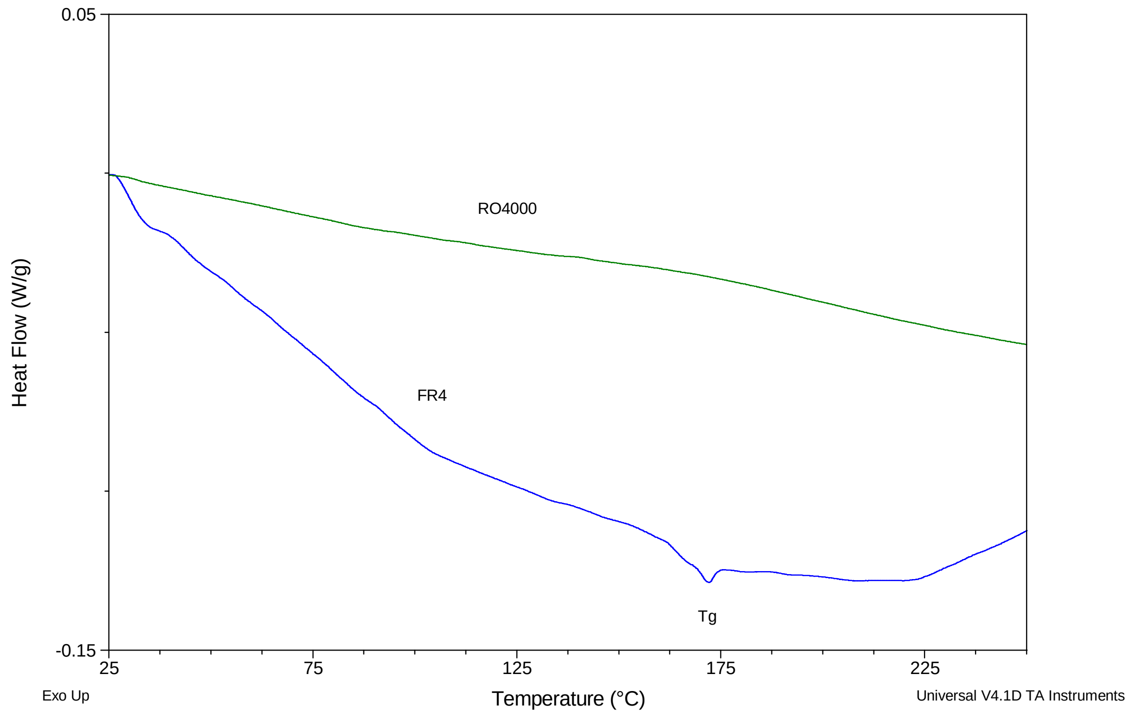
Question: Are RO4000® materials compatible with lead-free processes?
Answer: RO4000® cores and prepregs are among the most temperature stable products available. They easily meet or exceed all expectations for lead-free compatible PCB substrates whether you're considering **thermal properties, retention of copper adhesion, or reliability of multi-layer boards**.

THERMAL PROPERTIES: The thermal properties that are currently considered somewhat predictive of a material's compatibility with lead-free processing conditions include glass transition temperature, degradation temperature, Z-axis CTE, and time to delaminate at a given temperature.

The **glass transition temperature (Tg)** is the temperature or temperature range where a thermoset material transitions from being rigid and glass-like (below Tg) toward becoming rubbery and more compliant (above Tg). Although many opinions exist regarding the significance of Tg (including whether it helps predict lead-free compatibility), this property is often among the first considered when selecting a dielectric material. In the PWB industry, surpassing a material's Tg is believed to result in a significant reduction in copper adhesion, an increased risk of measling and a reduction in the reliability of plated-through holes. Tg can be measured by Differential Scanning Calorimetry (DSC), Thermal-Mechanical Analysis (TMA), or Dynamic-Mechanical Analysis (DMA). DSC has been the most broadly used method of measurement in the PWB industry.

The Tg of FR4-like materials in use today ranges from 125°C to 220°C. When measured by DSC, RO4000 materials do not experience detectable glass transitions at temperatures below 300°C. The chart below provides a comparison of curves generated when testing RO4000 cores vs. 175°C Tg, phenolic cured epoxy/glass cores. Observations to be made include the linear nature (e.g., no transitions detected) of the RO4000 material curve as compared to the changes to slope (Tg near 175°C) in the FR4 curve and the improved heat flow characteristics of the RO4000 material as compared to the epoxy/glass product.

