A Combination Flame Retardant Curing Agent Material
For Non-Halogen PCB Laminates

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Abstract

As interest continues in the development of non-halogen flame retardants for printed circuit boards, the requirements for robust thermal stability and lead-free solder compatibility also continue. With respect to developing “greener” electronic materials, one option available to the formulator is to use compounds that are reactive so they will become part of the cross-linked laminate matrix when cured. A well-understood example for doing this is to develop laminate formulations for epoxy resin systems that incorporate the flame retardant tetrabromobisphenol A, since it is completely reacted into the system. The advantages of using a reactive system can also be achieved with certain non-halogen flame retardants, such as the curing agent discussed in this paper. These types of reactive systems also become part of the cross-linked laminate matrix. This new flame retardant material was developed as a reactive phosphorus-containing flame-retardant curing agent with very high thermal and hydrolytic stability. It is intended for use in conjunction with epoxy resin formulations in use today. This paper describes the development of this flame retardant and the performance in laminates with comparison to some existing non-halogen systems.

Introduction

Over the past 10 years there has been a growing interest for developing flame retardant (FR) materials for printed circuit boards and other electronic applications that are not based on halogen chemistry. Driven by pressure from special interest groups, many OEM’s have adopted a marketing strategy to use non-halogen flame retardants. As a result, the catch phrases “non-halogen”, “halogen-free”, or “low-halogen” have become associated with claims of being “environmentally friendly” or “green”. This paper discusses the definition of “green chemistry” and how this concept is applied in new FR development. Next, it is shown how this translates into the strategy we used in the development of new flame retardant materials.

The developmental approach used and the key performance criteria that were established are presented for a new flame retardant product (PFR-1). The different approaches to making halogen-free laminates are discussed and the properties of laminates made with the new PFR-1 product are compared with some existing formulations.

Experimental Procedure

All reagents, solvents, and resins for laminate formulations were used as received without additional purification. Dowanol PM and DMF were obtained from Aldrich. DEN 438 was obtained from the Dow Chemical Company. SD-1708, EPON 164, EPON 828, EPON 1124, and EPON SU-8 were obtained from Momentive. Aluminum trihydrate (ATH) is Micral 9400 and was obtained from Huber Engineered Materials. Laminates were made using the hand lay-up method. For a typical laminate a flask was charged with a novalac resin, the non-halogen curing agent PFR-1, and acetone, heated with mixing to make the co-curing agent solution, and then cooled to room temperature. Epoxy resin in acetone, Micral 9400 ATH, and 2-methylimidazole catalyst was then added and stirred, using a paddle mixer, at room temperature for at least 30 minutes. Eight plies of 7628 glass cloth (12 × 12 in) were individually coated, using a paint brush, with the above varnish and hung on a rack for 30-60 minutes. The impregnated sheets were then placed into a laboratory oven at a temperature of 170 °C for 1-3 minutes to form the prepregs. The time in the oven depended on the stroke-cure of the formulation. Then the eight prepreg plies were stacked together (with or without copper foil) and sandwiched between steel plates with a Tedlar release sheet and pressed together at 36 psi in a hydraulic press for 2 1/2 hrs at 190 °C to produce a consolidated laminate. The laminate was trimmed and cut for testing. All laminate testing was done according to IPC recommended procedures unless otherwise stated, as summarized in Table 1.

Table 1. Laminate Test Methods and Instrumentation.

Test	Method	Instrument
TMA T_g, z-CTE	IPC-TM-650 # 2.4.24	TA Instruments model 2940
TMA T-288, T-260	IPC-TM-650 # 2.4.24.1	TA Instruments model 2940
TGA T_d	IPC-TM-650 # 2.4.24.6	TA Instruments model Q500
UL-94	UL-94, IPC TM-650 # 2.3.10	
Copper (Cu) Peel Strength	IPC-TM-650 # 2.4.8	MTS Sintech 2/G
PCSD (pressure cooker/solder dip)	IPC-TM-650 # 2.6.16	
Flex	ASTM D790	MTS ReNew Model 1123

For the tests using TMA and TGA, the samples were run as-is and not preconditioned. The laminate decomposition temperature (T_d) was determined by TGA analysis at the 5% weight loss temperature using a 10 °C / minute heating rate under nitrogen. The laminate press cycle was chosen to achieve a fully cured laminate straight from the press, which was checked by post-curing in the oven and checking the T_g for any signs of deviation greater than 5 °C. For the UL-94 test, standard conditioning was followed. For Cu peel strength, Condition A: as received, was followed. Sample dimensions were as specified in the test methods. For flexural testing, the sample dimensions were 0.5 x 5 in. and the samples were tested at a strain rate of 0.05 in/min.

Results and Discussion

Background and Motivation

In recent times, there has been a growing trend by electronic OEMs to manufacture and market "green" or "sustainable" products. In an effort to standardize criteria for determining that a product is "green" a multitude of eco-labels and certification standards have been developed. The website ecolabeling.org lists no less than 370 labels, with as many different criteria. Because most of these labels are privately developed, the criteria often lack scientific objectivity. Facing the risk of being tagged by certain environmental special interest groups as environmentally irresponsible, OEMs are choosing to convert to non-halogen flame retardant systems. According to a recent market survey by IPC, "It is widely believed in the industry that the movement toward halogen-free is not based on good science, but on marketplace pressures."[1]

While "green" in the marketing context is not always well defined, the definition of green from a scientific perspective is well-advanced. The seminal book, Green Chemistry; Theory and Practice by Paul Anastas and John Warner introduced to the world "The 12 Principles of Green Chemistry".[2] Since that time numerous methodologies have also been developed to consider the environmental and health impacts of chemicals using a life cycle perspective, looking not just at the chemical of interest itself when developed but also broader cradle to grave or even cradle to cradle impacts.[3] Life cycle analysis generally considers factors such as energy use, carbon footprint, societal and environmental impacts, and socioeconomic impacts not only for the chemical itself but also for the raw materials used to make the chemical, the useful life of the product that is made from the chemical, as well as the final disposition of the product at its end of life.

Given the criteria associated with green chemistry and life cycle analysis it is easy to see that developing a "Greener" or more "Environmentally-Friendly" product is a complicated matter. To ensure that society is not adversely impacted by uninformed decisions, chemicals should be evaluated and assessed each on their own individual merits using sound science, the principles of green chemistry and life cycle thinking in order to be truly confident that better and greener materials result. In fact, and as a matter of principle, IPC understands, appreciates and advocates the importance of science based life-cycle thinking rather than arbitrary decision making to achieve separate agendas.[4]

With this information in mind, a guide to our new product development efforts was created in a program termed "Greener is Better". This encompasses applying these principles of green chemistry to new products, seeking ways to eliminate environmental and health concerns associated with FR products, designing products that are inherently unlikely to enter the environment during use or end of life management, and designing products that are inherently non-bioavailable. This boils down to three key areas of concern that need to be addressed:

- Are the materials persistent?
- Are the materials bioaccumulative?
- Are the materials toxic?

These characteristics are typically referred to as the "P-B-T" profile of the chemical and one must look at the overall P-B-T profile to make an assessment. Ultimately it is the toxicity of a substance that is the primary concern, whether it is ecotoxicity or human health effects. The persistence or bioaccumulation of a substance are factors affecting the potential long-term build-up in the environment and thus the exposure. If however, substances are designed such that the potential for release to the environment, transport, and bioavailability are negligible, the potential for bioaccumulation and toxicity can be mitigated by design. It is important to recognize that plastic materials and the additives often must have some level of stability that allows for high heat processing and ensures the end product is durable. The required stability means that the 'P' characteristic, persistence, will typically be present in the plastic and flame retardant. With proper end-of-life management, such as post-consumer recycling or waste incineration, the long-term stability of plastics is effectively managed without adverse impact to the environment.

Persistence is not the only criteria that must be considered; bioaccumulation and toxicity must also be considered to fully understand the P-B-T profile. As part of the registration process for new chemicals, an assessment of the characteristics of the molecule with respect to its toxicological profile is conducted. This assessment provides the reassurance that the substance does not pose a risk to human health and the environment. One way to address the P-B-T profile is to have additive materials that are non-toxic and/or non-bioavailable in their own right. For example, the use of aluminum trihydrate (ATH) as an additive flame retardant in certain applications. Another scientifically sound alternative for minimizing the potential for environmental release and bioavailability is increased molecular weight. Higher molecular weight FR materials are inherently unlikely to be migratory or bioavailable. Another established means of preventing environmental release and bioavailability which has been demonstrated as achievable for the printed circuit board industry is to use reactive flame retardants. Reactive flame retardants become part of the polymer matrix, meaning that they are themselves transformed into much larger molecules and will neither migrate into the environment, nor be bioavailable (i.e. the reactive FR molecule no longer exists in it's monomeric form after reaction). Thus, the use of flame retardants that are polymeric or reactive is an effective strategy for developing sustainable and environmentally responsible products.

