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Resin Options for Lead-Free Printed Circuit Boards

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The Dow Chemical Co.

IPC Midwest 2007

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Outline

- New laminate requirements for lead-free solder application
  - Thermal resistance test
  - Prediction of lifetimes for given time & temp using TGA
  - Expansion (z-CTE) and moisture absorption
- New resin products that meet these requirements
  - Brominated
  - Non-brominated
- Cross properties relationship
  - Effect on toughness / adhesion
  - Toughness measurements
- Future laminate requirements

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IPC Lead-Free Specs

- Thermal resistance tests
  - Time to delamination at specific temperatures (T260, T288, T300)
    - IPC-TM-650 2.4.24.1 and 3.10.1.12 - TMA
    - Internal pressure from decomposition products is sufficient to cause the sample to delaminate and change dimensions
  - Thermal decomposition - Td (or Thermal stability)
    - IPC-TM-650 2.3.40 - TGA (@ 10 ° C/min)
    - Temperature at which 5 wt% of the sample is lost to volatile decomposition products
- Additional requirements
  - Z axis CTE and % expansion (50-260 ° C)
    - IPC-TM-650 2.4.24
  - Reduced moisture absorption (0.5% max)
    - IPC-TM-650 2.6.2.1

IPC 4101B

- Combination of key properties

IPC Specification Number	Tg (degC)	Td (deg C)	T288 (min.)	Moisture Absorption (max %)	CTE (ppm/deg C)	% Expansion (50-260 C)
IPC-4101B/26 (FR4 high Tg)	170 minimum	-	-	0.8	-	-
IPC-4101/101 (filled)	110 minimum	310	5	0.5	60/300	4
IPC-4101/121 (no filler)	110 minimum	310	5	0.5	60/300	4
IPC-4101/99 (filled)	150 minimum	325	5	0.5	60/300	3.5
IPC-4101/124 (no filler)	150 minimum	325	5	0.5	60/300	3.5
IPC-4101/126 (filled)	170 minimum	340	15	0.5	60/300	3
IPC-4101/129 (no filler)	170 minimum	340	15	0.5	60/300	3.5

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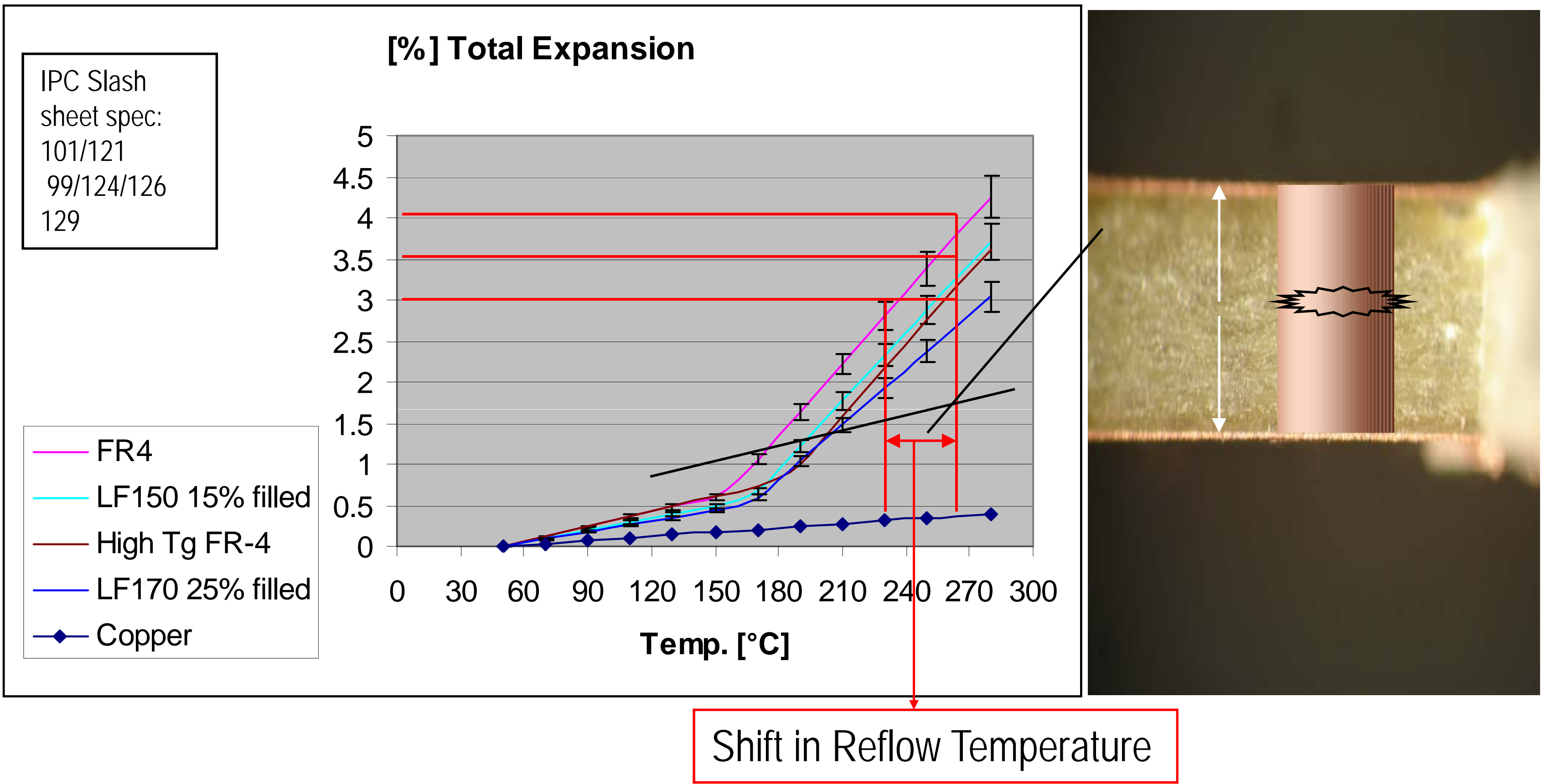
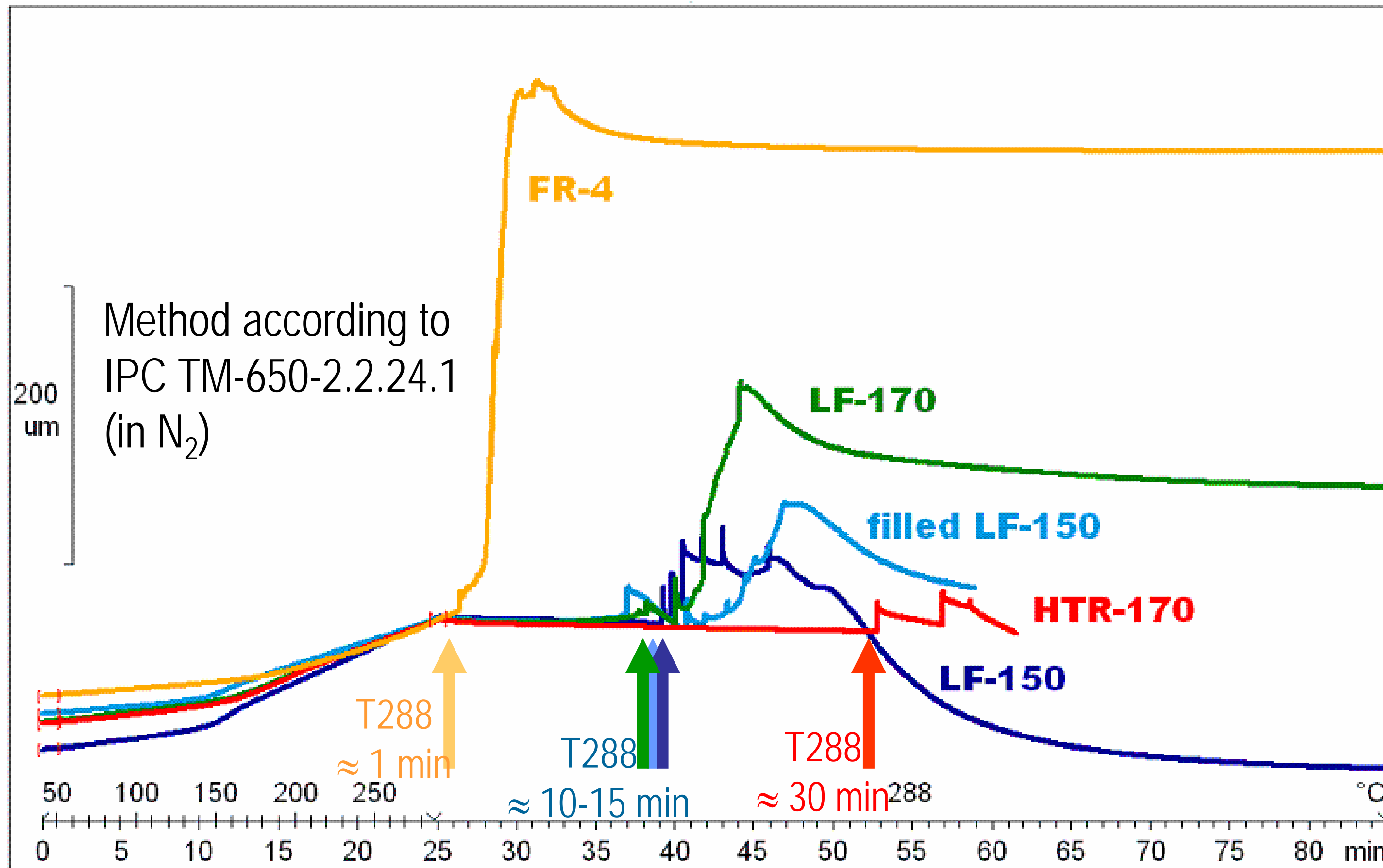
Z Axis Expansion



