Effect of Lead-free Soldering on Key Material Properties of FR-4 Printed Circuit Board Laminates

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Abstract
The high temperature exposures associated with lead-free soldering of printed circuit boards (PCBs) can alter the laminate material properties thereby creating a shift in the performance and reliability of the PCB and entire electronic assembly. The knowledge of PCB laminate material properties and their dependence on the material constituents, combined with their possible variations due to lead-free soldering exposures, is an essential input in the selection of laminates for appropriate applications.

An experimental study is conducted on fourteen types of commercially available PCB laminate materials to assess the effects of lead-free soldering process on key thermomechanical and physical properties. The laminates are classified on the basis of their glass transition temperature (high, mid and low), type of curing agents (dicyandiamide (DICY) and phenolic), type of flame retardants (halogenated and halogen-free), and presence or absence of fillers. Laminate material properties [glass transition temperature (T_g), coefficient of thermal expansion (CTE), decomposition temperature (T_d), time-to-delamination (T-260), and water absorption] are measured as per the appropriate IPC-TM-650 test methods before and after subjecting to multiple lead-free soldering cycles (namely, three reflow cycles, six reflow cycles, and a combination of one wave and two reflow cycles).

The lead-free soldering exposures resulted in variations in the material properties of certain FR-4 laminate material types. The extent of variations in the thermomechanical and physical properties under investigation are discussed as a function of material constituents. It was found that the type of curing agent has a more pronounced effect on the response of materials to exposures than the type of flame retardant or presence of fillers. For example, a significant variation in the T_g and CTE of certain DICY-cured materials is observed after the exposures. Also, time-to-delamination of DICY-cured materials decreased whereas phenolic-cured materials could retain their thermal stability even after exposures. An increase in water absorption after the exposures is observed in most of the materials. The exposures did not affect the laminate materials to an extent of changing their decomposition temperatures.

Keywords: Printed circuit board, FR-4, lead-free soldering, halogen-free, glass transition temperature

1 Introduction

FR-4[1] laminate is a composite of epoxy resin with woven fiberglass reinforcement, and it is the most widely used printed circuit board (PCB) material. The typical constituents of FR-4 laminate and the steps involved in the fabrication of printed circuit assembly are shown in Table 1 and Figure 1 respectively.

The woven glass (generally E-grade) fiber cloth acts as reinforcement for the laminate, primarily providing mechanical and electrical properties. Glass fabric is woven with two sets of fiber yarns (fibers are combined into strands of multiple fiber yarn). Warp yarn fibers lie in the machine direction of the fabric while those of fill yarn lie perpendicular to the warp direction. Coupling agents such as organosilanes are coated onto the fabric to improve adhesion between inorganic glass and organic resin.

The resin system acts as a binder and load transferring agent for the laminate and primarily consists of bi, tetra or multi-functional epoxy groups. Additives such as curing agents, flame retardants, fillers and accelerators are added in the resin to tailor the laminate material properties. Curing agents such as dicyandiamide (DICY) and phenol novolac (phenolic) enhance the cross-linking of epoxy matrix. Phenolic-cured epoxy systems have better thermal resistance, chemical resistance, humidity resistance, and improved mechanical properties but poor processability (e.g., drilling) compared to DICY-cured systems [1]. Flame retardants are added into the epoxy matrix to reduce flammability of the laminate material. Tetrabromobisphenol-A (TBBPA) is the most commonly used halogenated flame retardant for epoxy resin systems.

[1] FR-4 is the National Electrical Manufacturers Association (NEMA) grade. FR represents flame retardant (to UL94 V-0) and type 4 indicates woven glass reinforced epoxy resin.

Phosphorous based compounds are commonly used halogen-free flame retardants. Fillers such as silica and aluminum hydroxide are added to the epoxy resin primarily to lower the coefficient of thermal expansion (CTE) of the laminate while enhancing the flame retardancy and reducing material costs. Accelerators such as Imidazole are used to increase the rate of curing reaction and to control the cross-linking density of the epoxy system.

Table 1: Typical constituents of FR-4 laminates

Constituent	Major function(s)	Example material(s)
Reinforcement	Provides mechanical strength and electrical properties	Woven glass (E-grade) fiber
Coupling agent	Bonds inorganic glass with organic resin and transfers stresses across the laminate	Organosilanes
Resin	Acts as a binder and load transferring agent	Epoxy (DGEBA)
Curing agent	Enhances linear/cross polymerization in the resin	Dicyandiamide (DICY), Phenol novolac (phenolic)
Flame retardant	Reduces flammability of the laminate	Halogenated (TBBPA), Halogen-free (Phosphorous compounds)
Fillers	Reduces thermal expansion and cost of the laminate	Silica, Aluminum hydroxide
Accelerators	Increases reaction rate, reduces curing temperature, controls cross-link density	Imidazole, Organophosphine

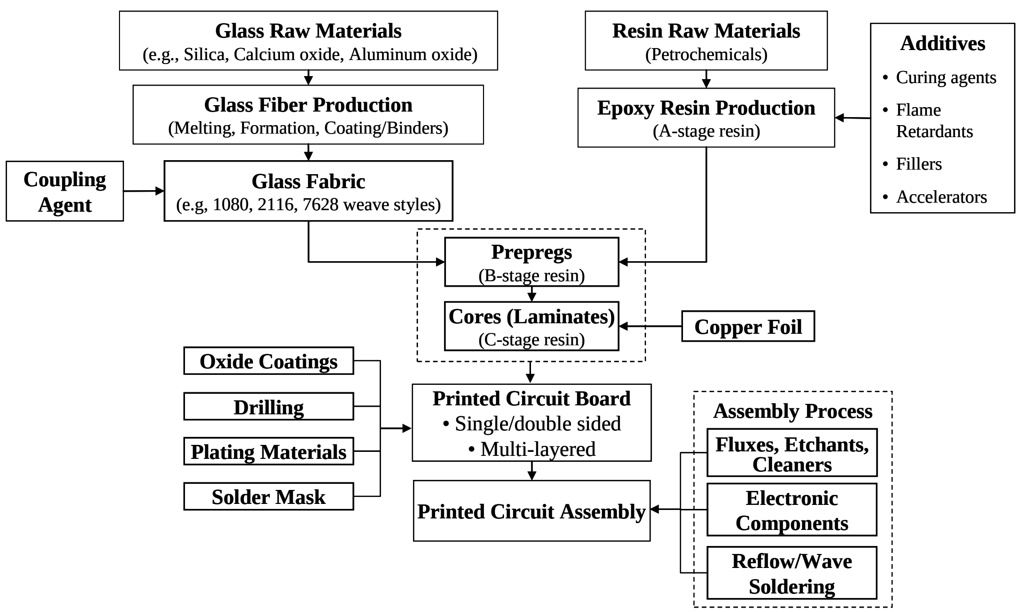

Figure 1: FR-4 printed circuit assembly fabrication

A prepreg is fabricated from a glass cloth impregnated with the semi-cured epoxy resin. Multiple prepregs are thermally pressed to obtain a core or laminate. Copper foil is then typically electrodeposited to obtain a copper clad laminate. Several prepregs and cores (with copper cladding etched as per the circuit requirements) are stacked together under temperature and pressure conditions to fabricate a multi-layered PCB. Through-holes and micro-via interconnects are drilled in the PCB as per the application-specific design data and then plated with copper. Solder mask is applied on the board surface exposing the areas to be soldered. Flux is applied at regions where the electronic components are to be soldered. The boards are then subjected to reflow and/or wave soldering process depending upon the type of components (surface mount or through-hole) to obtain the printed circuit assembly.

The transition to lead-free soldering of printed circuit boards using solder alloys such as Sn/Ag/Cu has resulted in a peak reflow temperature increase of 30-40^{o}C for longer time periods during assembly compared with eutectic Sn/Pb solders [2]. Rework and repair of assembled circuit boards also contribute to additional high temperature exposures.
These high temperature exposures can alter the circuit board laminate material properties thereby creating a shift in the expected reliability of the board and the entire electronic assembly.

The knowledge of laminate material properties and their dependence on the material constituents, combined with their possible variations due to lead-free soldering exposures, is an essential input in the selection of laminates for appropriate applications.

This paper addresses the effects of thermal exposures associated with lead-free soldering conditions on the key laminate material properties of glass transition temperature (T_g), coefficient of thermal expansion (CTE), decomposition temperature (T_d), time-to-delamination (T-260), and water absorption. Previous studies ([3], [4], [5], [6]) have identified these specific properties as some of the primary metrics in assessing the lead-free process compatibility of laminates.

2 Experimental Study

Fourteen commercially available FR-4 PCB laminates from two suppliers (I and II) were used in this study. This paper reports the measurement results of five laminate material properties on as-received materials and materials exposed to multiple lead-free soldering cycles.

2.1 Test materials

The laminates used for the study were broadly categorized (see Table 2) on the basis of glass transition temperature as high T_g (T_g>165°C), mid T_g (140°C<T_g<165°C), and low T_g (T_g<140°C) materials. Under each T_g category, laminates were grouped based on the type of curing agent (dicyandiamide [DICY] or phenol novolac [phenolic]), presence or absence of fillers, and type of flame retardants (halogenated or halogen-free). Laminates marketed for the high frequency applications (materials E and K) were also considered for the study. Coupling agents and accelerators were not controlled in the laminate materials.

Table 2: Classification of laminate test materials

Supplier	Material ID	Material classification			
		Glass transition temperature (T_g)	Curing agent	Fillers	Halogen-free
I	A	High T_g (T_g > 165°C)	DICY	No	No
I	B			Yes	Yes
I	C1		Phenolic	No	No
I	C2			Yes	No
II	D1			No	No
II	D2			Yes	No
II	E			Yes	Yes
I	F	Mid range T_g (140°C<T_g<165°C)	DICY	Yes	Yes
I	G1		Phenolic	No	No
I	G2			Yes	No
II	H			Yes	No
II	I			Yes	Yes
I	J	Low T_g (T_g <140°C)	DICY	No	No
I	K			Yes	No

Laminates with a nominal thickness of 1.2 mm with 0.036 mm (1 oz) copper cladding were used to evaluate all the properties except time-to-delamination. Laminates from supplier I have 6-plies of 7628 glass weave style[2] with a resin content of 41%, and those from supplier II have 6-plies of 7629 glass weave style. Time-to-delamination was measured on bare fabricated boards. The fabricated boards consist of a 12-layered stack up (nominal thickness of 2.5 mm) with alternative layers of cores and prepregs of 1080, 2116 and 7628 glass weave styles. The inner layers consist of staggered circular copper etch pattern and the outer layers of copper did not have any etch pattern. Fabricated boards were available only for materials A, B, C1, C2, G1, J and they span the range of T_g, curing agents, flame retardants and fillers.

2.2 Exposure conditions

Laminate samples from all the material types were divided into four lots. The first lot refers to control and represents the samples as-received from the laminate suppliers. The second lot was exposed to three reflow cycles (3X-R), the third lot to six reflow cycles (6X-R), and the fourth lot to a combination of two reflow cycles and one wave soldering cycle (2X-R+1X-W). The lead-free reflow test profile (measured using thermocouples placed at different locations on the first test board) is shown in Figure 2 and meets the IPC/JEDEC-J-STD-020D [7] recommended lead-free reflow profiles.

[2] The type of glass weave style depends on the parameters such as glass fiber bundle diameter, number of fiber bundles, and linear density of the fabric.

For the lead-free wave soldering exposures, samples were passed through two preheat zones maintained at 94°C and 155°C respectively (belt speed: 1 m/min), followed by the lead-free solder wave (Sn-0.7Cu-0.05Ni+Ge, commonly known as SN100C) with a maximum pot temperature set at 260°C.