The rationale for adopting this strategy can be found by reference to the regulatory treatment of such substances. Polymers are generally considered to be of low concern to human health and the environment and as such are recognized as presenting limited concern. As a result, chemical regulatory programs that have been adopted by many governmental agencies around the globe have established reduced requirements for polymers. For example, in the mid-1980's the U.S. Environmental Protection Agency (EPA) established the Polymer Exemption Rule in recognition that the manufacture, processing, distribution in commerce, use, and disposal of most polymers would not present an unreasonable risk of injury to human health or the environment. Under the terms of the Polymer Exemption Rule (as amended in 1995), the manufacture and distribution of polymers meeting the exemption criteria can take place without notification. EPA arrived at this decision based on many years of experience studying a wide variety of types of polymers. In the US Federal Register notice 40 CFR 723 it is stated that 1) In order to cause an adverse health or ecological effect, a chemical must first be absorbed by an organism, and 2) Substances with a number average molecular weight above 1,000 g/mol are not readily absorbed through the intact digestive tract. Secondly, in toxicology there is a "Lipinski Rule of 5" that is used in pharmacology to predict the biological activity of chemical compounds based on molecular weight and lipophilicity. It also suggests that a poor permeation of cell membranes occurs at molecular weights over 500.[5]

Note that this strategy does not look at halogen or halogen-free as a requisite part of the criteria. In many instances, especially when life cycle criteria are considered, halogen chemistry offers distinct advantages over alternate chemistries, including phosphorus chemistry. In other instances, non-halogen chemicals can offer advantages over halogenated chemistries. **We work under the principle that each chemical, whether halogenated or non-halogenated, should be judged on its own characteristics for its intended use from a life cycle perspective.** Rather than focus simplistically on halogen versus non-halogen as the way to achieve a green product, we instead look at the individual compounds. Designing flame retardants that are polymeric or reactive is one of the best ways to ensure a favorable P-B-T profile and to provide a sustainable fire safety solution. A perfect example of this concept is tetrabromobisphenol A (TBBPA) used for the manufacture of epoxy laminates, which is fully reacted into the resin, as discussed below.

Strategy and Literature Approaches for New FR Development

With these points in mind, there are several approaches available to get an FR material into an epoxy-cured laminate, as summarized in Figure 1. One can simply add the FR material as a filler-type of product or even add it as a soluble additive compound. Usually the latter approach generates process and/or quality issues with the resulting laminate. Alternatively, you can chemically incorporate your FR product into the epoxy resin or into the curing agent system. Combinations of these approaches can also be used. Each of these approaches will be discussed briefly.

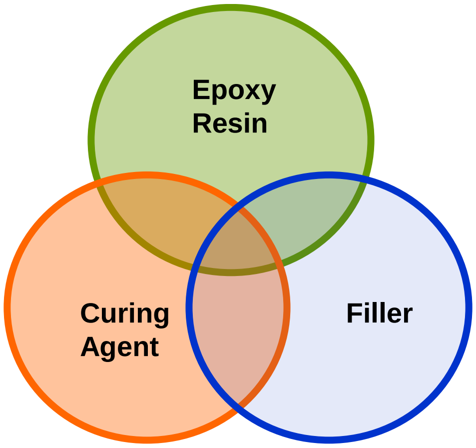


Figure 1. Methods to Incorporate FR Materials into Epoxy Resin Formulations.

A summary of the potential issues associated with each type of FR approach is provided in Table 2. Regardless of the approach used, in order to meet fire safety requirements in the laminates used for printed circuit boards, the resulting laminate must meet the prescribed fire retardancy level, typically "V-0" in the Underwriters Laboratory test method "UL-94". To meet that requirement, different loading levels of FR products are used, depending on the material, the resin matrix, and the way in which it is incorporated into the laminate.

Table 2. Summary of Flame Retardant Approaches and Potential Issues.

FR Type	Potential Issues	"Green" Strategy
Additive / Filler	• Migration / Leaching • V-0 Load level ➢ Rheology ➢ Adhesion ➢ Processing / dispersion • Properties	• Non-toxic additives • Not bioaccumulative
Reactive – epoxy resin or curing agent	• Reactivity profile • Properties	• Not bioaccumulative • Part of polymer matrix

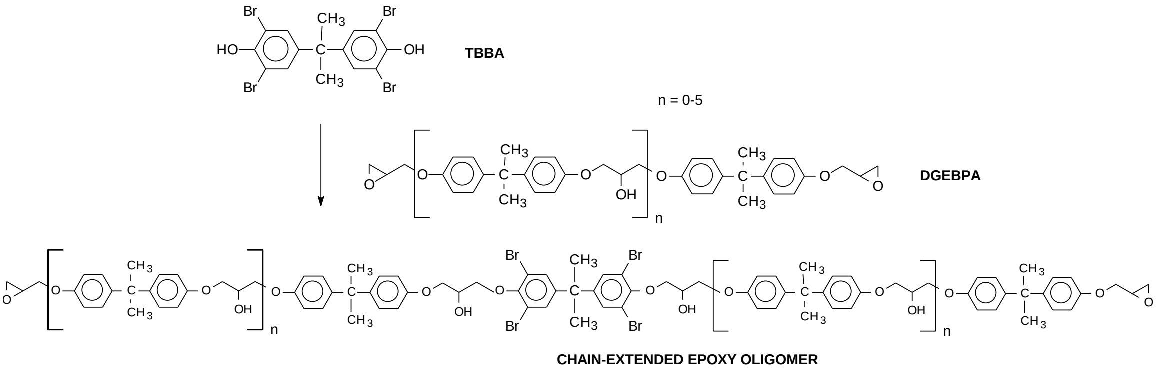
The different approaches to flame retarding PWB materials without the use of halogen chemistry have been reviewed extensively.[6] The approaches discussed below are intended to highlight the main methods that are being used for non-halogen PWB materials as background information only and is not comprehensive.

One example of the filler approach is to use inorganic metal hydrates as additives. The most popular of these has been the use of aluminum trihydrate (ATH). This material is non-toxic and releases water via endothermic decomposition to remove heat and to dilute the concentration of gaseous fuels. The product is usually used in conjunction with other FR materials because extremely high loadings of ATH are required to meet V-0 requirements alone, which severely impacts the PWB physical properties. Without other FR materials, a loading of 250 phr was reported to meet V-0 requirements for an epoxy laminate.[7] A second example of the filler approach is the use of salts of substituted phosphinic acids, such as OP-930 from Clariant.[8] This material is also not soluble in processing resins or solvents, but incorporates phosphorus into the formulation as an additive to function as the flame retardant. A typical load level required to meet a V-0 rating in a DEN-438 / DICY formulation was 9.5%.[9] It was suggested that this material may be used as a synergist with other FR compounds.[10]

Another additive approach is based on melamine polyphosphate, such as Melapur 200, available from Ciba Corporation.[11] This material was stated to be an FR synergist (or FR adjuvant) and was used in combination with other FR materials to achieve the desired properties. A host of other newly developed phosphorus based additive FR materials has been described in the review literature, which can be consulted for the details.

The most common example of delivering the FR performance via the epoxy resin can be found in TBBPA. This material and approach has been used for several decades and is a well-known approach with properties and toxicity that has been extensively studied.[12, 13] A comprehensive Risk Assessment published in the Official Journal of the European Union, June 2008, concluded that TBBPA presents no risk to human health. The Risk Assessment identified no risk to the environment when TBBPA is used in reactive applications such as printed wire boards.[14]