Shift in Reflow Temperature

TMA - Time to Delamination at 288 C



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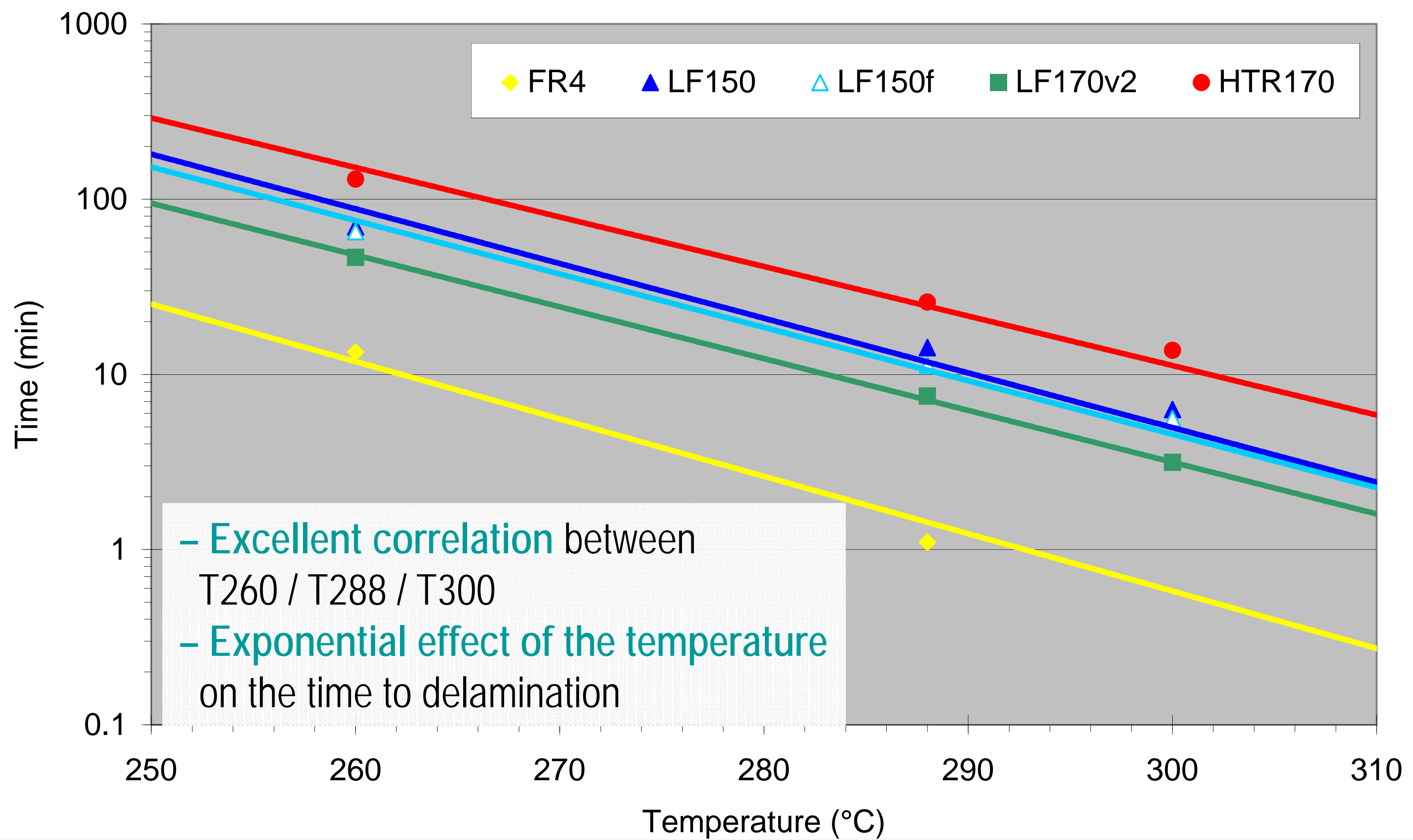
TMA Results