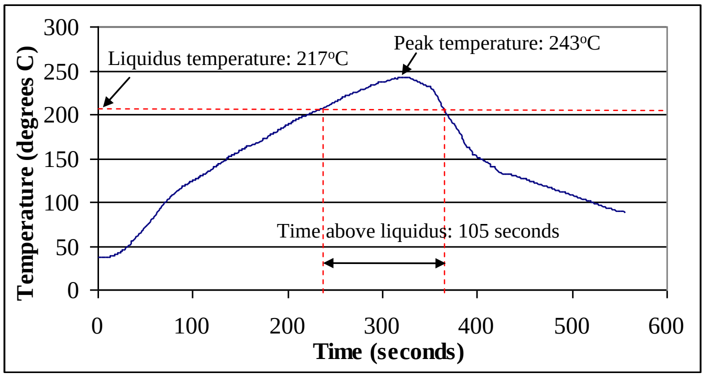

Figure 2: Lead-free reflow profile used for the exposures

2.3 Test methods

The test methods and equipment used to measure the properties are listed in Table 3. All the properties were measured as per the IPC-TM-650 test methods. The measurement procedure for each of the properties is discussed in the following sections.

Table 3: Measurement methods

Property	Units	Test method	Equipment
Glass transition temperature (T_g)	°C	IPC-TM-650 2.4.25	Differential scanning calorimeter (DSC)
Coefficient of thermal expansion (CTE, out-of-plane)	ppm/°C	IPC-TM-650 2.4.24	Thermomechanical analyzer (TMA)
Decomposition temperature (T_d)	°C	IPC-TM-650 2.4.24.6	Thermogravimetric analyzer (TGA)
Time-to-delamination (T-260)	minutes	IPC-TM-650 2.4.24.1	Thermomechanical analyzer (TMA)
Water absorption	%	IPC-TM-650 2.6.2.1	Micro-balance

2.3.1 Glass transition temperature (T_g)

Glass transition temperature (T_g) of a resin system is the temperature at which material transforms from a rigid state to a compliant state due to the reversible breakage of Van der Waals bonds between the polymer molecular chains. The T_g of laminates was measured using a Perkin-Elmer differential scanning calorimeter (Pyris 1 DSC) as per IPC-TM-650 2.4.25 test method [8]. Two samples weighing between 15-30 mg were used for the measurements. Copper cladding was etched from the samples using sodium persulphate solution. Samples were then baked at 105°C for 2 hours and cooled to room temperature in a dessicator prior to the measurements. Samples were subjected to a temperature scan of 25°C to 220°C at a ramp rate of 20°C/min, and T_g was identified as the midpoint of step transition in the DSC measurement plot.

2.3.2 Coefficient of thermal expansion (CTE)

Coefficient of thermal expansion (CTE) of a laminate is the fractional change of linear dimensions with temperature. The out-of-plane CTE of laminates was measured using a Perkin-Elmer thermomechanical analyzer (Pyris TMA 7) as per IPC-TM-650 2.4.24 test method [9]. Two samples of 7 mm x 7 mm size were used for the measurements. Copper cladding was etched and the samples were baked at 105°C for 2 hours followed by cooling to room temperature in a dessicator prior to the measurements. Samples were subjected to a temperature scan of 25°C to 250°C at 10°C/min ramp rate. The T_g was identified as the temperature at which slope of the TMA measurement plot change, and CTE was measured below and above T_g.

2.3.3 Decomposition temperature (T_d)

Decomposition temperature (T_d) is the temperature at which a resin system irreversibly undergoes physical and chemical degradation with thermal destruction of the cross-links, resulting in weight loss of the material.
The T_d of laminates was measured using a Shimadzu thermogravimetric analyzer (Shimadzu TGA 50) as per IPC-TM-650 2.4.24.6 test method [10]. One test specimen from each material type weighing between 8-20 mg was used for the measurement. Copper cladding was etched and the samples were baked at 110°C for 24 hours followed by cooling to room temperature in a dessicator prior to the measurement.

Sample was subjected to a temperature scan of 25^{o}C to 450^{o}C at a ramp rate of 10^{o}C/min in an inert nitrogen atmosphere. The change in weight of the sample was obtained as a function of temperature, and T_d was recorded at 2% and 5% weight loss (compared to sample weight at 50^{o}C as per the test method).

2.3.4 Time-to-delamination (T-260)

Time-to-delamination is the time taken by a fabricated board to delaminate (defined as the separation between layers of prepregs and copper clad cores in a multilayered structure), when exposed to a constant temperature. It is a measure of the ability of a board material to withstand multiple soldering cycles without delamination. The time-to-delamination at 260^{o}C (T-260) of fabricated boards was measured using Perkin-Elmer thermomechanical analyzer (Pyris TMA 7) as per IPC-TM-650 2.4.24.1 test method [11]. Two samples of 7 mm x 7 mm size were used for the measurement. Samples were baked for 2 hours at 105^{o}C and cooled to room temperature in a dessicator prior to the measurement. Samples were then subjected to a temperature scan of 25^{o}C to 260^{o}C at ramp rate of 10^{o}C/min and held at 260^{o}C until an irreversible change in thickness of the sample was observed. The test was terminated at 60 minutes for the laminate materials that did not delaminate until then. Time-to-delamination was determined as the time between onset of isotherm (260^{o}C) and the onset of delamination.

2.3.5 Water absorption

Water absorption is a measure of the amount of water absorbed by laminate materials immersed in distilled water for 24 hours at ambient temperature. Water absorption of the laminates was measured as per IPC-TM-650 2.6.2.1 test method [12]. Three samples of 50 mm x 50 mm size were used for the measurements. Copper cladding was etched and the samples were baked at 105^{o}C for 1 hour followed by cooling to room temperature in a dessicator prior to the measurements. Samples were weighed using microbalance before and after immersion in distilled water for 24 hours and percentage water absorption was calculated.

3 Results and Discussion

In all the properties considered, pre-exposure measurement results were used to characterize the laminate materials. The effects of laminate material constituents (such as curing agent, fillers, and flame retardant) in relationship to changes in the material properties due to lead-free soldering exposures are discussed in the following subsections.

3.1 Glass transition temperature (T_g)

The pre and post-exposure T_g measurement results were grouped by material (e.g., A, B, C1) as shown in Figure 3. Under each material group the results of four sets of data are represented. The first set of data points shown in each group corresponds to the results of control samples, the second set to 3X reflowed samples, the third set to 6X reflowed samples, and the fourth set to the samples that were exposed to a combination of 2X reflow and 1X wave soldering cycles. This pattern of data representation is followed in all other properties considered. The materials that underwent a mean-to-mean variation of greater than 5^{o}C in T_g after the exposures are highlighted in Figure 3.

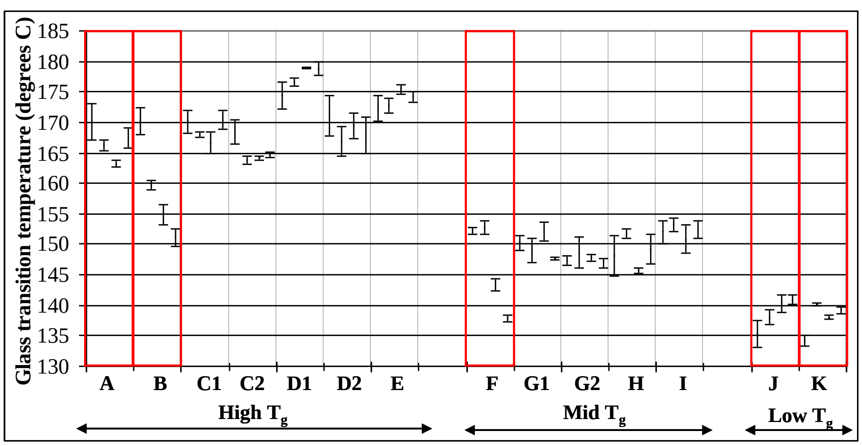

Figure 3: Effect of lead-free soldering exposures on T_g of the laminates

The control sample results show a similar T_g range for the laminates, irrespective of the type of curing agent, the type of flame retardant, and the presence of fillers. For example, materials A to E have a T_g range of 165^{o}C to 180^{o}C even though they differ by the material constituents. The T_g of a laminate system primarily depends on the type of epoxy (bi, tetra or multi-functional) and its percentage composition. Higher cross-linking density in the multi-functional epoxy systems compared to their bi-functional counterparts results in a higher T_g.

The post-exposure results show that five out of seven high T_g and four out of five mid T_g materials have relatively stable T_g with a variation of less than 5^{o}C. All of these are phenolic-cured materials. The materials (A, B, F, J and K) that underwent a mean-to-mean variation in T_g of greater than 5^{o}C are all DICY-cured. A decrease in T_g was observed in high and mid T_g DICY-cured materials, whereas an increase in T_g was observed in low T_g DICY-cured materials. The highest variation in T_g (a reduction of about 20^{o}C from control) was observed in the high T_g DICY-cured halogen-free material (B).

3.2 Coefficient of thermal expansion (CTE)

The out-of-plane CTE (below and above T_g) measurement results are shown in Figure 4. The materials that underwent a mean-to-mean variation of greater than 15% in (above T_g) CTE after the exposures are highlighted in the figure.

The control results show that a high T_g material (A) has lower CTE compared to a low T_g material (J) with similar constituents (DICY-cured with halogenated flame retardant). This could be due to the higher cross-linking density in the epoxy resin system of high T_g materials that resists the thermal expansion of the laminate. DICY and phenolic-cured materials have similar CTE range (A vs. C1). Filled materials have lower CTE values compared to unfilled materials (C2 vs. C1, D2 vs. D1, G2 vs. G1), as fillers replace the epoxy in filled materials. Halogen-free materials have lower CTE values than halogenated materials (B vs. A, I vs. H) [6].

The post-exposure results show a reduction of out-of-plane CTE in most of the materials, with a highest reduction of approximately 25% observed in the above T_g CTE of material B. The reduction in CTE could be due to further curing of the epoxy system, resulting in an increase in the cross-linking density.

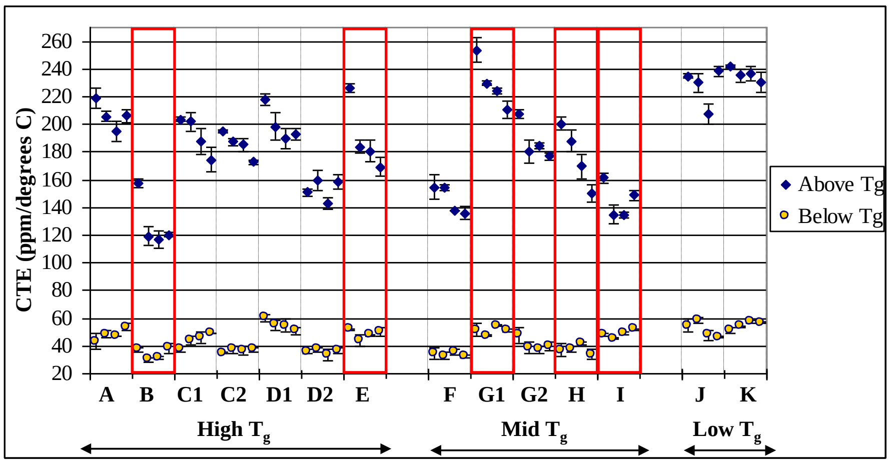

Figure 4: Effect of lead-free soldering exposures on out-of-plane CTE of the laminates

3.3 Decomposition temperature (T_d)

The decomposition temperature measurement results corresponding to 2% and 5% weight loss are plotted in Figure 5. Lead-free soldering exposures did not show noticeable variation (>10^{o}C) in T_d of the laminates, and hence none of the materials are highlighted in the figure.

