The Effects of RoHS, WEEE, Lead Free & Halogen Free on PCB's & CCL's

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M I C R O T E K L A B O R A T O R I E S

CCL Materials for Lead Free / Halogen Free

Base Material – “High Temp” FR-4

- Technical Definitions
  - Multifunctional Epoxy T_g 140-150°C
    - Standard difunctional epoxy resin with a minimal amount of multifunctional epoxy resin to yield marginal improvement in thermal performance. In these systems, 2% tetrafunctional resin is added for optical inspection. A T_g of this range can also be achieved via higher loadings of tetrafunctional resin.
  - High temperature epoxy T_g 150-190°c
    - High percentage blends of multifunctional epoxy resin with difunctional epoxy resin or 100% multifunctional epoxy systems designed to yield significant improvements in thermal performance, decomposition temperature and chemical resistance.
  - High performance T_g > 190°c
    - Specialty resins designed to yield significant improvements in thermal performance, decomposition temperature and chemical resistance. High performance epoxies can be used where higher continuous operating temperatures are required. These systems are normally patent protected.

Resin System Properties

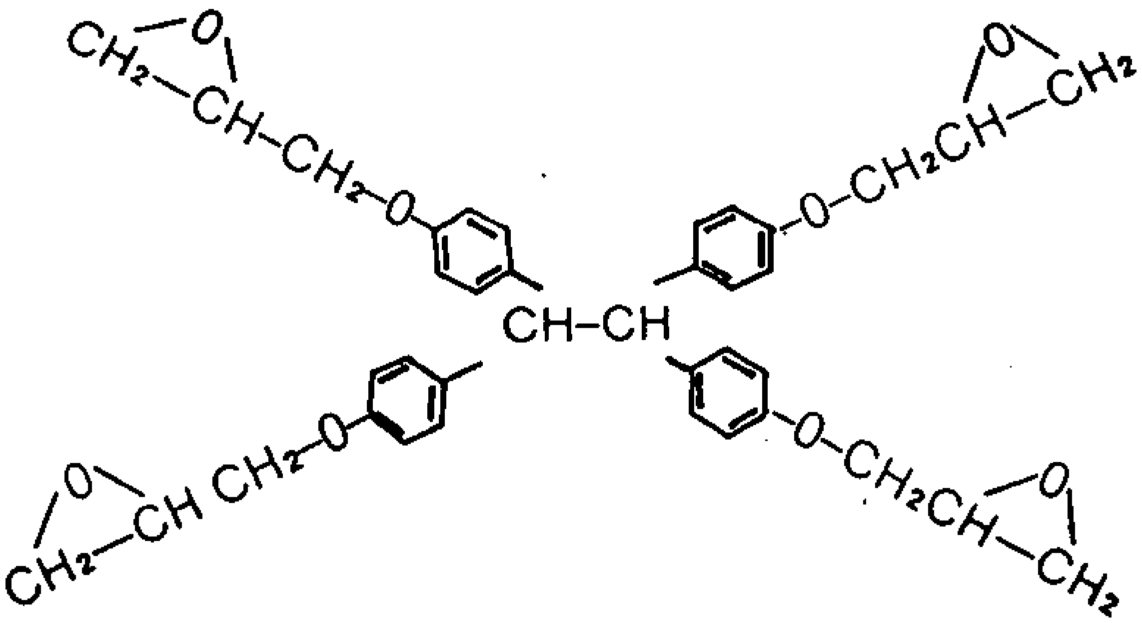
Environmental Properties of Common Dielectric Materials

Environmental Property	Material					
	FR-4 (Epoxy E-glass)	Multi-functional Epoxy	High Performance Epoxy	Bismaleimide Triazine/ Epoxy	Polyimide	Cyanate Ester
Thermal Expansion xy-plane (ppm/°C)	16 -19	14-18	14-18	~15	8-18	~15
Thermal Expansion z-axis below Tg[3] (ppm/°C)	50-85	44-80	~44	~70	35-70	~81
Glass Transition Temp. Tg (°C)	110 - 140	130 -160	165 - 190	175 - 200	220 - 280	180 - 260
Flexural Modulus ($\times 10^{10}$ Pa) [$\times 10^{6}$ psi] Fill[1] Warp[2]	 1.86 1.20	 1.86 2.07	 1.93 2.20	 2.07 2.41	 2.69 2.89	 2.07 2.20
Tensile Strength ($\times 10^{8}$ Pa) [$\times 10^{4}$ psi] Fill[1] Warp[2]	 4.13 4.82	 4.13 4.48	 4.13 5.24	 3.93 4.27	 4.82 5.51	 3.45 4.13
Water Absorption (wt%)	1.3	0.1	0.3	1.3	0.5	0.8

1 Fill – yarns that are woven in a crosswise direction of the fabric.
2 Warp (cloth) - yarns that are woven in the lengthwise direction of the fabric.
3 Z-axis expansion above Tg can be as much as four times greater. For FR-4 it is 240-390 ppm. Contact supplier for specific values of the other materials