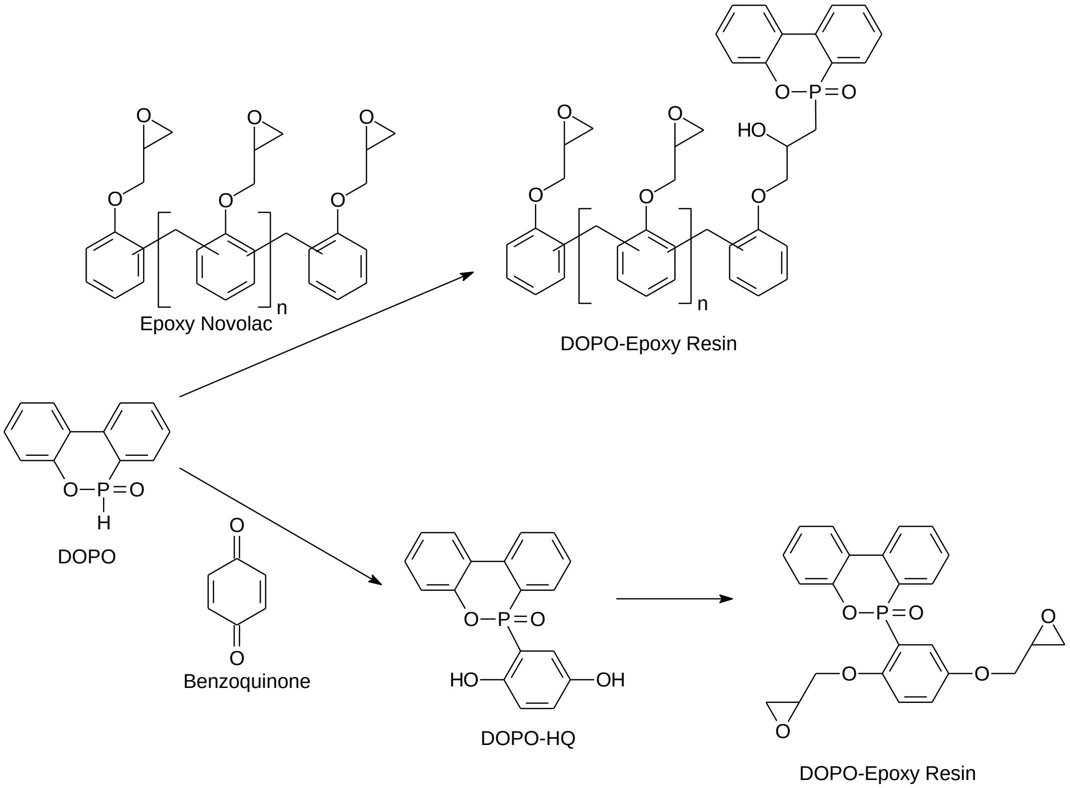
TBBPA is typically incorporated into the PWB by a reaction with difunctional epoxy resins to first form a chain-extended epoxy resin. That method can be summarized briefly in Scheme 1 where the TBBPA is first advanced into an epoxy resin and the newly formed resin, which contains TBBPA in the backbone, is then used by the laminator in various formulations. As a result, the TBBPA molecule is covalently bonded into the polymer backbone as part of the resin system. The resulting brominated resin is formulated with hardeners and accelerators and cured under heat and pressure to form the final laminate product. After the resin is cured in the laminate, the covalently bonded TBBPA property renders the TBBPA molecule unavailable to diffuse out of the circuit board into the environment. The TBBPA moiety provides flame retardancy by the well-known free-radical quenching of the fire chain reaction in the vapor phase.[15]



Scheme 1. Example of Making An Epoxy Resin Containing TBBPA.

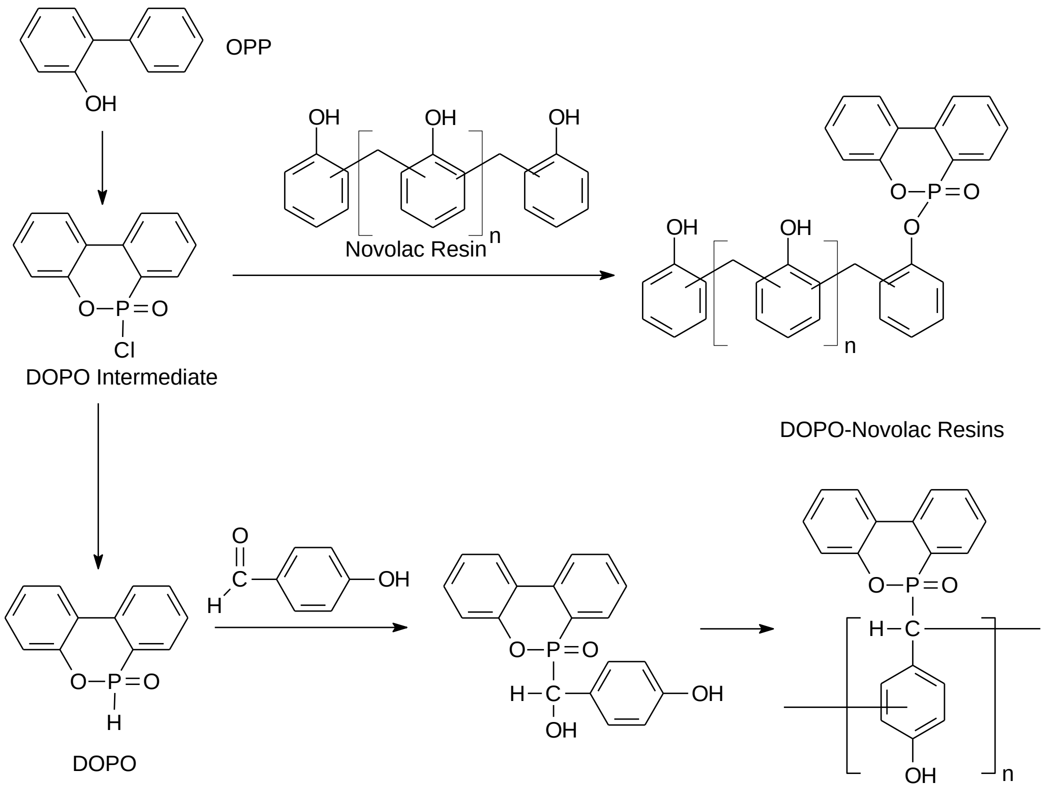
A non-halogen epoxy resin approach can be found with the many methods that incorporate the compound 9,10-dihydro-9-oxa-10-phosphaphenanthren-10-oxide; also known as "DOPO" (Scheme 2). This material was originally used for polyesters, but has seen resurgence in the epoxy resin area in the last several years.[16, 17] Because of its monofunctional nature (which can lead to a reduction in T_g), DOPO is usually reacted with epoxy novolac resins to make a phosphorus-containing resin as an additional step before use.[18] This is one way to compensate for the monofunctional nature of DOPO. By using this approach, some of the epoxy groups in the epoxy novolac resin are reacted with DOPO, leaving the remainder epoxy groups available for curing with the formulation. Another approach to compensate for the mono-functional nature of DOPO is to convert the DOPO into a difunctional compound and chain-extend into difunctional epoxy resins. Typical examples of that approach would be in the form of DOPO-HQ and the subsequent epoxy resins that are derived from that product. These approaches tend to limit the P content that can be present in the resin to avoid compromising the T_g of the final laminate.

The DOPO material can also be incorporated into the curing agent resin. In this case, a reactive DOPO intermediate is treated with a phenolic novolac resin to make a resin where some of the phenolic groups are end-capped with the DOPO structure (Scheme 3).[19] Alternatively, DOPO may be treated with a hydroxybenzaldehyde to make a different type of DOPO-based novolac resin.[20] Another curing agent approach was recently reported as Fyrol PMP, available from ICL-Supresta.[21] This compound was reported to function as a curing agent, but through a different cure mechanism than the standard phenolic based curing.[22]



Scheme 2. Selected DOPO-Epoxy Chemistry Approaches.

A fourth approach, not shown in Figure 1 is to change the base resin chemistry and develop completely new resin systems that are designed to be inherently flame retardant. This approach is usually reserved for niche applications that can afford the added expense or that require some of the special properties these resins may bring. These types of resins are typically highly aromatic in nature and contain a high degree of functionality to allow for some char formation. For example, the use of a dihydrobenzoxazine system with a triazine-modified novolac resin and 60 phr ATH has been reported to give V-0 performance.[23] Alternatively, a highly cross-linked specialty resin formulation has been reported that uses reduced quantities of additive type flame retardants to achieve V-0.[24] The basic strategy with these resins that typically meet V-1 requirements on their own is to use lower loadings of an FR adjuvant to push the specialty resin system to V-0 performance. Although a variety of approaches exists using this strategy, the specialty resins would be at a relatively higher cost than existing commercial resins and may not be as widely available.



Scheme 3. Incorporation of the DOPO Moiety into a Curing Agent.

These brief summaries of the typical approaches can be reviewed in more detail by consulting the previously mentioned review literature. Regardless of the approach used, the FR performance can be attributed to either a vapor or condensed phase mechanism.[25] This FR action is highly dependent on the structure of the cured system as a whole for non-halogen materials and no single PFR solution exists for all epoxy resin systems.

Emerald ™ 2000 Non-Halogen Curing Agent (PFR-1)

Based on the above considerations, it was decided to develop an FR material that will be reacted into the resin formulation in some fashion to minimize the likelihood of environmental release or bioaccumulation. In looking at the two approaches available, epoxy resin or curing agent, it appeared as though the DOPO materials were extensively used in the epoxy resin area and required an additional processing step to get the compound into a form that can be useful to the laminator. If we could develop a phosphorus-based flame retardant that could be used directly by the laminator without the additional processing step, the possibility is opened up for some additional flexibility for formulations development and also the potential would increase for improved economics by elimination of some steps.

So focus was placed on developing the curing agent aspect with an FR material that would function as both flame retardant and curing agent. The properties of the material that was developed are summarized in Table 3. The PFR compound is phosphorus-based and contains phenolic functionality. Phenolic functionality was chosen as the reactive group because a great deal of the epoxy curing agents for increased thermal stability is based on phenolic novolac resins, which would cure by similar reaction mechanisms. Being a phenolic compound, the material could also conceivably be used to make other resins that are derived from phenolic materials, like polycarbonates, benzoxazines, and epoxy resins to name a few.

Table 3. Physical Properties of PFR-1 Flame Retardant.

