

High Tg Bromine-free Laminates for PWB Applications

Marty Choate
Isola

Abstract

The development of halogen free materials has been a focus of the PWB industry for many years. The development of these materials has highlighted many technical challenges in substituting alternative flame retarded hardeners for t-bromobisphenol A. However, by tailoring these prepolymers to incorporate the proper chemical reactivity, alternative flame retardant systems can be incorporated into the thermoset resin matrix that will achieve the desired flammability resistance while maintaining the physical properties of current epoxy resin systems. This paper will describe some of the chemical approaches that have been evaluated and the effects of those approaches on the performance of these laminates in the fabrication of circuit boards.

Introduction

Halogen free materials have been available in certain laminate market areas for many years. At the time some of the first halogen-free products were being introduced, the vast majority of applications required primarily lower DSC Tg products similar in performance to FR-4 laminates. Since that time, laminate application requirements surrounding halogen-free as well as halogenated laminates have changed, requiring improved thermal and electrical performance. The recent drive for higher Tg and improved thermal performance laminates has been primarily driven by the concurrent development of lead free solder processing and higher temperature application environments. In Japan, low-temperature, incomplete incineration processing of halogenated materials has also been a primary driver of halogen free requirements.

Although recently proposed regulations to ban the use of halogenated flame retardants in Europe and North America have been extended, the development of higher thermal performance laminates continues in preparation for what future applications may require.

Isola remains committed to developing products using environmentally friendly alternative resin chemistries whenever possible, which meet or exceed the performance and process standards of today's FR-4 materials. The role of halogen and alternative flame-retardant approaches will be discussed towards the development of higher Tg laminate systems.

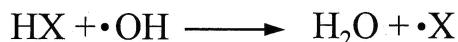
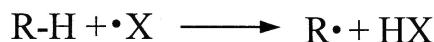
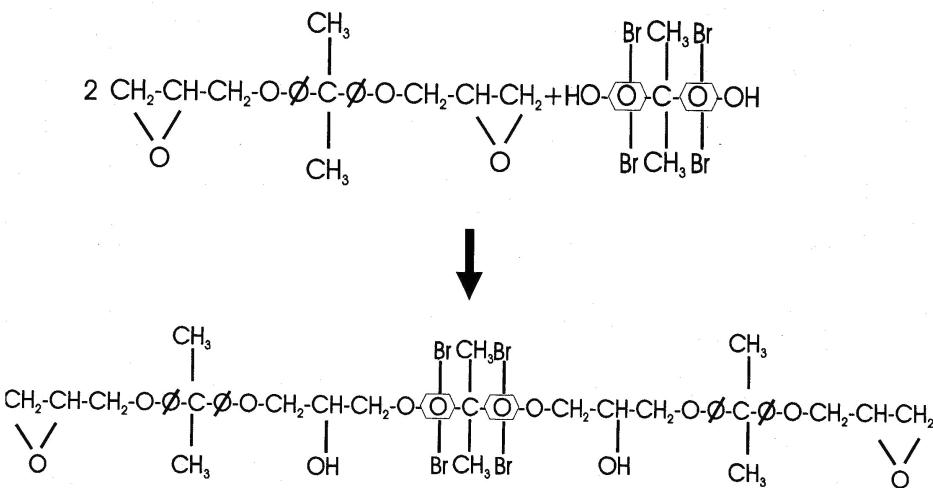
Tetrabromobisphenol-A (TBBA) in Laminate Chemistry

TBBA has played a very central role in the proliferation of traditional laminate chemistry. It

owes much of its versatility in laminate materials performance to several important characteristics.