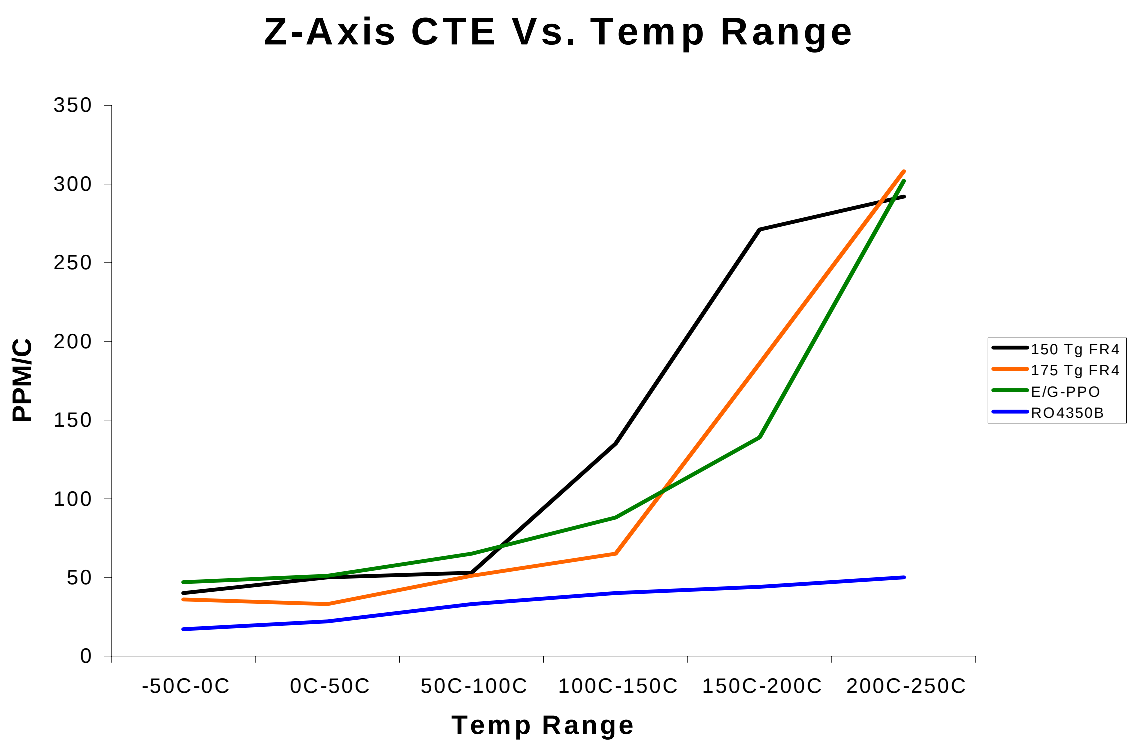


The **degradation temperature (Td)** of base PWB materials has become a property often used by designers to predict a material's compatibility with lead-free processing conditions. The Td of a material is considered the point where a material might be inclined to blister and/or delaminate due to pressures created by out-gassing. It may also be interpreted as the temperature at which a thermosetting resin system permanently degrades as cross-links are thermally destroyed.

Td is measured using Thermo-Gravimetric Analysis (TGA). A sample of material is placed into a TGA chamber and the temperature is increased at a rate of 10°C/Min. The degradation temperature is defined as the point where the sample has been reduced in mass by 5%. FR4-type products that are promoted as being lead-free compatible have Td's in a range of 300°C to 350°C. Depending on material grade, the Td of RO4000 materials range from 390°C to 425°C.