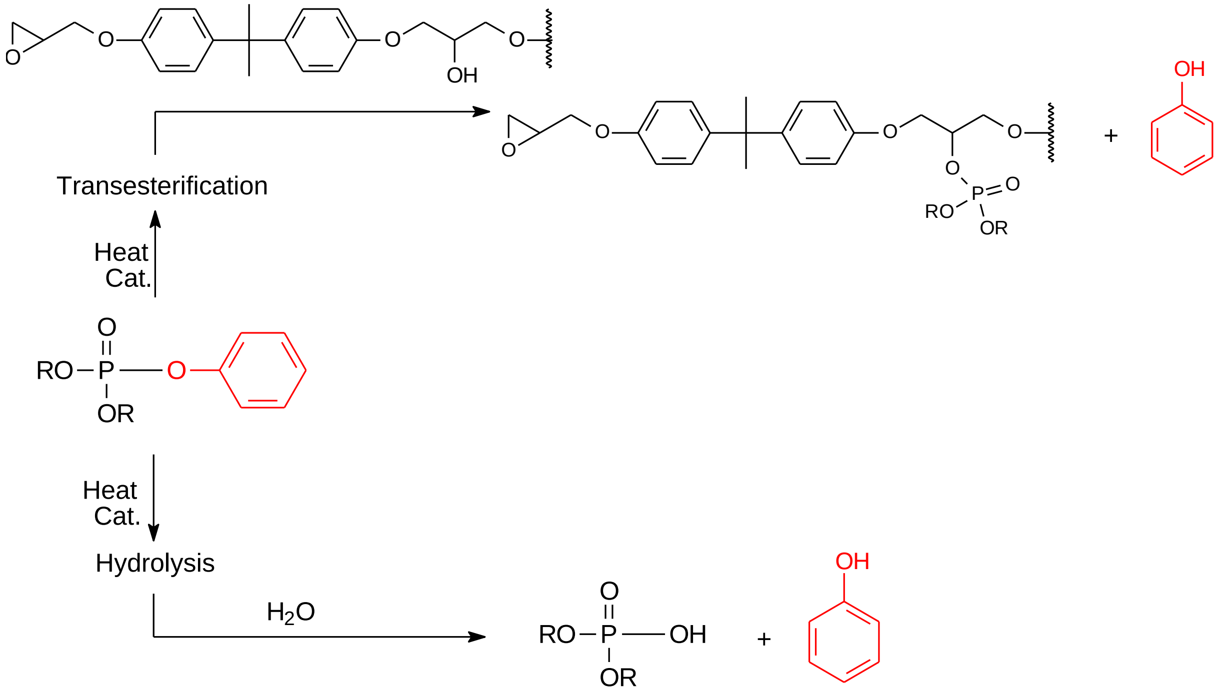
Physical Property	Value
Form	Solid, light amber flake or granular
Melt Range, °C	114 – 130
Functionality	Phenolic
Hydroxyl Equivalent Weight (g/Eq)	165 – 175
Phosphorus Content, %	9.7 – 9.9

In this development project, the following were established as the target performance criteria:

- Same processing conditions as comparable FR-4 laminates
- Soluble in processing solvents
- Laminate T_g > 150 °C
- Laminate lead-free compatible
- Cost-performance competitive

These goals were set to meet current and future needs of the marketplace regarding processing and thermal stability. Other factors, such as electrical properties would need to be assessed by laminators in their own formulations, since each company's formulations would be different.

To meet these goals, it was understood that the material must react via the phenolic functionality and not be subjected to other potential side-reactions that could occur during the laminate curing cycle. With phosphorus-based compounds, one potential side-reaction is transesterification or hydrolysis. The former occurs when a solvent molecule or other material with nucleophilic character, such as a hydroxyl group, an amino group, etc., reacts with a phosphorus material that contains phosphorus–oxygen–carbon bonds as shown in Scheme 4. The transesterification would bind the FR material to the reacting substrate, but would liberate part of the compound as a by-product. This by-product could continue to react with epoxy groups or it could volatilize, depending on the structure. The hydrolysis reaction would also liberate part of the compound as a by-product, but would also generate a phosphorus based acidic group, which may be an issue during the lifetime of the material.



Scheme 4. Transesterification or Hydrolysis of Phosphorus Esters.

Based on these concerns, the PFR-1 material was designed to not contain any phosphorus – oxygen – carbon bonds, so this would not be a point of concern. In addition to the increased chemical stability that this would bring, as described above, it would also increase the thermal stability, due to the strength of the phosphorus – carbon bonding.

If one were to use PFR-1 in a formulation as the sole curing agent, then the overall phosphorus content would be higher than necessary to achieve satisfactory FR performance. Therefore, the best way to apply the product in a formulation is to blend it with a phenol-novolac resin of your choice to make a co-curing agent package. This is how the product is applied in the subsequent formulations discussed below.

An added benefit to using a novolac resin as co-curing agent is that the solubility of the PFR-1 is significantly increased at room temperature. As shown in Table 4, one can achieve a 60% solids concentration of the co-curing agent package in either acetone or Dowanol PM solvent systems. The materials were heated to dissolve and then allowed to cool to room temperature for the blended solubility. The room temperature PFR-1 solubility was determined by stirring a slurry of PFR-1 in solvent for several hr, filtering, and weighing the filter cake.

Table 4. Solubility Properties of PFR-1 at Room Temperature.

Solvent	Solubility, g/100g
PFR-1	
Dowanol PM	33
Acetone	14
DMF	>100
PFR-1 / SD-1708 Novolac Resin 2.1/1.0 (w/w)	
Acetone	>150 (60% solids)
Dowanol PM	>150 (60% solids)

The first examination of the flame-retardant character of the PFR-1 material was in a load level study for 8-ply laminates made with the DEN 438 epoxy resin system and co-cured with PFR-1 and SD-1708 novolac resin, as shown in Table 5. ATH was used as the FR adjuvant and that load level was held constant at 23% on the formulation organics. As shown, V-0 FR performance was achieved at 2.75% phosphorus or higher, with the burn times extending slightly longer at lower %P loadings to give a V-1 rating. The phosphorus content is based on the total formulation organics throughout this discussion.

Table 5. PFR-1 Load Level in DEN-438 Epoxy Resin System.[a]

Run	%P	UL-94 Rating	Total Burn Time, s (T1, T2)
1	3.00	V-0	1, 22
2	2.75	V-0	4, 11
3	2.50	V-1	3, 35
4	2.25	V-1	8, 74

a) All formulations contained 23% ATH and were co-cured with SD-1708 novolac resin and PFR-1.

An understanding of the basic burn / FR behavior was continued with a study of the use of PFR-1 co-curing agent with different base epoxy resin systems, as shown in Table 6. The formulation and curing conditions used were similar to that used for the DEN-438 system. The possibility of using a phosphorus-based epoxy resin material in some of the systems was also explored. For that system, a commercially available DOPO-based epoxy resin was used that contained 3.2% P in the base resin.

Table 6. PFR-1 in Alternative Epoxy Resin Systems.[a]

Run	Epoxy Resin	FR System	%P	UL-94 Rating	Total Burn Time, s (T1, T2)
5	DOPO-Epoxy	DOPO	2.50	V-0	0, 30
6[b]	DOPO-Epoxy / DEN-438	DOPO + PFR-1	2.50	V-0	3, 23
7	Epon SU-8	PFR-1	3.00	V-1	3, 59
8	Epon 828	PFR-1	3.00	V-1	11, 59
9	Epon 164	PFR-1	2.50	V-1	6, 56
10	Epon 164 / DEN-438	PFR-1	3.00	V-0	2, 21

a) All formulations contained 23% ATH and were cured with SD-1708 novolac resin, or co-cured with SD-1708 novolac resin and PFR-1 as indicated.
b) 1.25% P from DOPO, 1.25% P from PFR-1.

In the alternative epoxy resin study, the DOPO-epoxy resin without PFR-1 gave a V-0 rating at 2.5% P content. The system with a combination of DOPO-epoxy and PFR-1 co-curing agent also gave a V-0 rating at 2.5% P content. Other epoxy resins were studied as shown and, in general, the resins that contain more aliphatic character tended to fall into the V-1 burn range and those with more aromatic character fell into the V-0 range in this limited study.

Having a base-resin system in hand that was a good V-0 in the DEN-438 epoxy system and also in the DOPO-epoxy systems, laminates were made both with and with out 1-oz. copper foil and the laminate properties were determined (Table 7). As shown in those examples, the CTE results were quite good for all of the laminates. However, the T-288 and T_d thermal properties increased significantly with increasing levels of PFR-1, confirming the stability of the material.

Table 7. Laminate Properties of PFR-1 vs. DOPO-Based Material.[a]

					CTE					
Run	**Epoxy Resin**	**FR System**	**%P**	**T_g, °C (TMA)**	**α1, ppm/°C**	**α2, ppm/°C**	**Total, % (50-250 °C)**	**T-288, min.**	**T_d (5%) °C**	**%Moisture**
5	DOPO-Epoxy	DOPO	2.50	126	2.1	213	2.67	0	367	0.29
6	DOPO-Epoxy / DEN 438	DOPO + PFR-1	2.50	152	6.4	265	2.57	3.9	379	0.32
2	DEN 438	PFR-1	2.75	156	16.3	242	2.52	>60	404	0.31

a) All formulations contained 23% ATH and were cured with SD-1708 novolac resin, or co-cured with SD-1708 novolac resin and PFR-1 as indicated.

b) The moisture absorption was determined from the pressure cooker test exposure.