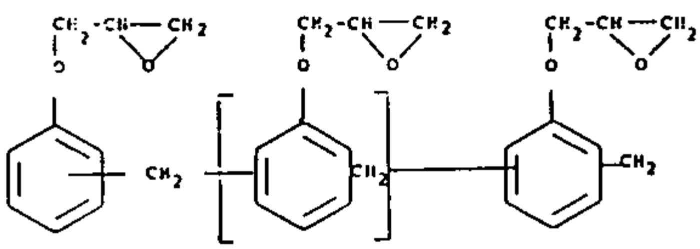
Base Material – “High Temp” FR-4

Tetrafunctional Resins

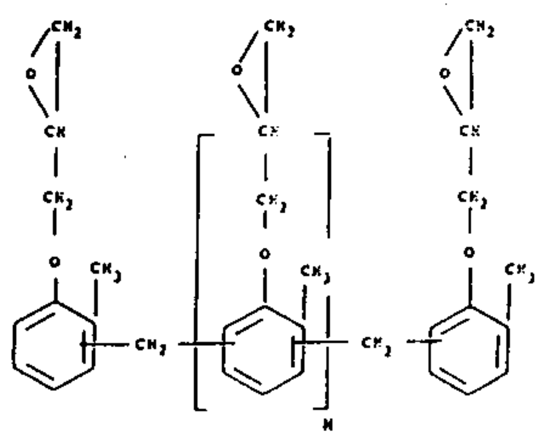


Base Material – "High Temp" FR-4

Multifunctional Resins



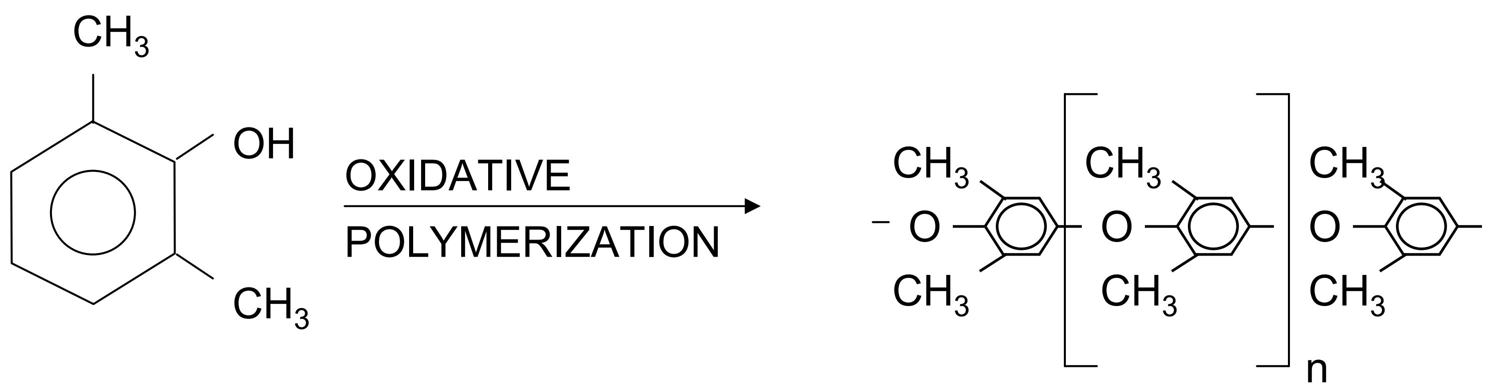
EPOXY PHENOL NOVOLAK



EPOXY CRESOL NOVOLAK

Base Material – "High Temp" FR-4

Epoxy / Polyphenylene Oxide Resins



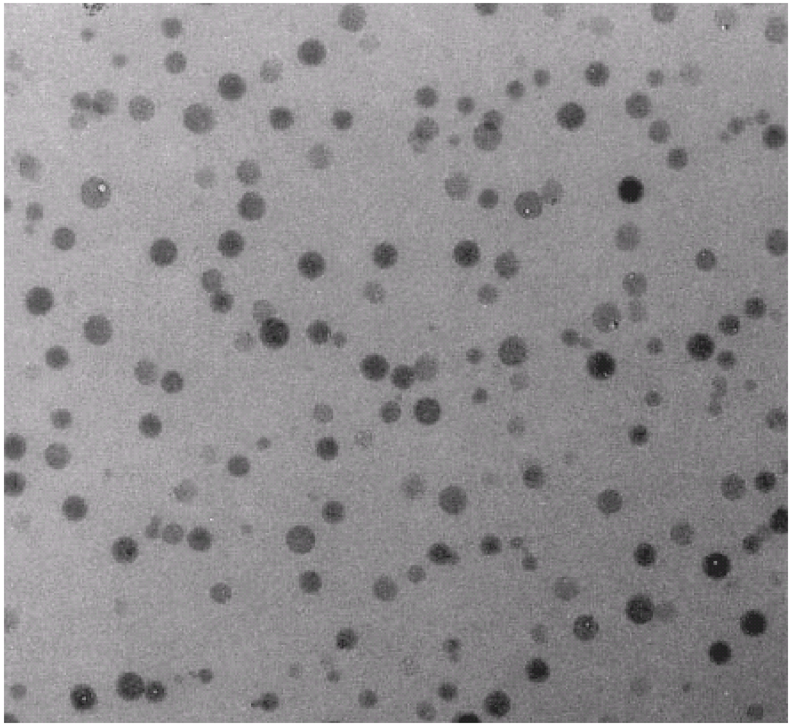
2, 6 XYLENOL

Base Material – “High Temp” FR-4

- Novalac Cured Systems
  - Advantages
    - Higher T_g (i.e. 170 degrees C).
    - Better thermal performance.
    - Improved chemical and moisture performance
  - Disadvantages
    - More difficult to drill
    - Shorter shelf life of prepreg

Core Shell Rubber Toughening Agents

- Improve Z-Axis expansion:
  - - alpha 1
  - - alpha 2
  - - overall %
- Improve T-260 and T-288 test results
- IncreasedPeel strength.
- Does not lower the Tg of the Material



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Base Materials – “Lead Free”

- Lead-Free Misconceptions*
  - Lead-free assembly will have only a minor effect on laminate and prepreg base materials.
  - New material types will not be needed, but more applications will switch to existing high T_g materials.
  - Most existing materials can be used in lead-free assembly without a significant problem.
  - 140°C T_g FR-4s are not compatible with lead-free assembly processes.

* Ed Kelley, Polyclad Laminates, Cookson Electronics

IEC "Lead-Free" Compatible Standards

- **IEC 61249-2-35** Materials for interconnecting structures – Part 2: Sectional specification set for reinforced based materials, clad and unclad – Section 35: Modified epoxide woven glass fabric copper-clad sheet of defined flammability for lead-free assembly

- **IEC 61249-4-15** Materials for interconnecting structures Part 4: Sectional specification set for prepreg materials, unclad (for the manufacture of multilayer boards) – Section 15: Multifunctional epoxide woven E-glass prepreg of defined flammability for lead-free compatible assembly

- **Requirements to be identical to IPC-4101B**

IPC "Lead-Free" Compatible Standards

- IPC-4101 Revision B.
- Includes specification sheets for lead-free assembly compatible materials.
  - Improved thermal resistance, Z-Axis and inter-laminar adhesion.
  - Requirements finalized for both 140 and 170°C T_g FR-4 materials.
  - UL forced separate specifications for filled and unfilled FR-4s.

IPC FR-4 Lead-Free Compatible Material (170 T_g)

Reinforcement:	Woven E-Glass
Primary Resin System:	Multifunctional Epoxy
Secondary Resin System:	Modified Epoxy or Non-Epoxy
Filler:	With Inorganic Fillers
Curing Agent:	Not specified
Flame Retardant:	RoHS Compliant Bromine

IPC-4101B/99

IPC FR-4 Lead-Free Compatible Material (140 T_g)

Reinforcement:	Woven E-Glass
Primary Resin System:	Multifunctional Epoxy
Secondary Resin System:	Modified Epoxy or Non-Epoxy
Filler:	With Inorganic Fillers
Curing Agent:	Not specified
Flame Retardant:	RoHS Compliant Bromine

IPC-4101B/101

IPC FR-4 Lead-Free Compatible Material (170 T_g)

Reinforcement:	Woven E-Glass
Primary Resin System:	Multifunctional Epoxy
Secondary Resin System:	Modified Epoxy or Non-Epoxy
Filler:	No Fillers
Curing Agent:	Not specified
Flame Retardant:	RoHS Compliant Bromine

IPC-4101B/124

IPC FR-4 Lead-Free Compatible Material (140 T_g)

Reinforcement:	Woven E-Glass
Primary Resin System:	Multifunctional Epoxy
Secondary Resin System:	Modified Epoxy or Non-Epoxy
Filler:	No Fillers
Curing Agent:	Not Specified
Flame Retardant:	RoHS Compliant Bromine

IPC-4101B/121

IPC FR-4 Lead-Free Compatible Material (170 T_g)

- Decomposition Temp: 325°C minimum
- Z-Axis Expansion:
  - Alpha 1 — 60 ppm maximum
  - Alpha 2 — 300 ppm maximum
  - 50 to 260°C — 3.5% maximum
- T260 Resistance: 30 minutes minimum
- T288 Resistance: 5 minutes minimum
- T300 Resistance: AABUS (as agreed upon between user and supplier)
- CAF Resistance: AABUS

IPC-4101B/99
IPC-4101B/124

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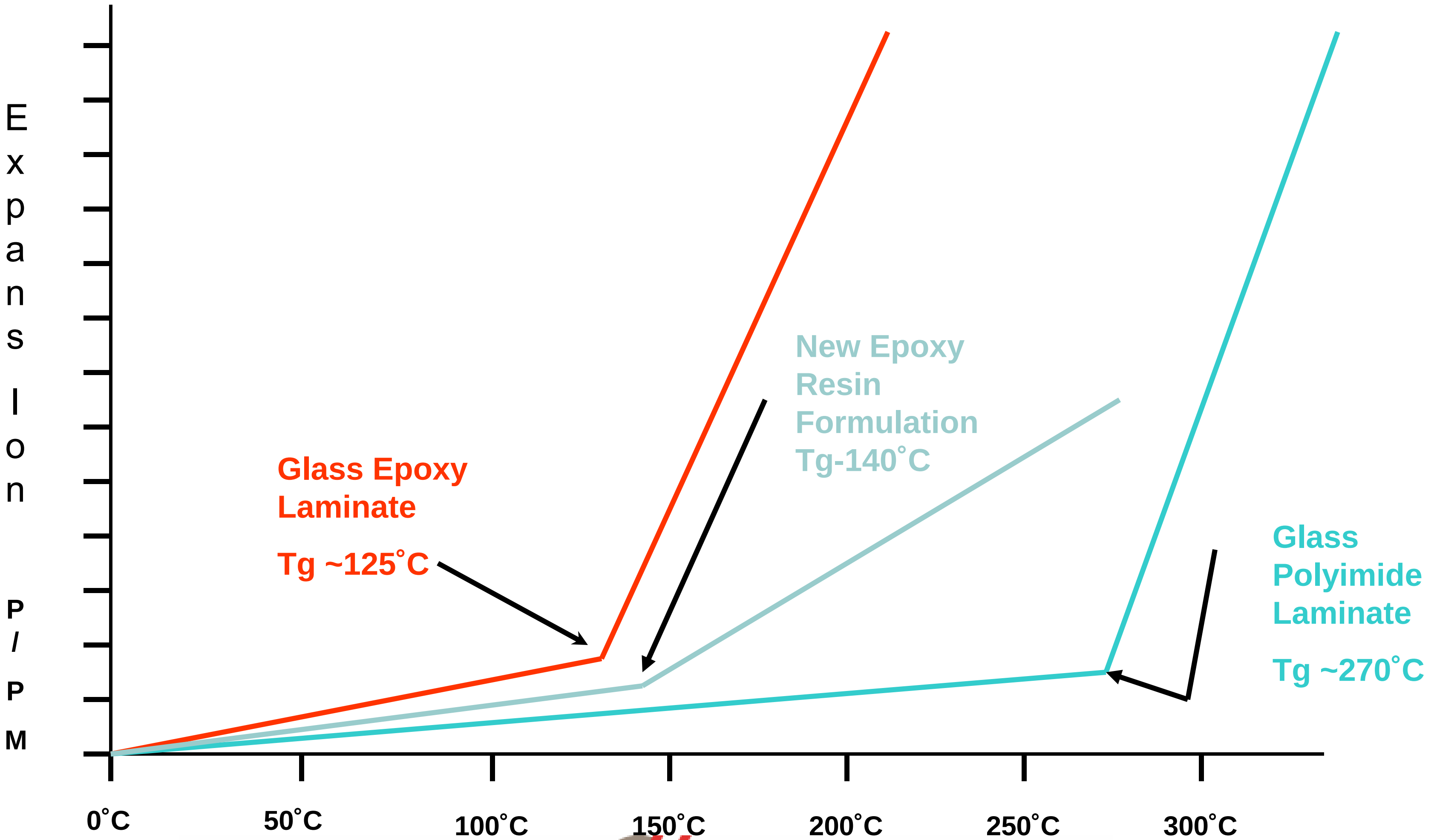
IPC FR-4 Lead-Free Compatible Material (140 T_g)