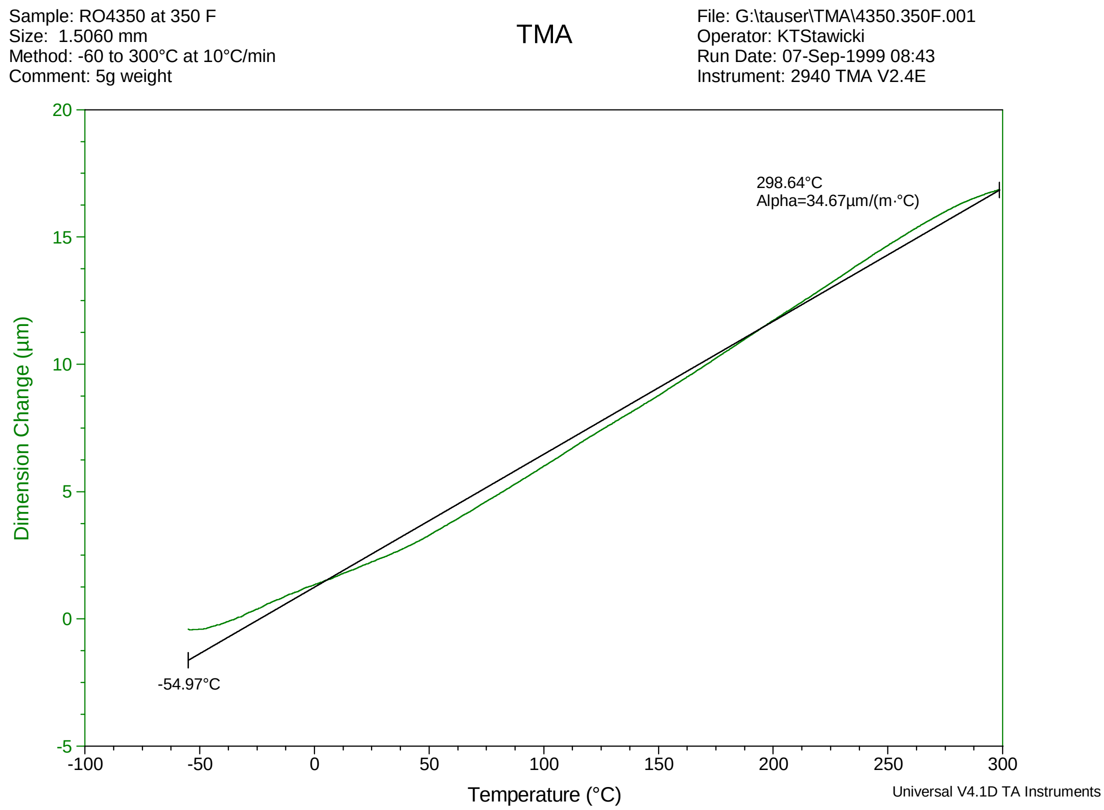
Z-axis CTE, as measured by Thermo-Mechanical Analysis (TMA), is the rate at which a material's thickness changes with changes to temperature. Understanding a material's thermal expansion characteristics as compared to those of copper is critical when trying to predict the reliability of plated-through holes (PTH's) in multi-layer constructions. As was previously mentioned, TMA equipment is also a tool used to identify the Tg of dielectric materials. The reason for this is the Z-axis expansion of most glass reinforced PWB materials at least quadruples when measured at temperatures above the glass transition point.

The data in the chart below was generated by testing the Z-axis CTE of RO4350B™ material, a 150°C Tg FR4, a 175°C Tg FR4, and an epoxy glass/PPO product over a temperature range of –50°C to 250°C. The CTE of each material was calculated over 50°C increments beginning at –50°C to 0°C and ending at 200°C to 250°C. The individual data points were charted and then connected by lines. As can be seen in the chart, the Z-axis CTE of the RO4350B material was low and remained relatively flat (no transitions) throughout the –50°C to 250°C temperature range. In contrast, the Z-axis CTE of the other products increased remarkably at temperatures above each material's glass transition. The CTE of these materials was nearly 300 ppm/°C in the 200°C to 250°C temperature range.



Historically, Z-axis CTE above Tg was not a major concern since a designer looking to improve the reliability of PTH's could simply choose a material with a higher Tg. Unfortunately, there are a scant few dielectric materials that possess Tg's at temperatures greater than the 260°C requirements of a lead-free assembly process. When calculated over a temperature range of –55°C to 288°C, the Z-axis CTE of most FR4-like materials is above 200 ppm/°C (6.9%). Over a similar temperature range, the Z-axis CTE of RO4000 core and prepreg is less than 50 ppm/°C (1.7%).

Figure 1 below provides a TMA curve that was generated while testing the Z-axis CTE of RO4350B material over a –55°C to 300°C temperature range. Two observations should be made of the graph. First, the Z-axis CTE over the entire temperature range is only 35 ppm/°C (1.2%). Second, the absence of points of inflection in the temperature vs. dimension curve again demonstrates the absence of glass transitions within the measurement range.



Time to delaminate tests were also run using TMA equipment. In this test, a sample of material, preferably a multi-layer construction, is held at a constant temperature until a delamination occurs. The delamination is detected as a sharp and sudden increase to the thickness of the test specimen. Clearly, survival time at a given temperature is used to predict a material's thermal reliability.

Epoxy/glass materials are promoted by their manufacturers as being lead-free compatible should they survive 260°C (T-260) for 30 minutes and 288°C (T-288) for ten minutes. As can be seen below in Figure 2, a 125 mil thick multi-layer board made using alternating 0.004" thick layers of RO4350B™ cores and RO4450B™ prepreg survived two successive 90-minute T-288 tests. A reduction to thickness that was noted at the onset of the first dwell at 288°C resulted from a temperature-induced advancement of cure in the prepreg layers. The sample was then removed from the TMA stage after the first 90-minute run, inspected for mechanical defects, and, when none were found, was returned to the TMA equipment for a second 90-minute exposure. The sample was cross-sectioned after the second run, and the absence of defects was confirmed.