The control sample results show that low T_g material (J) has higher T_d compared to high T_g material (A) with similar constituents [3]. Among the halogenated materials, all the phenolic-cured materials could withstand higher temperatures before 2% and 5% weight loss compared to the DICY-cured materials. The lower decomposition temperatures in DICY-cured epoxy systems could be attributed to the presence of linear aliphatic molecular bonds with amine linkages, compared to more thermally stable aromatic bonds with ether linkages present in the phenolic-cured systems ([1], [6], [13]).

Laminates with fillers have lower T_d compared to their counterparts without fillers (C2 vs. C1, D2 vs. D1, G2 vs. G1). Inorganic fillers such as silica or alumina accelerate the thermal decomposition process by lowering the activation energy required for decomposition, thereby acting as catalysts ([14], [15], [16]).

Halogen-free material that is DICY-cured (B) has higher T_d compared to the halogenated DICY-cured material (A). On the contrary, halogen-free material that is phenolic-cured (I) has lower T_d compared to its halogenated counterpart (H). Irrespective of the curing agent type, all the halogenated resin systems underwent degradation from 2% to 5% within a narrow temperature range (<10^{o}C), which was not observed in halogen-free systems (B, E, F, I).

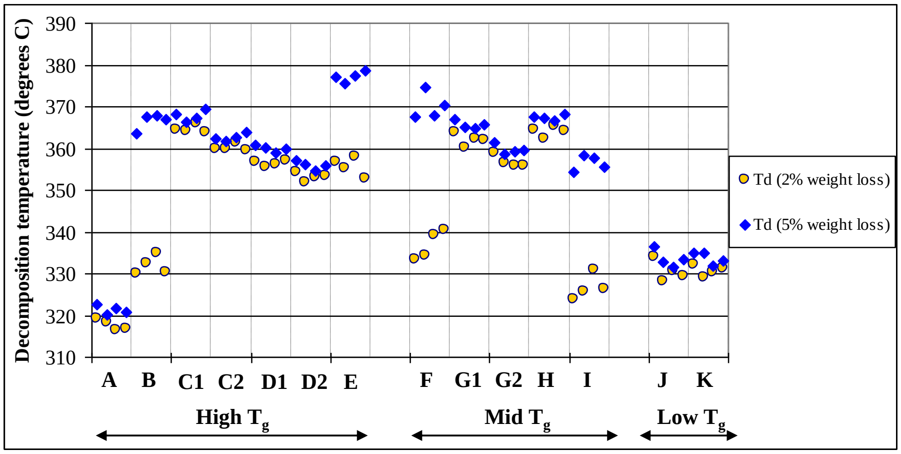

Figure 5: Effect of lead-free soldering exposures on T_d (2% and 5% weight loss) of the laminates

The post-exposure results show a maximum variation of 7°C in decomposition temperature of the laminates. The effect of material constituents such as curing agents, fillers, and flame retardants on the decomposition temperatures for the control samples remained the same after the exposures.

3.4 Time-to-delamination (T-260)

Time-to-delamination was measured for fabricated boards on a subset of materials i.e., A, B, C1, C2, G1, and J and the results are shown in Figure 6. Materials A, B and J delaminated before 15 minutes whereas C1, C2, and G1 did not delaminate until 60 minutes and the test was terminated.

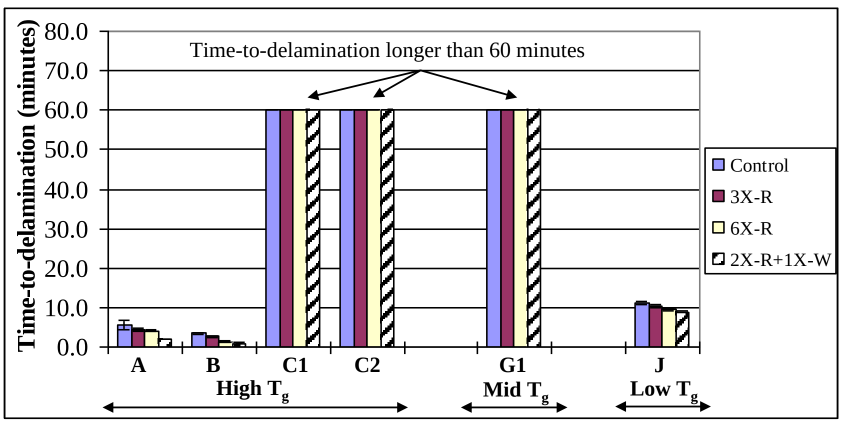

Figure 6: Effect of lead-free soldering exposures on T-260

The control results show that low T_g DICY cured materials (J) have higher T-260 compared to their high T_g counterparts (A, B) [3]. DICY cured materials (A, B, J) have lower time-to-delamination compared to phenolic cured materials (C1, C2, G1) irrespective of T_g. Lead-free soldering exposures tend to lower the time-to-delamination of materials A, B, and J all of which are DICY cured. Materials C1, C2 and G1 which are phenolic cured did not delaminate until 60 minutes even after exposures.

3.5 Water absorption

The pre and post-exposure water absorption measurement results are shown in Figure 7. Materials with a variation of greater than 25% in water absorption are highlighted in the figure.

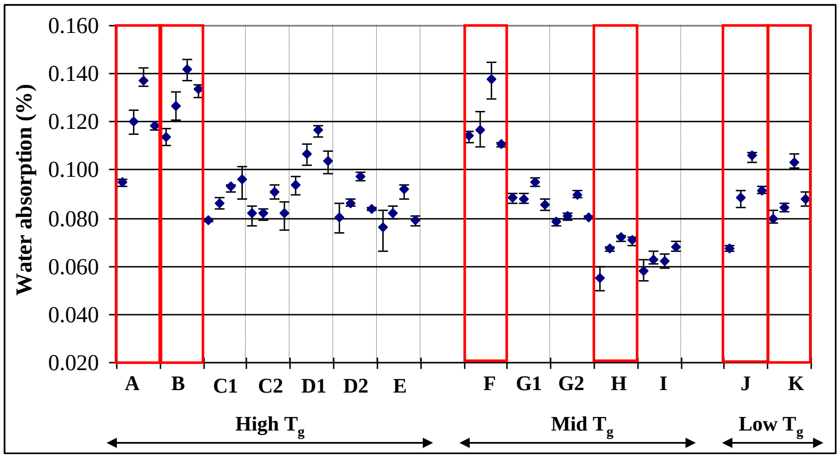

Figure 7: Effect of lead-free soldering exposures on water absorption of the laminates

The post-exposure results show an increase in water absorption due to lead-free soldering exposures for most of the materials. The material type with the highest increase in water absorption (55%) after 6X reflow exposure is a low T_g DICY-cured halogenated material (J).

4 Summary and Conclusions

Selection of PCB laminates compatible with lead-free processes is based upon their material properties, and is also impacted by factors such as application environment, cost, reliability, regulatory compliance, material sources, and availability. The laminate properties are determined by the constituents such as type of epoxy, curing agents, fillers, and flame-retardants present in the material.

In the materials studied:

- High T_g laminates have lower out-of-plane CTE compared to low T_g materials. Low T_g laminates on the other hand have higher T_d, T-260 and lower water absorption compared to high T_g materials with similar constituents.
- Although DICY and phenolic-cured laminates can have similar T_g and out-of-plane CTE, a higher T_d, T-260 and lower water absorption was observed in the phenolic-cured materials compared to similar DICY-cured counterparts.
- The presence of fillers lowers the out-of-plane CTE of the laminates, whereas the T_g, T_d, T-260 and water absorption does not have a strong dependence on fillers.
- Halogen-free and halogenated materials can have similar T_g, T-260 and water absorption, whereas lower out-of-plane CTE was observed in halogen-free materials compared to halogenated materials. Also, halogen-free material that is DICY-cured has higher T_d compared to the halogenated DICY-cured material. On the contrary, halogen-free material that is phenolic-cured has lower T_d compared to its halogenated counterpart.

$$\%\,\text{Water absorption} = \frac{\text{Wet weight} - \text{Conditioned weight}}{\text{Conditioned weight}} \times 100$$

The high temperature exposures associated with lead-free soldering assembly conditions result in variations in the material properties of certain FR-4 laminate material types. The type of curing agent has a more pronounced effect on the response of materials to exposures than the type of flame retardant or presence of fillers. For example, a significant variation in the T_g and CTE of certain DICY-cured materials is observed after the exposures. Also, time-to-delamination of DICY-cured materials decreased whereas phenolic-cured materials could retain their thermal stability even after exposures. An increase in water absorption after the exposures is observed in most of the materials. The exposures did not affect the laminate materials to an extent of changing their decomposition temperatures.

Based on the observations, it is recommended that the laminate manufacturers should conduct in-house qualification tests on the laminates to assess the variations in material properties due to lead-free soldering exposures. Corrective actions should be taken by tailoring the material constituents or laminate fabrication process conditions for achieving thermally stable laminates. Also, the electronic product manufacturers should gather the information about material constituents from the laminate manufacturers and consider the extent of variations in material properties due to lead-free soldering exposures before making a decision on the selection of appropriate laminates.

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[17] Diamant Y., Marom G., and Broutman L., "The effect of network structure on moisture absorption of epoxy resins", *Journal of Applied Polymer Science*, vol. 26, pp. 3015-3025, 1981.

Center for Advanced Life Cycle Engineering

Effect of Lead-free Soldering on Key Material Properties of FR-4 Printed Circuit Board Laminates

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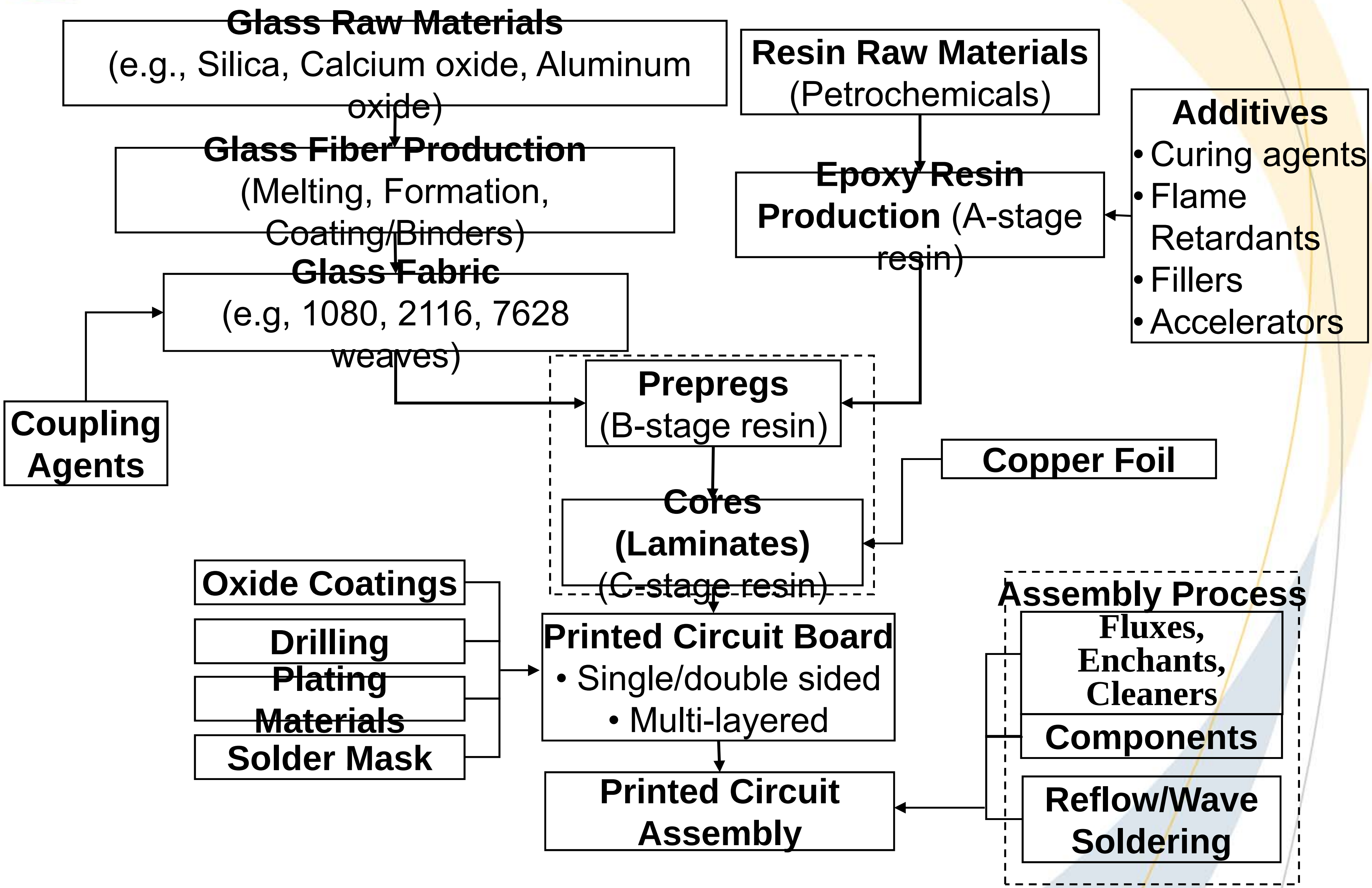
Background and Motivation

