More Robust Base Materials for Electronic Assemblies

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Abstract:
The proposed revision of *IPC-4101 - Specification for Base Materials for Rigid and Multilayer Printed Boards* contains new slash sheets describing FR-4 base materials compatible with lead free assembly. It has been reported in countless papers and presentations that the new silver/tin/copper and other lead free solders mandate processing temperatures 20-30°C higher than the time proven tin/lead solder. The six new lead free specifications were developed and incorporated into the IPC-4101B document in order specify FR-4 base materials with more robust processing windows for lead free assembly. While it is true that some "more mature" FR-4 products can be used successfully in lead free assembly, most fabricators and assemblers have found that no single FR-4 product works in all situations.

This paper discusses the new tests incorporated into IPC-4101B, the development of the requirements for lead free FR-4 and the solutions to various requirements / issues that have surfaced due to the lead free assembly movement.

Introduction:
The transition to lead free compatible base materials was initially assumed to be nothing more than a quick move to the 170°C glass transition temperature (Tg) products by many board fabricators and assemblers. Many base material suppliers felt that the products already developed and qualified would be satisfactory for lead free assembly even in lower Tg FR-4 materials. While in some cases both camps have been correct, the vast majority of the electronics supply chain have had to move to new FR-4 materials especially for more complicated designs and for multiple thermal shocks. **Figure 1** and **Figure 2** show how board design and complexity contribute to the need for different chemistries within the FR-4 family for tin/lead and lead free soldering respectively. Increasing the number of reflow cycles, overall board thickness and complexity of the design all require higher performing base materials.

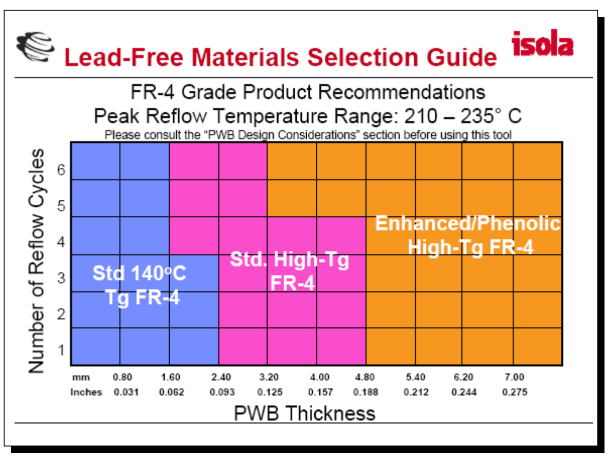

Figure 1 - Chemistry requirements for tin/lead assembly (compliments of Isola).

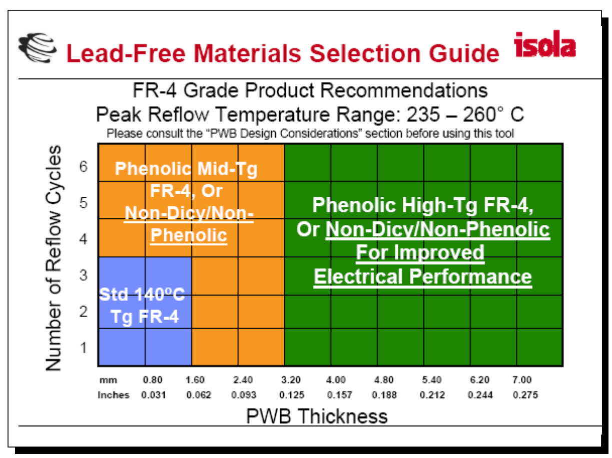

Figure 2 - Chemistry requirements for lead free assembly (compliments of Isola).

Many industry experts have worked on characterizing lead free compatible base materials. However, they can ony agree on one point – there is no single performance property that can be stipulated that will provide a soft landing to the lead free issue. In order to be more predictable, a number of thermal properties were then added as new performance characteristics in an attempt to provide some assurance to the assembler that the base material would survive soldering. Base material suppliers then developed new FR-4 materials with increased thermal performance. But some of the new materials that were were created were then found to have lower peel strength, poor interlaminar bond, and a new defect – "cratering". More development was still required.

As with any set of specifications, there is no quarentee that purchasing materials to any of the six lead free specifications will be satifactory under all conditions.