- Decomposition Temp: 310°C minimum
- Z-Axis Expansion:
  - Alpha 1 — 60 ppm maximum
  - Alpha 2 — 300 ppm maximum
  - 50 to 260°C — 4.0% maximum
- T260 Resistance: 30 minutes minimum
- T288 Resistance: 5 minutes minimum
- T300 Resistance: AABUS (as agreed upon between user and supplier)
- CAF Resistance: AABUS

IPC-4101B/101
IPC-4101B/121

Glass Transition Temperature (T_g)



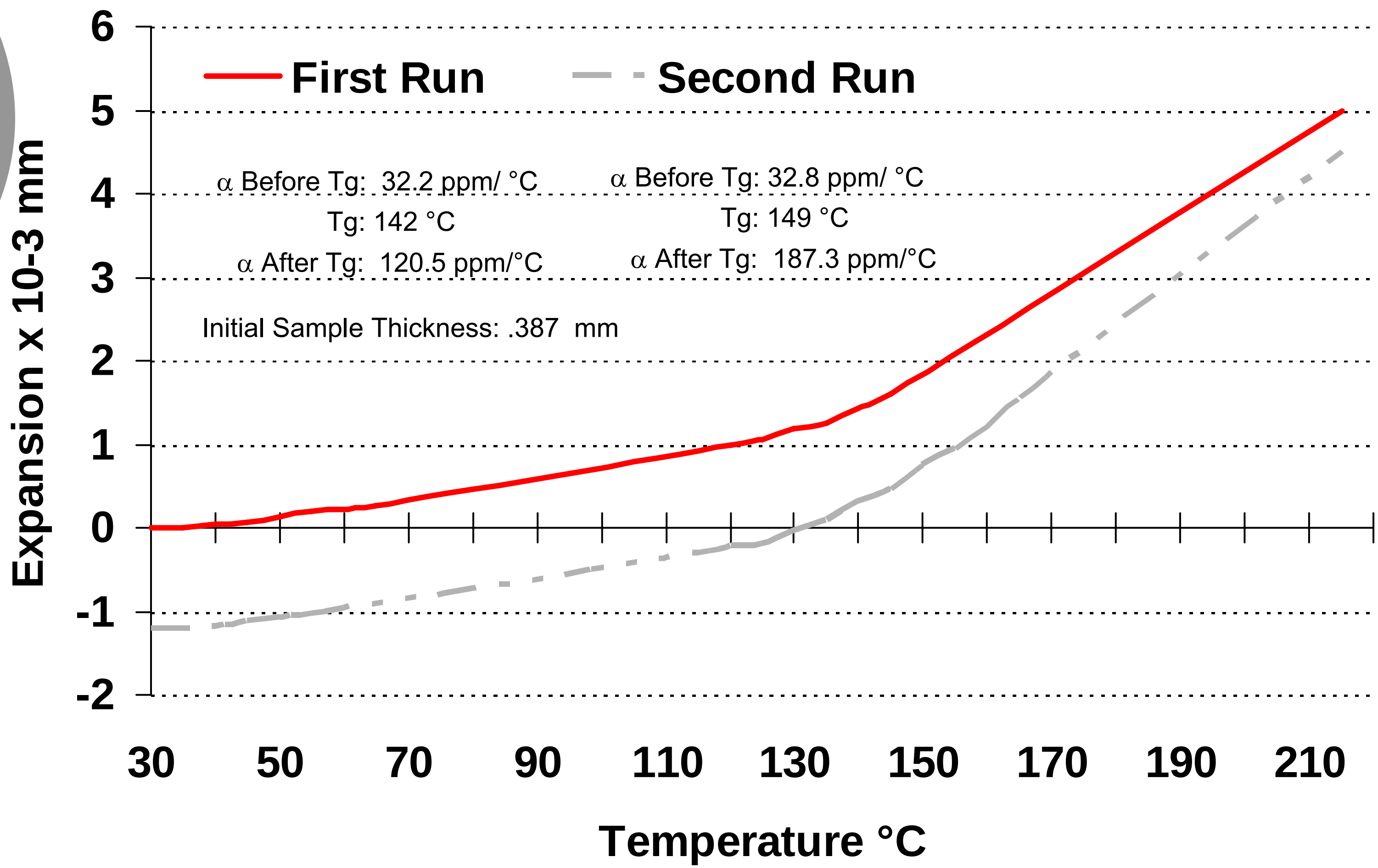
Testing Techniques
Thermal Mechanical Analysis (TMA)

- Evaluates expansion vs. temperature
  - Quartz rod measures actual expansion
  - Precise heater chamber
  - Small sample diameter (3-5 mm)
  - Sample should have no copper or soldermask
- Glass transition temperature (T_g)
  - Calculate using intersection of expansion rates
- Coefficient of thermal expansion (CTE)

Testing Techniques
Thermal Mechanical Analysis (TMA)

- Evaluate material cure with double run
  - Scans twice consecutively
  - Change in slope of expansion line evaluated
  - Change in glass transition temperature evaluated
- **Time to delamination (T-260)**
  - **Used to compare differences in materials**
  - **Possible use by UL to reduce testing of composite materials**
- **New lead free solder tests (T-288)**
  - **Used by communications/network companies/UL**

Testing Techniques
Thermal Mechanical Analysis (TMA)



