Dynamic Mechanical Analysis of Printed Circuit Board Laminates

J. Kuczynski
IBM Corporation
3605 HWY 52 N
Rochester, MN 55901 USA
Ph: 507-253-0746; Fax: 845-432-0764
Email: kuczynsk@us.ibm.com

Abstract

Printed circuit boards must meet stringent requirements imposed by elevated temperature processes required for mixed-solder and/or Pb-free assembly. To meet these requirements, laminate manufacturers offer a variety of resin formulations, reactive additives, and glass styles designed to impart specific properties. Both the coefficient of thermal expansion (CTE) and the glass transition temperature (Tg) have received considerable attention with respect to design of high-temperature laminates. CTE mismatch between the copper and the laminate within a PCB results in stress upon the copper that may manifest itself as opens within vias, at the interfaces between internal lands and plated-through hole barrels, as well as open traces. Since the CTE of resin materials below the Tg is typically on the order of 5X lower than the CTE above Tg, a typical laminate design strategy is to produce a resin that exhibits a high Tg without adversely impacting other properties. Numerous factors affect the ultimate Tg of the resin, including the functionality of the monomer(s), crosslink density, the cure profile, and absorbed moisture. Within the electronics industry, Tg is determined via differential scanning calorimetry (DSC) as per IPC-TM-650. However, due to the multilayer construction of current circuit boards coupled with sample size limitations, DSC has been shown to be an inadequate technique for measurement of the glass transition temperature. The endotherm in the DSC is often ill defined, of marginal quality, and may be convoluted with stress relaxation and/or volatile outgassing at elevated temperature. Dynamic mechanical analysis (DMA) has been demonstrated to provide far greater information relative to not only the Tg, but also physical property depression due to moisture plasticization and incomplete resin conversion in various high-Tg laminate systems. Several case studies regarding phenolic-cured epoxy resins, cyanate ester/epoxy blends, and/or polyphenylene oxide/triallylisocyanurate blends will be discussed.

Key words

Analysis, calorimetry, dynamic mechanical, laminates, printed circuit boards.

Introduction

The Restriction of Hazardous Substances (RoHS) legislation has generated tremendous reliability concerns throughout the electronics industry supply chain. One area of concern is printed circuit board (PCB) laminate compatibility for the elevated temperatures required for lead-free assembly processes. Two critical laminate material properties are the z-axis coefficient of thermal expansion (CTE) and the glass transition temperature. CTE mismatch between the laminate and copper in the plated through holes induces stress cracks. Attempts to minimize the CTE mismatch have focused on formulation of resin systems that exhibit elevated glass transition temperatures.

The glass transition temperature (Tg) of a resin system is the temperature at which the polymer material undergoes a second-order phase transition from a rigid

to a soft state. Various physical properties of a thermoset resin change upon exceeding the Tg, including an increase in both the specific volume and the CTE. The CTE is a measure of material expansion (which occurs both above and below the Tg), normally expressed in ppm/°C. Expansion in the z-axis (through the thickness of the board) is the primary concern due to its impact on plated thru hole (PTH) reliability often seen in cross-sections as barrel cracks [1]. Typical values for laminate materials are 50–90 ppm/°C below Tg (α1) and greater than 200 ppm/°C above Tg (α2). Considerable effort has been generated in the industry to formulate laminate materials with a significantly higher Tg than standard FR4 [2]. By driving the Tg to temperatures greater than the lead-free solder temperature, the z-axis CTE of the laminate will never exceed α1. Low z-axis expansion materials are desirable as they exert less stress on plated through holes during thermal excursions.

Within the PCB industry, Tg is typically determined in accordance with IPC specifications via thermomechanical analysis [3] or differential scanning calorimetry [4]. Measurement of the Tg via themomechanical analysis is of little use as it involves removal of copper cladding as well as the avoidance of internal metal cores, both of which are typically unavoidable in multilayer PCBs. Determination of the Tg via differential scanning calorimetry (DSC) per the IPC specification involves a pre-bake at 105°C for 2 hrs to remove moisture. However, in large multiplayer boards, the conditions necessary to ensure removal of adsorbed moisture vary depending on the board construction. Moreover, the DSC endotherm is often ill defined, of marginal quality, and may be convoluted with stress relaxation and/or volatile outgassing at elevated temperature. Consequently, a technique which requires no sample preparation yet provides the analyst with a wealth of physical property information is desirable.