- The transition to lead-free soldering of printed circuit boards (PCBs) using solder alloys such as Sn/Ag/Cu has resulted in an increase in peak temperature exposures (by 30-40^{o}C) and longer time above liquidus (by 15-30 seconds) during assembly compared with eutectic Sn/Pb solders [1]
- Rework and repair of assembled circuit boards also contribute to additional high temperature exposures
- The high temperature exposures associated with lead-free soldering can alter the circuit board laminate material properties and can affect the performance and reliability of the PCB and entire electronic assembly
- Knowledge of laminate material properties and their dependence on the material constituents, combined with their possible variations due to lead-free soldering exposures is an essential input in the selection of laminates for appropriate applications

Overview

- Fourteen types of commercially available laminate materials obtained from two suppliers were studied
- Laminate materials were classified on the basis of
  – glass transition temperature (high, mid and low)
  – curing agents (dicyandiamide (DICY) and phenolic)
  – flame retardants (halogenated and halogen-free)
  – fillers (presence or absence)
- Laminate materials were subjected to lead-free soldering exposures
  – 3 reflow cycles (3X R)
  – 6 reflow cycles (6X R)
  – Combination of 2 reflow cycles and 1 wave cycle (2X R + 1X W)
- Key thermo-mechanical, physical and chemical properties of laminates were measured in accordance with appropriate IPC/ASTM/UL test standards before and after lead-free soldering exposures
- Fourier transform infrared (FTIR) spectroscopy analysis and combinatorial property analysis were conducted to investigate the variations in material properties

PCB Fabrication

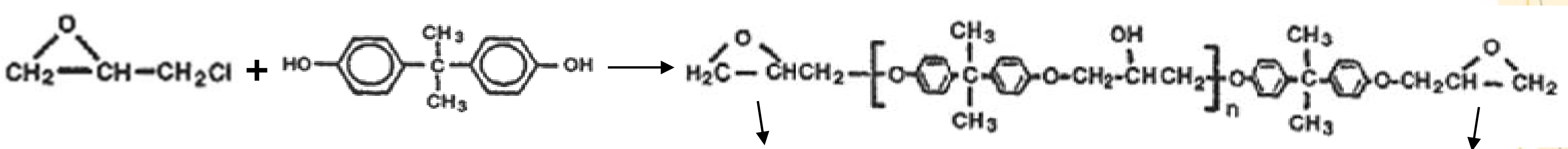


Constituents of FR-4 Laminates

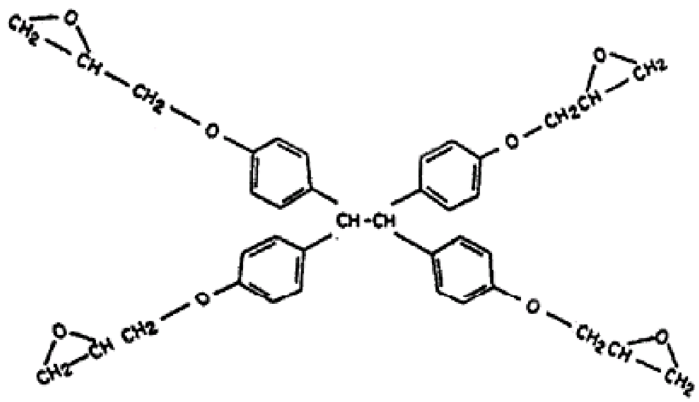
Constituent	Major function(s)	Example material(s)
Reinforcement	Provides mechanical strength and electrical properties	Woven glass (E-grade) fiber
Coupling agent	Bonds inorganic glass with organic resin and transfers stresses across the structure	Organosilanes
Resin	Acts as a binder and load transferring agent	Epoxy (DGEBA)
Curing agent	Enhances linear/cross polymerization in the resin	Dicyandiamide (DICY), Phenol novolac (phenolic)
Flame retardant	Reduces flammability of the laminate	Halogenated (TBBPA), Halogen-free (Phosphorous compounds)
Fillers	Reduces thermal expansion and cost of the laminate	Silica, Aluminum hydroxide
Accelerators	Increases reaction rate, reduces curing temperature, controls cross-link density	Imidazole, Organophosphine

Constituents of FR-4 Laminates
-Resin-

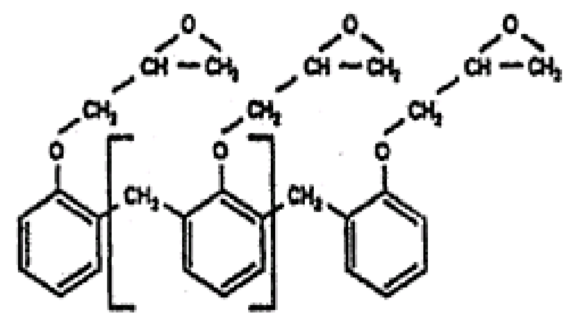
- Diglycidyl Ether of Bisphenol-A (DGEBA) is the epoxy resin used in FR-4 laminates
- DGEBA is derived from the reaction of Epichlorohydrin with Bisphenol-A



Epichlorohydrin **Bisphenol-A** Epoxide **DGEBA (Bi-functional epoxy resin)** Epoxide



Tetra-functional epoxy resin

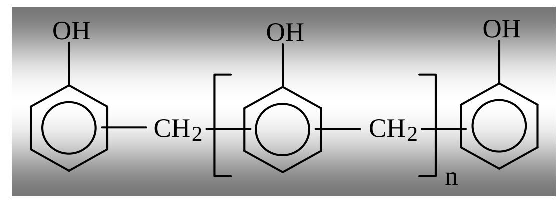
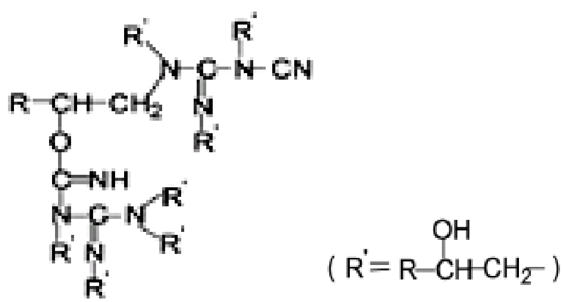
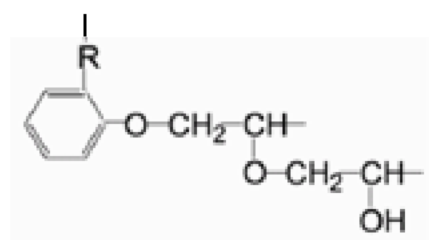


Multi-functional epoxy resin

- The epoxy groups react in subsequent resin polymerization and result in curing of the resin system

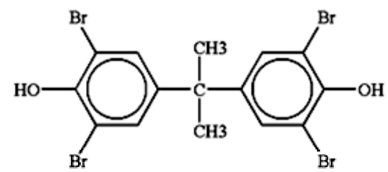
Constituents of FR-4 Laminates

-Curing Agents [7]-

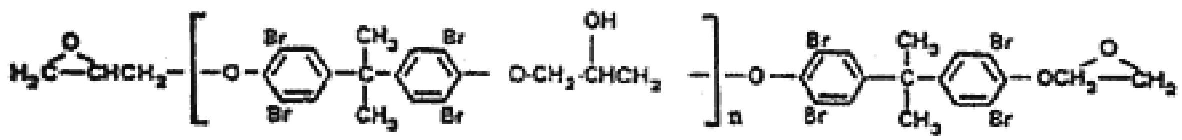
DICY	Phenolic
• **Curing agent:** – dicyandiamide – low molecular weight organic compound $H_2N\overset{NH}{\overset{\Vert}{C}}NHC\equiv N$	• **Curing agent:** – phenol novolac (resin) – high molecular weight organic compound with greater resonating structures 
• **Cured resin system:** – linear aliphatic molecule 	• **Cured resin system:** – Aromatic molecule 

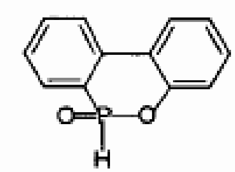
Constituents of FR-4 Laminates

-Flame Retardants-



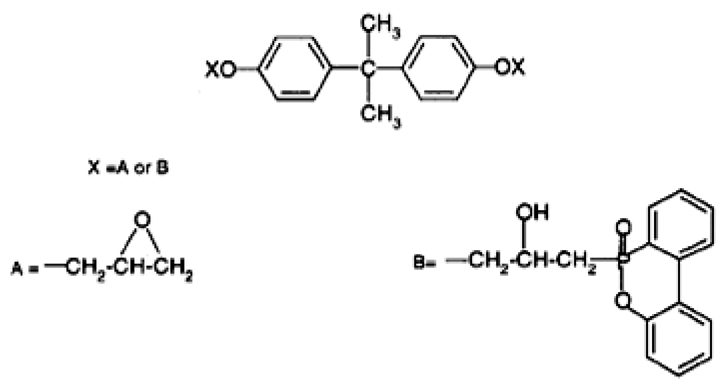
- **Brominated flame retardant [15]:**
  - Tetrabromobisphenol-A (TBBA)
  - Brominated flame retardant epoxy system (DGEBA+TBBA)





DOPO (I)

- **Organo-phosphorus based flame retardant [8]:**
  - 9,10-Dihydro-9-oxa-10-phosphophenanthren-10-oxide (DOPO)
  - Phosphorus based flame retardant epoxy system (DGEBA+DOPO)