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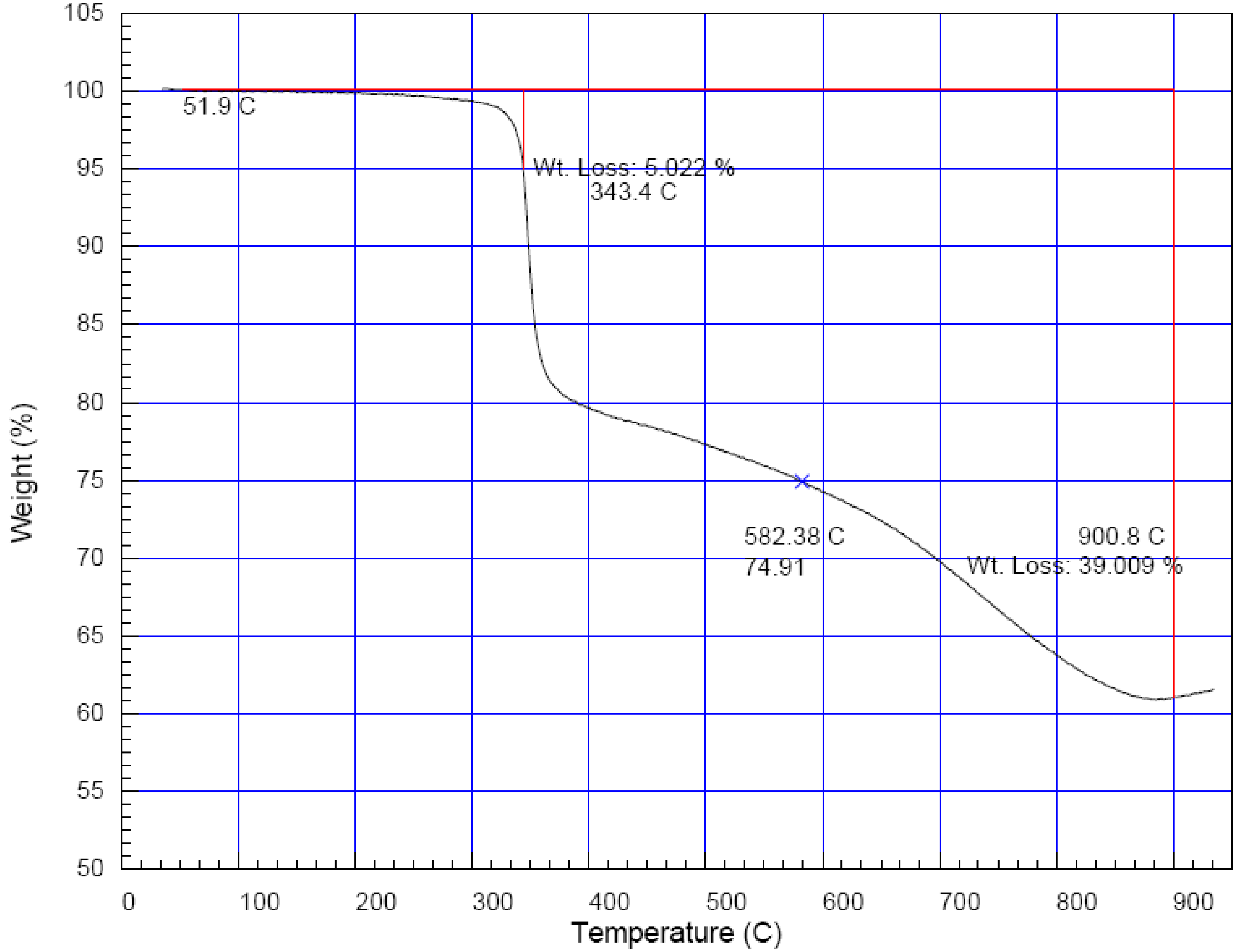
Testing Techniques
Thermo Gravimetric Analysis (TGA)

- Weight Loss vs. Temperature
  - Plot loss of weight as temperature increases
- Evaluate material Decomposition Temperature
  - 5% loss of weight from 30°C considered "decomposed"
- New IPC Test Method Proposal
  - Test Method 2.4.24.6
- IPC 4101 "Lead Free" slash sheets call out this test.

Testing Techniques
Thermo Gravimetric Analysis (TGA)



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Flame Retardants – Why Use Them?

- The major human health hazard is fire itself, not which materials are burning
- Flame retardants must balance:
  - Health
  - Environment
  - Performance
  - Cost

Why Use Flame Retardants

- Proper Flame Retardants:
  - Retard ignition
  - Delay or eliminate flashover
  - Reduce heat concentration
  - Reduce evolution of toxic gases
  - Increase time for escape

2003 US Fire Statistics

- Fire departments went to 1,584,500 fires
- Firefighters killed –111
- Civilians killed –3,925
- Civilians injured –18,125
- Direct property loss –$12.3 billion
- Structural fires –519,500 & 3,365 deaths
- 80% occurred in residential properties
- Vehicle fires –312,000 & 465 deaths
- Property damage ~ $1.3 billion

Brominated Flame Retardants are very diverse

- There are more than 75 different Brominates Flame Retardants
  - Only Common Point: All Contain An Element Widely Available In Nature, Bromine
- Environmental/Regulatory Scrutiny Focused primarily on a few BrFRs:
  - PBBs(Polybrominated biphenyls) –no longer produced
  - Penta-BDE: pentabromodiphenyl ether –no longer produced
  - Octa-BDE: octabromodiphenyl ether –no longer produced
  - PBDEs (Polybrominated diphenyl ethers)
  - Deca-BDE: decabromodiphenyl ether

EU Risk Assessment (RA)

- The most comprehensive assessment of chemicals' environmental and human health impacts
- This examines all aspects of a chemical
- Products are assessed individually, not as a class
- Nine Flame Retardants have or are undergoing RA
- If RA determines that risk reduction is necessary, then a Risk Management Program is developed

Why is this important "Now"

1. Legislative regulations
2. "Green" Marketing
3. Misinformation and misinterpretation

Early draft legislation confused marketplace

- Early drafts of the WEEE directive (Pre RoHS) targeted all Brominated Flame Retardants.
- This was corrected when the legislation split into WEEE and RoHS
- Many still confused

RoHS Compliant Bromine Requirement

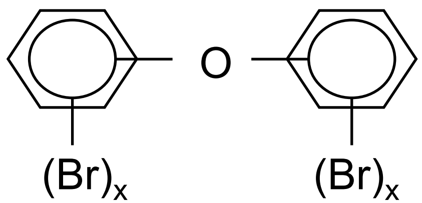
- RoHS does not ban all brominated materials used currently as a flame retardant for circuit boards.
- Bromine containing compounds that are outlawed by RoHS are those that remain as independent molecules within the polymeric matrix. These include:
  - poly biphenyl ethers or oxides (PBDE or PBBO)
  - poly brominated biphenyls (PBB)
- Bromine containing compounds that are acceptable by RoHS include those that react to become a chemical part of the polymeric matrix.
  - Tetra-Bromo-Bis-Phenol A (TBBPA)

Penta-& Octa–BDE EU Risk Assessment

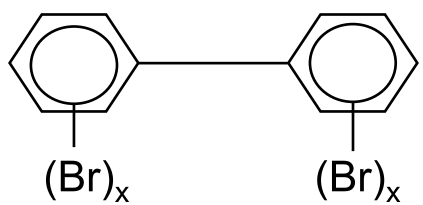
- Polybrominated diphenylethers (PBDEs)
  - Penta-BDE –Pentabromodiphenyl ether –Used predominately in PU foam
  - Risk Assessment was unfavorable
  - Ban of Penta-BDE in EU from August 15, 2004
- Octa-BDE –Octabromodiphenyl ether - Most use in automotive applications
  - Risk assessment indicated some risk
  - Ban of Octa-BDE in EU from August 15, 2004

RoHS Compliant Bromine Requirement

These brominated flame retardants <u>are banned by RoHS</u>



Polybrominated Biphenyl Oxide (PBBO or PBDE)



Polybrominated Biphenyl (PBB)

Deca-BDE EU Risk Assessment

- Ten years of evaluation
- EU risk assessment now covers 588 studies
- Deca-BDE is one of the most studies chemicals
- Risk Assessment on Deca-BDE concluded
  - Deca-BDE is **not toxic** to living organisms
  - Deca-BDE is **very poorly absorbed** if swallowed or inhaled
  - Deca-BDE **does NOT build-up or bioaccumulate** in humans over time
- The bottom line: No use restrictions needed based on current science