This paper investigates the use of dynamic mechanical analysis for the evaluation of PCB qualification. The effect of moisture, prepreg curing conditions, and lamination press ramp rate on the physical properties of the completed PCB will be discussed.

Experimental

Sample Preparation

Printed circuit boards for a power application were received from a preferred PCB supplier from their facility in China. The multilayer board was constructed from a phenol-cured, high temperature epoxy with a stated Tg of 170°C. As part of a routine qualification program, characterization of the PCB physical properties as well as the cure factor was undertaken. Sections of the PCB were excised from a card region devoid of plated thru holes. For DSC analysis, the sample was prepared as per the aforementioned IPC specification; for DMA, the card sections were used as received.

Prepreg and cores were received directly from the PCB supplier and refrigerated at -40°C in a vacuum bag until use.

Differential Scanning Calorimetry Analysis

Once excised from the PCB, the sample was preconditioned by baking for 2 ± 0.25 hours at 105 ± 2°C then cooled to room temperature in a desiccator for at least thirty minutes prior to testing. The card section was subsequently placed in an aluminum sample pan and an aluminum lid was crimped over the top of the sample. A suitable reference (multiple lids) was placed in the reference pan of a Perkin-Elmer Pyris 1 differential scanning calorimeter and the instrument instructed to scan at 20°C/min to 230°C. Following a cooling cycle to 25°C, the sample was re-scanned to 230°C. The Tg was determined from the endothermic shift in the baseline using the half-Cp method.

Dynamic Mechanical Analysis

Samples were centered on a stainless steel three-point bending fixture and placed under a normal load in order to achieve a minimum amplitude in excess of two microns (typical parameters: 5000 mN static force; 4000 mN dynamic force; frequency of 1 Hz). Following equilibration at the load temperature, the samples were subjected to the following thermal profile:

1) Heat from 25°C to 225°C at 5°C /min
2) Cool from 225°C to 25°C at 5°C/min
3) Heat from 25°C to 225°C at 5°C /min

Tg was reported as the peak in the loss modulus.

Simulated Lamination Stack Up

In order to investigate the effect of prepreg curing conditions on the DMA response of production cards, a simulated multilayer board was constructed from prepreg and cores. Stainless steel shims were used to sandwich prepreg and core layers that were cured

under various conditions (Fig. 1). For example, a sheet of prepreg was sandwiched between two cores and the layup cured for 30 min at 150°C. A second prepreg sheet (PP 2 in Fig. 1) was subsequently laid up between Core 2 and Core 3 and this stack up cured for 60 min at 150°C. Finally, two additional prepreg sheets (PP 3 and PP 4) were laid up on the top and bottom of Core 1 and Core 3, respectively. This stack up was then cured for 30 min at 150°C. Consequently, prepreg layers in the final stack up were subjected to incrementally increasing cumulative bake times of 30 min (PP 3 and PP 4), 90 min (PP 2), and 120 min (PP 1). In this fashion, cure advancement in a simulated multilayer board was evaluated.

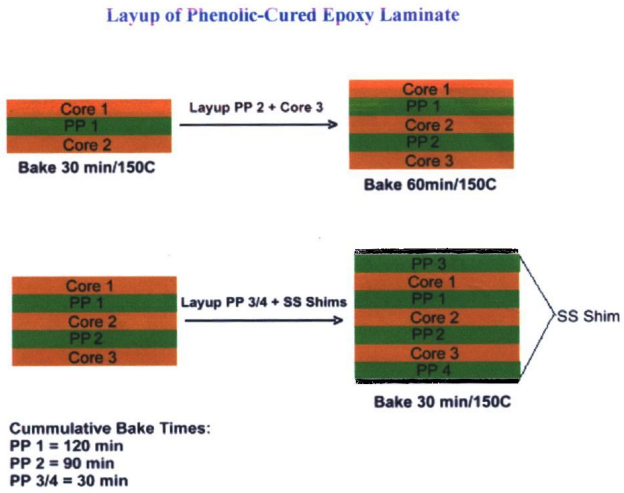

Figure 1. Protocol for the construction of a simulated multilayer board used to evaluate the effect of cure advancement.