Decomposition Temperature:
The decomposition temperature (Td) was one of the first new thermal properties that was reported to be a significant contributing factor to surviving lead free assembly. The first proposed requirement was that the minimum Td should be at least 340 degrees C. This was somewhat premature as there was no official test method for Td with the IPC-TM-650 document. Making matters worse, many argued that the Td should be defined as "the temperature at which there is a threshold 2% weight loss whereas others countered that it should be the temperature where a 5% weight loss was realized. Karl Sauter of Sun Microsystems led a team which developed the test method IPC-TM-650 Method 2.4.24.6, conducted round robin analysis and ultimately chose 5% as the definition of Td. **Figure 3** shows a typical thermalgram of FR-4. Note the very large difference between a 2% versus a 5% weight loss as far as the end-point temperature is concerned. Using a 2% weight loss would dictate much different requirements.

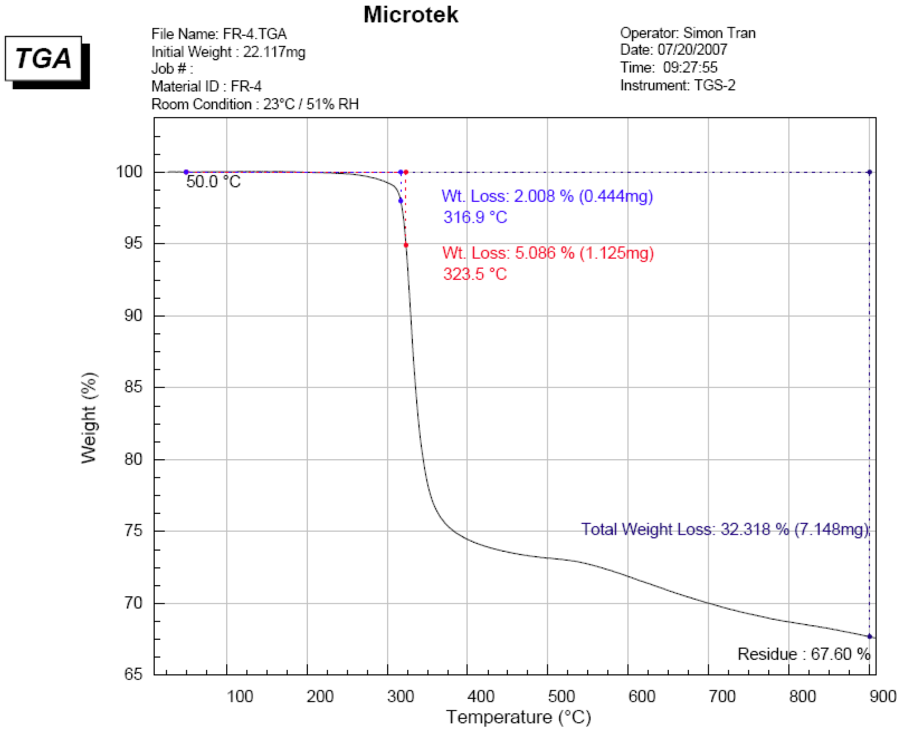

Figure 3 - Typical TMA thermalgram showing Td. (Compliments of Microtek)

With the test method complete, the next round of discussions centered on the actual requirement to be incorporated into IPC-4101B. The 340 degree minimum proposal was met with great resistance from the copper-clad laminate (CCL) manufactures due to the requirement being too high but also from the lack of precision if the test method. Therefore the compromise was to reduce the requirement to 325 degrees C for nominal 170 Tg FR-4 materials and to use 310 degrees C minimum for nominal 130 degree C Tg FR-4 materials.

The increase in the Td of the FR-4 materials usually involved using more multifunctional resins in the epoxy side of the recipe. FR-4 materials exhibiting a Tg of 130°C normally are comprised of only difunctional epoxy resin with about 2% tetra-functional epoxy added for improved AOI contrast. These include but are not limited to epoxidized novolak resins, epoxidized isocyanurate resins and epoxidized p-amino phenol resins. **Figure 4** shows some of the multifunctional resins added to the formulation to push up the decomposition temperature. **Figure 5** shows a tetrafunctional epoxy resin popular in FR-4.

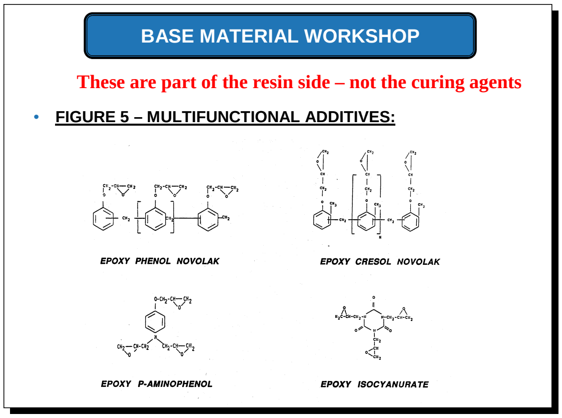

Figure 4 - Chemistry of multi-functional additives.