First, the terminally located hydroxyl groups (-OH) provide functionality for chain extension, shown in Figure 1. Secondly, the four bromine substituents provide flame-retardant characteristics via the mechanism shown in Figure 2. The unique combination of TBBA's relatively low molecular weight, polarity and functionality combine to give it excellent solubility in many solvents (including many environmentally friendly solvents). This third interactive feature also provides excellent compatibility with a wide variety of epoxy and other functional high Tg prepolymers. Whilst the Tg of the bisphenol-A backbone of TBBA is not particularly high, it's ability to cross-link with higher Tg prepolymers is key to the high Tg, high thermal degradation performance of many laminate materials today. Additionally, many of the commonly used chemicals in printed wiring board (PWB) fabrication for etching and soldering processes have been established in part around the characteristics of TBBA cured epoxies. Thus, the printed circuit board (PCB) laminate industry has been developed around the centrally pivotal role of TBBA as a highly versatile, economical and effective flame retardant to epoxy and other thermoset prepolymers.

The conversion of laminate systems away from TBBA and other halogenated flame-retardants will require very fundamental changes to the intrinsic flame-retardant mechanisms of the resins used in laminate materials. Conversion to these new systems will raise new performance challenges and possibly trade-offs for the designer and fabricator, and may take several years to establish the performance reliability database of TBBA-based FR-4 materials.



X = HALOGENES

Figure 2 – Mechanism of Halogenated Flame Retardants

Alternative Flame Retardant Approaches

There are a variety of approaches to replacing TBBA and other halogenated flame retardants in thermoset and other polymer matrices. Generally speaking, these may include:

1. Limiting fuel supply, especially oxygen and other readily combustible organic materials that support the oxidative process.
2. Increasing char formation through use of intumescing agents and backbones that upon initial surface combustion quickly build protective non-flammable layers preventing the further spread of oxidation throughout the matrix underneath.
3. Actively quenching and in some cases reducing temperature at the site of oxidation by releasing water of hydration or other oxidatively inert substances to stop the oxidative process.

The effectiveness and interactive timing of these different mechanisms vary during the oxidation process, depending on the relative amounts and type of resin formulation and flame retardant elements as well as available fuel (O_2) from the surrounding

atmosphere. These mechanisms play different roles at different, although somewhat overlapping, times during the combustion of a laminate structure.

Water of hydration precisely released upon heating from hydrated elements in the formulation initially aid in slowing the onset of ignition and also help to retard the flame spread rate and extinguish oxidation at its source, primarily through cooling, but may also participate in other synergistic mechanisms. Water of hydration in combination with phosphorous can also aid in the formation of acids in various forms. An example showing this mechanism with red phosphorous is shown in Figure 3. This mechanism primarily reduces flammability through oxygen scavenging and char promotion depending on the surrounding polymer backbone environment.

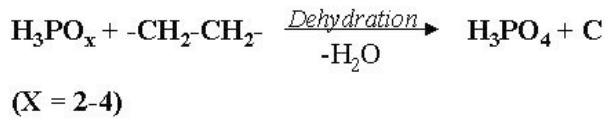
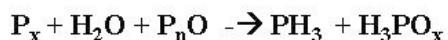


Figure 3 – Red Phosphorous Flame Retardant Reaction

A growing number of various organophosphorous and nitrogen containing compounds are being developed towards utilizing this type of mechanism for a variety of polymer environments and applications. Examples of common nitrogen containing prepolymers include materials such as melamine's and cyanurate and phosphorous containing materials such as phosphate esters and phosphonic acids.

An example of the properties of an earlier commercial halogen free product Duraver E-150 are shown in Table 1. It is an epoxy formulation composed of a polyarylisocyanurate, bisphenol F and

polyphosphonium acid combination, that provides a high Tg, good heat resistance, and is a non-halogen UL V-0 product.