Having obtained an understanding of the basic laminate properties, the focus was then shifted to adhesion properties. It was believed that the PFR-1 material could potentially be a chelator for certain metals. This property may manifest itself in an improved copper adhesion. This concept was examined in Table 8, which shows the copper adhesion was indeed improved when PFR-1 was present in the formulation vs. the DOPO-epoxy system without any PFR-1 present.

Table 8. Copper Peel Strength.[a]

Run	**Epoxy Resin**	**%P**	**FR System**	**Cu Peel Strength, N/mm (lb/in)**
5	DOPO-Epoxy	2.50	DOPO	1.18 ± 0.13 (6.72 ± 0.74)
6	DOPO-Epoxy / DEN 438	2.50	DOPO + PFR-1	1.47 ± 0.11 (8.38 ± 0.65)
2	DEN 438	2.75	PFR-1	1.50 ± 0.11 (8.56 ± 0.64)
1	DEN 438	3.00	PFR-1	1.46 ± 0.09 (8.36 ± 0.51)

a) All formulations contained 23% ATH and were cured with SD-1708 novolac resin, or co-cured with SD-1708 novolac resin and PFR-1 as indicated.

For non-halogen laminates, the subject has arisen regarding brittleness. It was decided to look at this aspect by measuring the flexural properties of the laminates. Test bars from the different unclad laminates were evaluated for flexural modulus and % strain at break to indirectly determine if certain laminates are more brittle than others. The modulus or stiffness is an indication of how much force is required to bend the material before it breaks. A high modulus means that the material is stiffer and it takes more force to cause it to yield. The % strain at break is an approximate indication of the degree of brittleness when comparing laminates while the area under the stress-strain curve depicts the 'toughness' of the material or how much energy the material will absorb. A high modulus with low % strain at break is a strong but brittle material. A high modulus with a fairly large extension at break means the material is stiff but it is also less brittle, comparatively.

The results are summarized in Table 9 and Figure 2 and compared to a brominated epoxy laminate with and without ATH present. All laminates were cured with phenolic novolac SD-1708 alone or in combination with PFR-1 as indicated. In the brominated epoxy case, the addition of ATH lowered the % strain at break somewhat, which makes sense because the addition of a filler material would somewhat disrupt the continuous resin phase. Bear in mind, however, that all of the materials had a very similar % strain at break centered near 2%. Interestingly, the DOPO system and the brominated systems all displayed essentially the same modulus. However, the system that used PFR-1 showed a ~20% higher modulus vs the DOPO and TBBPA cases, indicating this material may have somewhat better load carrying capabilities. The higher T_g SU-8 systems showed a more reduced modulus and slightly lower % strain at break, indicating that those very high T_g systems may be somewhat more brittle.

Table 9. Flexural Properties For Unclad Laminates.

Run	**Epoxy Resin**	**FR**	**%P**	**ATH, %**	**T_g, °C (TMA)**	**Modulus, GPa**	**% Strain at Break**
11	Epon 1124	TBBPA	---	23	134	20.8 ± 0.2	1.84 ± 0.05
12	Epon 1124	TBBPA	---	0	131	21.6 ± 0.3	2.44 ± 0.07
5	DOPO-Epoxy	DOPO	2.50	23	126	21.1 ± 0.2	2.11 ± 0.05
6	DOPO-Epoxy / DEN 438	DOPO + PFR-1	2.50	23	152	24.9 ± 0.6	2.38 ± 0.10
2	DEN 438	PFR-1	2.75	23	156	25.6 ± 0.6	2.24 ± 0.05
13	Epon SU-8	PFR-1	3.00	23	173	19.9 ± 0.6	2.20 ± 0.16
7	Epon SU-8	PFR-1	3.00	23	181	19.2 ± 0.4	1.97 ± 0.04

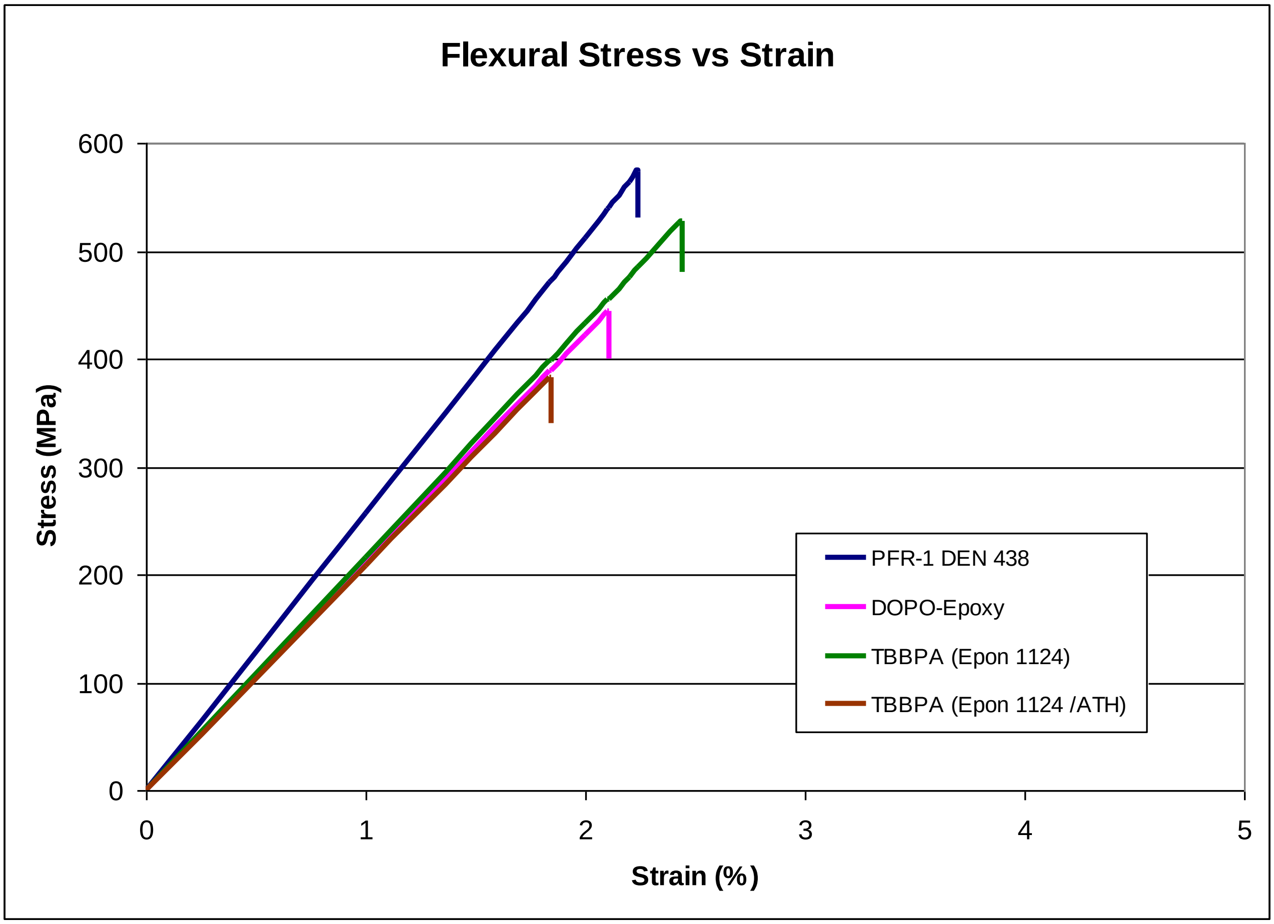


Figure 2. Flexural Testing of 8-Ply Laminates.

Conclusion

Emerald™ 2000 is a combination flame retardant / curing agent material that was developed to be consistent with our "Greener is Better" approach to molecule design. By nature of it being a reactive compound, it would likely exhibit a favorable P-B-T profile because it becomes part of the cured polymer matrix, much like TBBPA is also part of the cross-linked polymer system. The material was targeted for use as part of the co-curing agent package and has phenolic functionality so it would have reactivity that is very similar to phenolic novolac resin systems. The flame retardant material was shown to give V-0 performance in 8-ply epoxy laminates with very good thermal properties. Additionally, it was shown that the laminates made with this product may be able to absorb more energy under stress than comparable DOPO-based systems, indicating the material may be somewhat less brittle. The product was designed to not have any phosphorus – oxygen bonds, so hydrolysis and/or transesterification would not become potential problems downstream. We anticipate that this product can provide laminators with additional options and flexibility for developing customized FR epoxy formulations.

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For a Better Tomorrow

A Chemtura Business

A Combination Flame Retardant Curing Agent Material For Non-Halogen PCB Laminates

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AGENDA

- Non-halogen drivers
- Green chemistry and other considerations
- FR design strategy vs. other approaches
- Product properties and performance criteria
- Laminate preparations and evaluation results
- Conclusions

WHY A MARKET NEED?