Results and Discussion

Differential scanning calorimetry is an effective tool for determining cure kinetics as well as phase transitions in thermoset resins. However, as with any technique, certain limitations exist. Regarding multilayer PCB laminates, where internal power planes are comprised of copper and cores and prepreg consist of reinforced fiberglass, the actual thermoset resin content can be but a fraction of the overall construction. Moreover, as board thickness continues to increase beyond 130 mils, the full cross section of the board exceeds the depth of the DSC sample pan. Consequently, the thickness must be reduced (either by grinding the top/bottom layers or by slicing through the cross section) in order to accommodate the sample restrictions. Coupled with the prebake prescribed in the IPC specification, the integrity of the as-received PCB is more often than not compromised. For example, the prebake is designed to remove moisture, which acts as a plasticizer for epoxy thermosets. However, for large, multilayer PCBs, the IPC prebake is more than likely insufficient at removing absorbed water from the inner layers of the board. Residual moisture may result in a reduction of the Tg which can have deleterious consequences on board reliability. Since the OEM is concerned with raw card performance as the PCB is subjected to multiple solder reflow cycles, it is desirable to evaluate the board in the as-received condition. For thick multilayer PCBs, DSC analysis is not adequate.

Typical DSC results for a multilayer power card are depicted in Fig. 2.

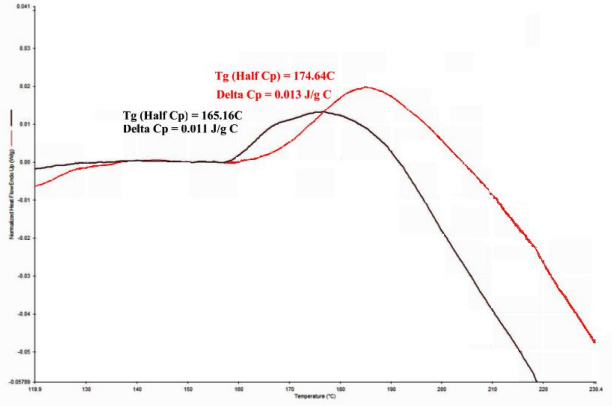

Figure 2. Thermograms for a multilayer power card; — initial heating cycle; — second heating cycle.

The normalized heat flow for the transition is extremely weak (less than 0.02 W/g) and is approximately 10X smaller than the neat resin (not shown). The insensitivity is due to the large fraction of both copper and fiberglass in the sample, both of which do not contribute to the phase transition and render its detection problematic. Cure advancement can be observed as the shift in the Tg (approximately 10°C). However, the increase in the Tg should have resulted in the observation of a residual exotherm, which is absent from the thermogram for the initial heat cycle.

The DMA response of the identical PCB as received is illustrated in Fig. 3. During the initial heating cycle, the storage modulus (E') clearly exhibits bimodal

behavior and two well defined peaks are present in both the loss modulus (E") and tangent delta curves. During the second heating cycle, the magnitude of E' increases 50% and exhibits monotonic behavior while the two peaks in E" and tangent delta collapse into a single peak shifted to much higher temperature (see Table 1).

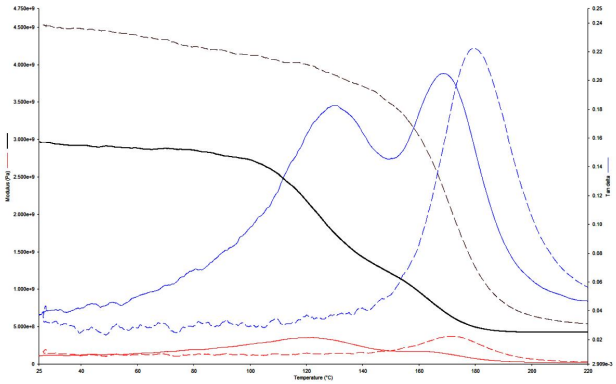

Figure 3. DMA response of a phenolic-cured laminate PCB for power applications: — storage modulus; — loss modulus; — tangent delta. Initial heating cycle curves are depicted as solid lines; second heating cycle curves are dashed.