EU RoHS Directive

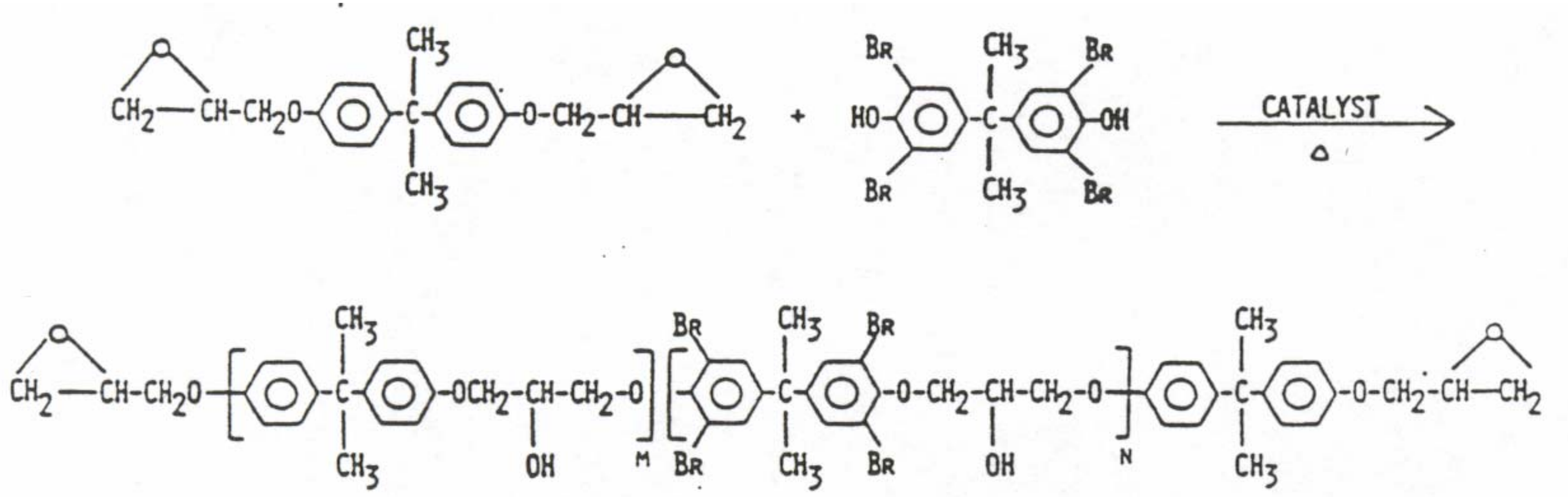
- On Oct 15, 2005, the EU Commission exempted Deca-BDE from the RoHS Directive (2005/717/EC)
- This decision --
  - Follows an intensive review of all available information
  - Is based on results of a comprehensive EU Risk Assessment beginning over 10 years ago, involving studies and independent review
  - Represents the final step in the RoHS regulatory procedure for adopting exemptions
  - Allows for continued use of Deca-BDE in electrical electronic equipment in the EU in all applications

Tetrabromobisphenol-A (TBBPA)

- TBBPA is the leading flame retardant used in circuit boards (95%) and computer chip casings
- TBBPA reacts into resin chemistries.
- TBBPA is very effective in low addition levels
- TBBPA is used because it is cost effective, compatible with circuit board components, and qualified for use on a worldwide basis
- TBBPA has also been used as an additive some electronic enclosures plastics
- The use of TBBPA is not currently banned in any country

RoHS Compliant Bromine Requirement

These brominated flame retardants are acceptable by RoHS



This Brominated epoxy resin is used for FR-4 production

TBBPA -EU Risk Assessment

- Human Health
  - Human Health assessment has been completed
  - No identifiable risks in any of the scenarios
  - No need for risk reduction measures
- Environmental
  - Expected to be completed in 2006
  - Classified in the EU as an R50/53 substance for the environment ("toxic to aquatic organisms" and "may cause long-term adverse effects in the aquatic environment"
  - This classification is effectively managed by good product stewardship to minimize or eliminate release to the environment

“Halogen-Free” Is Marketing Driven

- OEMs in Japan and Europe began “environmental friendly” campaigns with “lead-free”
- OEMs now pushing “halogen-free” with their supply chains
- OEMs now threaten cut-off of suppliers who fail to comply

Misinformation

- Electronics companies developing entirely halogen-free (i.e. bromine-free) systems to avoid extra costs of separation
- Yet some companies insist that Halogen Free = **Green**
- **Data does not bear this out**

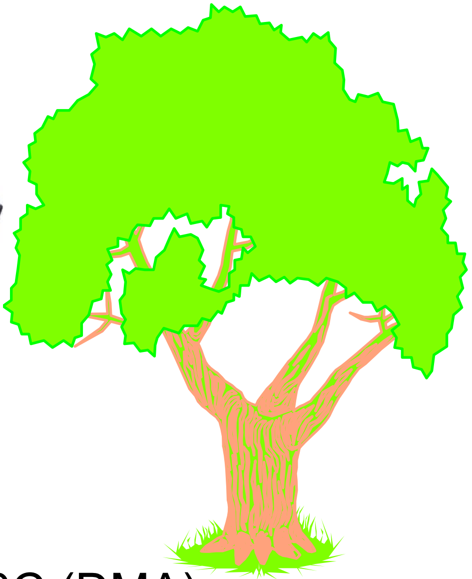
An Example of “Green” Marketing

Toshiba Chemical Corporation

<u>Environment Friendly Laminate</u>

Halogen-Free and Antimony-Free Glass Epoxy Copper Clad Laminate

TLC-555/Single side, TLC-W-555/Double Side
NEMA : FR-4, JIS : GE4F



*Halogen-Free Type
*Antimony-Free Type
*Flammability Class UL94 V-0
*Low Smoking Nature
*Easy Waste Disposal
*Higher Glass Transition Temperature (Tg) : 170-180C (DMA)
*Excellent Peel Strength for Long Term Aging
*UL Approval

Marketing Ecolabels

- Awarded products that meet specific environmental requirements
  - France
  - US
  - Germany
  - Japan
  - Canada
  - EU
  - Nordic Swan
  - Netherlands
- Enable consumers to know they are buying products that are environmentally sound
- Manufacturers use them as marketing tool

Non-Brominated Epoxy Resins are ***Not*** "Halogen-Free"

- Most PCB Resins are Epoxies
- Epoxy resins contain measurable levels of Chlorine (Saponifiable, Hydrolyzable and fixed Chlorides)
- Additional halogens are added to PCB laminates through glass sizes, wetting agents, curing agents and resin accelerators.

Halogen-Free Dielectric Substrates

- WEEE (Waste Electrical and Electronic Equipment Amending Directive 76/769/ECC – Current Draft
- Article 4, 4a "Member States shall insure the use of… PBB and PBDEs are phased out by 1 January 2004"
- Anex III, 1 "Components containing substances or preparations listed below have to be removed from any waste electrical and electronic equipment that is separately collected:… Halogenated flame retardants"

RoHS Compliant Bromine Requirement

- Being RoHS compliant does not mean the base material must be halogen free.
- Certain brominated flame retardants including the most popular brominated flame retardant for FR-4, TBBPA, are accepted by RoHS.
- Decabromo Diphenylether has been given an exemption by RoHS.

Halogen-Free Dielectric Substrate Considerations

- Performance Criteria
- 94-V0 Flame Rating
- Performance
  - Thermal
  - Electrical
  - Processability
  - Quality
  - Peel strength
  - Moisture absorption
- Cost

Halogen-Free Dielectric Flame Retardants

- Inorganic fillers
  - Alumina Trihydrate (ATH)
  - Magnesium Hydroxide Mg (OH_2)
  - Zinc Borate
- Mechanism:
  - Release of water (and may promote char)
- Advantages:
  - Relatively inexpensive
  - Useful as synergist
- Disadvantages:
  - High loading required
  - Frequently narrow in temperature range performance
  - T_g reduction
  - Typically inadequate without synergist
  - Moisture sensitivity
  - Low peel strength

Halogen-Free Dielectric Flame Retardants

- Intumescent Combinassions – Additive
  - Organophosporus compounds
- Mechanism
  - Foaming char formation acts as insulator
- Advantages
  - Relatively low loading required
  - Very effective
  - No toxic by products
- Disadvantages
  - High cost
  - Difficult to work with
  - Alteration of prepreg performance
  - T_g reduction
  - Phosphate restrictions in USA
  - Moisture sensitivity

Halogen-Free Dielectric Flame Retardants

- Organic (Phosphorus) Materials – Additive
  - Red Phosphorus
  - Organophosphorus compounds
- Mechanism
  - Char formation
- Advantages
  - Relatively low loading of phosphorus required
  - Wide temperature range performance
- Disadvantages
  - High cost
  - T_g reduction
  - Frequently toxic before encapsulation in epoxy resin matrix
  - Alteration of prepreg performance
  - Low solubility
  - Phosphate restrictions in USA
  - Moisture sensitivity
  - Low peel strength

Halogen-Free Dielectric Flame Retardants

- Organic Materials – Reactive
  - Epoxy reactive phosphorus compounds
- Mechanism
  - Char formation
- Advantages
  - Relatively low loading of phosphorus required
  - Wide temperature range performance
  - No dispersion issues
  - Less toxic
  - Good thermal performance
  - Good peel strength
- Disadvantages
  - High cost
  - T_g reduction
  - Moisture sensitivity

Failure Warning: Components Packaged with Phosphorus-Containing Molding Compound

- CALCE Posting Date: May 3, 2002
- Failure in components due to internal shorting within 6 to 12 months of operation.
- Root-cause is the presence of phosphorus particles (used a substitute fire retardant) bridging wire bonds.
- Suggest issue mesh size to sieve their molding compound material.