T260, T288, T300 vs temperature



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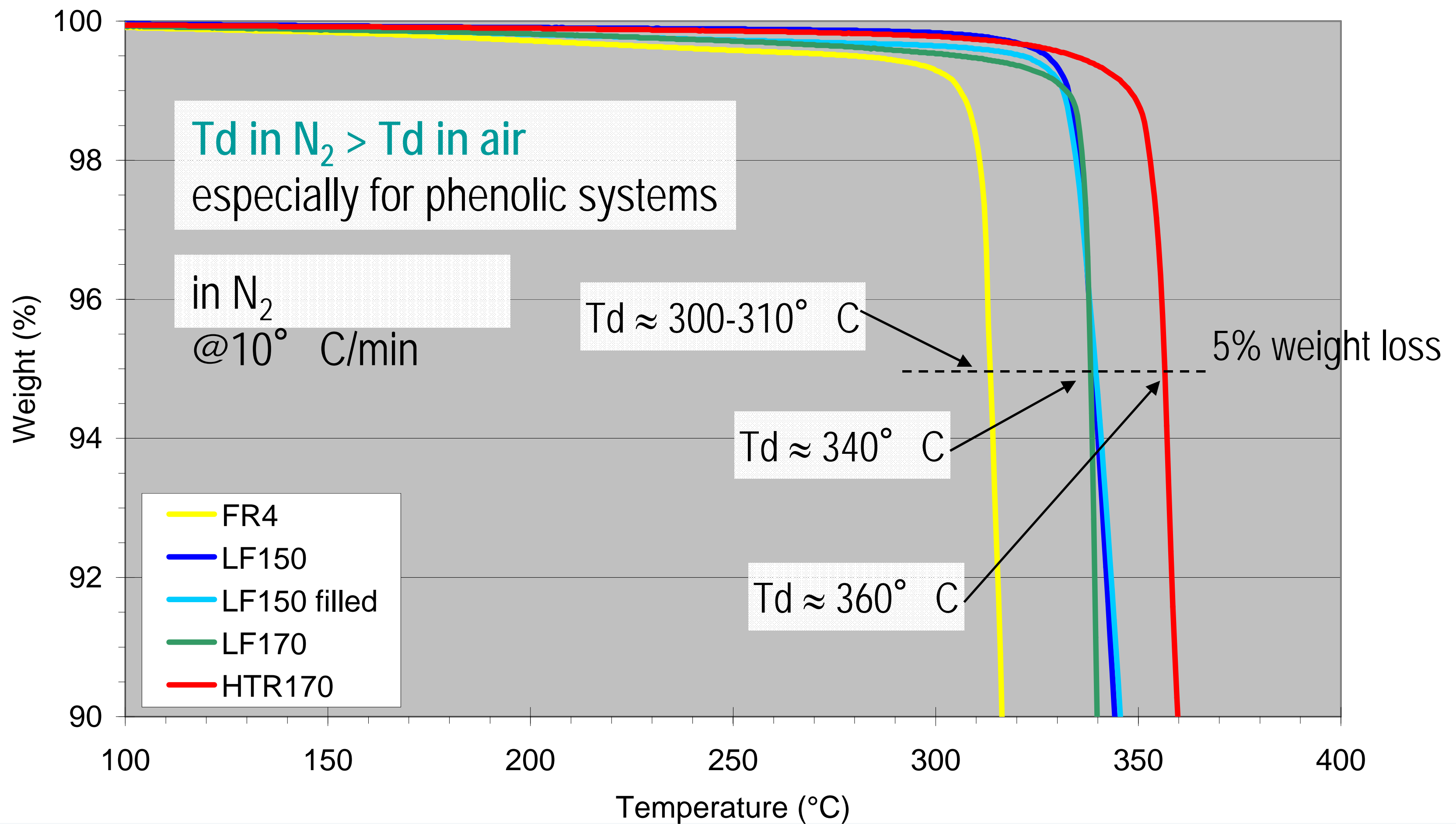
Td by TGA

Laminate weight loss vs temperature



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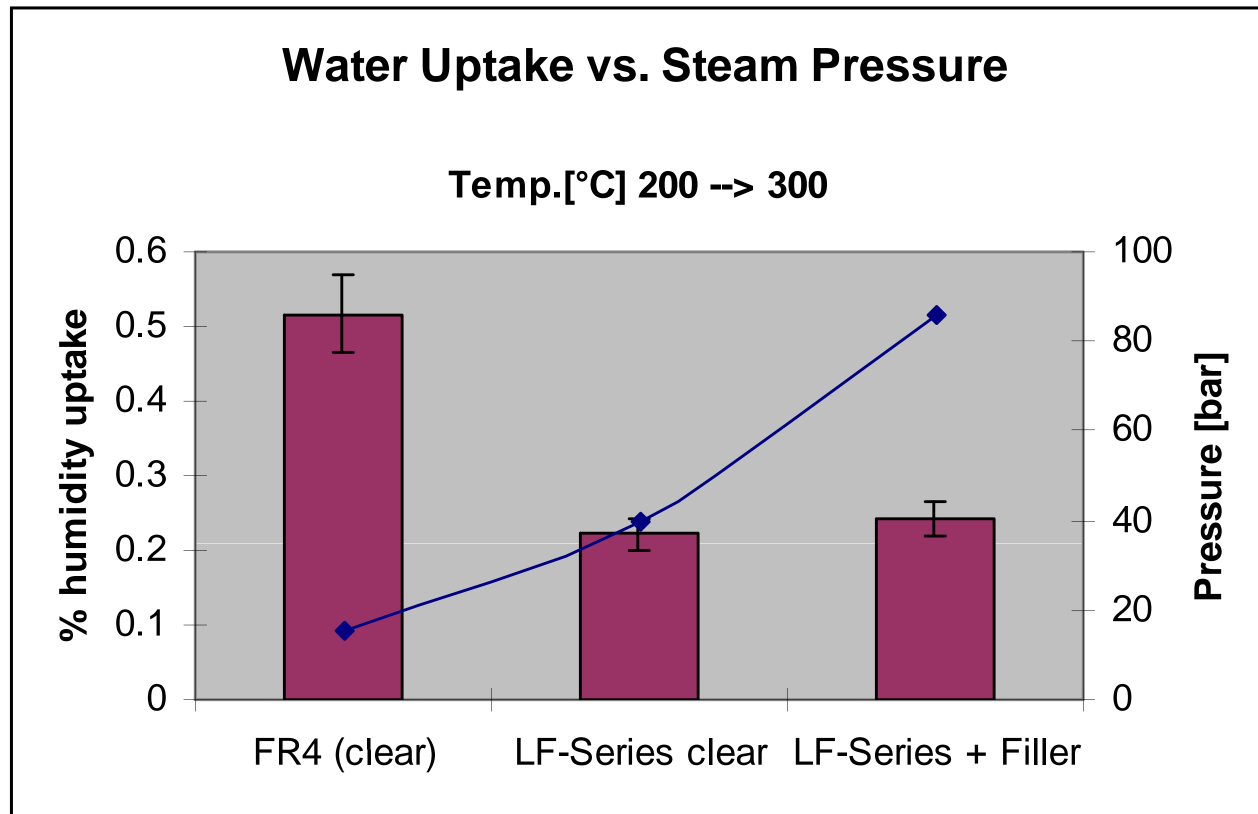
Moisture Absorption