Table 1 – Properties Early Halogen-Free Product

Properties	Conditions	Units	Halogen-Free Product
Surface Resistance	C-96/40/92	ohms	3×10^{10}
Volume Resistance	C-96/40/92	ohm-cm	9×10^{13}
Dielectric Constant (1 MHz)	C-96/40/92 + C-1.5/23/75		4.6
Dissipation Factor (1 MHz)	C-96/40/92 + C-1.5/23/75		0.016
Peel Strength	A	N/mm (lbs/in)	1.7 (9.7)
Solder Float (288 °C)	A	sec	>20
Water Absorption	E-24/50 + D24/23	%	0.3
NMP Absorption	E-1/105	T	0.25
Flammability (UL 94 V0)	A	Class	V0
Glass Transition Temperature	A	°C	160

Table 2 – Effects of Additives on Physical Properties

Property	Conditions	Units	Control	Red Phosphorous	Melamine Cyanurate	Phosphate Ester
Dielectric Constant	A, 100 MHz	ohms	4.61	4.89	4.64	4.56
Dissipation Factor	A, 100 MHz	ohms-cm	0.011	0.019	0.011	0.010
UL 94 V0	A		V0	Fail	V1	V1
Longest Individual Burn Time	A	sec	3	12	7	7
Average Burn Time	A	sec	2	9	4	5
Peel Strength	Thermal Stress	N/mm (lbs/in)	1.6 (9.2)	1.0 (5.6)	1.4 (8.2)	1.4 (8.1)
T-260 by TMA		sec	270	120	72	90
Tg by DMA		°C	175	165	148	153
Tg by DSC		°C	150	142	148	153
Moisture Absorption	D-24/100	%	0.9	2.5	1.3	1.1

Experimental Materials

Data comparing the effects of the three different types of flame-retardants in experimental laminate systems can be compared in Table 2. Like brominated materials, these phosphate and/or nitrogen containing prepolymers can be tailored to promote compatibilization and enhance a variety of polymer matrix properties. Their ability to enhance or degrade the properties of a given polymer matrix depend to some extent on their spatial arrangement and concentration in the polymer backbone. They can be made monofunctional, multifunctional or non-functional. The drawback to this approach stems from

the intrinsic affinity of phosphorous and nitrogen for moisture, greater susceptibility to oxidative attack and tendency to more readily degrade thermally depending on what they are attached to. To help protect these elements and replace the co-curing function of TBBA prepolymers, functionalization of the flame-retardants may also help to better protect key flame retardant elements from moisture attack and maintain higher Tg.

Another approach is to simply reduce the amount of resinous fuel and increase hydrated filler content of the system.

Figure 4 shows the effects of increasing concentrations of hydrated filler ATH on a 180 C DSC Tg epoxy based thermoset resin system on peel strength and T-288 thermal performance of a 20% by weight solids ATH system modified with an unreacted phosphate ester and nitrogen flame retardant. The phosphorous and nitrogen have very detrimental effects on what otherwise is a very thermally stable system. The increased levels of hydrated filler does not have a significant effect on the T-288 thermal properties but does have a significant detrimental effect on the peel strength. Hydrated filler systems are usually suggested for use

as synergists with nitrogen and phosphorous based flame-retardants to promote acid formation. This example is shown to simply demonstrate a trade-off of properties encountered when balancing organic and inorganic flame retardant loading on peel and thermal properties. The systems loaded with hydrated filler loading achieved only UL V-1, while the system modified with both unreacted organic and inorganic flame retardant was able to achieve V-0. All systems were evaluated in a 0.059 in thick eight-ply 7628 laminate with 18-um low profile copper using a typical FR-4 cure cycle.