Some alternatives actually worse

- Paper comparing economic and environmental impact of PCB manufacture with FR4 vs. halogen free flame retardant systems
- Used GrEEEN method of analysis
  - Production design, board manufacture, upstream manufacture, and downstream waste treatment
  - Materials consumption, energy, waste
  - Does not consider toxicity
- Cost increase of 10 – 50% for halogen free
- 0.3 – 1.3% increase in ecological impact for halogen free

Proceedings of Electronics Goes Green 2004

Assessment of Bromine Flame Retardant Alternatives

- Lifecycle impacts are key!
  - Design, Use, and End-of-Life
- Is alternative truly better for the environment?
- Can it meet same technical and functionality requirements?
- Are the alternatives compatible with higher lead-free processing temperatures?
- Will it decrease product safety or reliability?

UL Re-Classification of FR-4

- Project began in 1996.
- “What is FR-4” now?
- “What is FR-4” in the future?
- IR Scan is main criteria for new groupings.

UL Re-Classification of FR-4

- Group 1
  - Compare favorably to original IR scans for FR-4. Dicy-cured epoxy brominated resin (no fillers).
- Group 2
  - Some missing peaks (dicy). Novolak cured systems.
- Group 3
  - Inorganic filled systems (some additional peaks).
- Group 4
  - Everything not found in Groups 1, 2, 3. Non-halogen epoxy systems. Epoxy plus secondary resins.

UL Group 1 and 2

- 14 Reference Scans which now define FR-4:
  - Brominated Epoxy
  - Dicy or Novolak Cured
  - Woven E-glass Reinforcement
- Products from Group 1 & 2 only define references for standard FR-4.
- Testing must be conducted to demonstrate compatibility of mixed Groups.
  - Ie. Group 4 inner layers with Group 1 or 2 prepregs.

UL Re-Classification of Group 4

- Non-Epoxy Resins (BT, cyanate ester, hydrocarbon)
- Halogen-Free Systems
- Other Unusual Additives or Components

How Does Lead Free affect the PCB?

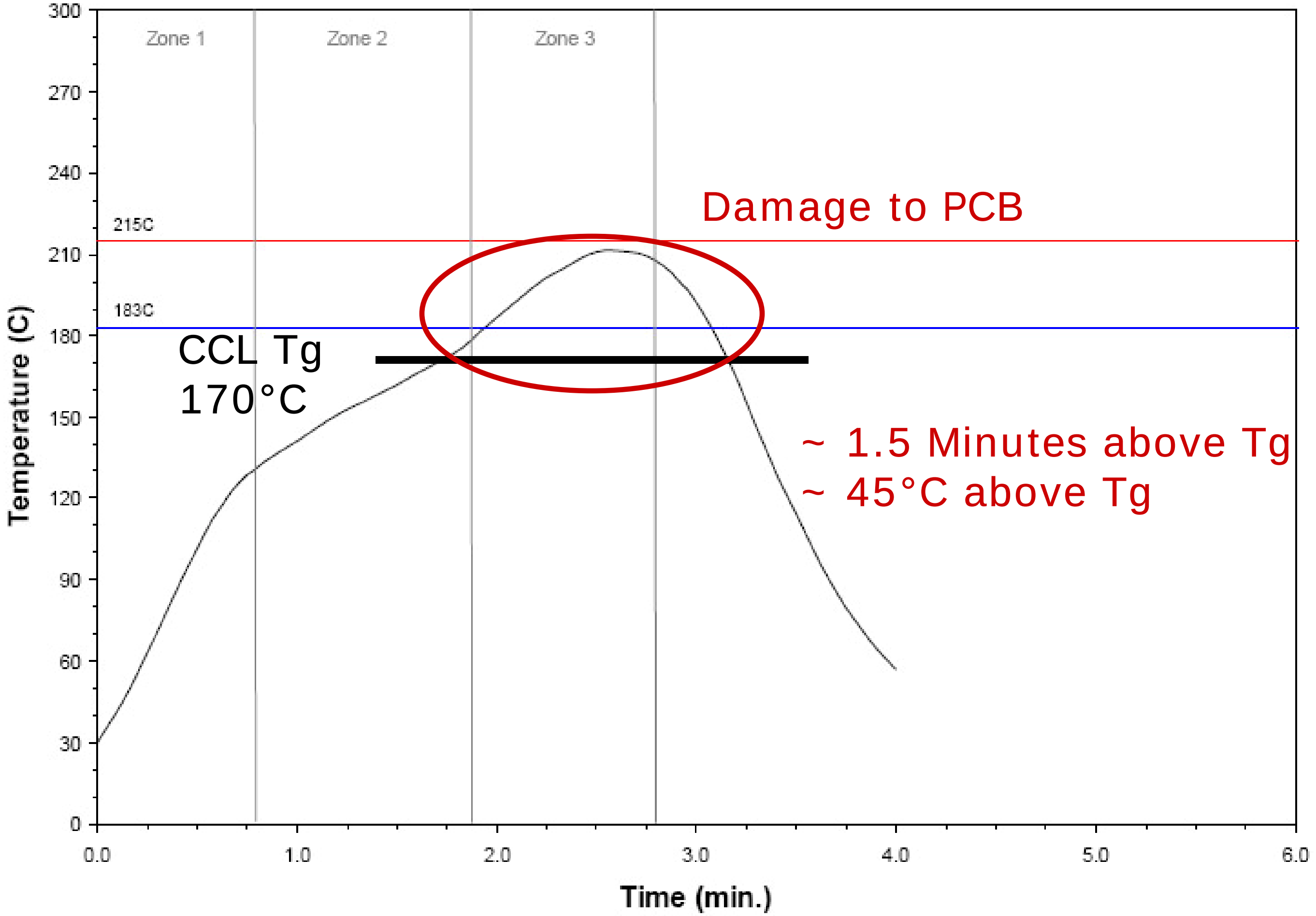
Lead Free Impact on Board Fabrication

- Common Mis-conceptions
  - “Lead-free assembly will have only a minor effect on laminates.”
  - “New material types will not be needed, but more applications will switch to existing high-Tg materials.”
  - “Most existing materials can be used in Lead-free assembly without a significant problem.”
  - “140°C Tg FR4 is not compatible with Lead-free assembly.”

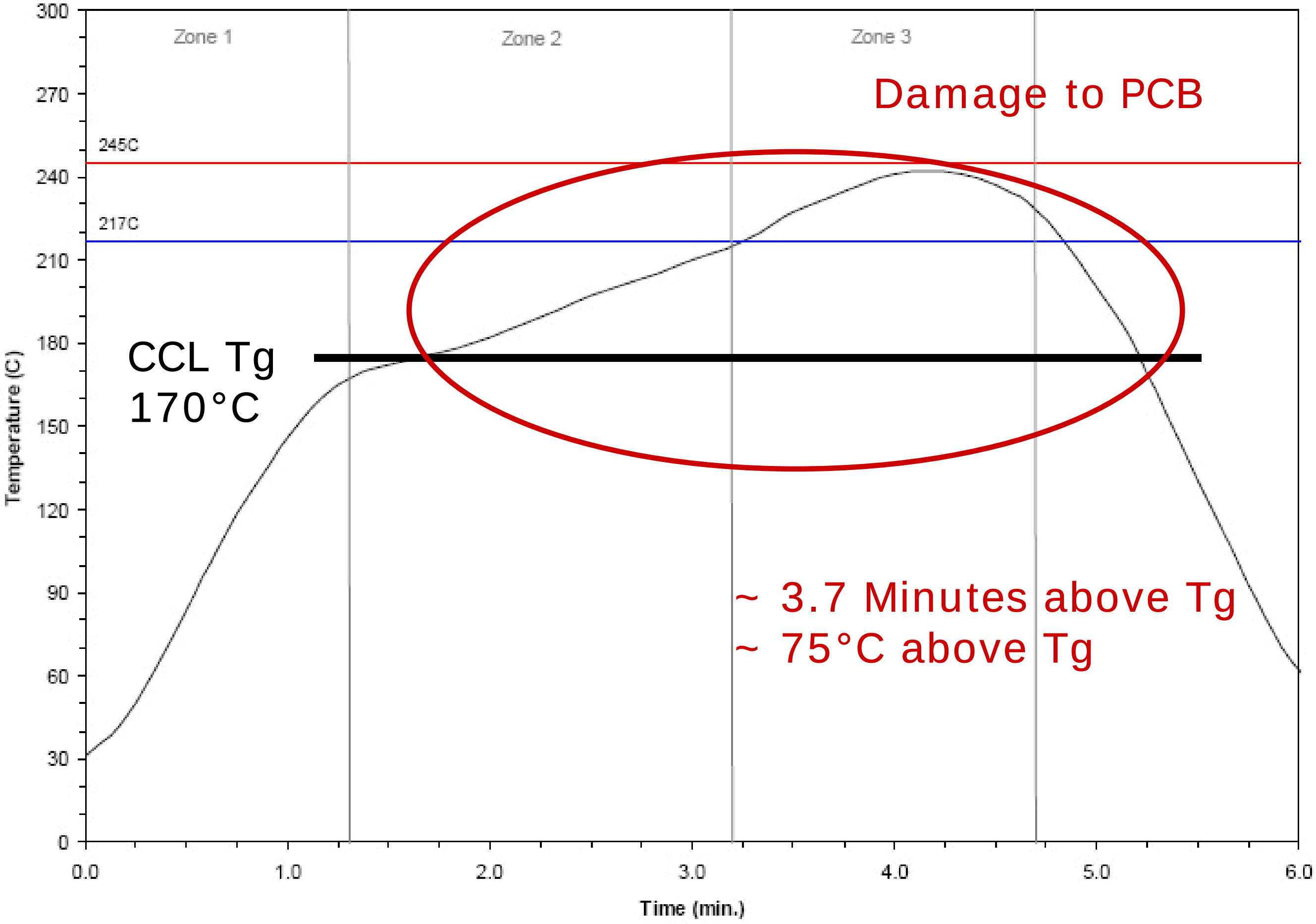
Component assembly temperatures for lead-free soldering