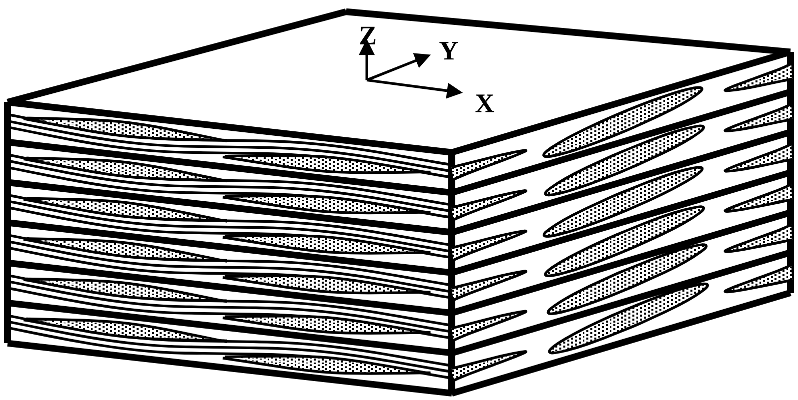


FR-4 Laminate Materials Studied

Supplier	Material ID	Laminate Material Classification			
		Curing agent	Fillers	Halogen-free	Glass transition temperature (T_g)
I	A	DICY	No	No	High T_g (T_g>165°C)
I	B	DICY	Yes	Yes	
I	C1	Phenolic	No	No	
I	C2	Phenolic	Yes	No	
II	D1	Phenolic	No	No	
II	D2	Phenolic	Yes	No	
II	E	Phenolic	Yes	Yes	
I	F	DICY	Yes	Yes	Mid T_g (140°C<T_g<165° C)
I	G1	Phenolic	No	No	
I	G2	Phenolic	Yes	No	
II	H	Phenolic	Yes	No	
II	I	Phenolic	Yes	Yes	
I	J	DICY	No	No	Low T_g (T_g<140°C)
I	K	DICY	Yes	No	

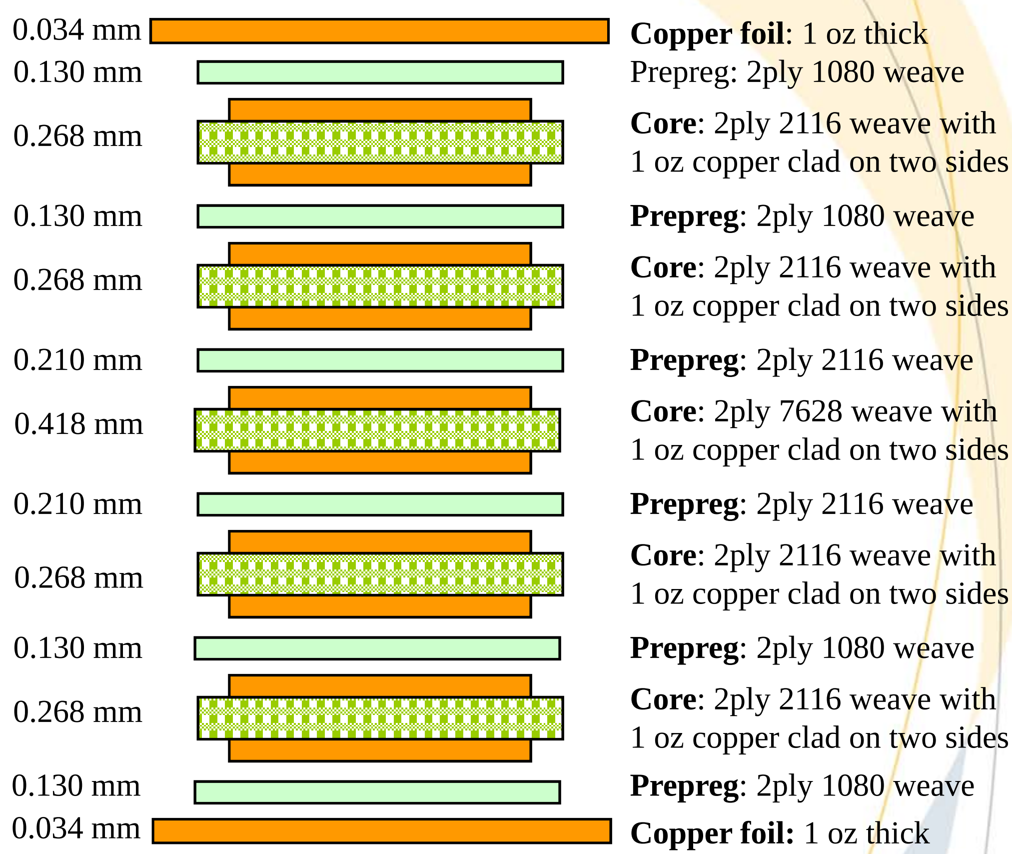
- Material types E and K are marketed for high frequency applications
- The T_g classification is based on the T_g measurement results by DSC equipment

Test Material Construction



6 ply laminate

Total thickness: 1.10 mm

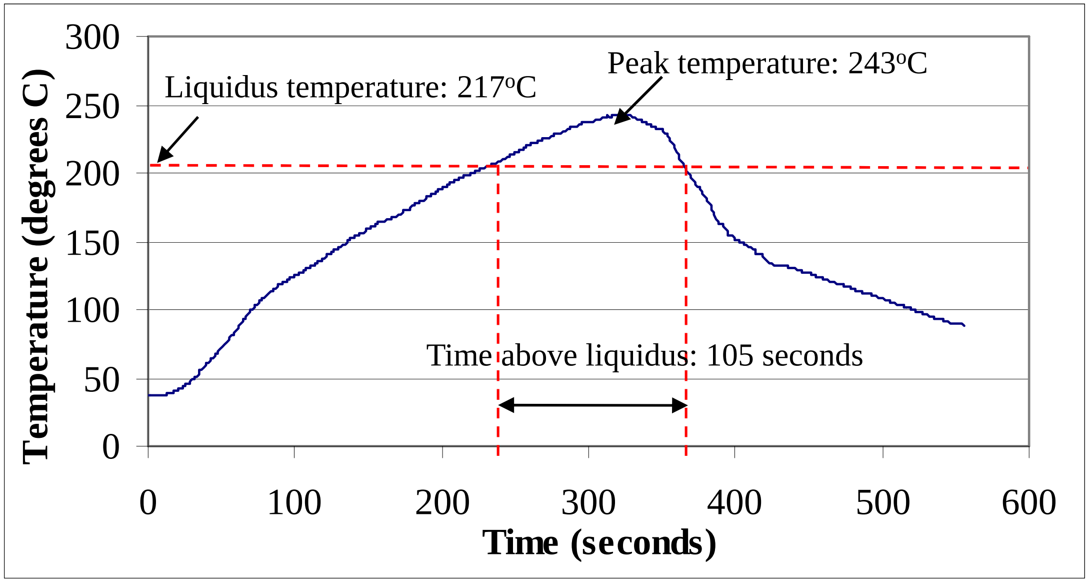


12 layer clad board

Total thickness: 2.50 mm

- Laminates are of 6 ply 7628 weave style (1.10 mm thick, 41% resin content), and were available for all the materials A to K
- Fabricated boards consist of a 12-layered stack up (2.50 mm thick, 53% resin content) with alternative layers of cores and prepregs of 1080, 2116 and 7628 glass weave styles, and were available for materials A, B, C1, C2, G1, J

Lead-free Soldering Exposures

Lead-free reflow exposure	Lead-free wave exposure
 • Average peak temperature: 243°C • Liquidus temperature of Sn96.5/Ag3.0/Cu0.5: 217°C • Time above liquidus: 105 seconds • Time between initial and peak temperatures: 324 seconds	• **Preheat zones:** – Zone 1: 175°C – Zone 2: 199°C • **Wave:** – Lead-free solder (Sn96.5/Ag3.0/Cu0.5) – Wave temperature: 295°C

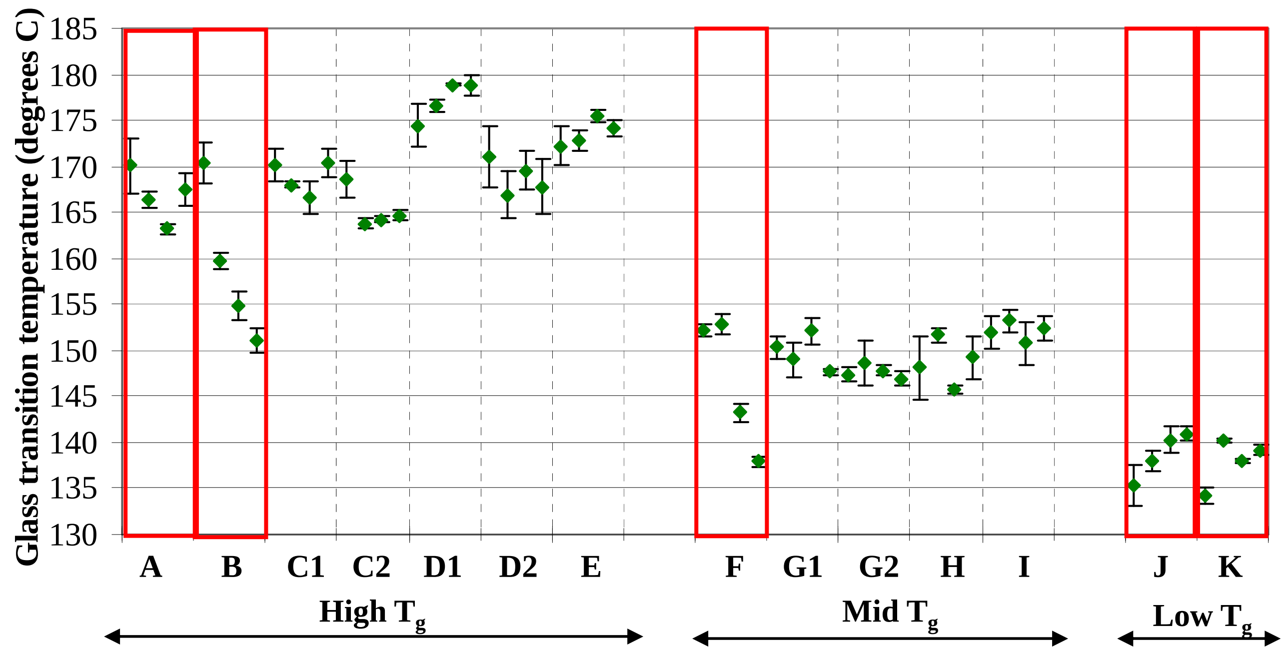
- **Lead-free soldering exposures considered for the study:**
  - 3 reflow cycles (3X R)
  - 6 reflow cycles (6X R)
  - Combination of 2 reflow cycles and 1 wave cycle (2X R + 1X W)

Measurement Matrix

Property	Unit	Test Method	Test Equipment
Glass transition temperature (T_g)	^oC	IPC-TM-650 2.4.25 [9]	Differential scanning calorimeter (DSC)
Coefficient of thermal expansion (CTE: out-of-plane)	ppm/^oC	IPC-TM-650 2.4.24 [10]	Thermo mechanical analyzer (TMA)
Decomposition temperature (T_d)	^oC	IPC-TM-650 2.4.24.6 [11]	Thermogravimetric analyzer (TGA)
Time-to-delamination (T-260)	minutes	IPC-TM-650 2.4.24.1 [12]	Thermo mechanical analyzer (TMA)
Water absorption	%	IPC-TM-650 2.6.2.1 [13]	Micro-balance
Flammability	-	UL 94 V-0 [14]	Bunsen burner/clamp

- All the properties except Time-to-delamination (measured on 12 layer clad board) were measured on the 6-ply laminate structure

Glass Transition Temperature (Tg): Results



- **Definition:** Temperature at which the laminate material transforms from rigid and glass like state to rubbery and compliant state
- **Test method:** IPC-TM-650 2.4.25
- **Equipment:** Differential scanning calorimeter (DSC)
- **Sample weighSt:** 15-20 mg
- **Preconditioning:** 2 hours@105°C
- **Temperature scan:** 25°C to 220°C @ 20°C/minute

#	Curing agent	Fillers	Halogen-free
A	DICY	No	No
B	DICY	Yes	Yes
C1	Phenolic	No	No
C2	Phenolic	Yes	No
D1	Phenolic	No	No
D2	Phenolic	Yes	No
E	Phenolic	Yes	Yes

