Lead Free Soldering: Impact on Laminates Requirements

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Abstract

Different legislations or draft directives target the restriction or the ban of the use of lead in the world. The law banning lead-bearing electronic products (with a few exemptions) in the European Union (EU) will be implemented in July 2006. China is considering adopting a similar law soon. In addition to the legislative pressure to reduce lead exposure, marketing rewards also explains the trend to lead-free solder, although usually more expensive. Several Japanese manufacturers have already commercialized products soldered with lead-free alloys. Finally technical requirements such as higher in-use temperature in automotive applications tend to favor higher temperature melting point solders. Consequently, it is expected that lead-free soldering will become the new standard in the future.

The change to higher temperature solder alloys will directly affect the reflow temperature profiles. In parallel, the complexity of the boards is increasing, leading to thicker multilayer structures. Laminates will thus be submitted to higher temperature for longer time through multiple reflow cycles. It is critical to understand how this translates into new technical requirements for the laminates, especially thermal resistance. Results suggest that conventional FR-4 resins might still be suitable for standard FR-4 applications that need only a few lead-free reflow cycles. When the number of cycles increases, enhanced resin systems must be considered to avoid in-process failure. Highly thermo-resistant products are suitable for complex multilayer build-up or for applications targeting high in-use temperature. In addition to thermal stability, other key laminate parameters are electrical properties, adhesion, toughness and coefficient of thermal expansion (CTE).

This paper also highlights new facets of the impact of lead-free soldering on the laminate requirements. The thermal stability data of various epoxy systems are described and related to specific applications needs. We propose a complete portfolio of epoxy systems available worldwide, from conventional FR-4 resins to highly thermo-resistant systems, halogenated or halogen-free, with standard or enhanced dielectric constants. Some systems are very suitable for filler loading, leading to low CTE laminates.

Introduction

Lead-free soldering is expected to become the new standard in the future. Different reasons explain this trend. First, different legislations or draft directives target the restriction or the ban of the use of lead in the world. The major ones are the Waste of Electrical and Electronic Equipments (WEEE) and the Restriction of Hazardous Substances (RoHS) Directives in the European Union (EU). The initial efforts of reducing the content of specific hazardous substances in the waste stream were not sufficient. The EU has decided to further restrict the incorporation of these hazardous substances in electronic products by enacting the RoHS Directive. From July 1, 2006, products that do not comply with these directives cannot be placed on the EU market. For instance, no more than 0.1% of lead shall be tolerated by weight of homogeneous material, e.g. which cannot be mechanically disjointed into different materials. Some exemptions apply however, such as automotive and industrial electronics, computing and communication infrastructure, medical and military electronics. Second, marketing rewards for “green” laminates also explains the trend to lead-free solder, although usually more expensive. This is one of the reasons why lead-free soldering was implemented very early in Japan. Third, technical requirements such as higher in-use temperature tend to favor higher temperature melting point solders. Conventional lead-based alloys sometimes show limitations due to extensive creep at in-use temperature.

The transition to lead-free soldering should be relatively smooth. The overall implementation to lead-free soldering by geographic areas is shown in Figure 1. The implementation forecast proposed in this paper has been developed based on the information collected in different sources, including several reports from Prismark Partner LLC (see the “References” section for details).

The lead-free implementation should reach about 60% globally in 2008, in a total market size of ca. $ 1250 Bn. Very different situations should be observed in the various geographic areas. The implementation should be completed in Europe and Japan at this date (respective market size ca. $ 240 Bn and $ 120 Bn), while it should remain in progress in Americas and in Asia (respective market size ca. $ 440 Bn and $ 450 Bn), even beyond 2010.

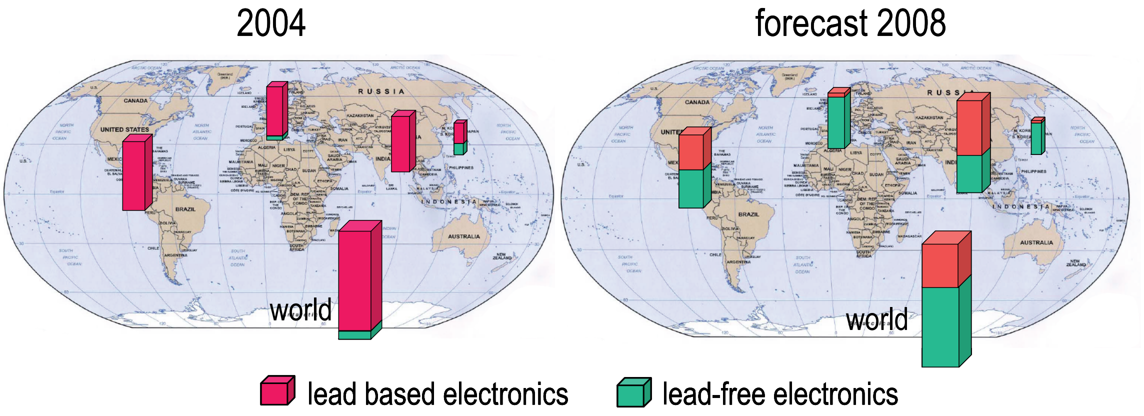


Figure 1 - Implementation to lead-free Soldering by Geographic Areas

The soldering temperatures will increase with lead-free solders because most of the lead-free solder alloys melt at higher temperature than that of the eutectic SnPb solder. The industry tends to recommend SAC alloys, i.e. SnAgCu alloys. The exact composition may vary but SAC alloys usually contain 2.5-4.0 % silver and 0.5-0.8 % copper. The change to higher temperature solder alloys will directly affect the temperature profiles for reflow soldering, wave soldering, rework and repair. Typical lead-free reflow profiles will reach peak temperature of 245°C to 265°C, while de-soldering, rework and repair will reach peak temperature above 300°C for a few seconds. There exist some solder alloys with lower melting points, such as SnBi or SnIn alloys. They can be used as drop-in replacements to lead-based alloys. These are very suitable when temperature-sensitive components are attached to the board.