There is reduced water uptake in products designed for lead-free applications

New Lead-Free Products

Dow Material Designation	D.E.R.*593	LF 150	LF 170	LF 180	HTR 180	XZ92567/ XZ92568
Material Type	Std. High Tg FR4	Mid Tg/Thermal Resistant	High Tg/Thermal Resistant	High Tg/Higher Thermal Resistant	High Tg/High Thermal Resistant/ Improved Dielectrics	High Tg/High Thermal Resistant/ Very low Dk/Df
Hardener/Cure Type		Phenolic	Phenolic	Phenolic	Phenolic	Anhydride
Laminate Requirement						
Glass Transition Temp	175-180	154	174	180	185	180-185
Decomposition Temp (Td) 5 wt % loss, 10 deg C/min	300	325	326	345	365	365
T-288 (10 deg C ramp)	0-1	10	6	14.5	39	>50
Z Axis Expansion (< Tg)	50-70	50-70	50-60	50-60	50-60	50-60
z Axis Expansion (>Tg)	250-270	250-260	250-260	250-260	250-260	250-260
Peel strength (std. foil)	9-10	8-9	8-9	10-11	8-9	5-6
Moisture Absorption	0.5-0.6	0.3	0.3	0.35	0.39	0.3-0.4
Permittivity, @ 1MHz	4.4-4.7	4.5-4.8	4.5-4.8	4.5-4.8	4.2-4.4	3.8-3.9
Loss Tangent @ 1 MHz	0.012-0.014	0.016	0.016	0.016	0.014	0.006-0.008
Flammability	V0	V0	V0	V0	V0	V0

All meet or exceed IPC specifications

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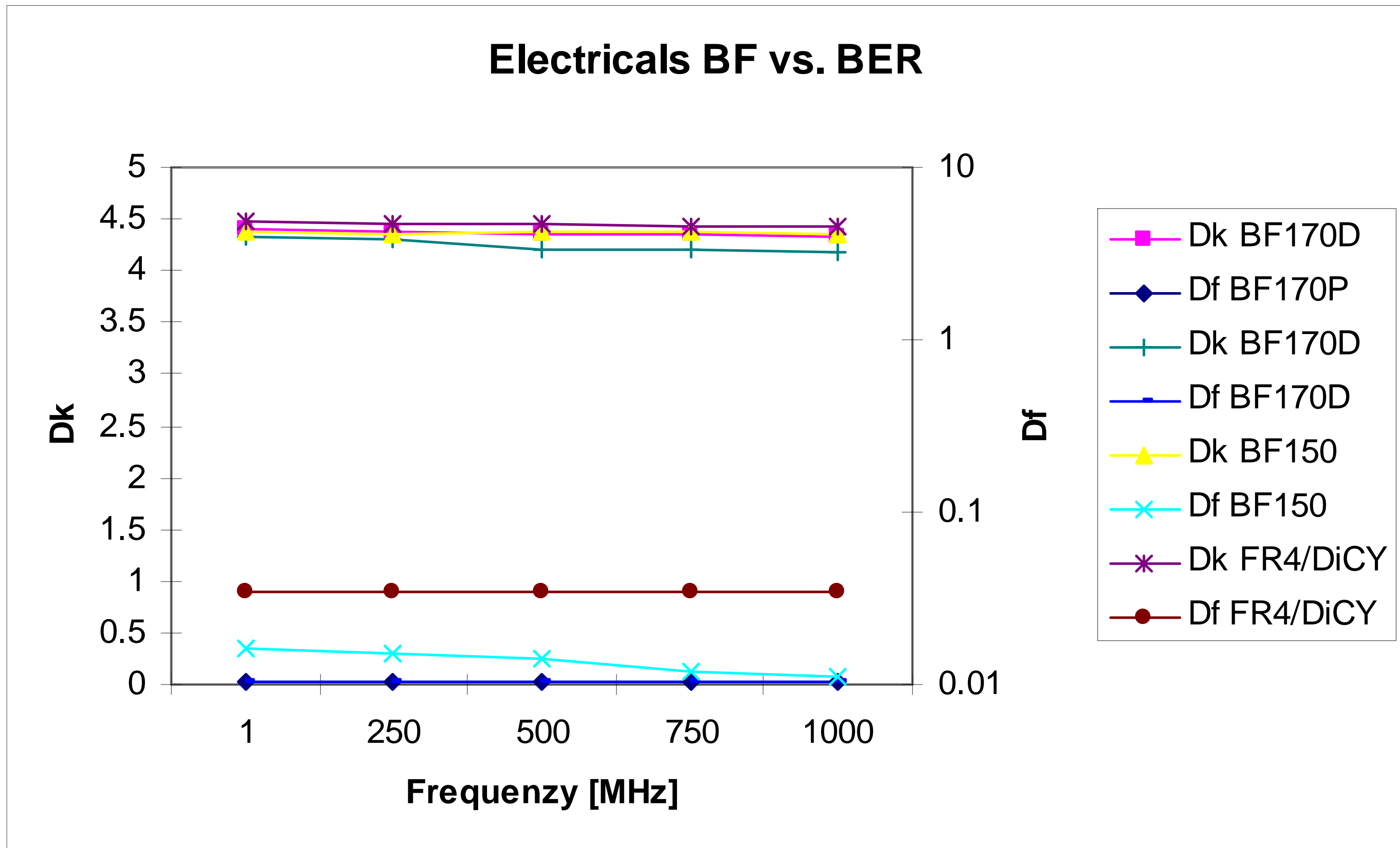
Bromine-Free Products