Table 1. Cure Factor of Phenolic-Cured Laminate		
DSC Results		
Tg (°C)		Cure Factor (ΔTg)
Initial Heat	Second Heat	
165.16	174.64	9.48
DMA Results		
Tg (°C)		Cure Factor (ΔTg)
Initial Heat	Second Heat	
139.16; 160.91	169.01	29.85; 8.10

These results raise potential reliability concerns for the printed circuit card. The low-temperature Tg (139°C) is well below the vendor specified minimum of 170°C and actually falls below the operating temperature of the card. The CTE above the low-temperature Tg is approximately 4-5X greater than it would be in a card exhibiting normal behavior. Consequently, expansion of the resin in plated thru holes is exacerbated and the potential for barrel cracks is increased. Additionally, the collapse of the dual peaks into a single peak at higher temperature is strongly suggestive of cure advancement in the epoxy resin. This implies that the resin will undergo further crosslinking (typically resulting in isotropic shrinkage) as it is subjected to the first solder reflow cycle. This dimensional instability in the PCB is extremely detrimental to card reliability.

Cure factor (or delta Tg) is a measure of the degree of cure in multifunctional and high-temperature epoxy systems. It is simply calculated as the absolute difference between the Tg observed in the first and second heating cycles. The Tg and cure factor determined via either DSC or DMA for the phenolic-cured laminate is shown in Table 1. Regarding the calorimetry results, a single Tg was observed in both the initial and second heat scans with no evidence of any residual exotherm associated with cure advancement of the epoxy resin. The Tg from the second heat scan was in line with the vendor specified value of 170°C. Delta Tg was calculated to be 9.48°C. In sharp contrast, the DMA results revealed the presence of a low-temperature transition. Delta Tg calculated from this transition results in a value of 29.85°C whereas the cure factor calculated from the high-temperature transition was 8.10°C. It is obvious that the DSC analysis is inadequate for fully characterizing the physical properties of the PCB. The techniques yield comparable results only if the cure factor is calculated from the high-temperature peak. However, the existence of the low-temperature transition has profound implications on PCB reliability. The nature of this transition was the subject of contention between the board manufacturer and the OEM with the board manufacturer asserting that absorbed moisture was responsible for the observed behavior.

Water plasticization of epoxy resins is known to result in a reduction of the Tg, in some reported cases to an extent of greater than 30°C [5]. In order to determine if the observed bimodal response in the storage modulus and the low-temperature peak in the loss modulus was due to water plasticization, sections of a power card were subjected to vacuum bake conditions of 50 torr at 125C for 48 hrs. The dynamic mechanical results revealed a very pronounced low-temperature peak with a clearly visible high-temperature shoulder in E". The cure factor was determined to be 32°C, comparable to results obtained on the as-received PCB. Although suggestive, complete removal of absorbed moisture was not confirmed. Therefore, water plasticization resulting in the observation of the low-temperature peak in the loss modulus could not unequivocally be rejected. Consequently, a test vehicle (TV) of similar thickness

constructed from the same phenolic-cured high temperature epoxy resin was subjected to either direct water immersion (50°C for 121 days or 25°C for 142 days) or 50°C/80% RH for 28 days. Moisture was driven out of these test vehicles by baking the card sections at 125°C for 48 hrs prior to exposure to direct water immersion or temperature/humidity conditions. Representative results are illustrated in Fig. 4.

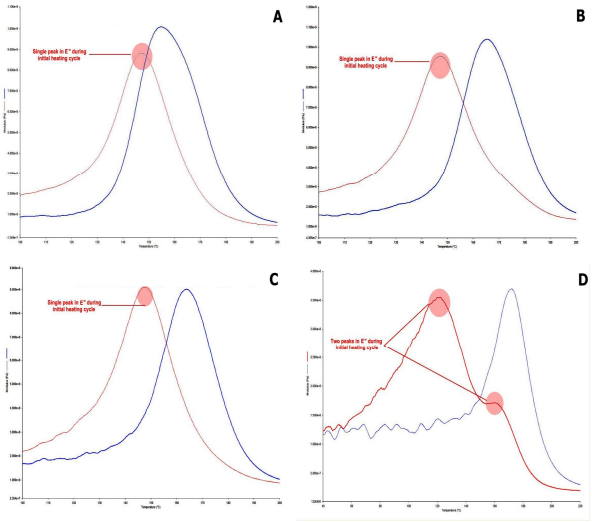

Figure 4. The effect of direct water immersion on the loss modulus of test vehicles and a power card constructed from a phenolic-cured high-temperature epoxy: – initial heating cycle; – second heating cycle. A) TV with PTHs, 50°C/121 days; B) TV without PTHs, 50°C/121 days; C) TV with PTHs, 25C for 142 days; D) Power card section, as received.