In addition to the higher soldering temperature, there is a general trend toward higher complexity of the boards, leading to thicker multilayer structures. Print circuit boards (PCB) will thus be submitted to higher temperature for longer time through multiple reflow cycles.
Consequently the laminates used to build lead-free PCB will face new challenges. They will have to fulfill minimum requirements on several key properties:[1,2]

- Thermal stability, defined by the temperature of decomposition, Td and the time to delamination at 288°C, T-288. It especially controls catastrophic failure during processing (blistering and delamination). It impacts overall in-use reliability as well.
- Coefficient of thermal expansion in the z-direction (perpendicular to the laminate surface), z-CTE. It plays a major role in through-holes reliability (mismatch between the laminate CTE and the copper CTE of the plated through-holes).
- Glass transition temperature, Tg. It improves interconnect reliability (impact on CTE).

The latest IPC proposed specifications for electrical laminates in lead-free solder applications (as of October 2005) are summarized in Table 1. The typical properties of a conventional high Tg FR-4 system are given as a reference. Most of the proposed specifications remain similar to the existing ones, except for the upgrade in thermal stability required for higher soldering temperature. The specifications on z-CTE are similar for the filled and the unfilled systems. z-CTE before Tg, $\alpha 1$ must be lower than 60 ppm/K and z-CTE after Tg, $\alpha 2$ lower than 300 ppm/K, for all products. The average expansion in the z-direction between 50°C and 260°C must be lower than 4.0% for mid Tg products and lower than 3.5% for high Tg products.

Table 1 - IPC Proposed Specifications for Electrical Laminates in Lead-free Solder Applications

IPC Specification Number	Filler	Cure	Tg (°C)	Td (°C)	T260 (min)	T288 (min)
B4101/121 – Mid Tg	No	Not specified	110 – 150	310	30	5
B4101/101 – Mid Tg	Yes	Not specified	110 – 150	310	30	5
B4101/124 – High Tg	No	Non dicy	150 – 200	330	30	5
B4101/99 – High Tg	Yes	Non dicy	150 – 200	330	30	5
Std High Tg FR-4	*No*	*Dicy*	*170 – 175*	*295 – 305*	*5 – 10*	*0 – 1*

In addition to these critical thermo-mechanical properties, the laminates must maintain sufficient toughness and adhesion to prevent the formation of in-process defects (cracking, delamination) that could lead to reliability issues.[3] This is especially important when filler is used to lower z-CTE. Inter-laminar delamination and copper peel strength tend to be lower than the neat resin system. It is consequently recommended to use resins with good filler acceptance, which depends on multiple parameters such as the chemical structure of the polymer backbone.

This paper aims to provide some experimental data related to the new requirements for lead-free soldering applications. The relevance of the different measurements (e.g. Tg, Td, T-288, z-CTE) is discussed. Correlation is proposed between the multiples thermal performance tests. Finally the performance envelopes of the various epoxy resins systems used to produce PCB (i.e. conventional FR-4, filled systems, high thermal performances brominated resins, halogen-free resins) are compared and correlated to the specific applications needs.

Experimental

The glass transition temperature Tg was measured by differential scanning calorimetry using a Mettler Toledo DSC822e, equipped with the sample robot TS0801RO and connected to a personal computer. Runs were performed with a heating ramp of 20°C/min, in nitrogen. Tg was determined by the transition midpoint, following the IPC TM-650-2.4.25C method. The typical experimental error was ± 1°C.

The thermo-mechanical analyzer was a TMA/SDTA840 from Mettler Toledo connected to a personal computer. All measurements were performed in N_2. The time to delamination method was performed according to IPC TM-650-2.4.24.1. The typical experimental error was ± 1 min.
The coefficient of thermal expansion in the z direction z-CTE (perpendicular to the laminate surface) was done according to IPC TM-650-2.4.24C. The typical experimental error was ± 10%.

We used a thermo-gravimetric analyzer TGA2950 from TA Instruments, fitted with an auto-sampling device and connected to a personal computer. TGA was operated under nitrogen flow (except otherwise mentioned, i.e. in air). The decomposition temperature Td was measured according to IPC-TM-650-2.3.40, with a heating ramp of 10°C/min (except otherwise mentioned, i.e. 5°C/min). Td was determined at 5% weight loss (except otherwise mentioned, i.e. 1%, 2%, or 10% weight loss). The typical experimental error was ± 1°C.

Results and Discussion

Thermo-Gravimetry Analysis (TGA)

Thermo-Gravimetry Analysis (TGA) was used in dynamic mode (heating ramp) to measure the degradation temperature (Td). The IPC specifications call for Td measurements determined at 5% weight loss. It has been observed that the internal pressure from the decomposition products is sufficient to cause damage in the laminate (delamination, blister) at much lower weight loss.[4] Consequently we evaluated the change of Td when it was determined at different weight losses, i.e. 1%, 2%, 5%, and 10% weight loss. A typical TGA plot is shown in Figure 2. The Td results obtained the different weight losses were then plotted as a function of Td measured at 5% weight loss, $Td^{5\%}$, as displayed in Figure 3.