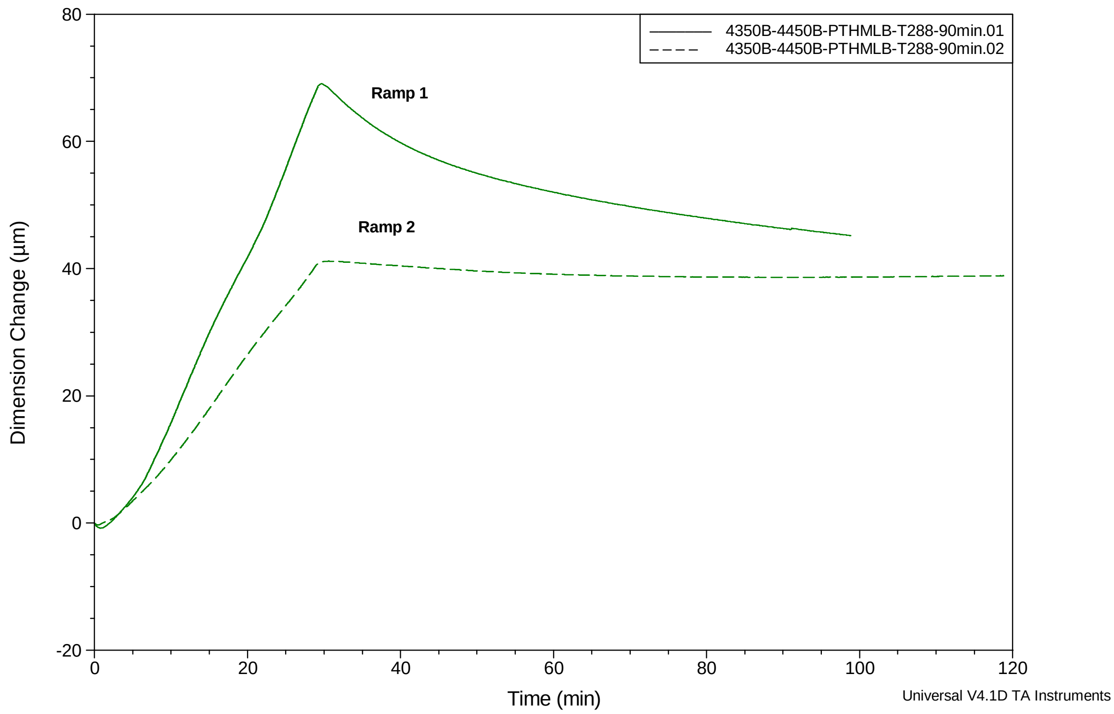


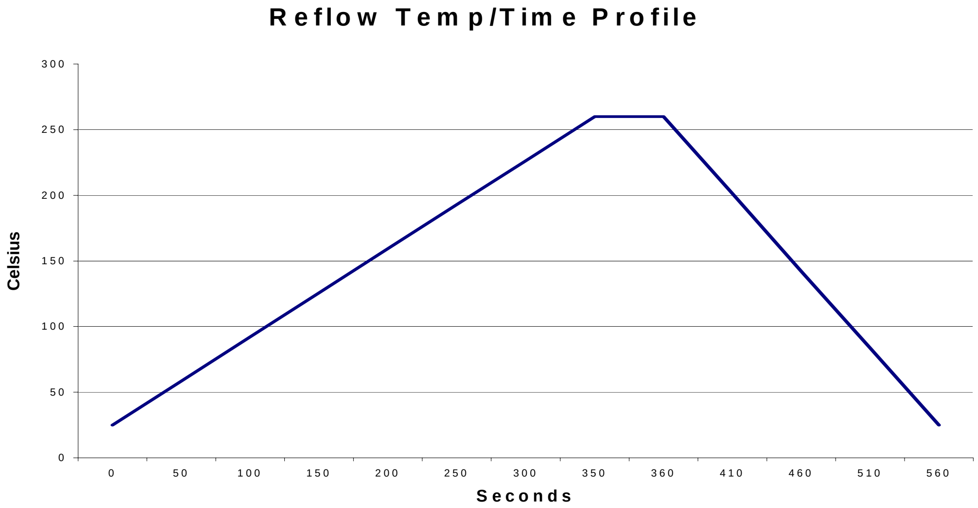
Table 1 summarizes the key thermal properties of RO4003C™ and RO4350B™ cores and RO4450B™ and RO4403C™ prepreg materials:

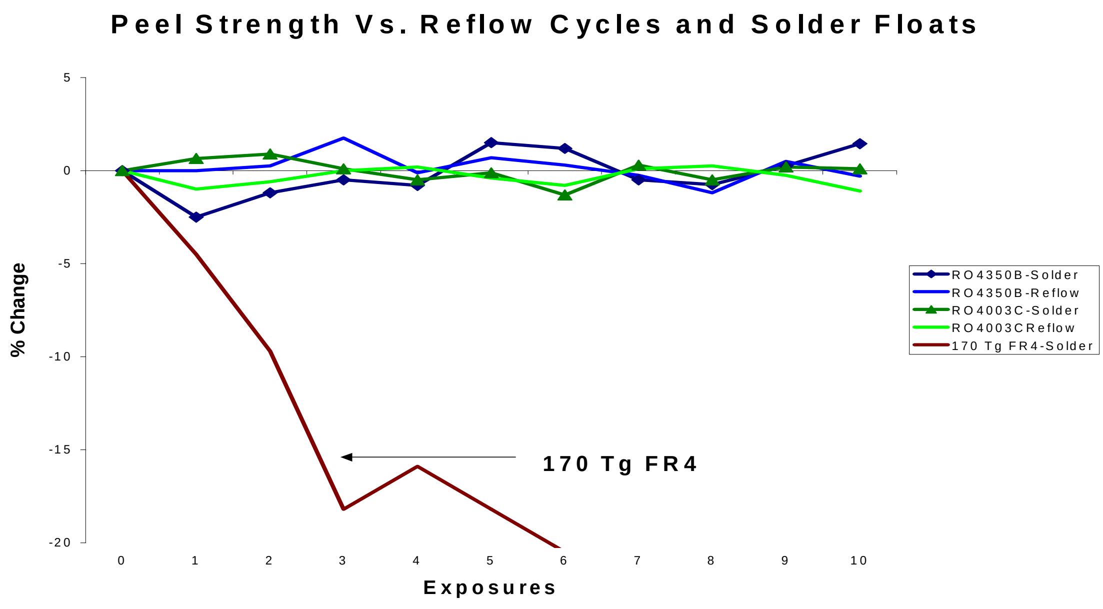
	Unit	RO4003	RO4350B	RO4450B	RO4403C
Tg-DSC	°C	No	No	No	No
Tg-TMA	°C	No	No	No	No
Td-TGA	°C	425°C	390°C	390°C	390°C
Z-Axis CTE -55 to 288°C	ppm/°C	<40	<40	<60	<80
T-288	Min	>90	>90	>90	>90

RETENTION OF COPPER ADHESION:

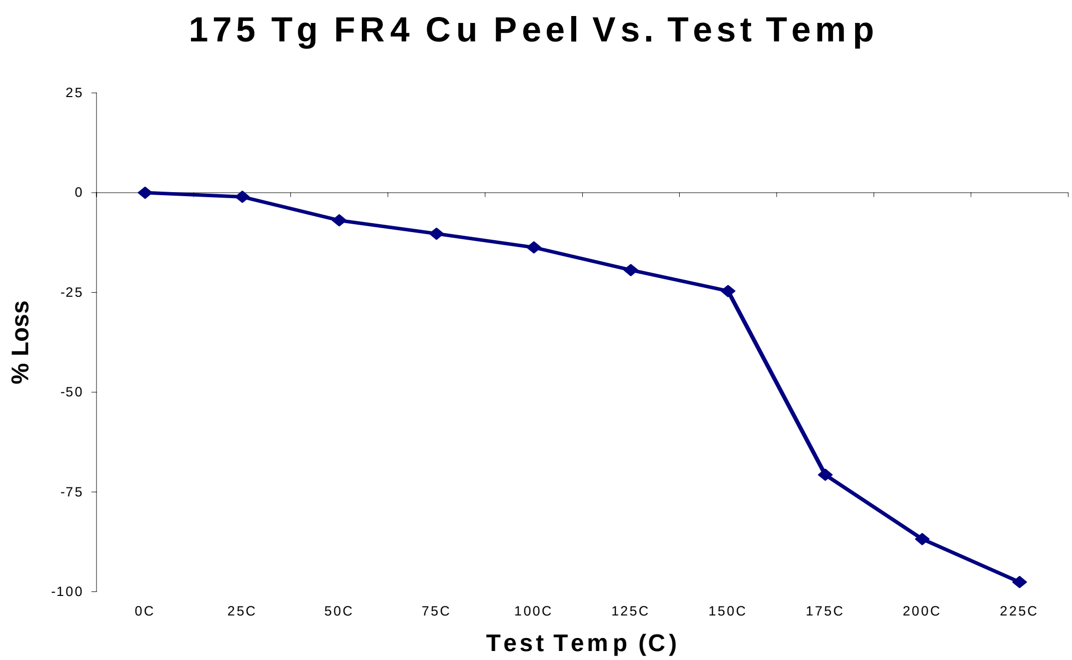
Thermal Stability of Copper Adhesion: It is expected that the copper bond to most epoxy/glass materials will degrade slightly each time the material is exposed to temperatures above the glass transition point. While the level of bond loss will vary among material types, it's pretty much a given that the bond loss for all substrates will be time and temperature dependent. The higher temperatures and exposure times associated with lead-free processing would result in greater damage than the times and temperatures associated with a traditional Sn/Pb process.