In every case, direct water immersion of a TV resulted in monotonic behavior of the storage modulus and the appearance of a single peak in the loss modulus during the initial heating cycle. The peak shifted to higher temperature during the second heating cycle—the calculated cure factor is shown in Table 2. Similar results were obtained for TVs subjected to T&H exposure. It is clear that both the DMA response and the cure factor are distinctly different for the as-received power card and the TVs subjected to extended moisture exposure. Moreover, the immersion and/or T&H conditions are extreme and result in much greater moisture absorption than could reasonably be attributed to normal card processes. Consequently, the observed DMA behavior of the PCB must be attributed to some other effect other than water plasticization. Phenolic-cured epoxy resins undergo cure advancement if the temperature is raised above the Tg. Assuming that the low-temperature peak observed in E" is due to incomplete conversion of the resin, then the Tg will shift to higher temperatures following the initial heating cycle in the DMA. Although the results are consistent with this interpretation, direct evidence was required to institute a process change during fabrication of the PCB.

Table 2. Cure Factor of Test Vehicles Subjected to Water Immersion

Sample ID^	Tg (°C)		Cure Factor
	Initial Heat	Second Heat	
A	140.5	156.1	15.6
B	147.3	165.6	18.3
C	147.5	163.9	16.4
D	121.2; 160.0	166.8	45.6

^ See Fig. 4 for details

Differential scanning calorimetry was used to evaluate the curing kinetics of the B-staged epoxy resin. Shown in Fig. 5 are the results from a curing kinetics analysis of the prepreg used in the construction of the PCB. Depicted in the insert is the initial scan (black trace) of an as-received sample illustrating the low-temperature Tg (65°C) with enthalpic relaxation and the onset of cure advancement at 140°C. The large residual exotherm (approximately 42 J/g) is characteristic of a B-staged resin. Cure advancement occurs as the temperature is swept above the Tg and chain mobility increases. Following a cooling cycle, the second heating curve (red trace) results in a Tg of 162°C with no further evidence of any residual exotherm suggesting that complete conversion has occurred. The curing kinetics were calculated based on the prepreg residual exotherm. Various cure times were input and the extent of reaction was calculated from the instrument software as a function of isothermal temperature. It can be seen that for any given temperature, the % reaction increases with cure time. For example, at 160°C, 30 min cure time results in 65% reaction, 60 min cure time results in 85% reaction, and 240 min cure time results in 98% reaction. If the isothermal curing temperature is increased to 170°C, 30 min cure time yields 85% reaction, 60 min cure time yields 96% reaction, and 240 min cure time yields 100% reaction. Theses results were used to subsequently fabricate prepreg/core samples to evaluate the effect of incomplete conversion of the prepreg in the PCB.

Prior to construction of the multilayer prepreg/core samples, the DMA response of the prepreg used in the

fabrication of the PCB was evaluated (Fig. 6). Inspection of the tangent delta curve during the initial heating cycle reveals several noteworthy observations. A glass transition (or multiple transitions) occurs at

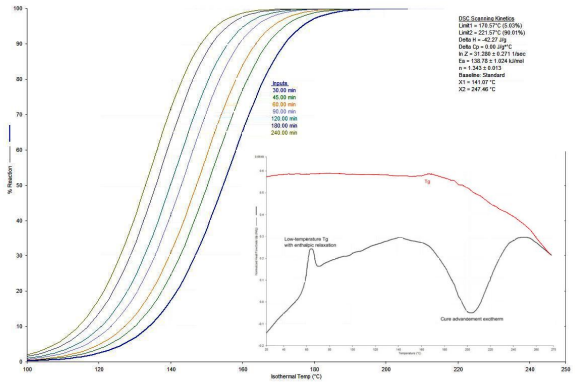

Figure 5. Curing kinetics of a phenolic-cured epoxy resin prepreg used in the fabrication of the PCB. The nested curves from left to right are decreasing cure times (as indicated in the figure). Insert: ─ initial heating cycle; ─ second heating cycle.

