Halogen Free Base Materials for PWB Applications

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Abstract
Since the introduction of FR-4 laminates in the early 1960's, *t*-bromobisphenol A (TBBPA) has been used as a reactive component to flame retard epoxy laminates and impart many of the desired properties of FR-4 laminates for printed wiring board (PWB) fabrication. Due to several influences including environmental concerns, recycling strategies and proposed European Union (EU) regulations there has been growing demand to develop alternative materials for PWB applications. Isola has developed a range of non-brominated materials to address this growing demand. This paper will discuss some of the challenges and concerns highlighted through these development efforts as they relate to material attributes and PWB processing characteristics of the different approaches evaluated.

Introduction

The development and commercialization of environmentally responsible products continues to be a key emphasis for the electronics industry, driving the need for environmentally friendly materials such as bromine free laminates and non-lead solders. This industry demand has driven by many factors. The most recent demand was highlighted by proposed legislation in the EU where all brominated materials would be banned from use. Since those initial proposals, legislators have backed away from this position focusing only on poly-brominated diphenyls and diphenyl ethers. However, some proposed restrictions on end-of-life recycling of brominated materials still remain in place. Additionally, public sentiment and concerns over the risks of chlorine and bromine containing materials continues to fuel the need for solutions, and has generated a market need to provide consumers with "green" alternatives.

In terms of laminate production, Isola's focus has been to refrain from the use of hazardous substances in the production of laminate materials, insure that no toxic components are in the base laminate material, and that no banned substances are introduced into the production waste stream. For the purposes of our development efforts we have focused on eliminating the use of brominated flame retardants in FR-4 laminates, and in particular the elimination of TBBPA. Our goal has been to develop products using alternative resin chemistries which meet or exceed the performance and process standards of today's FR-4 materials.

FR-4 Laminate
The versatility of epoxy resins typically used to formulate FR-4 laminates has developed into a very broad range of material offerings by the industry. This versatility has been a direct result of the ease of formulating with various hardeners and catalysts to impart unique properties to the base epoxy. However, one constant is that they all contain TBBPA as part of the polymer backbone (Figure 1). It's primary use is to impart flame retardancy by incorporating bromine into the molecule (Figure 2). However, TBBPA is also a hardener for the epoxy resin, it imparts much of the mechanical and thermal performance necessary for today's PWB fabrication, and it's very cost effective.

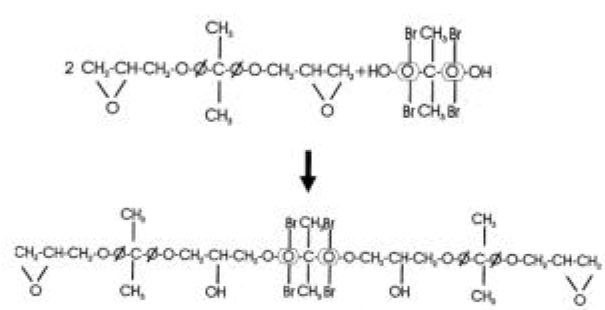

Figure 1 – Brominated Epoxy Resin

$$R\text{-}H + \bullet X \longrightarrow R\bullet + HX$$

$$HX + \bullet OH \longrightarrow H_2O + \bullet X$$

$$X = \text{HALOGENES}$$

Figure 2 – Mechanism of Halogenated Flame Retardants

Some other key considerations to replacing TBBPA are that much of the industry infrastructure has been designed around TBBPA systems. PWB fabrication processes such as drilling, plating, etching, and lamination can be significantly impacted when different materials are introduced into a standard process. For example, currently commercially available non-halogen systems require extended press cycles and higher press temperatures to achieve full cure. Product reliability history is also well established on TBBPA based chemistries. Conversion to new systems will raise a new list of performance trade-offs for the designer and fabricator, and it will take several years to establish the performance reliability database that exists with FR-4 materials.

Alternative Flame Retardant Approaches

One might expect that a direct substitution of TBBPA with bisphenol A would result in a thermoset epoxy with very similar properties with the exception of flame retardancy. However, because of the differences in reactivity and chemical structure there is a significant change in thermal properties and the kinetics of the curing reaction, dropping the glass transition temperature (Tg) by nearly 30 °C thus requiring extended press cycles.