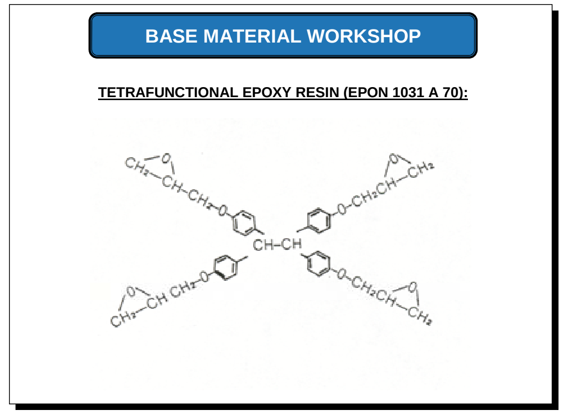

Figure 5 - Chemistry of tetra functional epoxy

In addition to the resin side of the chemistry, the curing agent side can also be changed to push up the Td. Traditionally; dicyano-diamide (dicy) has been the curing agent of choice for decades for FR-4. However, the dicy cure materials for the most part did not exhibit the thermal robustness for the lead free assembly process. In fact at one time there was a compositional requirement for the six lead free specification sheets that restricted the use of dicy for these base materials. The restriction was not part of the final draft but much skepticism still exists concerning dicy as a viable curing agent for in complicated board designs. The chemistry of a simple FR-4 with dicy versus phenolic cure can be seen in **Figure 6**.

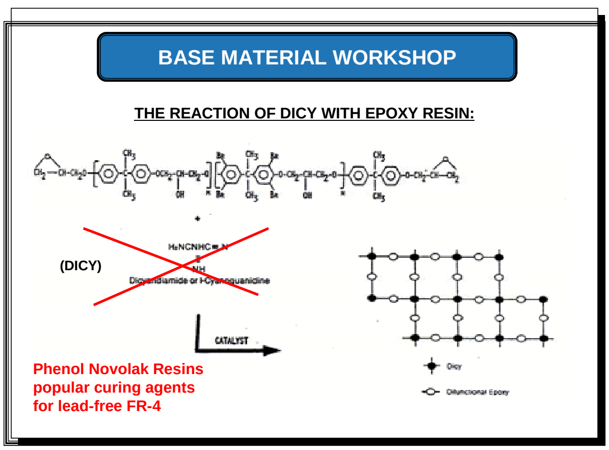

Figure 6 - Phenolic cure vs. dicy of FR-4

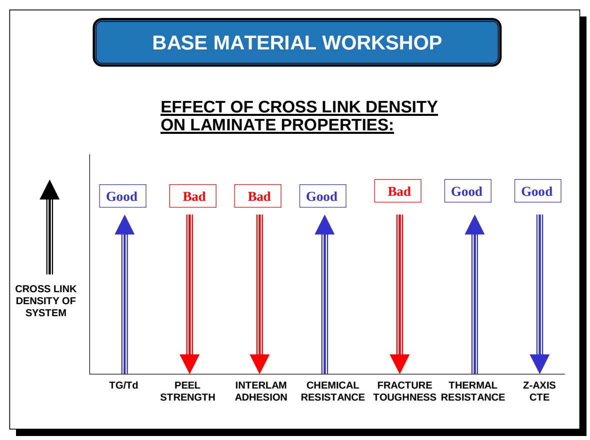

Figure 7 - Performance properties as a function of the polymer cross link density

All of the "better performance through chemistry" activities have in the past been directed at higher Tg. However most have learned the hard way that an increase in the cross-link density of the polymeric matrix has side effects as shown in **Figure 7**. While it is true that Tg (and now Td) is improved, the system tends to be more brittle resulting in cohesion failures in the polymer itself. Cracks that form by whatever mechanism propagate easily and quickly through the resin phase. Properties even more critical to board performance and fabrication such as the weak inter-laminar bond, crazing during drilling and lack of fracture toughness tend to suffer with these systems. Therefore, a chemistry change to improve thermal properties must at the same time involve chemistry changes to improve resin cohesive failures.