65-70°C and another Tg appears at 145°C during the heating cycle. This Tg is attributed to cure advancement in the analyzer and is supported by the storage modulus results. A bimodal increase in E' was observed in the initial heating cycle in the 60-75°C range; the storage modulus more than doubled in magnitude throughout the initial heating cycle indicating that the prepreg was becoming stiffer as the epoxy cure was driven toward complete conversion. Following a cooling cycle, both the storage and loss moduli behave as expected: a monotonic decrease in E' was observed with increasing temperature and a well defined peak in E" was observed at 170°C. Moreover, the magnitude of E' at the start of the second heating cycle is nearly 10X greater than E' for the initial prepreg sample. These results indicate that transitions in the prepreg, in particular cure advancement, can be readily observed in the DMA response.

A similar analysis was undertaken on a core fabricated from the phenolic-cured epoxy resin used in the construction of the PCB (Fig. 7). Only a single peak is evident in the loss modulus and tangent delta during the initial heating cycle and the storage modulus exhibits a well-behaved decrease with increasing temperature as the glass transition temperature is approached. The second heating cycle results in an increase in the magnitude of E' (roughly 2X) and a slight shift to elevated temperature for the peak in E" or tangent delta. The calculated cure factor for the core was 4.9°C. These results are typical for this type of laminate.

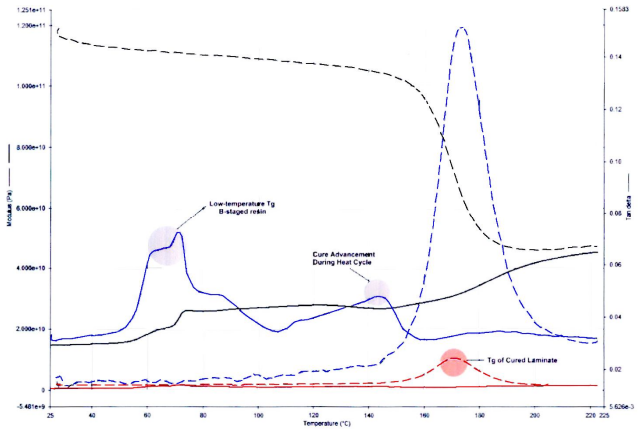

Figure 6. DMA response from a phenolic-cured epoxy prepreg (2313 cloth; 57% resin content) used in the construction of the PCB: ─ storage modulus; ─ loss modulus; ─ tangent delta. Initial heating cycle curves are depicted as solid lines; second heating cycle curves are dashed.

Having established the DMA response from both the prepreg and core separately, multilayer prepreg/core samples were prepared as previously described with intentionally under cured prepreg layers. Representative DMA curves for the simulated multilayer board are depicted in Fig. 8. It is immediately obvious that the results from the simulated multilayer stackup are virtually identical to those for the as-received PCB. Namely, during the initial heating cycle, the storage modulus clearly exhibits bimodal behavior and two well defined peaks are present in both the loss modulus and tangent delta curves. Following a cooling cycle, the magnitude of E' increases approximately 50% and exhibits monotonic behavior while the two peaks in E" and tangent delta collapse into a single peak shifted to much higher temperature. The calculated cure factor for the simulated stackup was 47°C. If the curing time at 150°C is increased, the cure factor is decreased as the low temperature peak is shifted to higher values. At 120 min, the two peaks in E" collapse into a single peak; the cure factor for this sample was 2.3°C. The low-temperature peak can be ascribed to the prepreg Tg whereas the high-temperature peak arises from the core. Increasing cure time at 150°C drives the epoxy conversion to higher values and pushes the prepreg Tg

to higher temperatures. At 120 min, prepreg cure has advanced as far as possible at 150°C (Fig. 9).