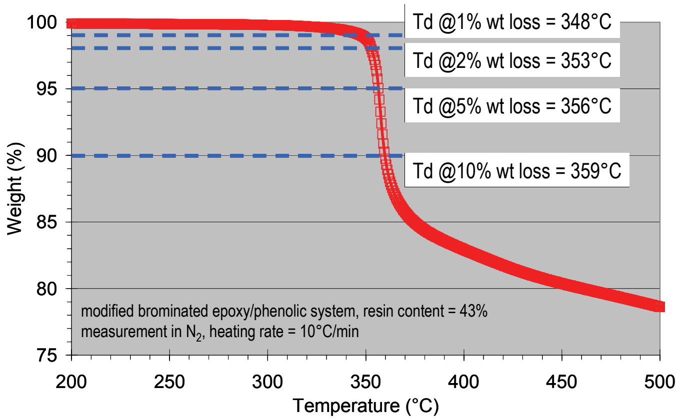


Figure 2 - Typical TGA Curve

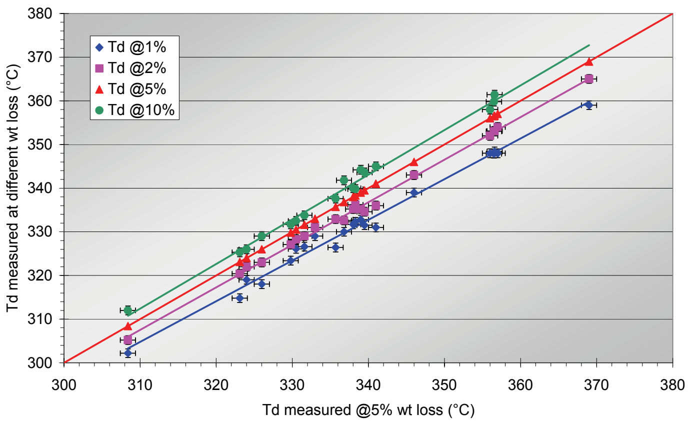


Figure 3 - Td Measured at Different Weight Losses

For most of the brominated epoxy resins cured with phenolic hardeners, the decomposition profile was very sharp. As seen in Figure 2, the laminate was stable up to high temperature without any significant weight loss. Very limited weight loss (<< 0.5 wt%) can be observed sometimes at low temperature (typically in the range of 100 – 150 °C) if the laminate has not been dried prior to the TGA measurement. This was due to moisture absorbed during storage and did not influence the overall thermal stability of the laminate. When temperature reached the onset temperature, the resin started to degrade and to release low molecular weight by-products,[5] such as HBr and brominated phenols, propane, acetone, and phenol. The onset temperature strongly depended on the chemical structure of the network, including the nature of the epoxy resin, the type of hardener, and the presence of specific additives. In most of the cases however, most of the degradation took place within a very narrow temperature range. As a consequence, there was an excellent correlation between the decomposition temperatures measured at 1%, 2%, 5%, and 10% weight loss (see Figure). In the case of brominated epoxy resins cured with phenolic hardeners, the following relationships were obtained:

$$Td^{1\%} = Td^{5\%} - 7°C, \pm 2°C$$
$$Td^{2\%} = Td^{5\%} - 3°C, \pm 1°C$$
$$Td^{10\%} = Td^{5\%} + 3°C, \pm 1°C,$$

where all temperatures are in °C. It is noteworthy that the largest experimental errors were observed for the measurement of $Td^{1\%}$. Therefore we recommend not using Td at 1% weight loss to characterize the thermal stability of the laminates. Measurements should be performed at 2% or 5% weight loss. Although $Td^{2\%}$ and $Td^{5\%}$ represent a significant volume of volatile by-products, they are a reliable measurement of the overall thermal stability of the polymer network. The automatic detection of the degradation onset or the degradation peak should not be used because they strongly depend on the shape of the TGA curve.

A series of Td measurement were performed with a slower heating ramp, i.e. 5°C/min. The correlation of the Td's obtained with the different heating ramp was excellent. The faster heating ramp led to higher Td's, as expected. It appeared that ΔTd between 10°C/min and 5°C/min was about constant for the laminates tested in this study, equal to 15°C. For these products:

$$Td(@5°C/min) = Td(@10°C/min) - 15°C, \pm 2°C$$

where all temperatures are in °C. This relationship seems to be valid for many brominated epoxy systems cured with phenolic hardeners.

Another series of Td measurements were performed in air. All Td's measured in air were lower than the respective Td's measured in nitrogen in the same conditions. The difference was between 2°C and 9°C, depending on the composition. No correlation was performed. The major effect of the TGA gas purge was observed on residual charring at 700°C. The residual weight was much lower in air than in nitrogen because oxygen was necessary to achieve pyrolysis (thermo-oxidation).

Thermo-Mechanical Analysis (TMA)

Thermo-Mechanical Analysis (TMA) was used in the isothermal mode to measure the time to delamination at a given temperature (T-260, T-288, T-300) and the coefficient of thermal expansion along the z-axis (z-CTE).

A conventional FR-4 laminate failed after about 1 minute in a T-288 test. The sample showed significant delamination after the test. The more thermally stable "lead-free" laminates usually displayed the first delamination after 10 to 15 minutes. The extent of delamination after the test was much less than for the FR-4 laminate. The very thermally stable laminates failed after 20 to 30 minutes, or even more for non-brominated resins. They do not show real delamination after the test but only small cracks not visible to the eye.