Z-Axis Expansion:

Early analysis by IST and HATS testing indicated that the Z-Axis expansion would be more significant a factor than with tin/lead solders. Almost all supplier data sheets reported Z-Axis expansion for FR-4 but there was no formal requirement for any specification outlined in IPC-4101. For the six lead free documents, an alpha 1 requirement (below the Tg) and an alpha 2 requirement were added. In addition, a total expansion from 50°C to 250°C on a percentage basis was also added. From the start there was almost universal agreement on the requirement. Regardless of the Tg of the FR-4, the alpha 1 was stated as 60 ppm / °C maximum while the alpha 2 value must be lower than 300 ppm / °C. The only difference reflects the actual Tg of the material which has been taken into account in the percent expansion. The low Tg sand high Tg materials have requirements of 3.5% and 3.0 percent respectively. This difference again is simply the difference in the inflection point between the low and high Tg materials as shown in **Figure 8**.

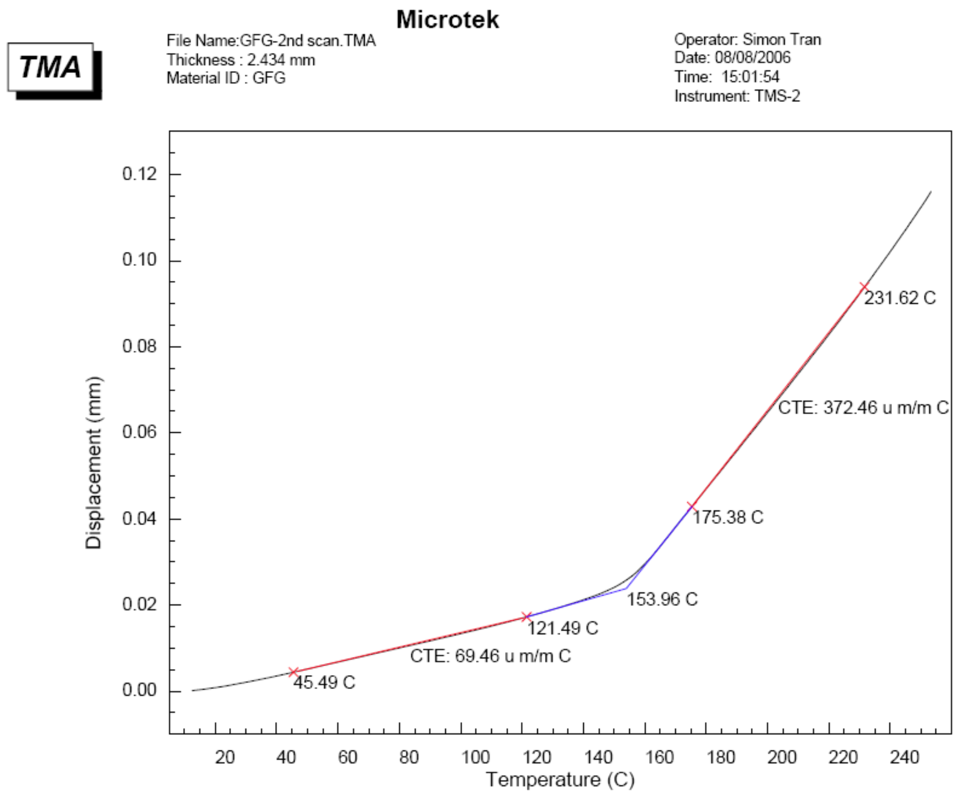

Figure 8 - Z-Axis expansion of FR-4 materials. (compliments of Microtek)

Z-Axis expansion has been achieved generally by the addition of inert fillers to know and qualified resin systems. The most common is silica dioxide (SiO2) or magnesium dioxide (MgO2) but similar analogs or mixtures of fillers can also be used. Note that the material under test in **Figure 8** does not pass the Z-Axis expansion requirements of IPC-4101B. The performance reflects a polymeric system that is not filled. In order to assist the industry in bringing these new materials to market faster, Underwriters Laboratories has new rules for qualification of recognized resins systems where the only change is the addition of a filler.

T-260/T-288/T-300:
The T-260 test was originally used to determine the bond between the black oxide coating on an inner layer and the prepreg. The application of this test has been expanded to include simple blister resistance. The thought being that the higher a temperature and time that a base materials can withstand, the more likely the resulting multilayer board will be withstand lead free assembly. The IPC-4101B expanded the temperatures which the test could be run and requirements were added to the six lead free specifications. The T-260 and T-288 requirements are 30 minutes and 8 minutes minimum respectively. The T-300 requirement is left as an AABUS – "As Agreed upon Between User and Supplier" for commodity type FR-4 materials.