- Tin-lead attachment (Sn37Pb) alloy melts at 183°C with typical reflow temperatures of **205-220°C**.
- SnAgCu lead-free alloy's melting point is 217°C with typical reflow temperatures of **235-250°C**.

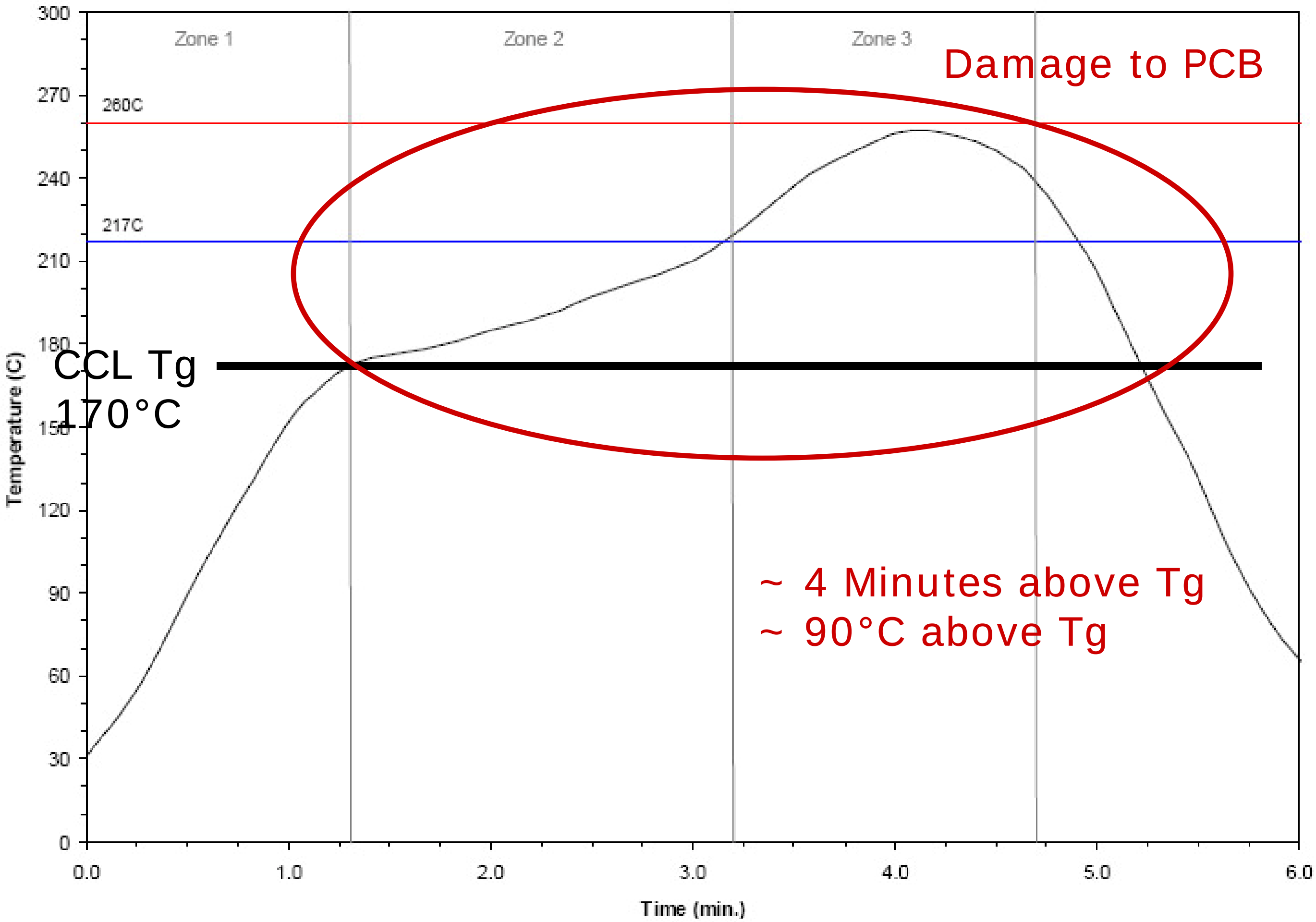
Leaded Solder Reflow Profile



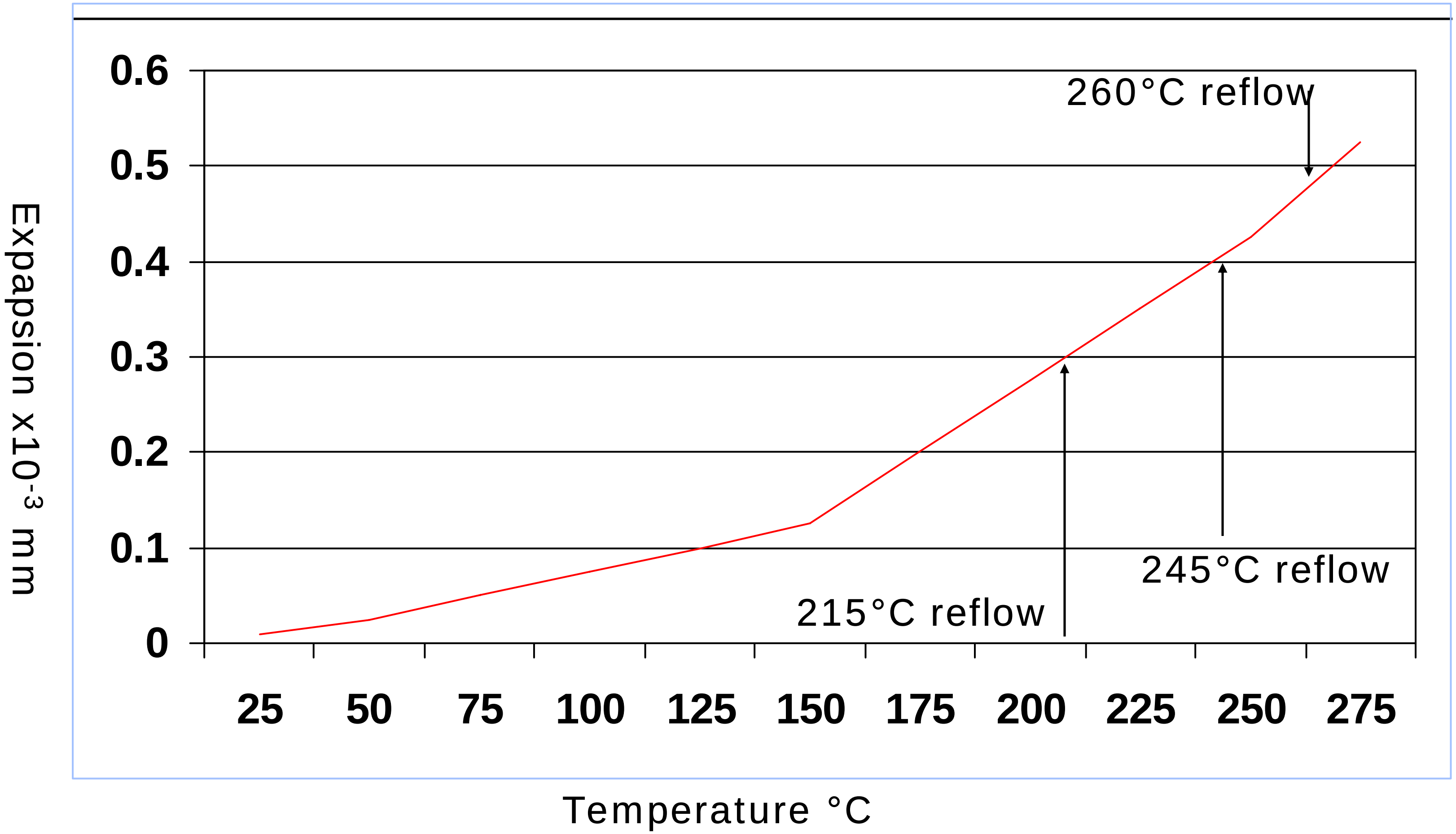
245°C Lead Free Reflow Profile



260°C Lead Free Reflow Profile



Z-Axis Expansion vs. Temperature



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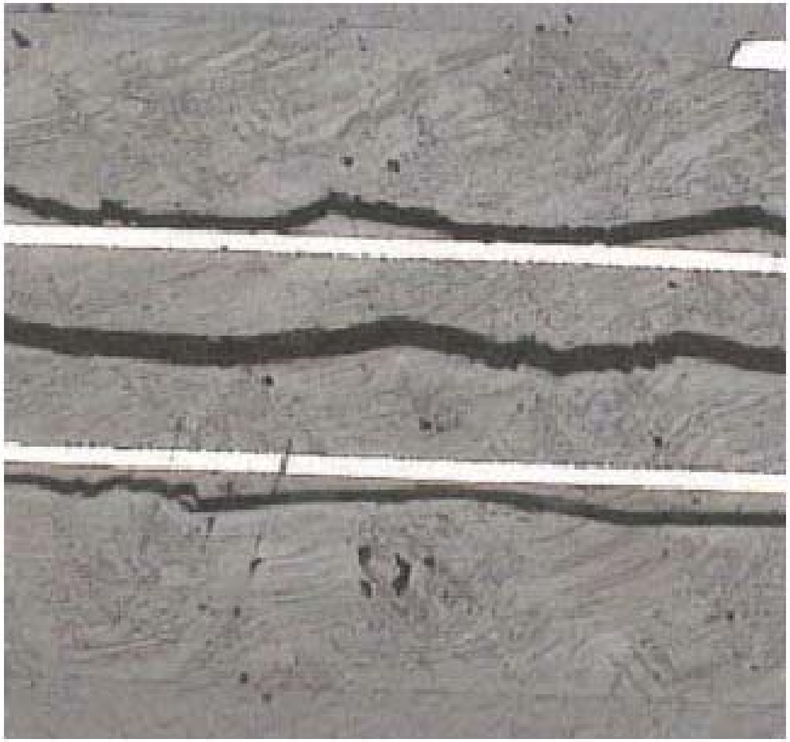
Lead Free Impact on Board Fabrication

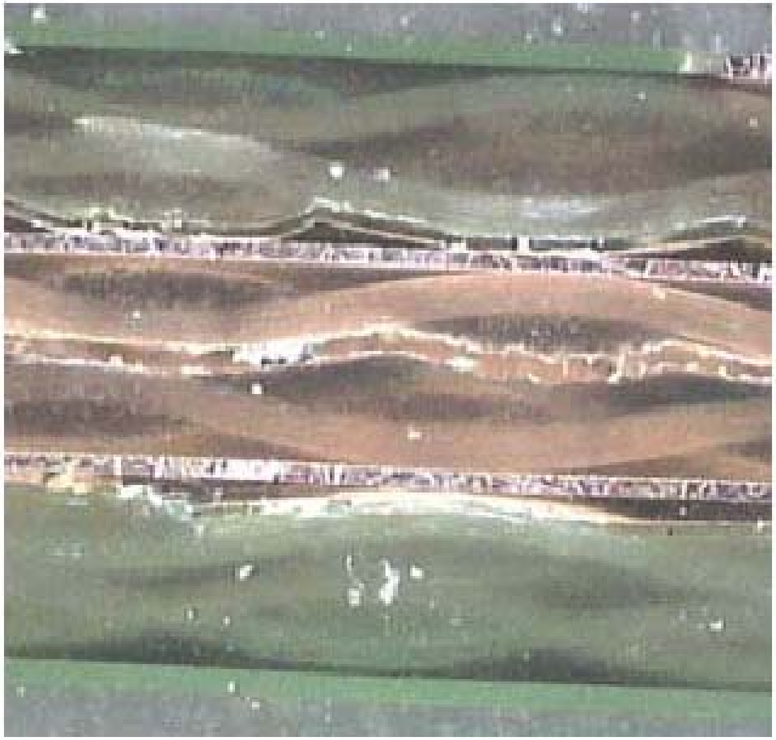
Challenges as a result of Higher Temperature Processing

Problems	Through hole reliability Delamination Measles Blister resistance
Mechanisms	Z Axis expansion Thermal stability
Key Base Material Properties	Degradation temp/Tg Time at temperature performance

Lead Free Impact on Board Fabrication
Worst Case Results

A Common 175°C Tg FR-4 After Lead-Free Assembly





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Lead Free Impact on Board Fabrication Processing

- More difficult to drill
- Lower tool life
- Lower chip load required
- Under cut drill bit geometry, high helix angle required
- Fracturing at array break-off

This equates to ¥¥¥ someplace along the line

Lead Free Impact on Board Fabrication CAF (Conductive Anodic Filaments)