The time to delamination measured by TMA was plotted as a function of decomposition temperature measured by TGA in Figure 3. There was an excellent correlation between Td and T-260 / T-288 / T-300. The time to delamination at a given temperature, noted T-xyz, was proportional to the exponential of the decomposition temperature:

$$T_{XYZ} \propto a \cdot \exp(b \cdot T_d)$$

where a and b are constants for a given TMA temperature.

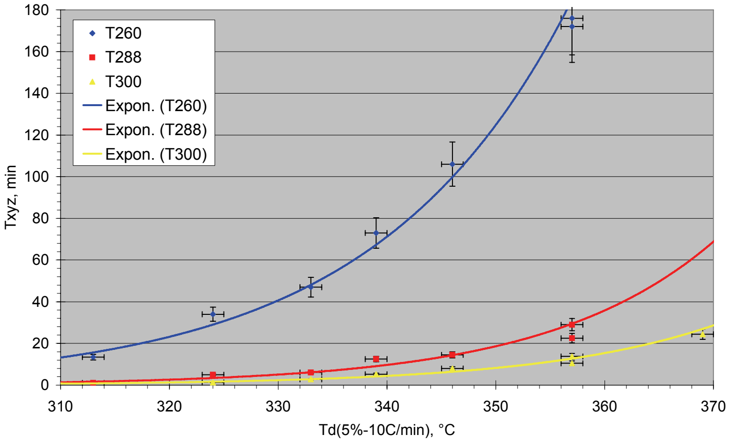


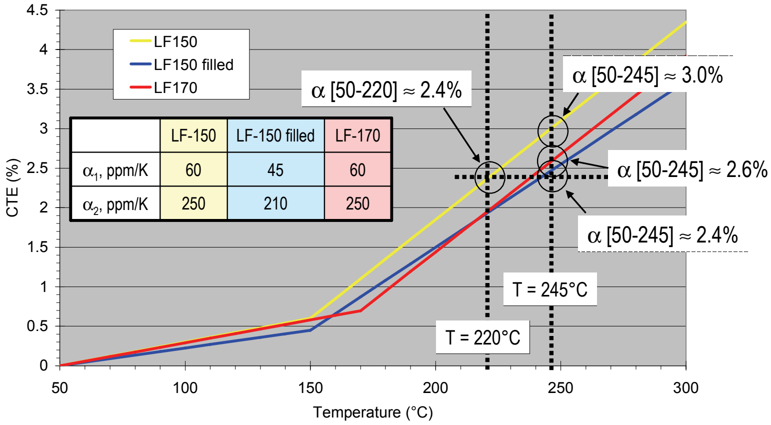
Figure 3 - Time to Delamination Measured by TMA as a Function of Decomposition Temperature Measured by TGA

Based on the best fits obtained in Figure 3, it was possible to model the theoretical time to delamination at a given temperature measured by TMA as a function of the decomposition temperature measured by TGA (10°C/min heating ramp, in N_2). A few examples are given in Table 2. From this set of data, it can be concluded that to achieve T-260 = 30 min and T-288 = 5 min, Td must be between 320°C and 330°C.

Table 2 - Theoretical T-260, T-288, and T300 as a Function of Td (@5% wt loss, @10°C/min, in N_2)

Td, °C	320	330	340	350
T-260, min	23	40	71	> 120
T-288, min	2.6	5	10	19
T-300, min	1.3	2.4	4.4	8

The coefficient of thermal expansion in the z direction z-CTE (perpendicular to the laminate surface) is a critical parameter for through-hole reliability.[6,7] It is often described as the overall thermal expansion between 50°C and 260°C, z-CTE [50-260]. During reflow soldering process, the board temperature can increase up to the temperature of the solder alloy. With SnPb alloy, the maximum temperature was about 220°C. With SAC alloys, we can expect that the maximum temperature will become about 245°C. We study the effect of the temperature increase on the overall in-process z-CTE, changing from z-CTE [50-220] to z-CTE [50-245]. In the latter case, the coefficient of thermal expansion post-Tg will play an even more significant role. This is schematically described in Figure 4. LF-150 stands for “lead-free, Tg ≈ 150°C” and LF-170 stands for “lead-free, Tg ≈ 170°C”. They are made of brominated epoxy resins cured with proprietary modified phenolic hardeners. The LF-150 filled laminate was produced with the LF-150 system and 25 phr of silica flour.



	LF-150	LF-150 filled	LF-170
α_1, ppm/K	60	45	60
α_2, ppm/K	250	210	250

Figure 4 - Schematic Effect of Tg and Filler on the Thermal Expansion Before and After Tg

By considering typical coefficient of thermal expansions for LF-150, z-CTE [50-220] was about 2.4%. The increase of temperature to 245°C led to z-CTE [50-245] equal to 3.0%. The resulting mismatch of thermal expansion between the organic resin of the laminates and the copper barrels will significantly increase. The use of a higher Tg system LF-170 brought down z-CTE [50-245] to 2.6%, assuming similar coefficient of thermal expansions pre- and post-Tg for LF-150 and LF-170. The use of filler in LF-150 allowed the mid Tg laminate to achieve z-CTE [50-245] equal to 2.4%. As a consequence, the higher Tg system or the filled mid Tg system should not induce more thermal stress at 245°C than the unfilled mid Tg system at 220°C. This could be important for the board in-process reliability.