Generally speaking the higher Tg and higher Td resin systems perform more poorly than the lower Tg FR-4s. A lot of work has been done to make the more highly cross-linked systems perform better in these series of thermal tests. Most of the improvement has been due to improvement in fracture toughness which will be discussed later.

Moisture Absorption:
One overlooked characteristic of a base material as a candidate for lead free assembly is moisture absorption. The higher temperatures of the silver/tin/copper solders and the like have generated a much higher vapor pressure than the conventional soldering temperatures. According to Isola as shown in **Figure 9**, the vapor pressure at 260 degrees C is almost double that at 230 degrees C. Increased vapor pressure can cause laminate and multilayer boards to delaminate and blister as well as cause blow holes and other reliability issues in plated through holes. The reason that moisture absorption is not normally considered is due to the fact that conventional FR-4 materials have very low water pick-up. However, this is not true for most of the low-halogen FR-4 materials where the required moisture absorption properties are almost twice as high as the

brominated versions. In addition phenolic cured materials generally pick up moisture faster than dicy cured materials meaning that storage of prepreg, laminates and multilayer boards during processing is more critical.

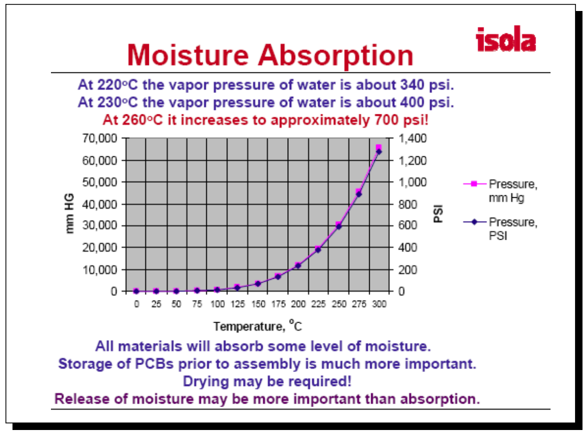

Figure 9 - Vapor pressure as a function of temperature. (Compliments of Isola)

Pad Cratering:

In the spring of 2006, many OEMs were reporting failures associated with the cracking within the polymeric matrix itself. In the most severe cases the pad itself would fall off along with the attached part leaving behind a crater". Pad Cratering as it is now called has been investigated at a frantic pace in order to develop a solution. **Figure 10** shows a schematic on the types of defects related to cratering. The cracks form initially in the resin layer. The cracks then can propagate though the trace leaving an open circuit as shown in **Figure 11**. In **Figure 13** the micrograph shows the initial crack which ultimately leads to failure do to pad cratering. The crack will continue to propagate until the entire pad is isolated. Eventually, the pad will be dislodged from the surface leaving a large hole.

What has been learned about pad cratering over the last 18 months. First the issue is the combination of two factors. The first is that the more thermally robust resins systems developed for lead free assembly were inherently more brittle than the standard FR-4 materials. Secondly, the new lead free solders tend to be less ductile and therefore transmit more stress to the pad and the underlying base material. Combine these factors with multiple solder shocks and some rough physical handling and craters appear.

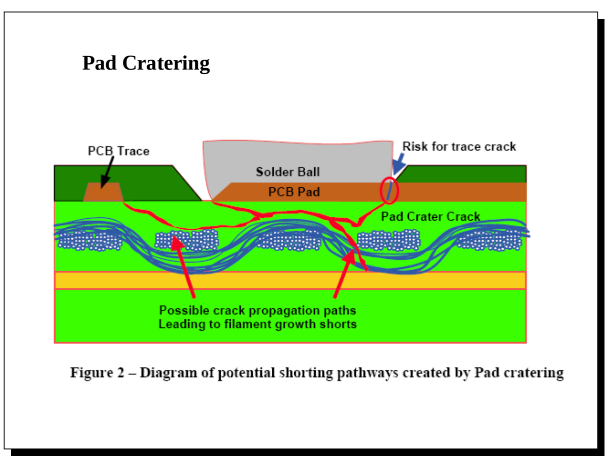

Figure 10 - Schematic of pad cratering issues (compliments of Intel).