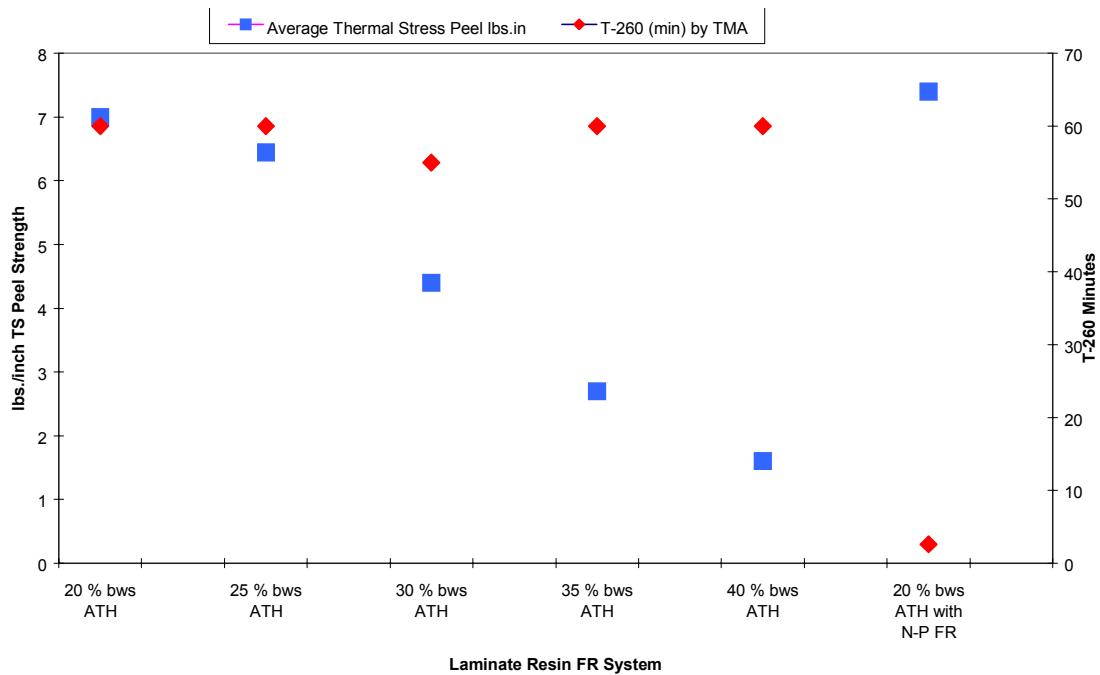


Figure 4 – Effects of Increasing Hydrated Filler Loading on a 180°C Tg Epoxy Thermoset System Thermal Stress Peel & T-268 Thermal Performance

Commercial Materials

Table 3 compares three commercially available products. Product A uses a high Tg resin formulation with an inert filler as the flame retardant. This product has a relatively high Tg with a lower dissipation factor than standard FR-4. Product A is completely compatible with alternate oxide etching chemistry but is strongly attacked by sodium

hydroxide etchants. Product B is based on the same chemistry and filler as A only using a different halogen-free flame retardant that yields a significantly lower Tg, slightly higher CTE and about the same electrical performance, but is designed to be more resistant to sodium hydroxide etch. Duraver-E-Cu 156 is a phosphate ester modified epoxy with no fillers.

Table 3 – Commercial Materials

Property	Conditions	Units	Product A	Product B	High Tg Epoxy
Dielectric Constant	A, 100 MHz	ohms	4.86	4.91	4.35
Dissipation Factor	A, 100 MHz	ohms-cm	0.0076	0.0086	0.0146
UL 94 V0	A		V0	V0	V0
Longest Ind. Burn Time	A	sec	6	6	1
Average Burn Time	A	sec	2	3	1
Tg by DMA		°C	214	180	140
Tg by DSC		°C	186	162	126
Tg by TMA		°C	178	131	120
Coefficient of Thermal Expansion (23 – 160 C)		ppm	34.5	41	140 (RT-200C)
Peel Strength 18 um		N/mm (lbs/in)	1.25 (7.5)	0.82 (4.5)	1.7(9.95)
Moisture Absorption	D-24/100	%	0.41	0.65	0.35
Etchant Computability			Alt. Oxide Only	NaOH	NaOH

Summary

Development of halogen free materials continues to be of interest and will evolve as the many new flame-retardant systems are developed and designed for specific applications. There are several commercially available non-halogen materials today with more being developed. Some rely solely on inorganic fillers, others an organic flame-retardant and still others combinations of both. Each of these systems will ultimately have to be evaluated on their own

merits at the OEMs, fabricators and designers. The industry will ultimately define the direction and scope of development during the coming decade. Halogen-free PCB system development offers new opportunities for the resin, flame retardant, laminate and fabricator and OEM component industries to explore new chemistries and perhaps develop improved properties and processes of laminates, as a whole, previously not considered with halogenated materials.