The sequence of data points shown is:
Control — 3X R — 6X R — 2X R+1X W

#	Curing agent	Fillers	Halogen-free
F	DICY	Yes	Yes
G1	Phenolic	No	No
G2	Phenolic	Yes	No
H	Phenolic	Yes	No
I	Phenolic	Yes	Yes

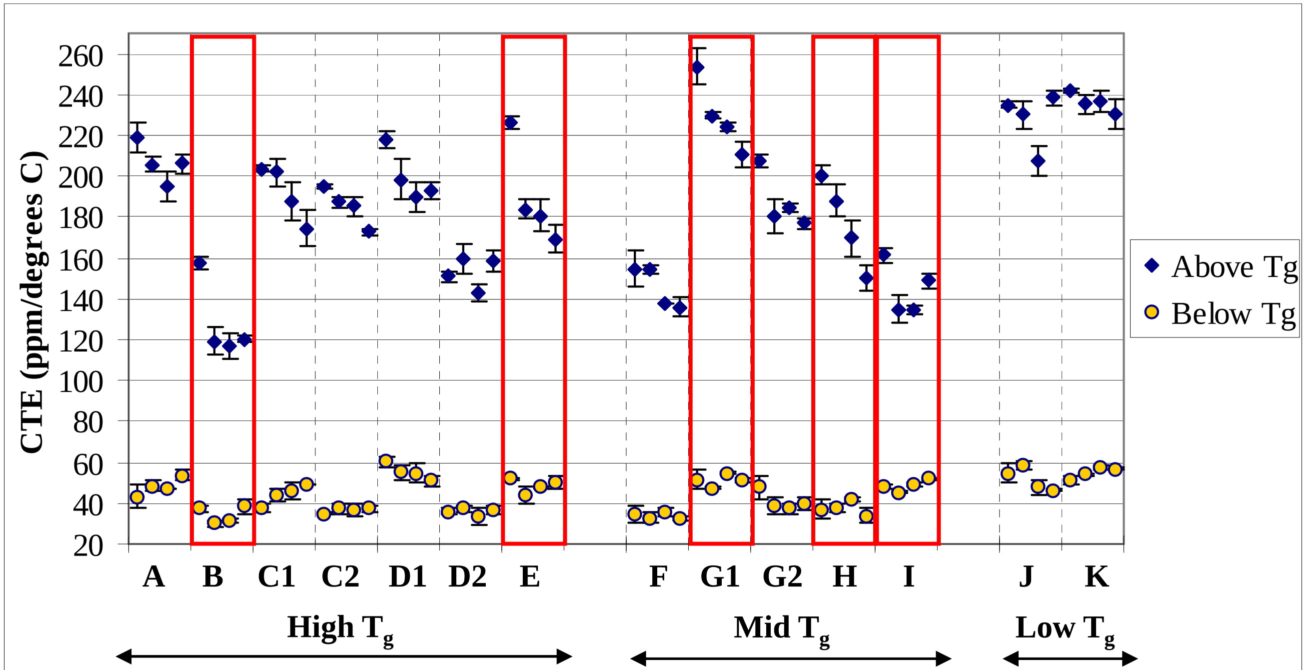
Material types with a T_g variation of greater than 5°C from control		
3X	6X	2X-R+1X-W
B	A, F, B	K, J, F, B

#	Curing agent	Fillers	Halogen-free
J	DICY	No	No
K	DICY	Yes	No

Glass Transition Temperature (T_g): Discussion

- **Control (pre-exposure) results:**
  - Laminates have similar T_g range irrespective of type of curing agent, flame retardant and presence or absence of fillers
- **Post-exposure results:**
  - Phenolic cured materials have relatively stable T_g with a variation of less than 5°C due to lead-free soldering exposures
  - Materials that underwent a variation of greater than 5°C were all DICY cured (A, B, F, J and K)
  - A decrease in T_g was observed in high and mid T_g DICY cured materials (A, B, F) whereas an increase in T_g was observed in low T_g DICY cured materials (J, K)

Coefficient of Thermal Expansion: Results: Out-of-Plane CTE



- **Definition:** CTE of a material is the fractional change in linear dimensions with temperature, expressed in ppm/°C
- **Test method:** IPC-TM-650 2.4.24
- **Equipment:** Thermomechanical analyzer (TMA)
- **Sample dimensions:** 7 x 7 mm
- **Preconditioning:** 2 hours@105°C
- **Temperature scan:** 25°C to 250°C @ 10°C/minute

#	Curing agent	Fillers	Halogen-free
A	DICY	No	No
B	DICY	Yes	Yes
C1	Phenolic	No	No
C2	Phenolic	Yes	No
D1	Phenolic	No	No
D2	Phenolic	Yes	No
E	Phenolic	Yes	Yes

The sequence of data points shown is:
Control — 3X R — 6X R — 2X R+1X W

#	Curing agent	Fillers	Halogen-free
F	DICY	Yes	Yes
G1	Phenolic	No	No
G2	Phenolic	Yes	No
H	Phenolic	Yes	No
I	Phenolic	Yes	Yes

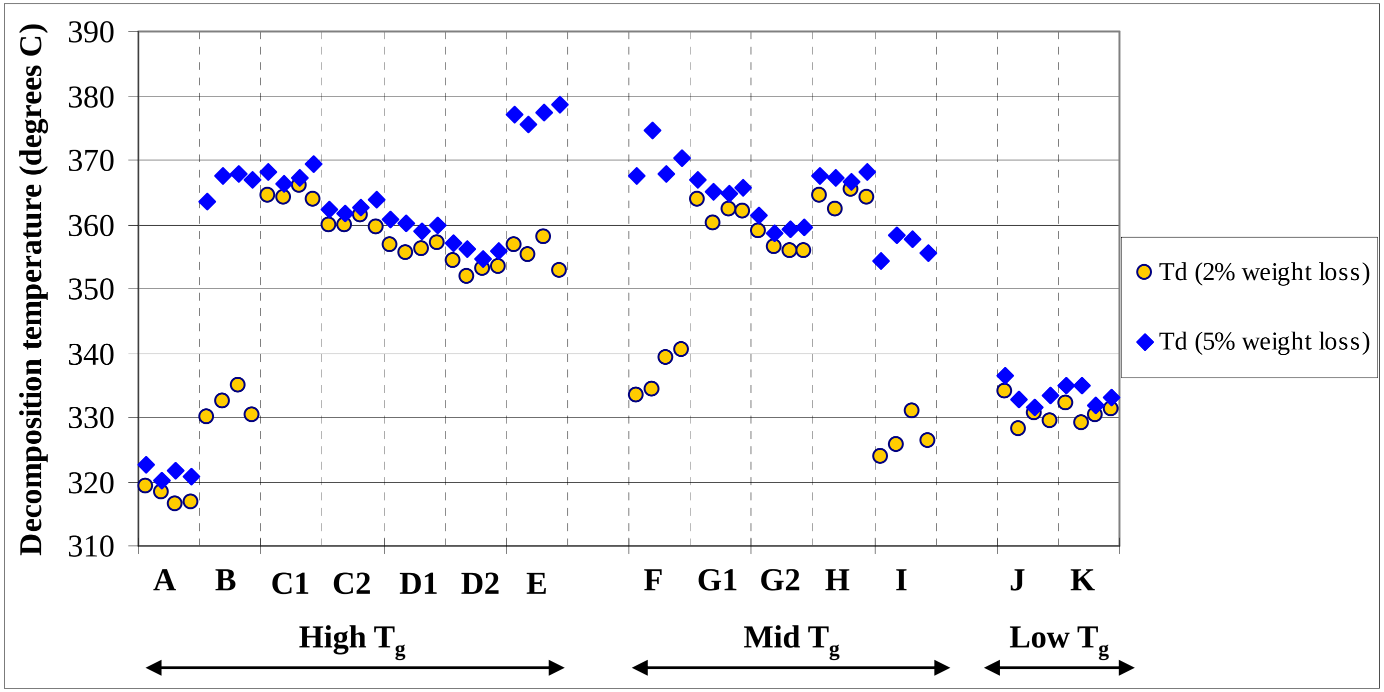
Material types with a CTE variation of greater than 15% from control		
3X	6X	2X-R+1X-W
I, E, B	H, I, E, B	G1, B, E, H

#	Curing agent	Fillers	Halogen-free
J	DICY	No	No
K	DICY	Yes	No

Coefficient of Thermal Expansion: Discussion Out-of-Plane CTE

- Control (pre-exposure) results:
  - High Tg laminate (A) has lower CTE compared to low Tg laminate (J) with similar constituents (DICY cured with halogenated flame retardant)
    - High Tg epoxy systems have higher cross-linking density compared to low Tg
  - The effect of type of curing agent was not observed in the CTE results
  - Filled materials (D2, G2) have lower CTE values compared to unfilled materials (D1, G1) due to lower epoxy content
  - Halogen-free materials (B, I) have lower CTE values than halogenated materials (A, H) with similar constituents [5]
- Post-exposure results:
  - A decrease in above Tg CTE due to lead-free soldering exposures was observed in most of the materials
  - A reduction of about 25% in above Tg CTE was observed in material B, whereas a variation of more than 15% was observed in below Tg CTE of materials B, C1 and G2

Decomposition Temperature (Td): Results



- **Definition:** T_d is the temperature at which a resin system irreversibly undergoes physical and chemical degradation with thermal destruction of the cross-links, resulting in weight loss of the material
- **Test method:** IPC-TM-650 2.4.24.6
- **Equipment:** Thermo-gravimetric analyzer (TGA)
- **Sample weight:** 8-20 mg
- **Preconditioning:** 24 hours@110°C
- **Temperature scan:** 25°C to 400°C @ 10°C/minute

#	Curing agent	Fillers	Halogen-free
A	DICY	No	No
B	DICY	Yes	Yes
C1	Phenolic	No	No
C2	Phenolic	Yes	No
D1	Phenolic	No	No
D2	Phenolic	Yes	No
E	Phenolic	Yes	Yes

The sequence of data points shown is:
Control — 3X R — 6X R — 2X R+1X W

#	Curing agent	Fillers	Halogen-free
F	DICY	Yes	Yes
G1	Phenolic	No	No
G2	Phenolic	Yes	No
H	Phenolic	Yes	No
I	Phenolic	Yes	Yes

#	Curing agent	Fillers	Halogen-free
J	DICY	No	No
K	DICY	Yes	No

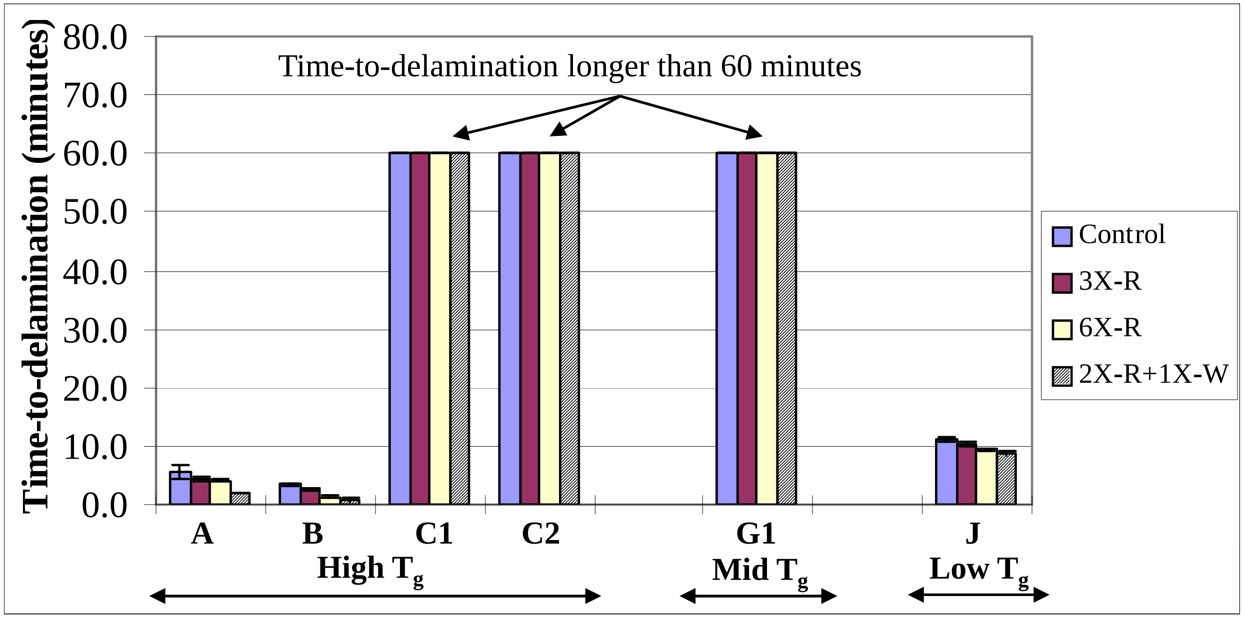
Decomposition Temperature (Td): Discussion