- Environmentally Friendly
- Green
- Sustainable

- Eco-Labels
- Unique Technical Reasons
- Marketing
- Legislation

What does it all mean?

Lots of conflicting information in the marketplace

Drivers

- OEM desire to manufacture and market “Green” or “Sustainable” products.
- 370 different eco-labels (ecolabeling.org)
  - Privately developed
  - Scientific objectivity?
- IPC: “It is widely believed in the industry that the movement toward halogen-free is not based on good science, but on marketplace pressures”[1]

[1] Starr, S., *IPC White Paper: Report on Phase 1 of IPC Market Research on Electronics Technology Trends: Insights about 10 Key Trends from Interviews with Industry Experts* (**2010**).

Green Chemistry[1]

1. **Prevent waste:** Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
2. **Design safer chemicals and products:** Design chemical products to be fully effective, yet have little or no toxicity.
3. **Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
4. **Use renewable feedstocks:** Use raw materials and feedstocks that are renewable rather than depleting.
5. **Use catalysts, not stoichiometric reagents:** Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times.
6. **Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible.
7. **Maximize atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
8. **Use safer solvents and reaction conditions:** Avoid using solvents, separation agents, or other auxiliary chemicals.
9. **Increase energy efficiency:** Run chemical reactions at ambient temperature and pressure whenever possible.
10. **Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
11. **Analyze in real time to prevent pollution.**
12. **Minimize the potential for accidents:** Minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

[1] From: Anastas, P. T.; Warner, J. C.; *Green Chemistry: Theory and Practice*, Oxford University Press: New York, **1998**, p.30.

Other Potential Considerations

- Life cycle analysis
  - Cradle to grave or cradle to cradle (recycling)
  - Carbon footprint
  - Societal and environmental impacts
- Science based life-cycle thinking is needed rather than arbitrary decision making to achieve separate agendas[1]
  - Elimination of bromine / chlorine from materials, regardless of the chemical structure is not a sound scientific approach
  - Each material needs to be evaluated on it's own merits

It's Complicated!!

Lot's of information to consider

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[1] Abrams, F. *Circuitree*, p. 30, **October 2009**; McGuirk, D. *IPC InTOUCH*, **February 2010**.

Our Strategy

“Greener Is Better” philosophy includes:

- Apply the Principles of Green Chemistry and Engineering to present and future products
- Assess existing and new products from a life-cycle perspective and look for opportunities for improvement
- Design products that are inherently unlikely to enter the environment during use or end of life management
- Design products that are inherently non-bioavailable

P-B-T profile

P-B-T Profile

- Persistent
  - Present for most plastics / a.k.a. “stability”
  - Can be addressed by proper end-of-life management
- Bioaccumulative
  - Must be addressed in the molecule design
- Toxic
  - Must be addressed in the molecule design or potential for exposure

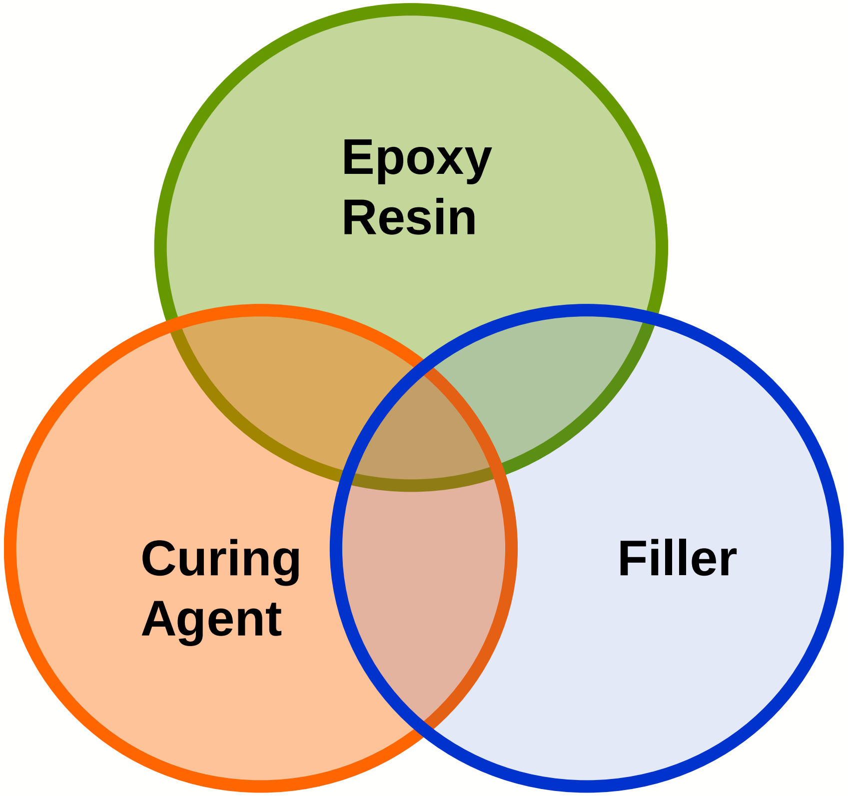
Strategies for “Greener” FR

“Greener is Better” Flame Retardant Approaches

- Non-Toxic additives
- Increased molecular weight (polymers)
- Reactive compounds (become polymers during processing)

- THIS DOES NOT CONSIDER HALOGEN OR HALOGEN-FREE AS A CRITERION.
- EACH MATERIAL NEEDS TO BE ASSESSED INDIVIDUALLY ON ITS OWN MERITS
- CONSIDERS INTENDED USE AND LIFE CYCLE PERSPECTIVE

PCB FR APPROACHES



Multiple approaches are possible.

Reactive curing agent approach was chosen

Potential Issues

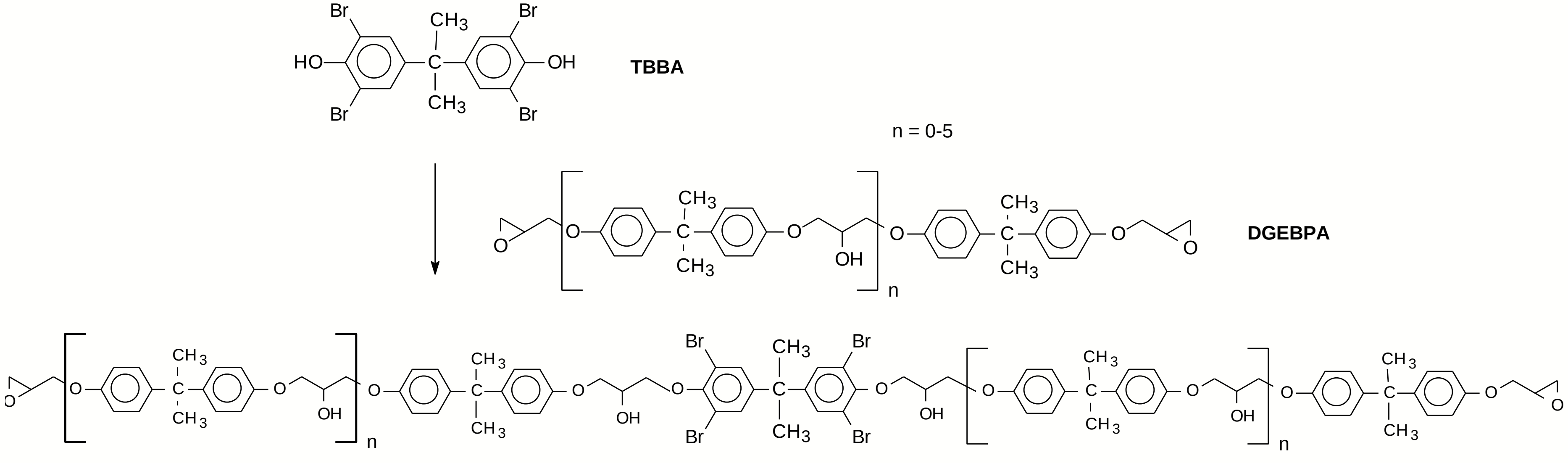
FR Type	Potential Issues	"Green" Strategy
Additive / Filler	•Migration / Leaching •V-0 Load level ➢Rheology ➢Adhesion ➢Processing / dispersion •Properties	•Non-toxic additives •Not bioavailable or bioaccumulative
Reactive – epoxy resin or curing agent	•Reactivity profile •Properties	•Not bioavailable •Part of polymer matrix

There are pros and cons associated with the various approaches

Common FR Approaches

- Additive
  - ATH
  - OP-930
  - Melapur MP® 200
- Reactive – Epoxy Resin
  - TBBPA
  - DOPO based
- Reactive – Curing Agent
  - Fyrol® PMP
  - DOPO analogs
  - PFR-1 Our New Approach