To determine bond retention through lead-free thermal exposures, RO4003C™ and RO4350B™ cores were patterned with 1/8" wide peel test strips. Peel strength was measured after each of ten exposures to lead-free reflow conditions. The temperature profile is provided below in Figure 3. Peel strength was also measured after each of ten 60 second floats on 288°C. As can be seen in Figure 4 and as might have been predicted by the thermal properties of the dielectric materials, the copper peel strength of RO4003C and RO4350B materials remained stable through the thermal exposures. Provided in the same graph are the results obtained when testing copper bond retention on a 170 Tg FR4 material through ten solder floats.

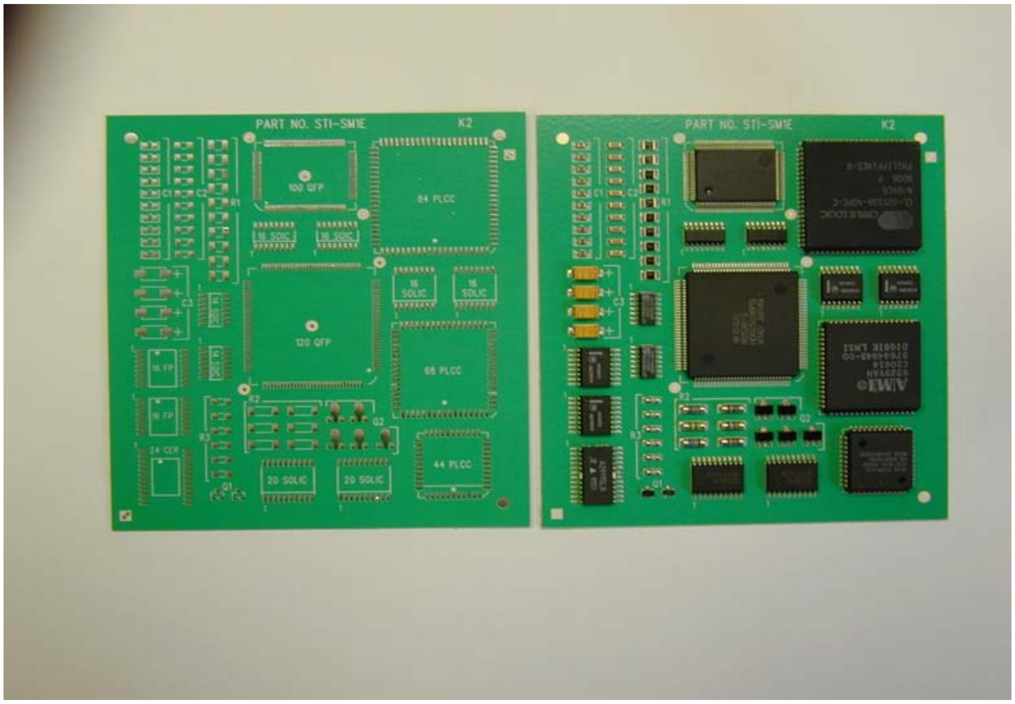




Copper Bond Though Component Re-Work: The freedom to replace defective components on finished assemblies offers a significant cost savings to a contract manufacturer. Indirect tests that might predict how a material would perform through re-work aren't very functional. Thermal properties such as Tg and Td might be helpful in pre-determining whether a resin system would degrade, but they are of marginal help in predicting how well copper is bonded at elevated temperatures. When tested in compliance with IPC-TM-650 2.4.8.2, peel strength at elevated temperatures can be more misleading than insightful. These tests at 150°C, almost always below the Tg of the resin system, ignore the significant reductions to copper bond that result when most materials are exposed to temperatures in excess of their Tg. The chart below shows the copper adhesion to a 175°C Tg, phenolic-cured epoxy/glass material system when it was measured at temperatures ranging from 0°C (submerged in an ice bath) to 225°C (submerged in reflow oil). As can be observed, the loss to copper bond at the IPC-prescribed test temperature of 150°C is a respectable 25%. However, copper adhesion is reduced significantly when the tests are performed at temperatures in excess of the substrates' glass transition point. At 225°C, the material experienced a 97% loss to copper bond, and this temperature was still more than 100°C cooler than temperatures used to complete re-work on boards populated using lead-free solders.