- **Control (pre-exposure) results:**
  - Low T_g material (J) that is DICY cured has higher T_d compared to high T_g DICY cured material (A) with similar other constituents [3]
  - Amongst the halogenated materials, phenolic cured materials (G1, C1) could withstand higher temperatures before 2% and 5% weight loss compared to their DICY cured counterparts (A, J)
    - DICY cured materials have linear aliphatic molecular bonds with amine linkages compared to thermally stable aromatic bonds with ether linkages in phenolic cured materials [5], [7]
  - Laminates with fillers (C2, D2, G2) have lower T_d compared to their counterparts without fillers (C1, D1, G1)
    - Inorganic fillers such as silica or alumina accelerate the thermal decomposition process by lowering the activation energy required for decomposition [16], [17], [18]

Decomposition Temperature (Td): Discussion

- **Control (pre-exposure) results: (continued)**
  - Halogen-free material that is DICY cured (B) has higher T_d compared to the halogenated DICY cured material (A). On the contrary, phenolic cured halogen-free material (I) has lower T_d compared to its halogenated counterpart (H)
  - Irrespective of the type of curing agent, halogenated resin systems (A, H) underwent degradation from 2% to 5% within a narrow temperature range, which was not observed in halogen-free systems (B, I). Similar findings were observed with materials E and F both of which are halogen-free.
- **Post-exposure results:**
  - Relationship of curing agents, fillers, and flame retardants with the decomposition temperature for the control samples remained the same after lead-free soldering exposures
  - A maximum variation of $7^{o}C$ in decomposition temperature due to the exposures was observed

Time-to-Delamination (T-260): Results



#	Curing agent	Fillers	Halogen-free
A	DICY	No	No
B	DICY	Yes	Yes
C1	Phenolic	No	No
C2	Phenolic	Yes	No

#	Curing agent	Fillers	Halogen-free
G1	Phenolic	No	No

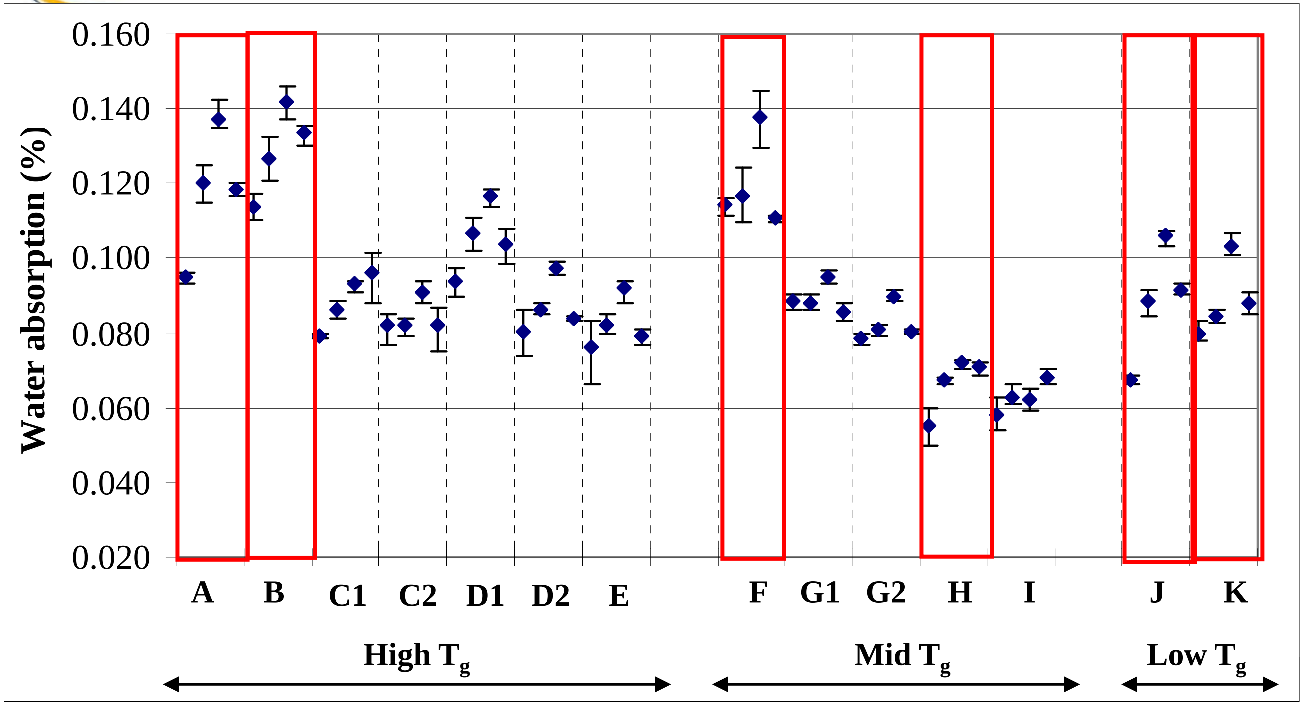
#	Curing agent	Fillers	Halogen-free
J	DICY	No	No

- **Definition:** T-260 is the time taken by a fabricated board to delaminate (defined as the separation between layers of prepregs and copper clad cores in a multilayered structure), when exposed to a constant temperature
- **Test method:** IPC-TM-650 2.4.24.1
- **Equipment:** Thermomechanical analyzer (TMA)
- **Sample dimensions:** 7 x 7 mm
- **Preconditioning:** 2 hours @105°C
- **Temperature scan:** 25°C to 260°C @ 10°C/minute and hold until delamination
- 12-layered bare boards

Time-to-Delamination (T-260): Discussion

- **Control (pre-exposure) results:**
  - DICY cured materials (A, B, J) have lower time-to-delamination compared to phenolic cured materials (C1, C2, G1) irrespective of T_g
  - Low T_g DICY cured material (J) has higher T-260 compared to the high T_g DICY cured materials (A, B) [3]
  - The effect of type of flame retardant and presence of fillers is not as prominent as that of curing agent
- **Post-exposure results:**
  - Lead-free soldering exposures tend to lower the time-to-delamination of materials A, B, and J, all of which are DICY cured
  - Materials C1, C2 and G1 which are phenolic cured did not delaminate up to 60 minutes even after exposures

Water Absorption: Results



- **Definition:** Water absorption is a measure of the amount of water absorbed by laminate materials when immersed in distilled water for 24 hours at room temperature
- **Test method:** IPC-TM-650 2.6.2.1
- **Sample dimensions:** 50 mm x 50 mm
- **Preconditioning:** 1 hour@110°C

#	Curing agent	Fillers	Halogen-free
A	DICY	No	No
B	DICY	Yes	Yes
C1	Phenolic	No	No
C2	Phenolic	Yes	No
D1	Phenolic	No	No
D2	Phenolic	Yes	No
E	Phenolic	Yes	Yes

The sequence of data points shown is:
Control — 3X R — 6X R — 2X R+1X W

#	Curing agent	Fillers	Halogen-free
F	DICY	Yes	Yes
G1	Phenolic	No	No
G2	Phenolic	Yes	No
H	Phenolic	Yes	No
I	Phenolic	Yes	Yes

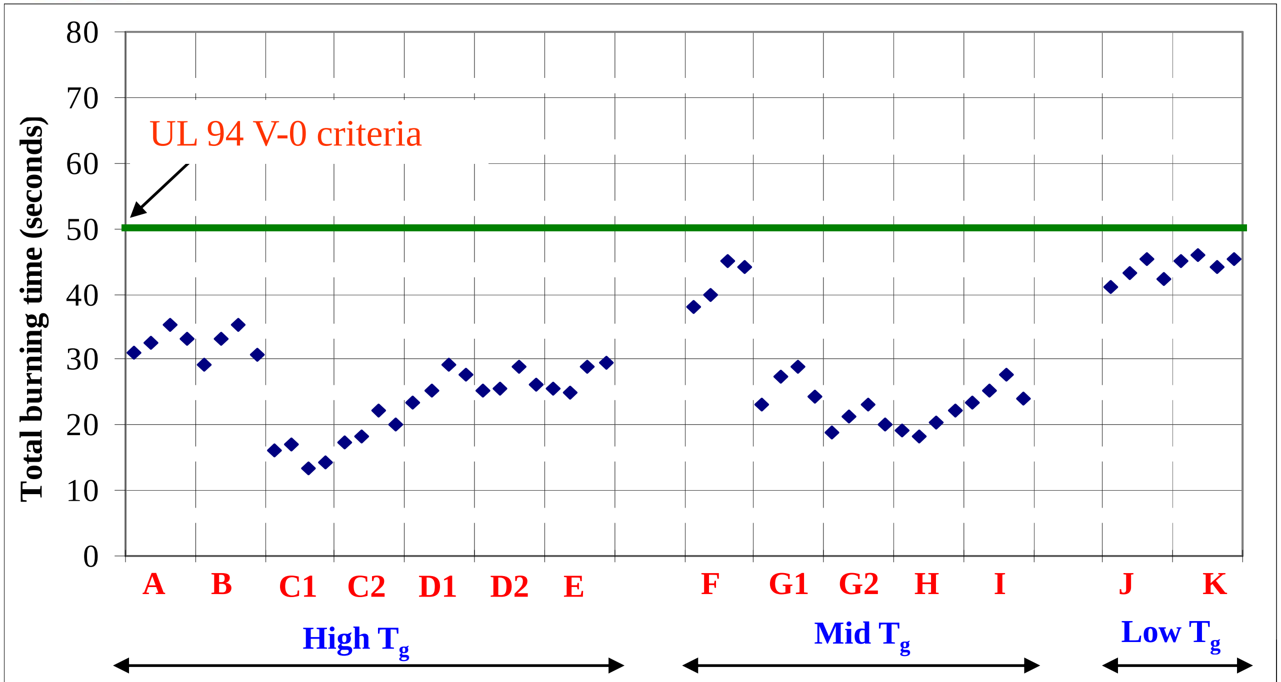
Material types with a variation of greater than 25% in water absorption from control		
3X	6X	2X-R+1X-W
A, J	F, B, K, H, A, J	A, H, J

#	Curing agent	Fillers	Halogen-free
J	DICY	No	No
K	DICY	Yes	No

Water Absorption: Discussion

- **Control (pre-exposure) results:**
  - High T_g materials (A, B) have higher water absorption compared to low T_g materials (J, K) with similar constituents
    - Higher free volume due to higher cross-linking density is available in the high T_g materials compared to low T_g materials [19]
  - DICY cured materials (A, F) are more hydrophilic compared to phenolic cured materials (C1, I)
    - DICY cured systems have highly polar bonds compared to phenolic cured systems [7]
  - The effect of presence of fillers and type of flame retardant is not as prominent as that of type of curing agent
- **Post-exposure results:**
  - An increase in water absorption due to lead-free soldering exposures was observed for most of the materials