Laminate properties	BF 150	BF 180	unit
Tg (20 ° C/min)	**162**	**183-185**	° C
PCT 90 min + solder 288° C 20 sec x 5 times, water pick	**0.30 and 100 passed**	**0.47 and 100 % passed**	%
Copper Peel Strength	**12-14 (7-8 lb/in)**	**17-18 (10-11 lb/in)**	N/cm
T300	**>60**	**➢60**	min
TGA in N2 at 10 ° C/min (5 wt% loss)	**405**	**382**	° C
Dk (1/10/100/500/1000 MHz) @ approx. 43 % RC	**4.46 / 4.36 / 4.25 / 4.15 / 4.05**	**4.43 / 4.34 / 4.26 / 4.19 / 4.14**	
Df (1/10/100/500/1000 MHz) @ approx. 43 % RC	**0.009 / 0.013 / 0.012 / 0.012 / 0.011**	**0.0098 / 0.010 / 0.010 / 0.010 / 0.0091**	
UL 94	**47 (Vo)**	**46 (Vo)**	sec

Excellent thermal resistance and electrical properties for lead-free

Br-Free Dielectric Properties



Improved electrical properties with bromine-free materials

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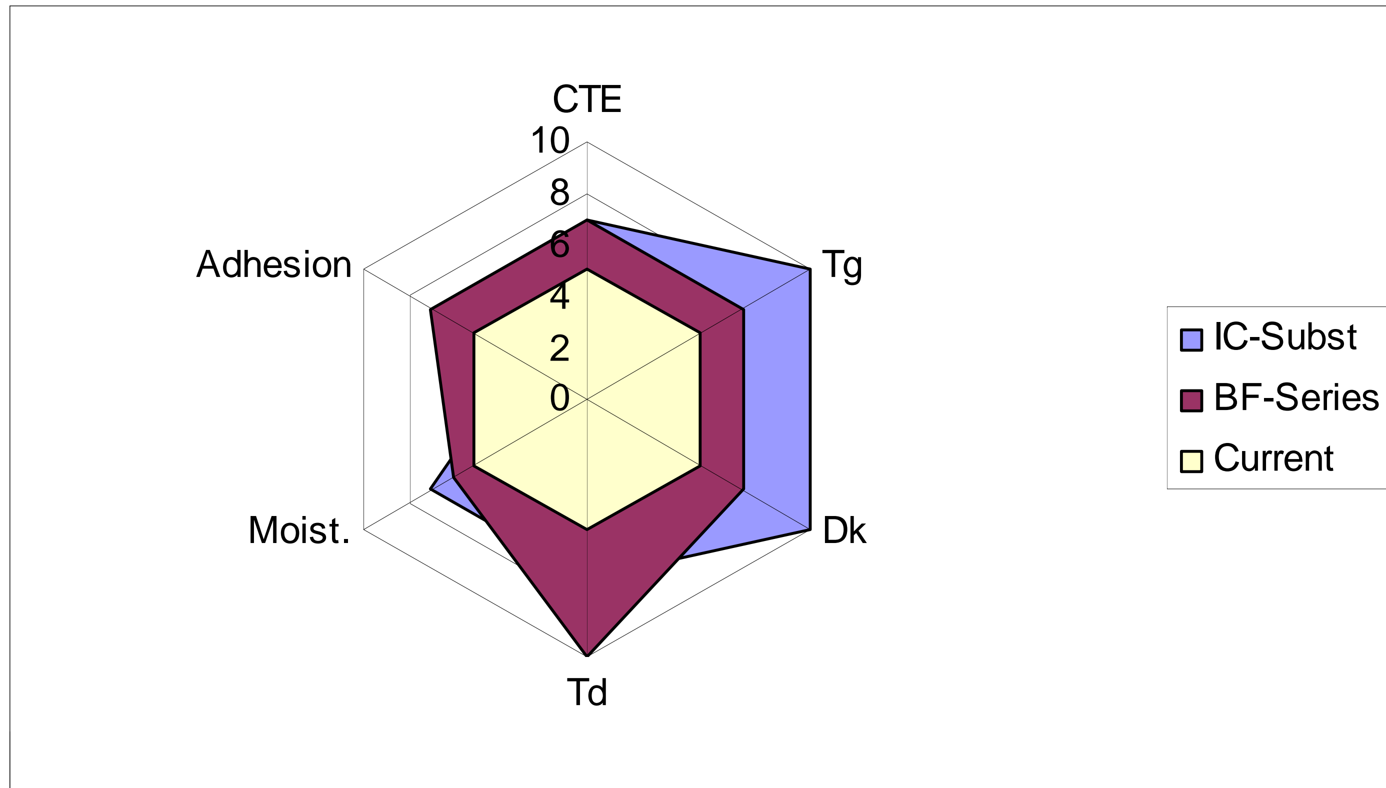
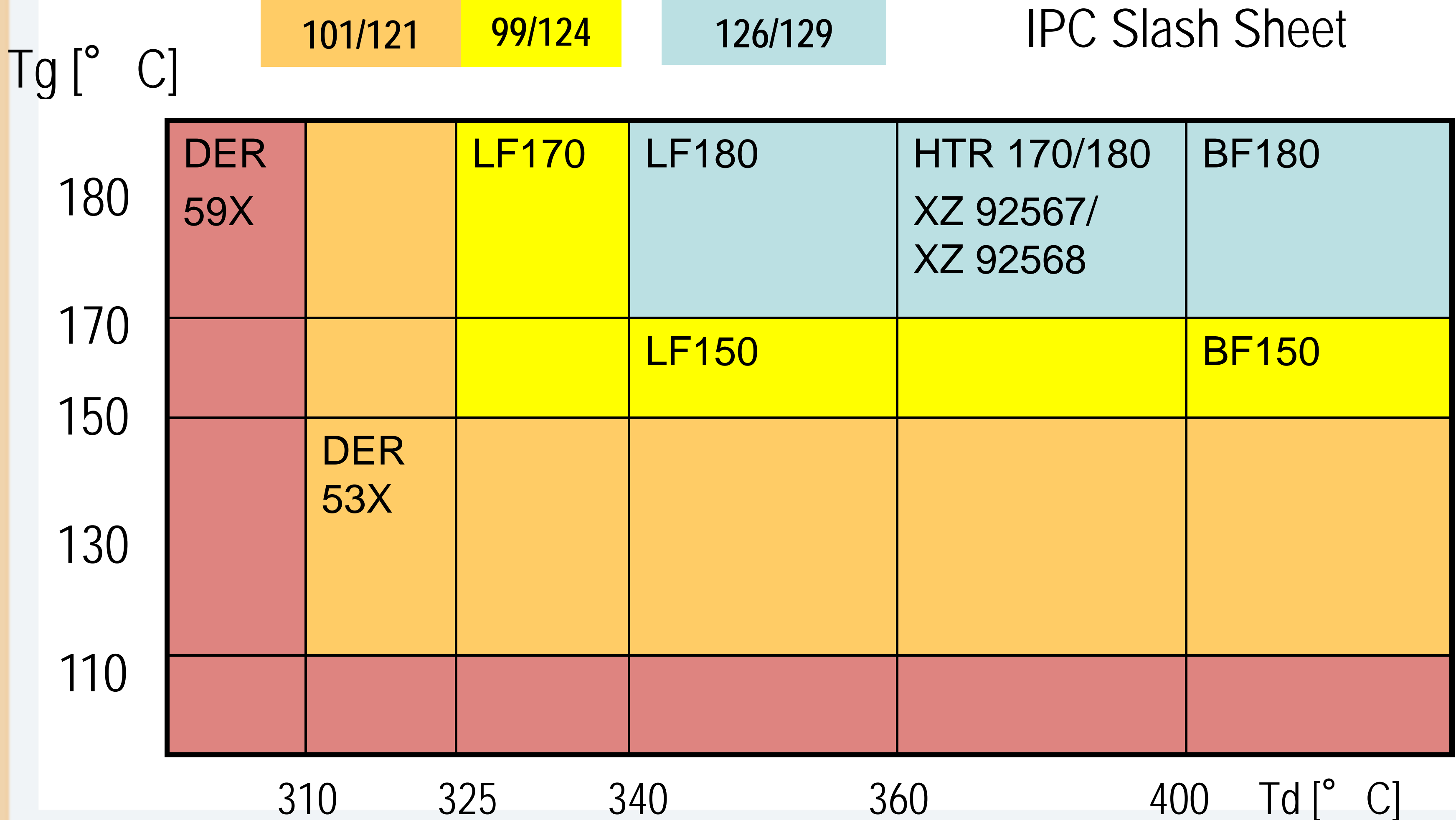
Br-Free Performance