Performance Envelopes of PCBs and Cross-properties Relationship Tables

Performance Envelopes of PCBs

The performance envelopes consist in a convenient and schematic representation of the overall performance of a given system. Due to the increasing complexity of the requirements on boards, it is no longer possible to consider the separate properties only. It is a must to combine the most relevant information into one single figure. The performance envelopes were prepared on the base of spider charts or radar plots. A conventional FR-4 laminate was used as the control baseline. The different properties (e.g. Tg, Td, z-CTE, cost) were then normalized against this reference. In a 0 to 10 scale, all the properties of the FR-4 laminate were assumed to be at 5. As described on Figure 5, higher numbers lead to better performances (except for cost). The performance envelopes presented in this paper apply for the majority of materials within a given series. Their purpose is to draw the main trends, but exceptions exist. Data are coming from the large experience that The Dow Chemical Company has built through years of global presence in the electrical laminates market, with the Research & Development centers and the Technical Service & Development organizations.

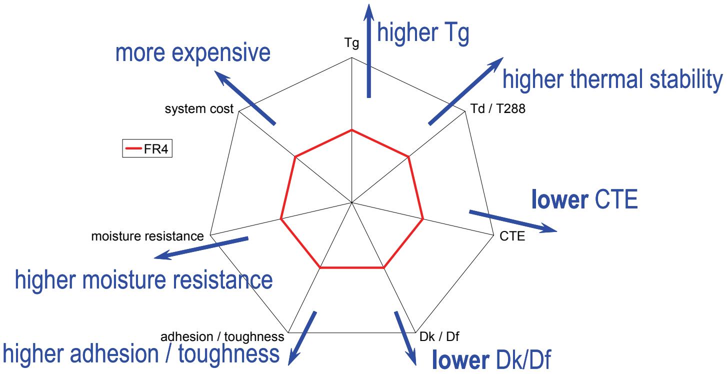


Figure 5 - Performance Envelope of a Conventional Standard Tg FR-4 Laminate

Figure 6 shows the comparison of two conventional FR-4 laminates with different Tg's, standard Tg (Tg ≈ 130-140 °C) and high Tg (Tg ≈ 170°C). In addition to the higher glass transition temperature, the major advantage of higher Tg systems is that the average coefficient of thermal expansion is reduced. In general, the individual coefficients of thermal expansion before and after the glass transition, α1 and α2, remain very similar for standard Tg and high Tg laminates. α2 might be slightly lower because of the higher cross-linking density that is often observed in high Tg materials. However as described earlier in the paper, the transition from α1 to α2 is shifted to higher temperature because of the higher Tg. Consequently the average expansion over a temperature range (e.g. from 50°C to 260°C) is reduced. This is an important feature for the mechanical thermal reliability,[8,9] in opposition to the chemical thermal reliability that is not affected by Tg. The thermal resistance of specimens subjected to moisture can also be marginally improved, depending on the chemistry. The main drawback of higher Tg systems is that they are usually more brittle because of the higher cross-linking density of the epoxy network. Some specific products have been developed to solve this problem. For instance, a proprietary technology has been developed to increase the rigidity of the molecules leading to higher Tg while maintaining excellent toughness, along with improved dielectrics.

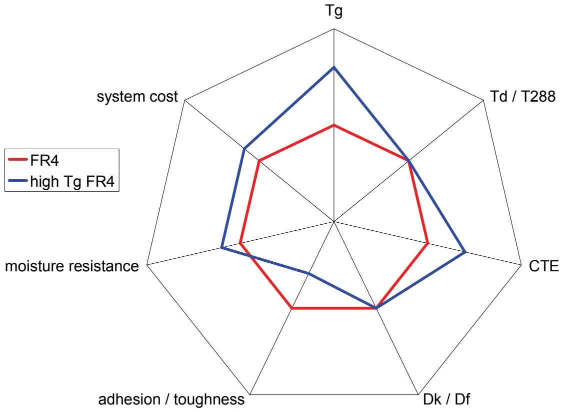


Figure 6 - Comparison of the Performance Envelopes of the Conventional Standard Tg FR-4 and high Tg FR-4 Laminates

The following performance envelopes differ from the previous ones in the sense that series of products (or families of products) are compared. As a consequence, the performances are not represented by a line anymore, but by a surface. The width of the surface represents the spread of performances within a given series. The wider the spread is, the more freedom one would have to fine tune a specific system. A simple example is Tg. It can be adjusted to standard, mid, or high Tg in all performance envelopes shown below. Of course, a change in Tg will impact other properties, leading to wider spread. The specific impact of a given properties on the others will be discussed in a later section.

The influence of filler in conventional FR-4 laminates is presented in Figure 7. The addition of filler is a very effective solution to produce low CTE laminates. The higher the concentration of filler is, the lower the CTE. It is important to note that, in first approximation, the addition of filler will impact α1 and α2 in a proportional manner, and that the reduction of CTE will be linear with the filler concentration (at least at relatively low incorporation levels). The major negative drawbacks of filler addition are the increase of viscosity of the varnish and the higher brittleness of the laminates. Dispersing agents and adhesion promoters (e.g. silanes) are efficient to reduce these negative effects. The most suitable resins to disperse filler have low viscosity and excellent intrinsic toughness. Inert fillers are neutral respect to the chemical thermal stability of the network. However they can increase the mechanical thermal reliability by reducing the CTE mismatch between the PCB matrix (organic phase) and the inorganic phases (glass reinforcement, copper, silica). Depending on the nature of the filler, the dielectric properties can vary significantly. For instance, talc increases Dk and Df, unlike quartz that lowers Dk and Df.