Flammability: Results



- **Definition:** Flammability is the measure of material's tendency to extinguish the flame once the specimen has been ignited and separated from the flame source
- **Test method:** UL 94 (V-0)
- **Sample dimensions:** 127 x 12.7 mm
- **Preconditioning:** 48 hours@ 25°C, 50% RH
- Total burning time = sum of burning times during two flame applications per sample

Parameter	V-0
Time of burning per specimen after either application of test flame	≤ 10 seconds
Total burning time for the 10 flame applications for a set of 5 specimens	≤ 50 seconds

#	Curing agent	Fillers	Halogen free
A	DICY	No	No
B	DICY	Yes	Yes
C1	Phenolic	No	No
C2	Phenolic	Yes	No
D1	Phenolic	No	No
D2	Phenolic	Yes	No
E	Phenolic	Yes	Yes

The sequence of data points shown is:
Control — 3X R — 6X R — 2X R+1X W

#	Curing agent	Fillers	Halogen free
F	DICY	Yes	Yes
G1	Phenolic	No	No
G2	Phenolic	Yes	No
H	Phenolic	Yes	No
I	Phenolic	Yes	Yes

#	Curing agent	Fillers	Halogen free
J	DICY	No	No
K	DICY	Yes	No

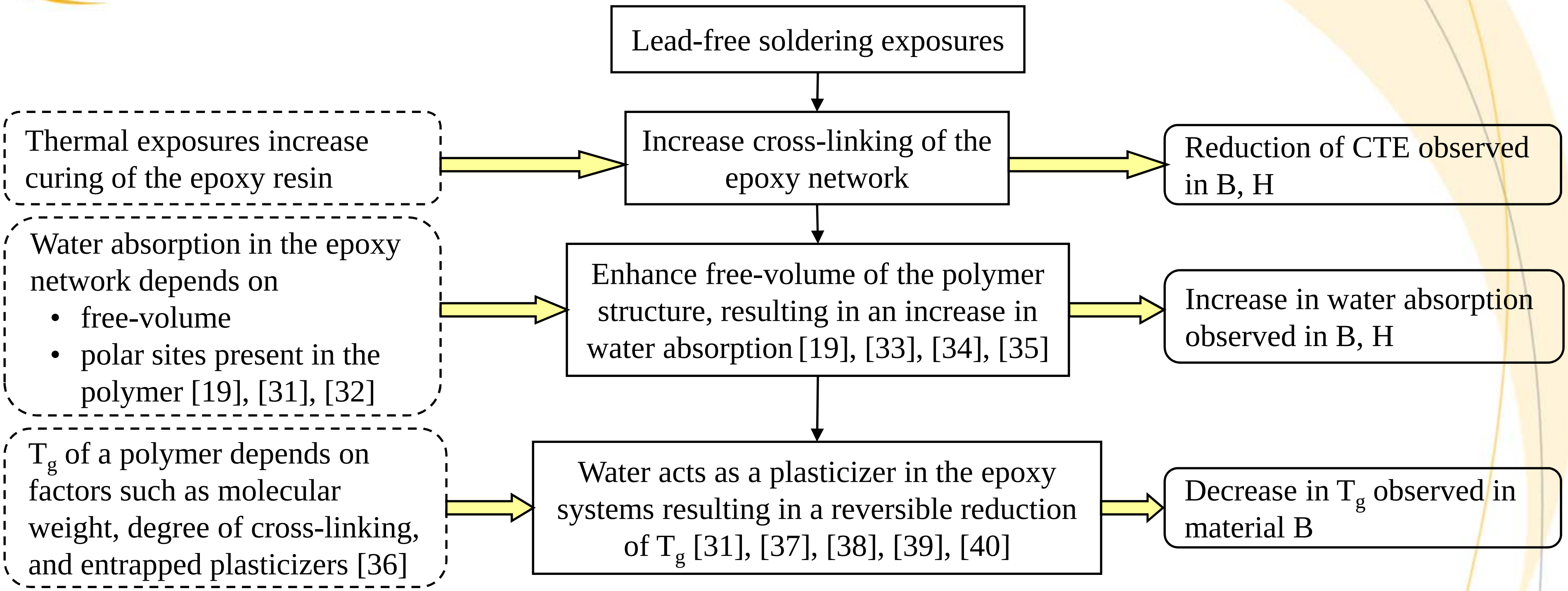
Flammability: Discussion

- **Control (pre-exposure) results:**
  - UL 94 V-0 flammability criteria are satisfied by all the samples
  - DICY cured materials (A, B, F, J, K) have longer burning times compared to phenolic cured systems irrespective of T_g, type of flame retardant and presence of fillers
    - Phenolic cured systems are highly aromatic structures that can produce a substantial amount of char (carbonaceous non-volatile residue that results during decomposition of polymer) which forms a protective boundary layer between the flame front and the combustible material reducing the flame propagation [20]
    - Also, the flammable mixture of phenolic cured systems could still contain higher energy bonds compared to that of DICY cured systems
  - The effects of presence of fillers and type of flame retardant are not as prominent as that of the curing agent
- **Post-exposure results:**
  - The laminate materials still complied with UL 94 V-0 flammability criteria after lead-free soldering exposures
  - An increase in combustion times was observed in most of the laminate materials with the exposures

Analysis of Results

- High temperature exposures associated with lead-free soldering resulted in a noticeable variation in the material properties of some of the laminates
- The exposures could possibly result in cleavage of bonds
  - In the polymer backbone leading to a 'degraded' structure, or
    - Results in a change in the material structure due to loss of certain functional groups [15]
  - At the chain ends of the epoxy system leading to an 'enhanced-cure' structure
    - Results in an increase in the cross-linking density of the epoxy matrix
- Either of the mechanisms could result in variations in the laminate material properties
- Fourier transform infrared spectroscopy (FTIR) analysis was performed (in reference to [22]-[30]), to verify the possible degradation in the epoxy structure and combinatorial property analysis was performed to verify the enhanced-cure structure
- FTIR results did not show any noticeable change in the wave numbers corresponding to the functional groups in the spectra between control and 6X reflowed samples. This indicates that the variation in material properties could possibly be attributed to an increase in cross-linking of the resin system than to the degradation of the polymer network.

Combinatorial Property Analysis



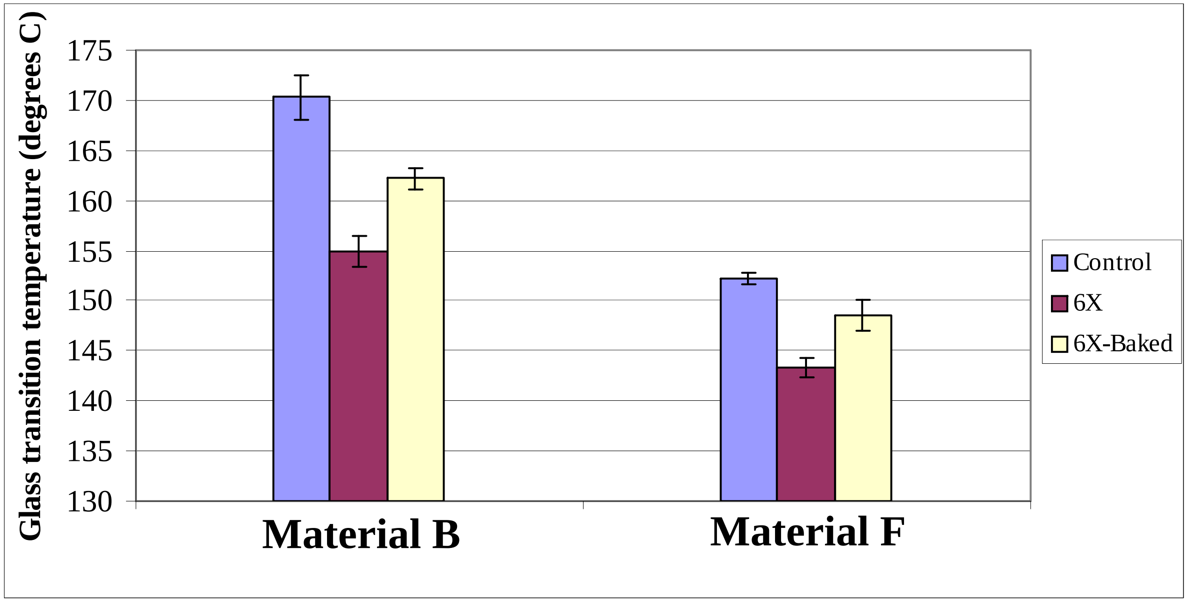
Property	Material ID	Observed variation*	Magnitude of variation*
CTE (out-of-plane)	B, H	Decrease	>15%
Water absorption	B, H	Increase	>25%
T_g	B	Decrease	>5°C

#	Supplier	T_g	Curing agent	Fillers present	Halogen free
B	I	170°C	DICY	Yes	Yes
H	II	148°C	Phenolic	Yes	No

- Variation refers to the difference of measurement results between control and 6X reflowed samples
- Low T_g materials (J, K) are an exception to this analysis as the exposures resulted in an increase in their water absorption and also T_g

Combinatorial Property Analysis

- T_g of the 6X reflowed samples of material B was measured after baking for 24 hours at 115°C [41]



- T_g reduction between control and 6X reflowed samples of material B decreased from 15°C to 8°C
- T_g of material F (mid T_g DICY cured) was also measured after baking for 24 hours at 110°C and a decrease in the reduction of T_g between control and 6X reflowed samples was observed
- Overall, the variation in properties due to lead-free soldering exposures could be related to the degree of cross-linking and the extent of water absorption in the exposed samples

Conclusions

- Laminate properties are determined by the constituents such as type of epoxy, curing agents, fillers and flame-retardants present in the material

Factor	Conclusions
T_g	• High T_g laminates have lower out-of-plane CTE and flammability compared to low T_g materials • Low T_g laminates have higher T_d, T-260 and lower water absorption compared to high T_g materials with similar constituents
Curing agent	Although DICY and phenolic cured laminates can have similar T_g, out-of-plane CTE; a higher T_d, T-260 and lower water absorption, flammability was observed in the phenolic cured materials compared to similar DICY cured counterparts
Filler	The T_g, T_d, T-260, water absorption, and flammability of laminate materials does not have a strong dependence on fillers, whereas presence of fillers lower the out-of-plane CTE of laminates
Flame retardant	Halogen-free and halogenated materials can have similar T_g, T-260, water absorption and flammability whereas lower out-of-plane CTE was observed in halogen-free laminates compared to halogenated laminates

- Lead-free soldering exposures result in
  - decrease in the T_g, out-of-plane CTE, and T-260
  - increase in the water absorption and flammability
  - minimal effect on the decomposition temperature (T_d) of the laminate materials

Recommendations and Contributions

- **Recommendations**
  - Laminate manufacturers should conduct in-house qualification tests to assess the variations in laminate material properties due to lead-free soldering exposures and take corrective actions by fine tuning the material constituents and/or laminate fabrication process conditions for achieving thermally stable laminates.
  - Electronic product manufacturers should gather the information about laminate material constituents, and the possible extent of variations in material properties due to lead-free soldering exposures, from the laminate manufacturers before making a decision on the selection of appropriate laminates.
- **Contributions**
  - Characterized a range of commercially available FR-4 laminates by assessing the influence of material constituents on thermo-mechanical, physical, and chemical properties. The analysis of characterization provides a guideline for the selection of laminates for appropriate applications.
  - This is the first published study demonstrating the effects of lead-free soldering exposures on FR-4 laminate material properties.
  - Illustrated the laminate material types that are most affected by lead-free soldering exposures.

Thank you !

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