotted as a function of \( 1/T \), and the fitted straight line was determined by the least squares method.

Fig. 9 shows the plots of \( \ln(f) \) versus \( 1/T_p \) and the corresponding linear fit while the inset shows the \( E_a \)-conversion relationship obtained from DSC measurement. At all conversions, the R-square values for the fitting are above 0.99, which means within the current frequency range (1 Hz, 2 Hz, 5 Hz, and 10 Hz), the frequency variation of \( T_p \) with \( 1/T \) follows an Arrhenius dependence. Hence, we applied this method to all the prepregs, to easily determine the activation energy for different curing conversions.

We can find a very unusual similarity of \( E_a \) tendency from the results tested by DMA of \( T_g \) transition and those by DSC of curing, i.e. the \( E_a \)-conversion relationship obtained by DSC and DMA displays similar pattern starting from curing conversion 60%. Activation energy from DMA measurements reflects the energy barrier to overcome in order to induce cooperative segmental movement of polymer chain. While \( E_a \) measured by DSC at relatively high conversion also reflects the mobility of the polymer chain, since at this stage, the curing conversion is diffusion controlled rather than reaction controlled.

From the activation energy data of both DMA tested \( T_g \) and DSC tested curing process, it can be clearly found that there is similar tendency of these two process. In other words, both reflect the chain mobility of the epoxy networks at specific temperatures.

For a polymer with crosslinked parts and multi-segmental structure, the mobility of polymer chains varies depending on segmental diffusion ability. Low crosslink density and flexible parts always have high mobility at lower temperature, while high crosslink density parts or rigid backbone parts can only be activated at high temperature; i.e., chains rotated at high temperature may correspond to either high crosslinked parts or rigid parts, while the former has low activate energy and latter with high value.

During curing process, the reactivity of chemical groups governs the curing rate before gelation. However, the chain mobility or the chain end diffusion ability determines the curing process after gelation when the curing temperature is higher than the \( T_g \) of cured networks.

The detection of \( T_g \) has the similar effect like curing process, both reflect the chain mobility with heating process. Specific segments (with chemical bond length about 5–15) rotated at elevated temperature \( (T_g) \), which shows similar sequence as the curing process, even though the former related to glass transition while the latter results in crosslinking. Nevertheless, both results are from the intrinsic chain rotation of the networks.

As a result, the activation energy of \( T_g \) and curing process shows similar tendency. The value of \( E_a \) \( (T_g) \) is several times higher than that of curing, because \( T_g \) transition related to segmental movement while curing mostly related to chain ends.

### 3.5. Mechanical properties with different curing conversions

The mechanical properties of epoxy composites with different curing conversions were tested to evaluate their relationship. Table 1 lists the tensile properties of laminates of Sample a as an example. Young’s Modulus almost show a linear increase with curing conversion, while the tensile strength and elongation at break...
have not shown this tendency, which may due to the effect of glass fiber in the samples.

As the tensile test results in this study show large deviations, other mechanical properties, like peel strength, which is an essential index for PCB materials, were tested with conversion. Fig. 10 shows the influence of curing conversion on the average peeling strength for the prepregs using both unoxidized and oxidized (with black oxide layer) copper foil. All the prepregs showed similar peel property change with curing conversion. Maximum values appear at conversion between 90% and 95% either in unoxidized copper clad or oxidized copper clad.

The copper–epoxy interface after peeling was observed to testify the relationship morphology and peel strength. Fig. 11 shows the SEM images of Sample b and oxidized copper foil interface after peeling. The SEM graphs definitely show that the destruction occurred in the epoxy resin matrix rather than resin-copper interface. After analyzed by software ImageJ, and the roughness characteristics were calculated by Roughness Calculation plugin as shown in Table 2.

<table>
<thead>
<tr>
<th>Curing conversion</th>
<th>60%</th>
<th>70%</th>
<th>80%</th>
<th>90%</th>
<th>95%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength (MPa)</td>
<td>232 ± 32</td>
<td>164 ± 23</td>
<td>112 ± 18</td>
<td>108 ± 17</td>
<td>90 ± 24</td>
<td>101 ± 12</td>
</tr>
<tr>
<td>Modulus (GPa)</td>
<td>10.0 ± 0.4</td>
<td>10.8 ± 0.5</td>
<td>11.3 ± 0.7</td>
<td>12.1 ± 0.6</td>
<td>12.8 ± 0.5</td>
<td>12.9 ± 2.8</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>3.1 ± 0.6</td>
<td>3.4 ± 0.7</td>
<td>3.9 ± 0.5</td>
<td>4.5 ± 0.9</td>
<td>3.5 ± 0.4</td>
<td>3.3 ± 0.6</td>
</tr>
</tbody>
</table>

It can be found from Fig. 11 and Table 2 that both the root mean square and arithmetic mean roughness has been observed to increase with the increase of curing conversion, i.e. roughness of the peeled epoxy matrix increased with the curing conversion. From the energy consumption point of view, increased roughness means that more energy is needed for similar material construction.

However, it is generally accepted that peel strength is highly dependent on the adhesive strength of the copper-resin interface and the flexibility of matrix resin. While lowering down the Young’s Modulus and increasing the elongation at break of the resins will diminish the stress concentration during fracture process, and thus increase the peel strength. However, the dropping down of modulus always accompanies with lower cohesive strength of resin matrix, which results in smaller peel strength. In combination, high peel strength is a result of balanced modulus, elongation at break and tensile strength. In other words, the peel strength is closely related with the toughness of the materials.

In our studied systems, with the increase of curing conversion, more epoxy groups are polymerized or reacted with curing agents, which increased the crosslink density and lowered down the chain mobility of epoxy networks, thus results in higher modulus, higher tensile strength and lower elongation at break [32]. Therefore, it can be easily inferred that there would be a highest value of peel strength at a specific curing conversion (not 100%) with the
combination of above mentioned factors. Therefore, the maximum peel strength is located at about 90–95% curing conversion, which has been demonstrated in other systems and neat epoxy resins in our previous study.

4. Conclusions

The curing of epoxy composites for PCB substrates are complex phenomena of the prime importance in industry. DSC appears to be a valuable tool for qualitative analyses the curing process. Following dynamic or isothermal variations of exothermic areas from DSC allows extracting relevant kinetic parameters to get more insight about the specific reaction mechanism of curing process. Due to the complexity of PCB materials, prepregs follow various curing mechanisms with distinct differences.

Compared with Mid-IR and DSC, NIR and DMA were demonstrated to be reliable methods for curing conversion characterization of PCB materials either fully or partially cured. NIR testing of the epoxy band correlated well with DSC study of curing conversion. While DMA provided both glass transition temperature and viscoelastic properties of materials at different curing stage. For multi-component materials, the growth of Tg with conversion cannot be simply modelled by the well-known DiBenedetto equations based homogenous neat resins; while activation energy from both DSC curing study and DMA Tg detecting shows similar tendency with conversion because the chain mobility governs both diffusion-controlled curing and glass transition process.

Mechanical properties of cured materials are closely related to the curing conversions. Modulus from DMA and tensile test increased with conversion, while peel strength showed a maximum value at curing conversion between ca. 90–95%.

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