New BF-Series resins are approaching IC substrate performance targets

Product Positioning



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Performance Matrix

impact on →	*Tg*	*Td*	*CTE*	*Dk / Df*	*adhesion / toughness*	*moisture resistance*
Tg		ø	+	ø	-	+
Td	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	

Improving properties for lead-free solder application can have a detrimental effect on toughness and adhesion

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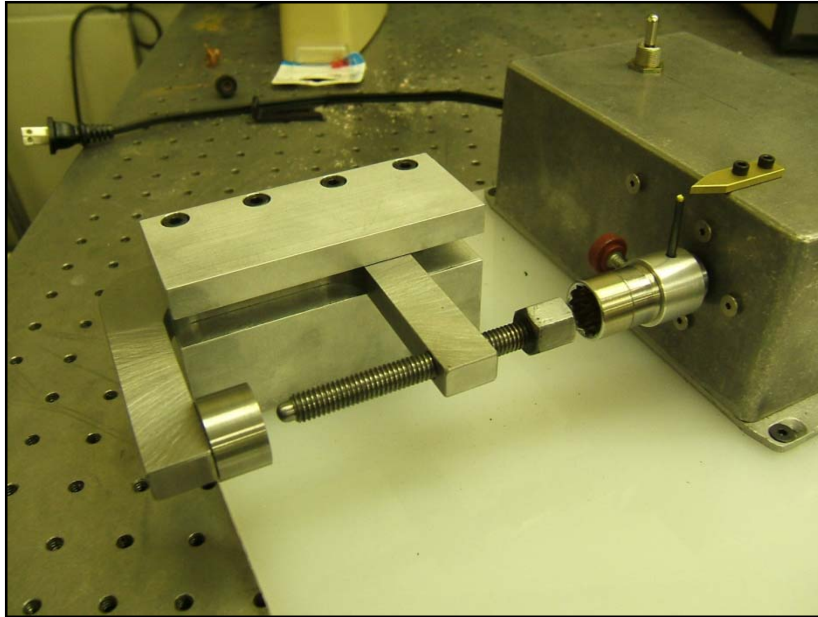
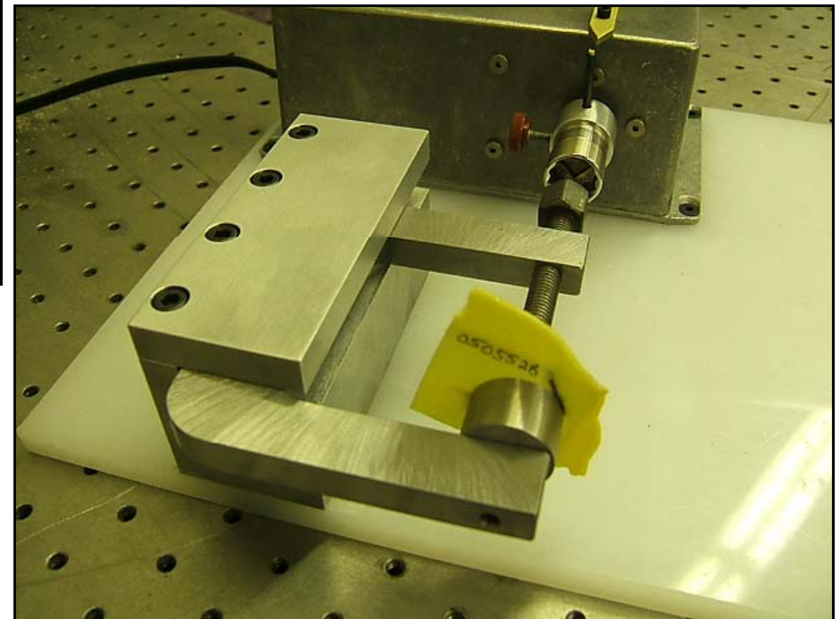
Toughness

- Standard FR-4 materials are tough and process well
- Conventional thermally resistant phenolic/anhydride cured materials tend to be brittle and non-process friendly
- Typically the higher the Tg and Td, the more brittle the system
- Toughening is required in these systems to make them more process friendly and reliable (e.g. CAF resistance)
- There is a direct correlation between adhesion to copper and toughness