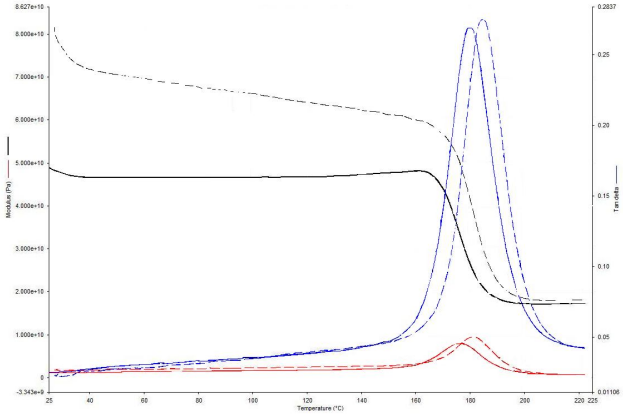

Figure 7. DMA response from a phenolic-cured epoxy core used in the construction of the PCB: storage modulus (black curves), loss modulus (red curves), tangent delta (blue curves). Solid traces are the initial heating cycle; dashed traces are the second heating cycle.

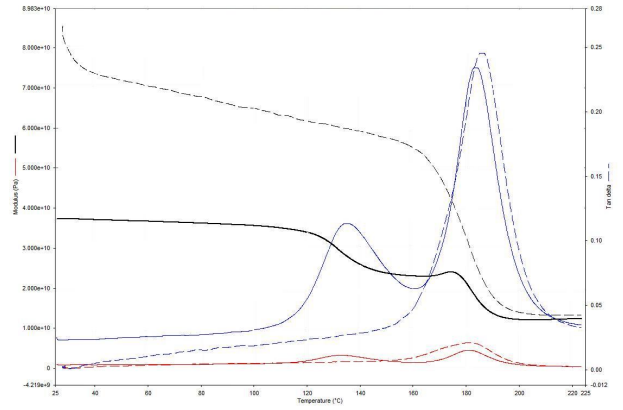

Figure 8. DMA response of a simulated multilayer stackup cured at 150°C/30 min: storage modulus (black curves), loss modulus (red curves), tangent delta (blue curves). Solid traces are the initial heating cycle; dashed traces are the second heating cycle.

These results provide strong evidence for cure advancement of the prepreg layers in the PCB. Further support for this assertion was obtained from FTIR analysis of the PCB as-received and following exposure to the thermal profile in the DMA. Shown in Fig. 10 is the fingerprint region for both samples. Of particular interest is the resonance at 940 cm^{-1} attributed to the C-O-C stretch of the expoxide functionality in the resin. Although weak, a clearly defined peak was observed in the as-received sample which decreases to a shoulder following exposure to the thermal cycle in the DMA. Upon ring-opening polymerization, the C-O-C linkage is broken and the resonance in the IR associated with it decreases. Taken in conjunction with the DMA results, it is clear that the as-received PCB is comprised of adequately cured cores and undercured prepreg. Incomplete cure of the prepreg layers poses a serious reliability concern as the dimensional stability of the PCB will be rapidly changing as the board is subjected to solder reflow processes. It is imperative to eliminate the undercured condition to assure high reliability product. During PCB fabrication, there are multiple processes that may contribute to incomplete conversion of the B staged epoxy resin. However, a likely process is the lamination press ramp rate which can vary by at least a factor of two. Throughout the lamination process, two competing phenomena occur: an initial reduction in resin viscosity due to an increase in temperature and an increase in resin viscosity as crosslinking and vitrification become dominant. The lamination press rate is selected to account for this complex interplay as well as board thickness and construction.

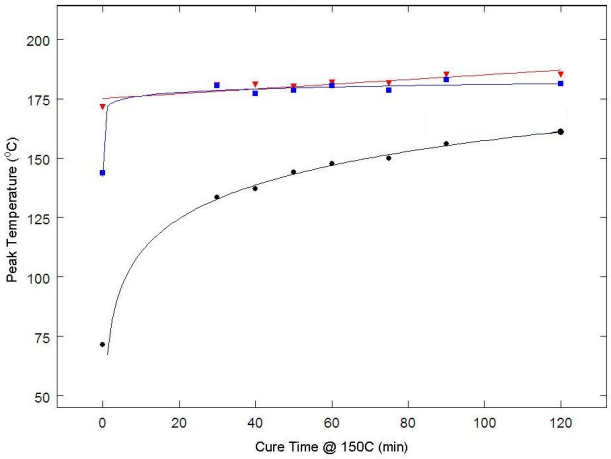

Figure 9. The effect of cure time at 150°C on the peaks in E" for the simulated multilayer stackup: ● low temperature peak, initial heating cycle; ■ high temperature peak, initial heating cycle; ▼ low temperature peak, second heating cycle.