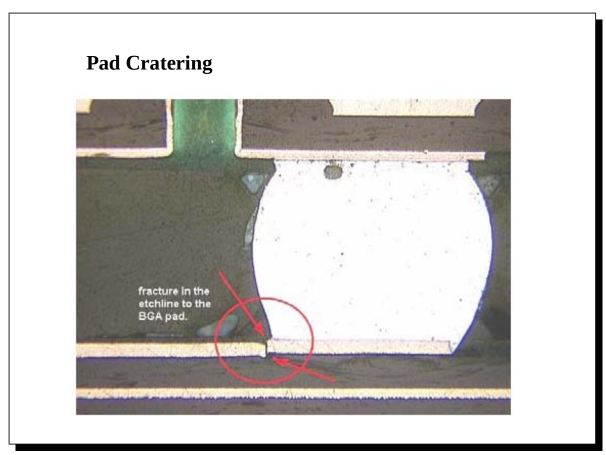

Figure 11 - Micrograph showing open circuit (compliments of Intel).

Toughness Testing:

Figure 13 shows the Fracture Toughness test fixture as described in ASTM 5045. The test specimen is supported in two places and then the specimen is notched midway between the supports. The test measures both the force (K1C) and the energy (G1C) required to propagate this initial crack. This test measures directly the crack termination performance of the resin system. Cohesion failure in the polymer is directly related to fabrication and assembly issues such as lower peel strength, poor inter-laminar bond, crazing during drilling and pad cratering. This test can be used to predict the performance of control and test resin systems for copper-clad laminate and prepreg production.

The IPC Laminate and Prepreg Subcommittee is currently investigating including this test method into IPC-TM-650 and developing requirements for lead free compatible base materials. This test method has been used for decades in aerospace and sports / recreation composites but up to now the electronics supply chain has not utilized this performance testing tool.

Laminate and prepreg materials can be toughened to improve the performance in the ASTM 5045 fracture toughness test. Current tougheners include high molecular weight epoxies (Hexion et al.), CTBNs (Emerald et al.) and Core Shell Rubber (Kaneka et al.) Fracture toughness can be improved 200-400% for both K1C and G1C using these materials. Some modifiers lower the Tg and Td when incorporated in levels required for increased toughness but others have no Tg / Td depressing effect whatsoever.

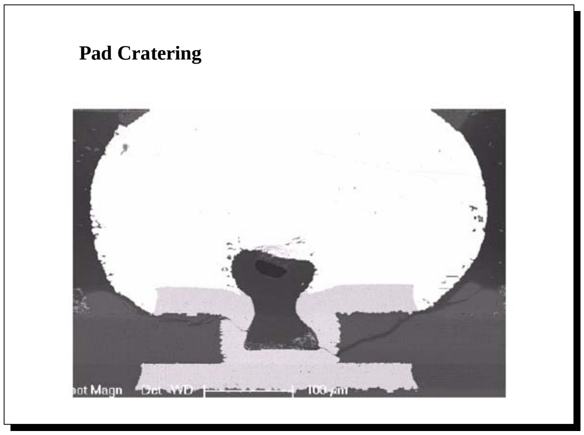

Figure 12 - Micrograph showing initiation of "pad cratering" (compliments of Intel).

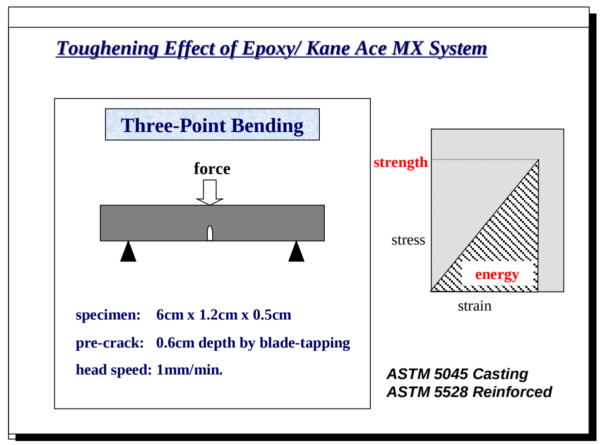

Figure 13 - ASTM 5045 Fracture Toughness test.

Summary:
The six specification sheets associated with lead free compatible FR-4 base materials covers almost all of the products currently on the market. There is no one product that satisfies all of the commercial factors of performance, availability and cost. The most common solution for the lead free assembly market is a brominated, multifunctional epoxy resin which when cured with phenolic resin provides an FR-4 laminate with a glass transition temperature of approximately 170°C. Although these systems provide improved thermal stability for the higher eutectic temperatures of the lead free solder, the polymeric matrix is generally more brittle resulting in lower inter-laminar bond, poor drillability and lower resistance to microcracks resulting in craters. There are test methods to compare various materials and additives that can be utilized to improve already qualified resin systems for fracture toughness.

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