As bond at elevated temperatures can be misleading, the ability of RO4000 materials to survive the thermal rigors of re-work in a lead-free environment was determined through real-world, re-work simulations. The test vehicle chosen for the re-work evaluations was the standard SMT design that is used to provide certification training to repair technicians. The design provided a variety of component types (i.e., capacitors, resistors, SOIC's, SOLIC's, QFP's, and PLCC's) and connection styles (J-leads, GullWings, and Leadless). A picture of bare and populated boards is provided below.



Test boards were processed onto 0.020" thick RO4350B™ and RO4003C™ cores. The boards were then finished with electroless nickel/immersion gold (ENIG), immersion silver, and OSP. All boards were populated using Sn/Ag/Cu solder paste and the temperature profile pictured in Figure 3. Three certified repair technicians were given three boards of each material type and each final finish type and were asked to complete three re-work cycles on all components. One re-work cycle entailed component extraction, excess solder removal, and component re-attach.

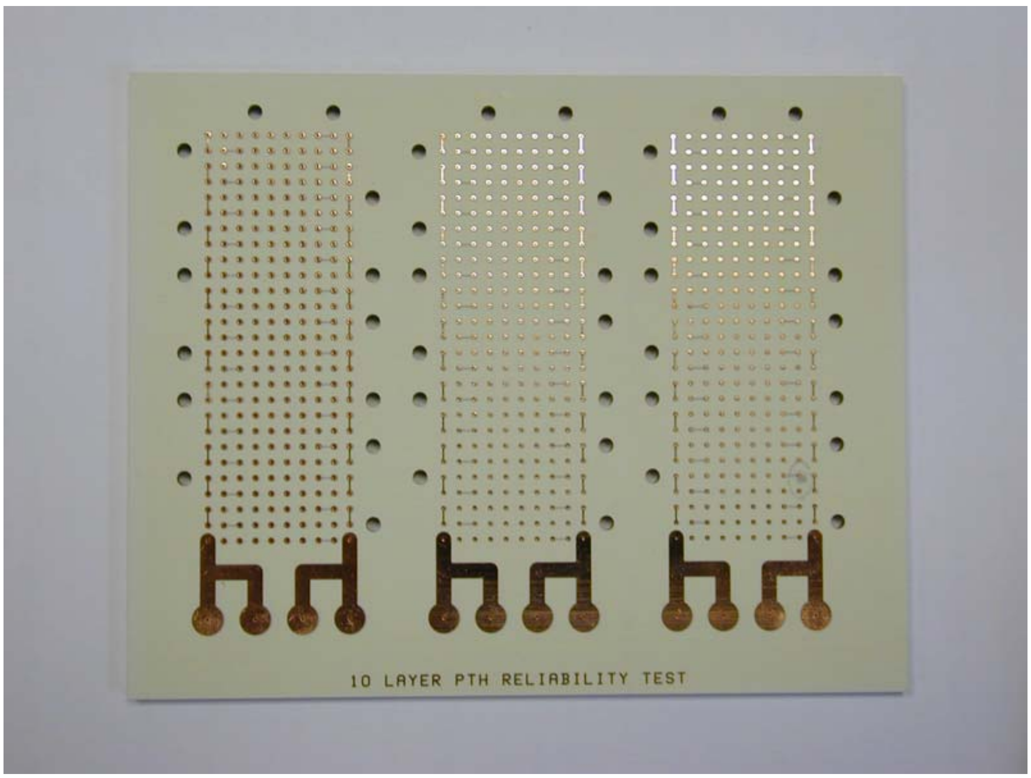
The component extraction techniques considered included solder tip, solder tip fixture, hot air, IR, and conduction oven. Solder wick and vacuum were the methods used to clean excess solder from the SMT pads. All components were replaced using soldering irons. Where applicable (all extraction, solder removal, and device re-attach techniques not using IR), operating temperatures were set at 700°F (371°C).

All repair regimens were successful regardless of re-work cycle number, operator technique, substrate material grade, final metal finish, extraction technique, or solder cleaning methodology. No failures in the form of lifted or dislodged SMT pads and measled or blistered dielectrics were observed. The only critical observation made during the re-work evaluations involved a thermal discoloration of the solder mask surrounding some of the SMT pads. The discoloration appeared worse when hot air was used to extract the component.

RELIABILITY OF MULTI-LAYER BOARDS: Lead-free processing conditions increase the reliability risk of multi-layer constructions in many ways. The risk of delamination, measling, and blister formation are increased due to the thermal degradation of resin systems and the increased pressures that are created by water vapors at temperatures required to process lead-free solders. The risk of PTH failures due to excessive Z-axis expansion of the base materials is also increased. The shock of the high-temperature exposures can result in immediate PTH failures or can contribute to an accelerated rate of fatigue failures during thermal cycling.