Since one cannot directly substitute a similar chemical for the TBBPA and maintain the majority of the performance attributes of standard FR-4 laminates, the formulator is forced to evaluate alternative resin chemistries in combination with other flame retardant additives. As with any new system there are necessary compromises that must be weighed in the development efforts. For example, products such as Isola's Duraver-E-150 highlight the performance trade-offs typically encountered in development. This product consists of a polyarylisocyanurate, bisphenol F and polyphosphonium acid. The product provides a high Tg, good heat resistance, and is a non-halogen V0 product. However, there are also issues with brittleness, drilling and punching, high moisture absorption, and cost (Table 2).

Table 1 – Physical Properties of Duraver-E-150

Properties	Conditions	Units	Duraver-E-Cu 150
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

More recent developments have improved on some of the early product offerings, however, many of the alternative flame retardants still represent significant challenges to the formulator in trying to develop systems that provide equivalent performance to existing FR-4 materials while eliminating TBBPA from the formulation.

Inorganic Additives

There are a variety of inorganic additives that have been widely used in thermoplastics to provide flame retardancy. These include red phosphorous, hydrated fillers such as aluminum trihydrate and magnesium hydroxide, and intumescent additives. The mechanism of reducing the flammability with each of these is different. However, with each ingredient the formulator must address concerns over uniformity and compatibility. To achieve V0 performance, loadings of these additives can be as high as 30% of the formulation. At these levels, inert fillers also tend to reduce peel strengths, increase moisture absorption, and reduce electrical properties. Because they are particulate materials dispersed in the resin matrix they can also reduce toughness, change rheological properties and some interact with the catalysts and alter the cure kinetics.

One example is shown in Table 2. Red phosphorous is an inorganic solid which can be dispersed into an epoxy formulation. The phosphorous will reduce the flammability of the product through the generation of phosphoric acid from water through the reaction mechanism shown in Figure 3. As shown in Table 2, even at 15-25% loading in this formulation V0 performance was not achieved and the dielectric constant, peel strength, moisture absorption, and Tg are negatively impacted.

Table 2 – Effects of Additives on Physical Properties

Property	Conditions	Units	Control	Red Phosphorous	Melamine Cyanurate	Liquid Phosphate
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

$$P_x + H_2O + P_nO \rightarrow PH_3 + H_3PO_x$$

$$H_3PO_x + \text{-}CH_2\text{-}CH_2\text{-} \xrightarrow[-H_2O]{Dehydration} H_3PO_4 + C$$

$$(X = 2\text{-}4)$$

Figure 3 – Red Phosphorous Flame Retardant Reaction

Organic Additives

Organic additives can be either reactive or non-reactive components. Reactive components are generally preferred because they will react into the polymer backbone, thus eliminating any concerns with extractability or leaching. However, this also tends to significantly alter the cure kinetics of the epoxy resin. Most of the organic additives are either nitrogen or phosphorous containing materials. To achieve a V0 flammability rating the loading is typically very high. This usually drops the Tg of the material while increasing moisture absorption, reducing electrical properties and increasing overall formulation costs.

Two examples of commercially available organic additives are also shown in Table 2. Both the melamine cyanurate and the liquid phosphate still did not achieve a V0 rating, but were improved relative to the red phosphorous formulation. However, thermal performance was reduced and moisture absorption was increased.

Commercial Materials

With the impacts of the various alternatives more clearly understood, several new bromine-free laminate materials have been introduced during the last year. Table 3 compares two commercially available products. The Product A uses a high Tg resin formulation with an inert filler as the flame retardant. This product has a good Tg with somewhat higher dielectric constant than standard FR-4. Duraver-E-Cu 156 is a phosphate ester modified epoxy with no fillers. Electrical properties are more consistent with standard FR-4 materials, but the Tg is depressed and moisture absorption is increased.

Table 3 – Commercial Materials

Property	Conditions	Units	Product A	Duraver-E-Cu 156
Dielectric Constant	A, 100 MHz	ohms	4.86	4.35
Dissipation Factor	A, 100 MHz	ohms-cm	0.0076	0.0146
UL 94 V0	A		V0	V0
Longest Individual Burn Time	A	sec	N/A	1
Average Burn Time	A	sec	N/A	1
Tg by DMA		°C	174	140
Tg by DSC		°C	151	126
Moisture Absorption	D-24/100	%	0.23	2.51

Summary

There are several commercially available non-halogen materials today with more being developed. Some of these are filled with inorganic fillers and others use various organic components containing nitrogen or phosphorous. As with all new materials in our industry, they each have their strengths and weaknesses. Ultimately, the fabricators and designers will decide how and where to utilize these new offerings. In the meantime, as formulators become more familiar with these products and new additives are developed, we can expect to see a variety of new product offerings in the next few years.