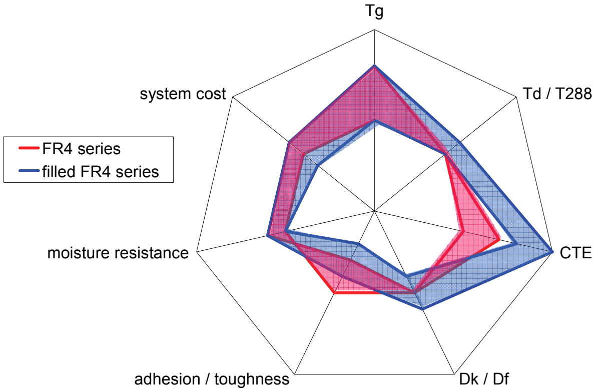


Figure 7 - Comparison of the Performance Envelopes of the Conventional FR-4 Laminates with or without Filler

Figure 8 presents the performance envelope of the lead-free materials (called LF materials) and compares it with the conventional FR-4 series. The LF series regroup a variety of technologies and chemistries. They all have in common the fact that they do not use dicyandiamide (dicy) as curing agent. Non-dicy cured epoxy systems, such as phenolic cured epoxy systems, are known to show better thermal resistance.[10,11] Consequently they are more suitable for complex lead-free soldering applications, although conventional FR-4 laminates will continue to be the most effective base materials for simple applications such as rigid boards with a few reflow cycles (i.e. few layers count). The thermal stability of the LF materials is spread over a wide range of temperature. The most conventional brominated epoxy resins cross-linked with phenolic hardeners have a Td in the range of 320°C to 330°C. Some of these proven technologies are being successfully used for lead free commercial applications. The next generation of high Td systems is aiming at Td > 330°C, usually between 330°C and 350°C. They are often based on modified phenolic hardeners, optionally with specific additives. They are very suitable for high-end lead-free solder applications, such as high layers count. A few brominated LF systems show outstanding thermal resistance, where Td > 350°C and T-288 > 20 min. Depending on the chemistry, the dielectric properties range from conventional FR-4 (Dk > 4.6 and Df > 0.02 @1GHz) to low Dk/Df (Dk < 4.2 and Df < 0.015 @1GHz). Some improved low Dk systems (systems with lower dielectric constant and lower loss factor) based on non dicy and non phenolic curing agents have been proven to be extremely thermally stable.[12] The non-dicy non-phenolic systems display in general a tendency for higher brittleness and better moisture resistance. Systems cost strongly depends on the level of performances.

The last series of epoxy materials used for PCB substrates are the relatively recent halogen-free products (called HF products). Although no risk assessment on TBBA ever demonstrates the toxicity of this molecule when reacted in an epoxy network, brominated flame retardants are currently under thorough scrutiny. It is noteworthy that the WEEE directive in Europe does not ban the use of TBBA in electrical and electronic equipments. In addition to the foreseen environmental advantage of HF systems, some of them have been reported to display better dielectric properties, especially lower Df[13] and much higher thermal resistance.[14] The extraordinary thermal resistance of the HF systems is explained by the replacement of the thermally labile Br atoms of the TBBA-derivative flame retardants. Phosphorus-based flame retardants are particularly effective. The thermal stability of such HF systems can be as good as Td >>

360°C and T-288 >> 60 min. The moisture sensitivity of HF systems tends to be higher than their brominated equivalent. It mainly comes from the P-O bonds. However the newest HF systems have been optimized to reduce moisture pick-up and to pass the requirement of the high pressure cooker tests. All the HF systems on the market are significantly more expensive than their brominated equivalent, TBBA-based molecules being the most cost-effective solution to produce flame-retardant laminates. HF systems currently target a niche market, which is growing very fast. Because of the superior thermal performances of HF resins, the market share might expand to replace brominated systems in highly demanding applications.

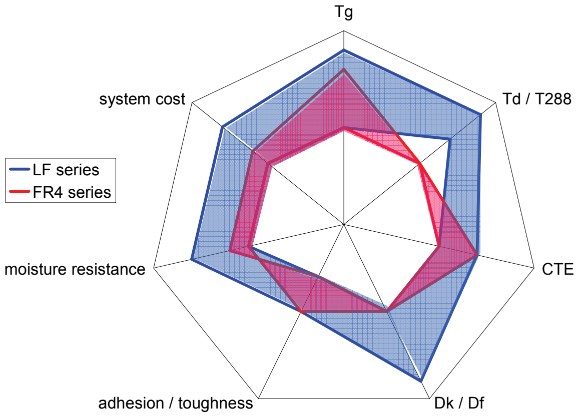


Figure 8 - Comparison of the Performance Envelopes of the Conventional FR-4 Laminates and the "lead-free" Laminates

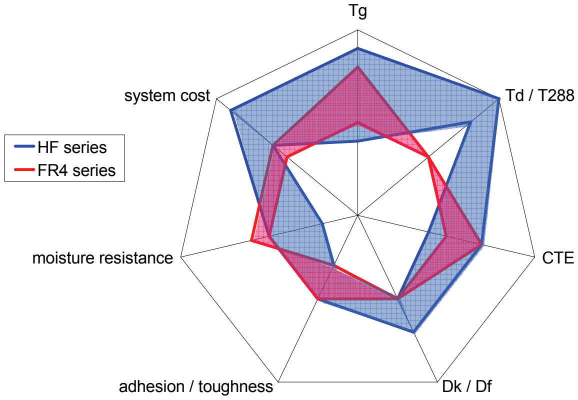


Figure 9 - Comparison of the Performance Envelopes of the Conventional FR-4 Laminates and the "halogen-free" Laminates

Cross-properties Relationship

The information collected in the previous sections are summarized in Table 3. It shows the impact of the resin characteristics (i.e. type of flame retardant, type of hardener, presence of filler) on the PCB properties. As already mentioned, the trends presented in this paper apply for the majority of the epoxy-based materials, but exceptions may exist.