Simple Toughness Testing





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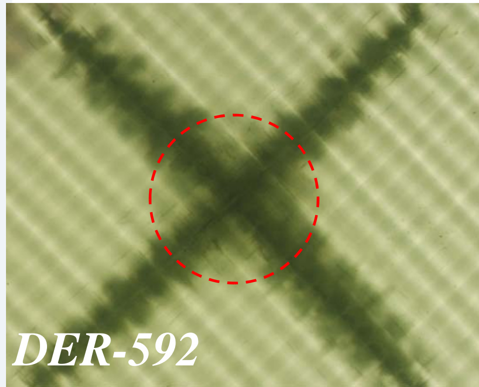
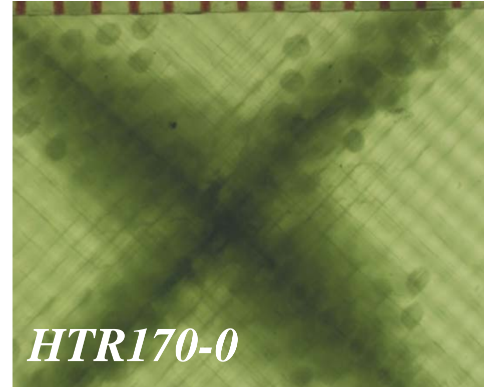
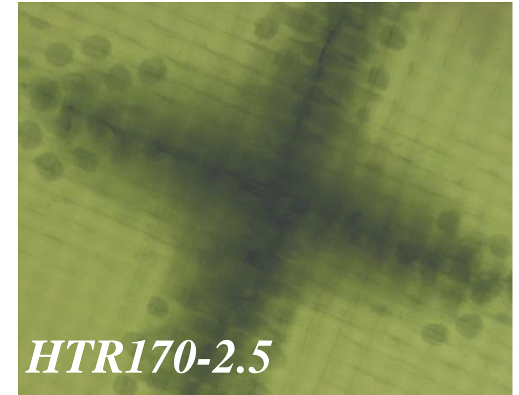
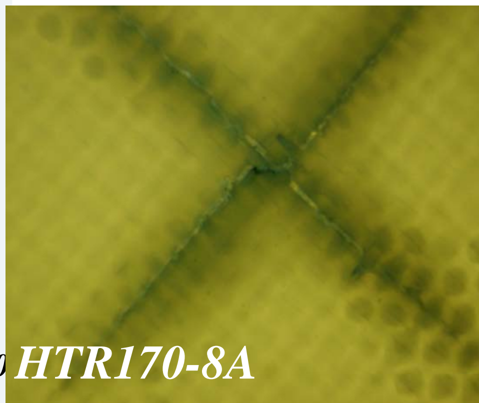
Results from Punch Test

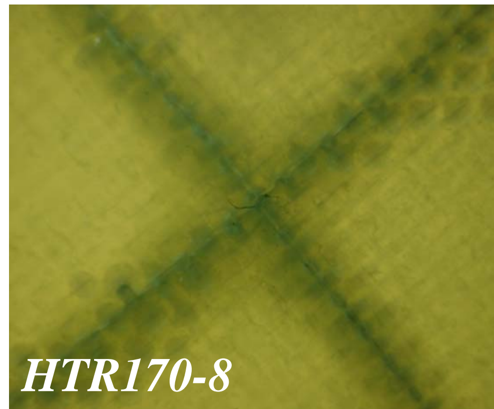
Low magnification optical microscopy

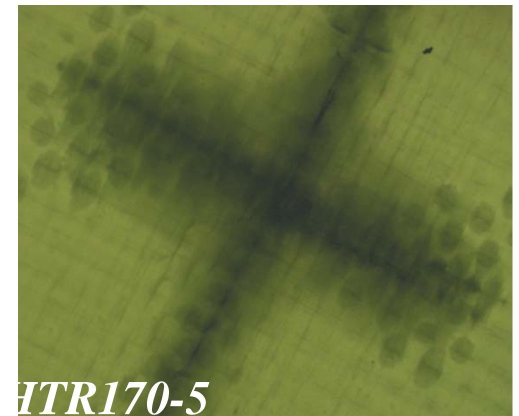












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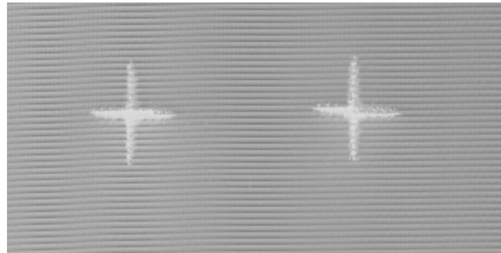
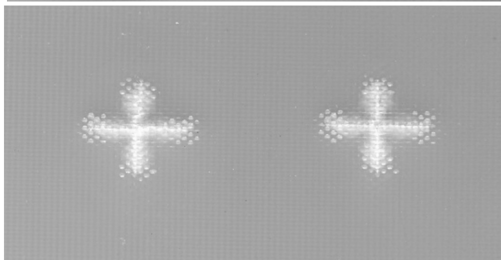
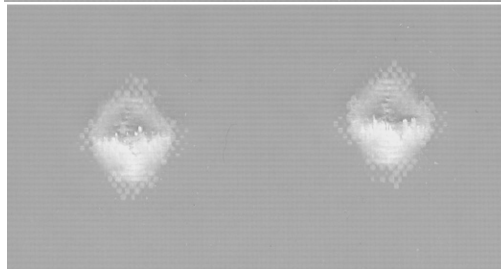
Toughness Ranking



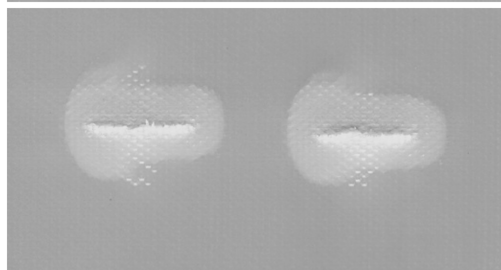
FR-4 Dicy cured:
Ranking = 5 (excellent)



Toughened Lead Free system:
Ranking = 4 (good)



Conventional Lead Free system:
Ranking = 2-3 (poor-fair)



Conventional filled Lead Free system:
Ranking = 1 (unacceptable)