Definition:

Conductive Anodic Filaments are copper corrosion by-products that emanate from the anode of a circuit and “grow” subsurface toward the cathode, frequently along separated fiber-epoxy interfaces.

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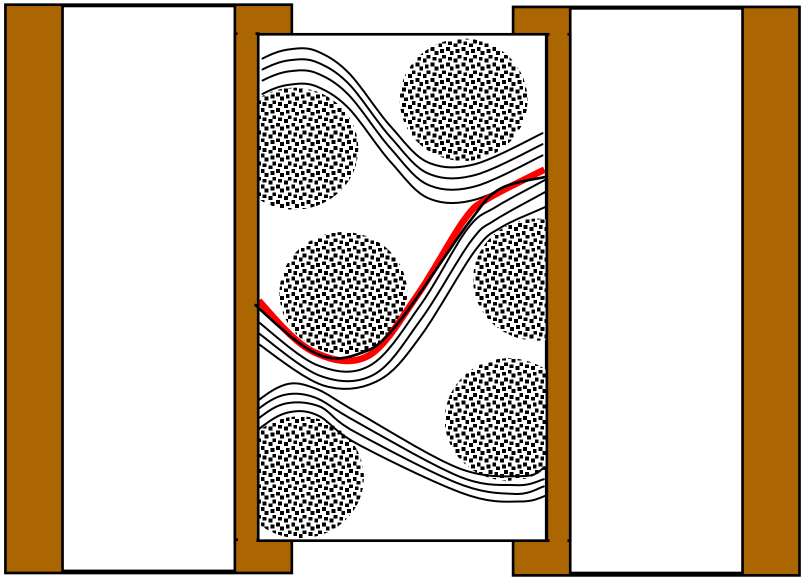
- Design Influences
  - High Density Circuits
    - Hole-to-hole
    - Hole-to-feature
    - Feature-to-feature, in plane
    - Feature to feature, out of plane



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- Physical Influences:
- High Humidity (~80%RH anytime during product life)
- High voltage gradient between anode and cathode (~3-8 V/mil)
- Hole drilling
- Multiple thermal Cycles during processing
- Certain soldering flux ingredients (polyglycol)

Material Selection Summary

- Specifying Tg may be necessary, but it is insufficient. Higher Tg is not always better.
- Decomposition temperature (Td) is a critical property to understand when specifying materials for Lead free assembly
- CTE values should be considered also.
- Time to delamination tests are increasingly relevant, but multilayer PCBs can be affected by other variables than just materials
- If switching materials, verify other performance characteristics also, e.g. Dielectric Constant and Dissipation Factor values.