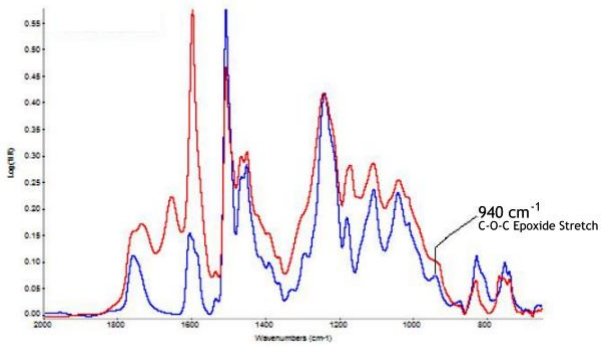

Figure 10. FTIR spectra of the PCB in the fingerprint region: – as received; – following exposure to the thermal cycle in the DMA.

The sensitivity of the prepreg Tg on cure ramp rate was demonstrated by constructing a sample comprised of a single prepreg layer sandwiched between two copper clad cores. Lamination press ramp rate was simulated by subjecting this sample to various ramp rates in the DMA furnace. Although this sample is very thin compared to actual PCBs, the results are noteworthy (Fig. 11). It can be seen that at least a 5°C increase in Tg can be realized by simply altering the cure ramp rate from 8°C/min to 2°C/min. In actual production, where the lamination stack is much thicker and thermal gradients exist within the press and sample, this effect is likely to be exacerbated.

Conclusions

As PCB thickness increases, traditional IPC test methods for determining Tg and cure factor have been shown to be inadequate. In particular, DSC analysis is not sensitive enough to detect the low-temperature transitions in the prepreg layers of incompletely cured epoxy resin laminates. Dynamic mechanical analysis is a far superior technique for determining PCB quality.

Water plasticization of the PCB was readily observed but does not result in the bimodal response in the storage modulus nor the dual peaks in the loss modulus or tangent delta curves. Simulated multilayer stackups were used to demonstrate that the low-temperature peak in E" in the PCB was due to incomplete conversion of the B staged epoxy of the prepreg layers.

Finally, the prepreg cure ramp rate was shown to shift the Tg to higher temperatures. These results were used to assist the board manufacturer in re-evaluating their lamination cycle parameters in order to avoid incomplete conversion of the epoxy resin. A collaborative effort resulted in the establishment of tighter process controls at the board manufacturer's overseas facility and the production of high-reliability power cards.

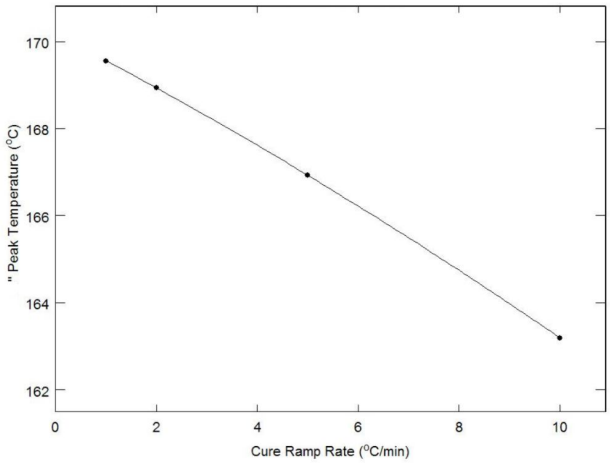

Figure 11. Effect of cure ramp rate on the Tg of a phenolic-cured epoxy prepreg.

References

[1] W. Rothschild and J. Kuczynski, "Lessons learned about laminates during migration to lead-free soldering", *IPC Printed Circuits Expo, APEX and Designers Summit 2007 Proceedings*, and references therein.

[2] S. Ehrler, "The compatibility of epoxy-based printed circuit boards with lead-free assembly," *Circuit World* 31(4), 3-13 (2005)

[3] IPC-TM-650 § 2.4.24C, Glass Transition Temperature and Z-Axis Thermal Expansion by TMA.

[4] IPC-TM-650 2.4.25C, Glass Transition Temperature and Cure Factor by DSC.

[5] A. Apicella and L. Nicolais, "Effect of water on the properties of epoxy matrix and composite", in *Epoxy Resins and Composites 1*, vol. 72, Heidelberg: Springer, 1985, pp 69-77.