It is rapidly becoming the protocol to monitor MLB reliability through moisture conditions followed immediately by high-temperature shock treatments and through thermal cycling after exposing the test boards to reflow conditions. The reliability of MLB's using RO4350B cores and RO4450B prepreg layers was monitored through exposures that most PWB materials are not expected to survive.

Ten-layer MLB's were processed using alternating layers of 0.004" RO4350B cores and RO4450B prepreg. The MLB's were made to thicknesses of approximately 0.060", 0.090", 0.125", and 0.175" by evenly spacing additional core and prepreg layers between the metal layers. Each multi-layer master panel provided sixteen 5"X4" test coupons with each test coupon having three daisy-chained clusters of 220 PTH's per cluster. Connections within each cluster were made from L1-L6, L2-L7, L3-L8, L4-L9, and L5-L10. The drilled hole diameters in one of each of the three clusters were 9.8 mils, 13.5 mils, and 19.8 mils. In considering all drilled hole diameters and the thickness of all constructions, aspect ratios in this evaluation ranged from 3:1 to 18:1. A picture of a 0.175" thick coupon is provided below.



The resistance of daisy-chained clusters was measured and coupons were exposed to the following conditions:

- -Ten 60-second floats on 288°C solder
- -60 minutes of pressure pot conditioning followed by a 60 second/288°C solder float
- -100 hours conditioning at 85C/85%R.H. followed by a 60 second/288°C solder float

-24 hour immersion in 50°C water (D-24/50) followed by a 60 second/288°C solder float

The resistance of the daisy-chained clusters was re-measured following the conditioning. Using a 5% increase over initial resistance readings as the threshold limit, no failures were detected in the continuity of the daisy-chained clusters regardless of board thickness or hole diameter. In addition, there were no visual signs of delamination, measling, or blistering during surface and cross-section inspections.

Resistance readings were taken on nine coupons of each board thickness before the boards were sent to an outside contractor for processing through ten reflow cycles (See Figure 3.). Resistance readings remained within tolerance and there were no visual signs of mechanical defects having formed. Six coupons of each thickness were forwarded to an independent laboratory where half of the boards were exposed to 1000 –55°C to 125°C air-air thermal shock cycles and half of the boards were exposed to 500 –55°C to 150°C air-air thermal shock cycles. The remaining three coupons of each thickness were exposed to 250°C to 225°C liquid-liquid thermal shock cycles. In the case of air-air cycling, the dwell at each temperature was 20 minutes and the transition time between chambers was less than 60 seconds. Resistance readings were taken during each hot cycle. The dwell time during liquid-liquid cycling was ten minutes at each temperature and the transfer time was immediate. Resistance readings were taken at room temperature after every fifth cycle. Once again using a 5% increase to resistance as the threshold, no failures were detected regardless of hole diameter, board thickness, or thermal shock conditions. Furthermore, there were no visual signs of measling, blistering, fracturing, or delamination during surface and cross-section inspections.

Conclusion: The following list of properties and performance clearly demonstrates that RO4000 materials are lead-free compatible.

RO4000 PROPERTIES/PERFORMANCE THROUGH LEAD-FREE COMPATIBILITY EVALUATIONS

THERMAL PROPERTIES

Tg (DSC, TMA)	No transitions below 300°C
Td (5% Weight Loss – TGA)	>390°C
Z-Axis CTE (-55°C to 300°C)	Low, stable through 300°C
T-288 (0.125" MLB)	>90 minutes (twice)

COPPER ADHESION

Copper Peel Strength	Stable through 10X 260°C reflow cycles
Copper Peel Strength	Stable through 10X 60 second, 288°C solder floats
SMT Re-Workability	Survived 3X 371°C re-work cycles

MLB/PTH RELIABILITY

(0.60"-0.175" Thickness, 3:1-18:1 Aspect Ratio)

10X 60 Second/288°C Solder Float	Electrical/Mechanical Pass
60 Minute Pressure Pot/288°C Solder Float	Electrical/Mechanical Pass

100 Hours 85C/85% R.H./288°C Solder Float	Electrical/Mechanical Pass
D-24/50/288°C Solder Float	Electrical/Mechanical Pass
10X 260C Reflow/1000 –55C-125°C Shock Cycles	Electrical/Mechanical Pass
10X 260C Reflow/500 –55C-150°C Shock Cycles	Electrical/Mechanical Pass
10X 260C Reflow/25 0C-225°C Shock Cycles	Electrical/Mechanical Pass