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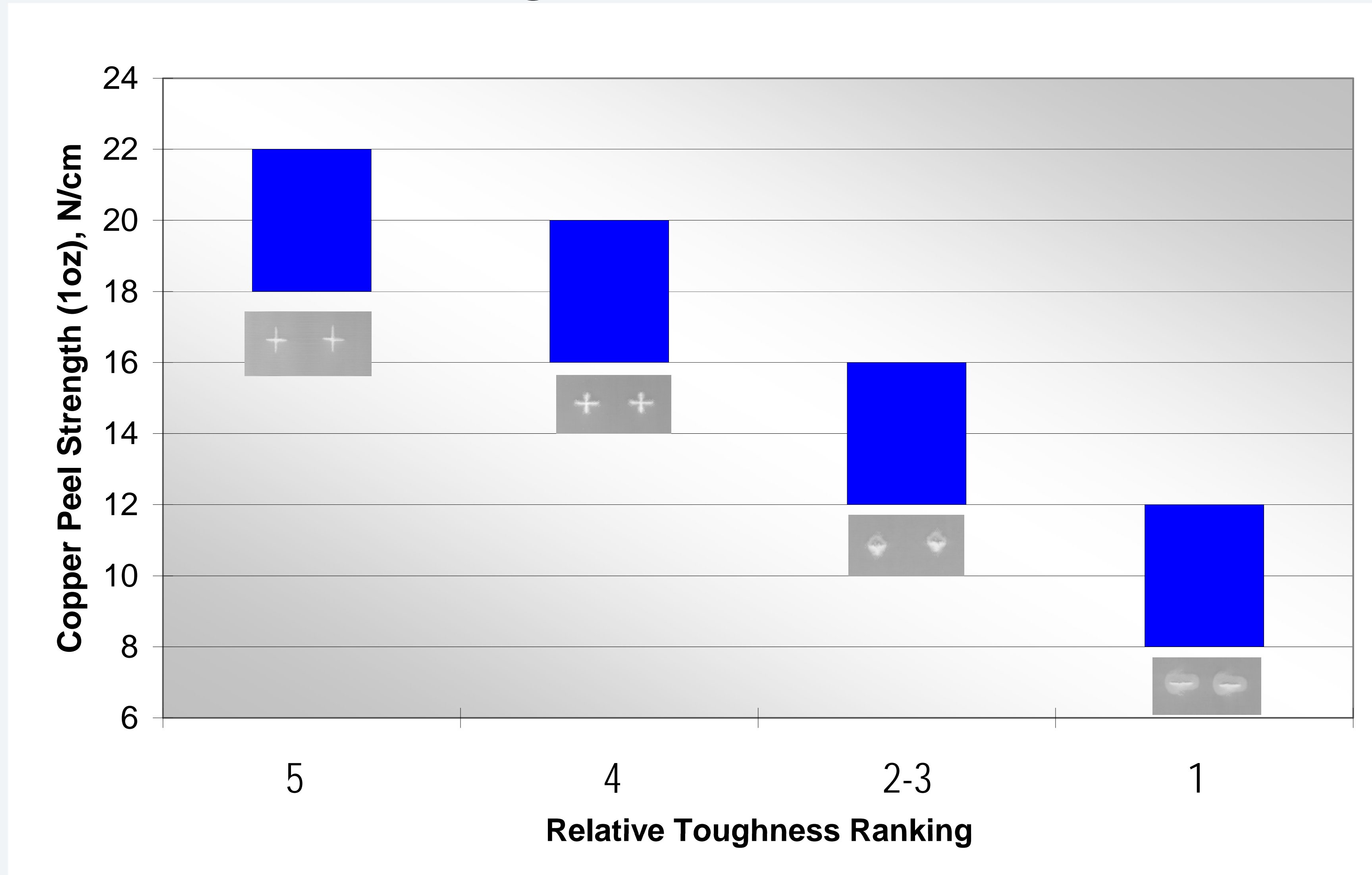
Toughness vs Adhesion



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Future Laminate Requirements

Performance requirements over time: State of the Art Materials (80% Laminate Market)

Year	Condition	Unit	2003	2005	2007	2009	2015
Price*	6 layer conven.	$/cm²$	0.055	0.04	0.03	0.03	0.03
Tg**	(DSC)	°C	130	150	165	185	200
Td***	2.4.24.6	°C	300	325	340	350	360
Dk*	(1MHz)		4.7	4.5	4.5	3.5	3.0
Df*	(1MHz)		0.02	0.015	0.015	0.013	0.010
CTEz*	Alpha 1	ppm/°C	60	50	50	40	30
Moisture abs.*	TM 2.6.2.1	%	0.25	0.20	0.10	0.10	0.08

*ex. iNEMI Road Map
** ex Jisso Road Map
*** Estimate b.o. IPC specs

Std. FR-4 Today

High Tg FR-4 Today

IC-Substrate performance today is benchmark for laminate performance in the future

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IC-Substrate Properties

	BT	BT-Equiv	PI	PTFE	FR-4/5	**2015 Target**	
Market Share	80	3	10	3	3		% sqm
Resin	BT-epoxy	PPO-Epoxy	Polyimide	Teflon	DER 592		
Rel. Cost.	5.3	3	6.5	32-78	1(ref)	**1**	
Customer	Isola	Isola	Isola	Rogers/Gore	Isola		
Reference	G200	GETEK	P96/26	RO2800/ Microlam	FR406		
Tg	185	175	260	220	170	**200**	[° C]
Td	320	345	382	400	300	**360**	[° C]
CTE	55/275	55/275	60/180	15/200	65/140	**30**	ppm/ ° C
Adhesion	9	>5.5	6	3	7		lb/in
Dk	3.7-3.8	3.5-3.6	3.8-3.9	2.6-3.2	3.8	**3.0**	
Df	0.012-0.013	0.009-0.011	0.018-0.024	0.002-0.004	0.018-0.019	**0.010**	
Moisture Abs	0.36	0.2	0.2-0.6	0.13	0.2	**0.08**	[%]
	V0	V0	V0	V0	V-0	**V0**	[Class]

Source: Prismark & TDS

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New building blocks

- Differentiated Hardener systems
  - Phenolics
    - High functional novolacs
    - FR phenolics
    - Phenolics with improved toughness
    - Phenolics with UV/fluorescence capability
    - Phenolics with improved electrical properties
  - New anhydride curing agents
  - New non-traditional curing agents
  - Hybrid curing systems
  - Dicy cure with good thermal properties (LF)

- High functionality epoxies with new backbone chemistry that can impart
  - Improved toughness
  - Improved thermal resistance
  - Improved electrical properties
  - Improved moisture resistance
- New chemistry - phosphorus based materials
- Add in toughening agents or premixed toughening agents
- Fillers (nanoscale – premixed or add in)

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Conclusions

- Brominated lead-free formulation meet all IPC specs, have different property balance
- Bromine-free resins are excellent for lead-free applications
- Continuing demands for property improvements

Motorola 68000 vs modern processor

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