First, one should recognize that there is no perfect system. All resin characteristics lead to a combination of positive, neutral, and negative impact on the PCB properties. As a consequence, the PCB performances must be optimized to achieve the targeted requirements, by combining the right properties together. Brominated flame retardant can be formulated with phenolic hardener to reach satisfactory thermal stability. Such combinations can result in very good balance of properties, but most of the time there is at least one compromise.

Brominated flame retardants are suitable to achieve high Tg because of the relative rigidity of the brominated polymer chains. TBBA-based molecules are effective flame retardant, produced in large quantities for a long time. They are therefore the preferred option to produce cost-competitive FR PCBs. Bromine has a negative impact on Dk, when compared to the same non-brominated product. We have observed an increase of Dk of 0.15 to 0.20 in fully cured laminates when bisphenol A epoxy resin was replaced by the equivalent tetrabromobisphenol A epoxy resin. The most dramatic effect of the TBBA-based epoxy is the lower thermal stability due to the early degradation of the bromine radicals. Phosphorus-based flame retardants usually show opposite impacts when compared to brominated FR. Tg tends to be lower, moisture resistance is reduced, system cost increases, but Df can be improved and thermal stability is drastically enhanced.

The hardener of the epoxy resin is also a key factor on the PCB properties, for a given type of flame retardant. Dicyandiamide is by far the most common one. Dicy-based epoxy formulations are extremely process-friendly, both for the laminators (e.g. wide processing window) and for the board shops (e.g. excellent drillability). In addition they can reach high Tg, still with excellent toughness and adhesion because of the polarity of the amine groups. The drawbacks of the polar network are that Dk is high and that the prepreg and laminates are relatively sensitive to moisture. Dicy negatively impacts thermal stability, especially with brominated resins. The nitrogen atoms appear to have a catalytic effect on the degradation of the bromine radicals. Phenolic hardeners tend to have opposite impacts when compared to dicy, although the multitude of available structures makes the comparison uneasy. The trends reported in Table 3 are valid for conventional phenol Novolac. They are less process-friendly than dicy because of narrower processing window and higher brittleness. They are not as effective to boost Tg, but they greatly improve the thermal resistance and reduce the sensitivity to moisture. The effect on the dielectric constants is relatively neutral, although the slight increase in Df has been noticed. The non-dicy non-phenolic hardeners aim to upgrade the conventional hardeners to fulfill unmet needs. Thermal stability can be significantly increased, as well as dielectric properties. Depending on the hardener, toughness and adhesion might be negatively impacted.

The last key factor on the PCB properties is the presence of filler. There are many types of fillers and the resulting impacts may change in a large extend. However from a generic viewpoint, the presence of filler in a PCB makes it more brittle, while the coefficient of thermal expansion is drastically reduced. Often the dielectric constants are negatively affected. The overall system cost is lowered because of the dilution effect of the organic resins.

It is also interesting to consider the cross-properties relationship in PCBs, i.e. what the influence of a given properties on the others is. This is shown in Table 4.

Higher Tg PCBs tend to have lower CTE and reduced moisture sensitivity due to higher cross-linking density. As a drawback, there are also more brittle. A direct correlation is that low CTE PCBs often show lower toughness. Although the dielectric properties do not have direct impact on other physical properties, low Dk systems are usually less polar than the conventional laminates. Consequently the adhesion is lowered and the sensitivity to moisture is improved. It has been observed that an improved toughness and an excellent adhesion between the resin and the glass reinforcement have a positive influence on moisture resistance. Indeed the number of micro-cracks located within the organic matrix or at the glass / resin interface is minimal, preventing the moisture to penetrate through the board. This is of particular importance for CAF resistance (cathodic-anodic filament). Reducing the moisture pick-up of the prepreg and the laminate ensures consistent Tg (moisture tends to plasticize the organic matrix) and Dk/Df (H_2O is extremely polar, Dk ≈ 70, and consequently even a small concentration of entrapped water impacts the dielectric performances). Note that the thermal stability is relatively neutral to the other properties.