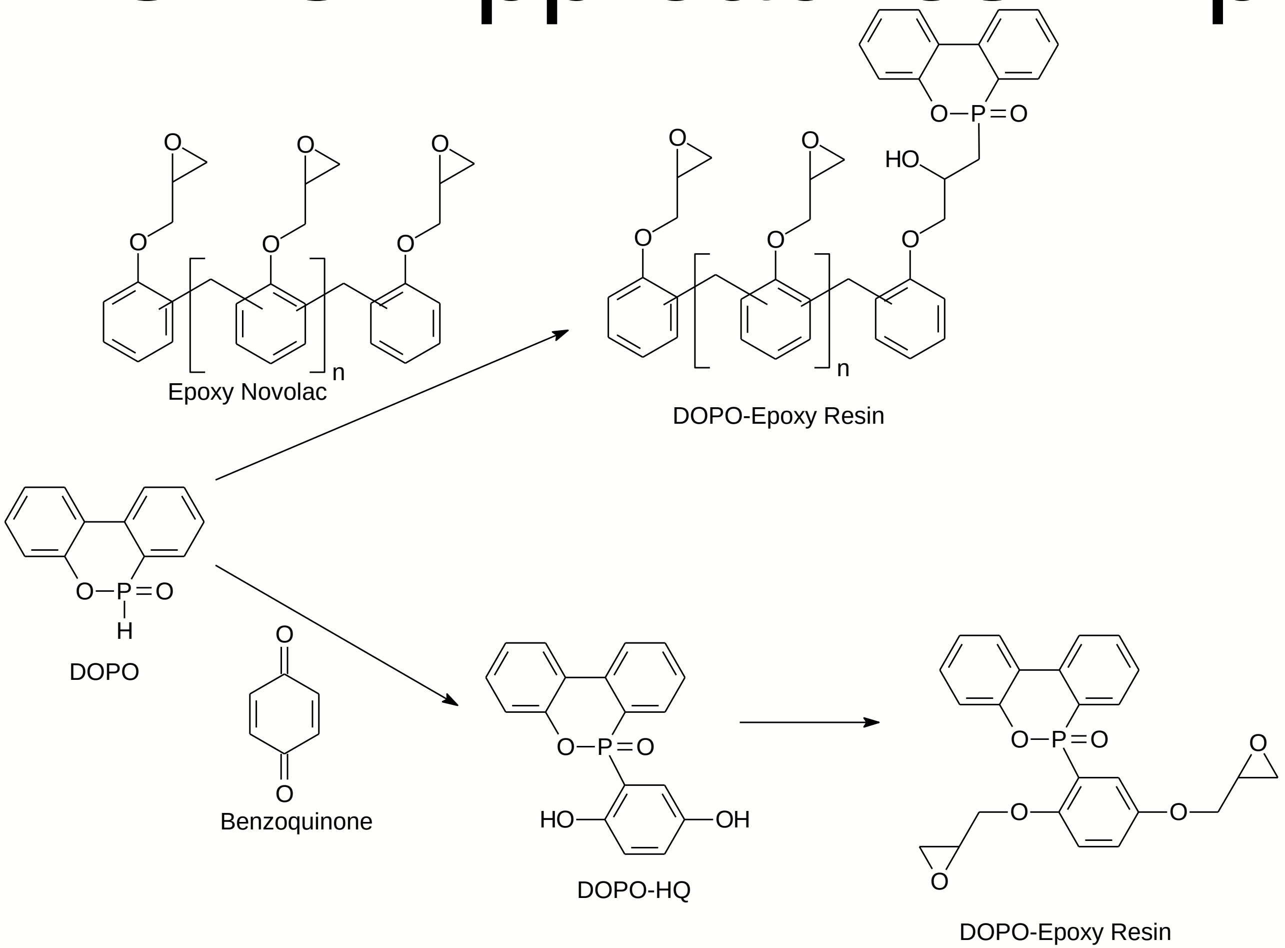
TBBPA Approach



CHAIN-EXTENDED EPOXY OLIGOMER

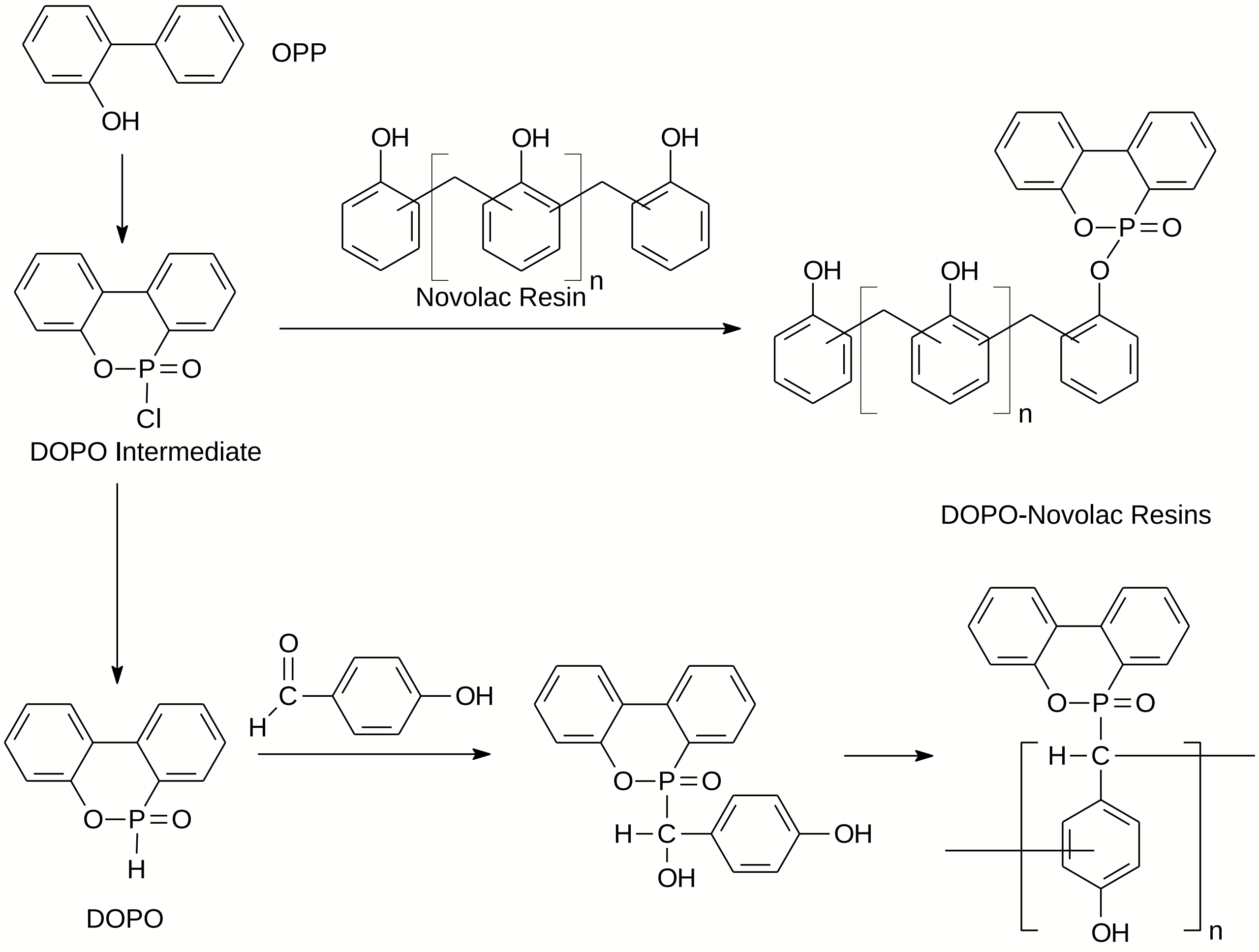
- TBBPA is incorporated into the polymer
- Meets our criteria under “Greener is Better”

DOPO Approaches - Epoxy



- Must overcome monofunctional nature of DOPO by making derivative resin. Necessary for Tg properties.
- These are the two main approaches being used.