Table 3 - Impact of the Resin Characteristics on the PCB Properties

impact on		Tg	Td / T288	CTE	Dk / Df	adhesion / toughness	moisture resistance	system cost
FR	Br	+	-	ø	-	ø	+	+
	P	-	+ +	ø	+	-	-	-
hardener	dicy	+	- -	ø	-	+ +	-	ø
	phenolic	-	+	ø	ø	-	+	+
	non dicy / non phenolic	ø	+ +	ø	+	-	+	-
filler	without	ø	ø	-	+	+	ø	-
	with	ø	ø	+ +	-	- -	ø	+

- Green cell with + (or + +) means positive (or very positive) impact
- Red cell with – (or – –) means negative (or very negative) impact
- Grey cell with ϕ means neutral effect

Table 4 - Cross-properties Relationship in PCBs

impact ↗ on	Tg	Td	CTE	Dk / Df	adhesion / toughness	moisture resistance
Tg		ø	+	ø	-	+
Td	ø		ø	ø	ø	ø
CTE	ø	ø		ø	-	ø
Dk / Df	ø	ø	ø		-	+
adhesion / toughness	ø	ø	ø	ø		+
moisture pick-up	+	ø	ø	+	ø	

- Green cell with + means positive impact
- Red cell with – means negative impact
- Grey cell with ϕ means neutral effect

An overview of portfolio positing with respect to thermal properties is shown in Figure 10. The epoxy-based PCBs can be segmented in 4 generic categories:

- Conventional FR-4: brominated, dicy cure
- Lead-free FR-4: brominated, phenolic cure (or modified phenolic cure)
- Low Dk/Df FR-4: brominated, non dicy / non phenolic cure
- Halogen-free FR-4: non brominated, dicy or phenolic cure

The thermal properties of these different segments do not differ with regard to the glass transition temperature. It is possible to find standard-, mid-, or high-Tg systems in each categories. The major difference lays in the chemical thermal stability. Conventional FR-4 systems show limited Td. Consequently they are more suitable for simple lead-free solder applications such as rigid boards with a few reflow cycles (i.e. few layers count). The thermal stability of the lead-free systems was greatly upgraded. They are the most effective base materials for complex lead-free soldering applications (i.e. high layers count). The low Dk and the halogen-free categories are also very reliable in lead-free applications. However they are over-engineered for most of the large volume applications and the materials cost does not allow them to have a wide market penetration, yet.

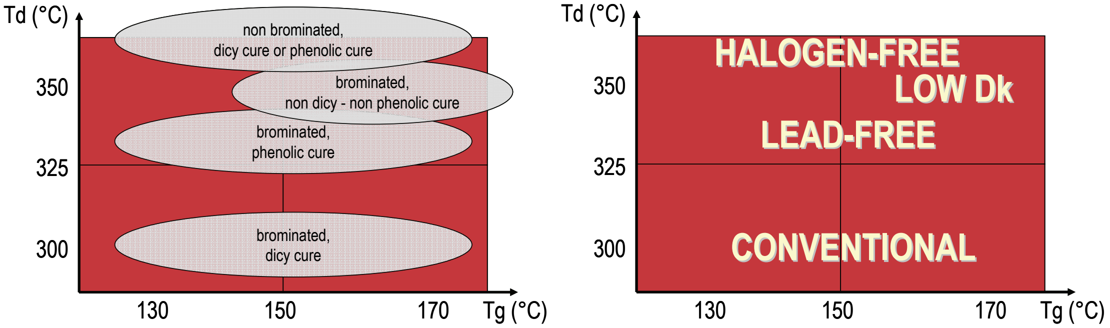


Figure 10 - Overview of Portfolio Positing with Respect to Thermal Properties

Conclusions

Lead-free soldering is expected to become the new standard in the future. Different legislations or draft directives target the restriction or the ban of the use of lead in the world. As an example, the European Union adopted the Restriction of Hazardous Substances (RoHS) Directive in January 2003. It will come into effect on July 1, 2006. Most of the lead-free solder alloys melt at higher temperatures than that of the eutectic SnPb solder. The change to higher temperature solder alloys will directly affect the temperature profiles for reflow soldering, wave soldering, rework and repair. In parallel, the complexity of the boards is increasing, leading to thicker multilayer structures. Laminates will thus be submitted to higher temperature for longer time through multiple reflow cycles. It is critical to understand how these new technical requirements will have an impact on the thermal resistance of electrical laminates.

This paper provided some experimental data related to the new requirements for lead-free soldering applications. The relevance of the different measurements (e.g. Tg, Td, T-288, z-CTE) was discussed. Correlation was proposed between the multiples thermal performance tests. The results obtained by thermo-mechanical analysis (TMA) and by thermo-gravimetry analysis (TGA) correlated well. The early decomposition species were critical for the overall thermal resistance of the laminates because they turned from solid to gas during decomposition. However there was also an excellent correlation between T-288 and Td measured at 5% weight loss (in nitrogen). All the results suggested an exponential effect of the temperature on the decomposition process.

Finally the performance envelopes of the various epoxy resins systems used to produce PCB (i.e. conventional FR-4, filled systems, high thermal performances brominated resins, halogen-free resins) were compared and correlated to the specific applications needs.

From these results and from our experience, we believe that conventional FR-4 laminates will continue to be the most effective base materials for simple applications such as rigid boards with a few reflow cycles. The more thermally resistant laminates will become the materials of choice for more complex applications such as thick boards with multiple reflow cycles. There will be no need to "over-engineer" the laminate materials. Td > 320-330°C should be enough in most cases. PCBs with Td > 330°C might be more suitable in case of very demanding process, e.g. high layer count. The use of filler was the most effective method to lower the coefficient of thermal expansion, as well as the use of higher Tg materials. Low z-CTE should improve reliability by reducing the expansion mismatch between the organic resin and the copper barrels. In any cases, the improvement of thermal stability must not be done at the expense of the mechanical properties. It will be critical to maintain good adhesion and sufficient toughness to avoid reliability issues. Users should choose the most suitable balance of properties for their specific process conditions and applications. In parallel, the specialty products such as low Dk and halogen-free materials will bring differentiation and additional benefits to the users.

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