DOPO Approaches - Cure

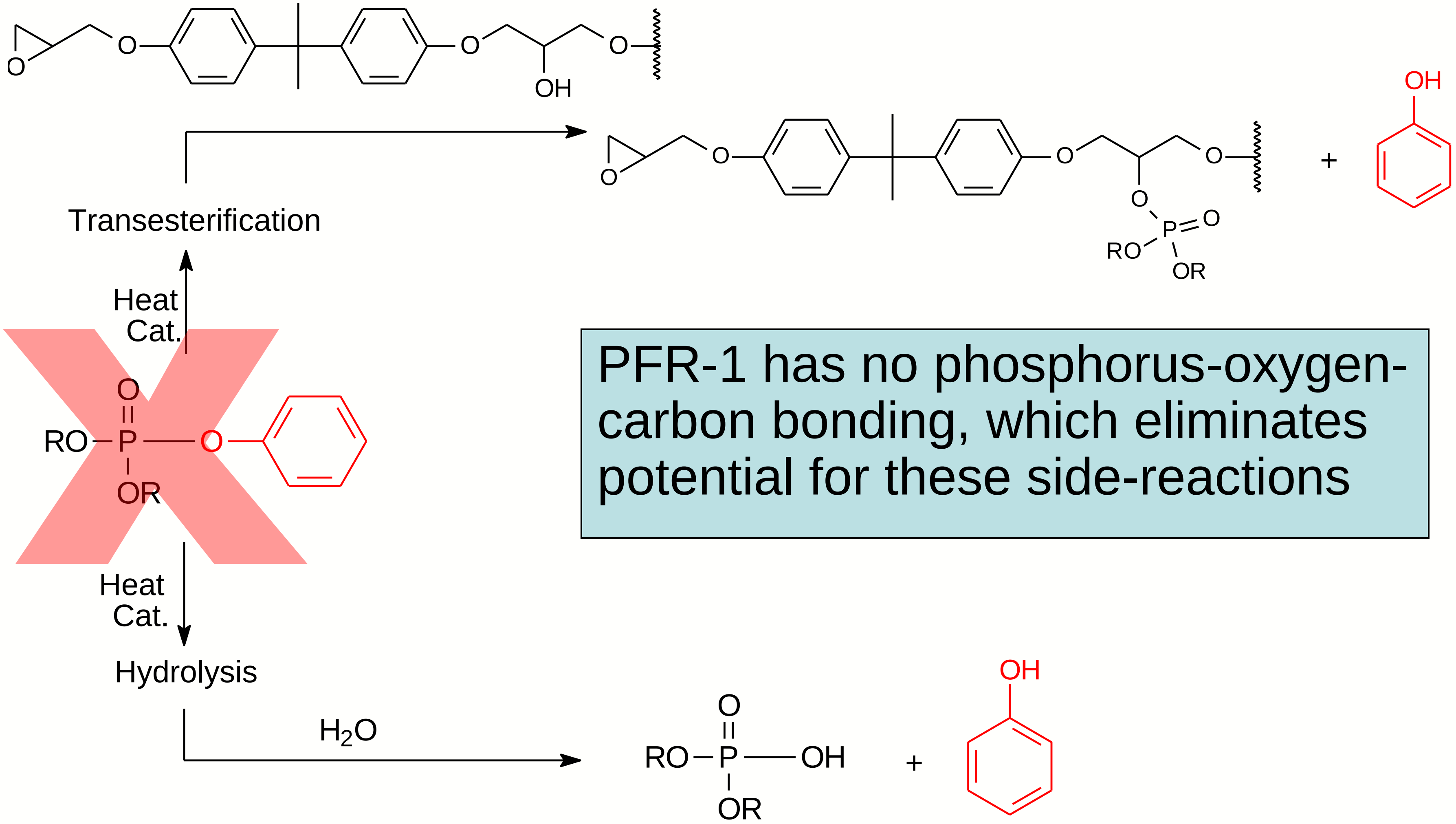


These approaches are seen more in academic literature

PFR-1 Approach

- DOPO appears to be used mainly as an epoxy resin derivative
- Thought was to use FR product <u>directly in formulation</u> without extra processing step to potentially reduce costs.
- To meet our Greener is Better criteria, we designed PFR-1 to be reactive.
- Therefore, selected phenolic based functionality in the new PFR-1 compound:
  - Similar reactivity to novolac resin curing agents already in use
  - Will be incorporated into the cross-linked structure
  - Improved thermal stability would be possible

Other Design Considerations



PFR-1 has no phosphorus-oxygen-carbon bonding, which eliminates potential for these side-reactions

Properties and Target Performance Criteria

Physical Property	Value
Form	Solid, light amber flake or granular
Melt Range, °C	114 – 130
Functionality	Phenolic
Hydroxyl Equivalent Weight (g/Eq)	165 – 175
Phosphorus Content, %	9.7 – 9.9

Targets:

- Same processing conditions as comparable FR-4 Laminates
- Soluble in processing solvents
- Laminate Tg >150 °C
- Laminate lead-free compatible
- Cost-performance competitive

PFR-1 Mode of Use

- Data was developed using a phenol-formaldehyde novolac resin as a co-curing agent to give best overall properties
- This also improved the formulation solubility

Solvent	Room Temperature Solubility, g/100g
PFR-1	
Dowanol PM	33
Acetone	14
DMF	>100
PFR-1 / SD-1708 Novolac Resin 2.1/1.0 (w/w)	
Acetone	>150 (60% solids)
Dowanol PM	>150 (60% solids)

Laminate Preparations

- All laminates were made by the hand lay-up method
- Solvents and reagents / resins were used as-received
- Used 8-plies of pre-preg with 7628 glass.
- Laminates were made with and without 1 oz copper foil and tested per standard IPC specifications unless otherwise indicated

UL-94 V-0 Load Level Study

System: DEN-438 Epoxy Resin, PFR-1 + SD-1708 Co-Curing Agent, 23% ATH

Run	**%P**	**UL-94 Rating**	**Total Burn Time, s (T1, T2)**
1	3.00	V-0	1, 22
2	2.75	V-0	4, 11
3	2.50	V-1	3, 35
4	2.25	V-1	8, 74

- Good FR behavior was observed in the base formulation system.
- %P is based on entire formulation organics

Additional UL-94 Testing

System: SD-1708 Co-Curing Agent, 23% ATH

Run	Epoxy Resin	FR System	%P	UL-94 Rating	Total Burn Time, s (T1, T2)
5	DOPO-Epoxy	DOPO	2.50	V-0	0, 30
6[a]	DOPO-Epoxy / DEN-438	DOPO + PFR-1	2.50	V-0	3, 23
7	Epon SU-8	PFR-1	3.00	V-1	3, 59
8	Epon 828	PFR-1	3.00	V-1	11, 59
9	Epon 164	PFR-1	2.50	V-1	6, 56
10	Epon 164 / DEN-438	PFR-1	3.00	V-0	2, 21

a) 1.25% P From DOPO resin and 1.25% P from PFR-1.

- Additional optimization appears to be possible
- Increased aliphatic character in the system tended to give longer burn times in these formulations

Full Laminate Properties

System: SD-1708 Co-Curing Agent, 23% ATH

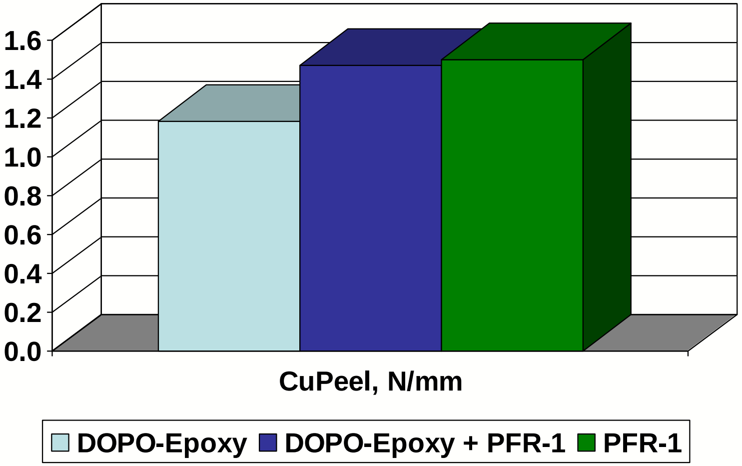
					CTE					
Run	**Epoxy Resin**	**FR System**	**%P**	**T_g, °C (TMA)**	**α1, ppm/°C**	**α2, ppm/°C**	**Total, % (50-250 °C)**	**T-288, min.**	**T_d(5%) °C**	**%Moist.**
5	DOPO-Epoxy	DOPO	2.50	126	2.1	213	2.67	0	367	0.29
6	DOPO-Epoxy/ DEN 438	DOPO + PFR-1	2.50	152	6.4	265	2.57	3.9	379	0.32
2	DEN 438	PFR-1	2.75	156	16.3	242	2.52	>60	404	0.31

- Good CTE results were seen for all systems
- Significant improvement in T-288 and T_d was observed in systems containing PFR-1

Copper Adhesion

Idea: Possible “chelator” properties of PFR-1 compound may lead to improved Cu peel strength

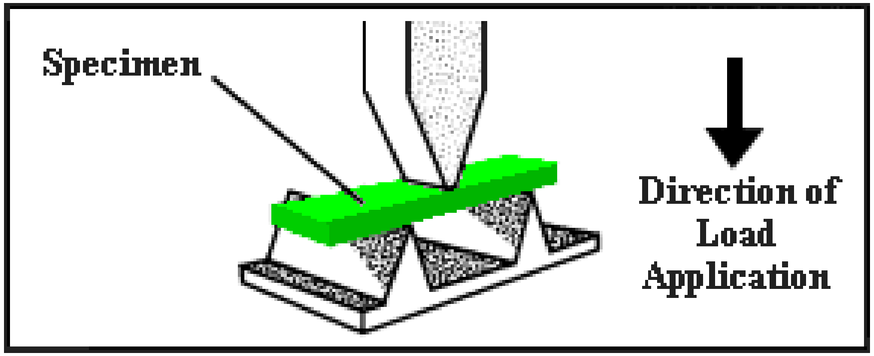
Run	Epoxy Resin	%P	FR System	Cu Peel Strength, N/mm (lb/in)
5	DOPO-Epoxy	2.50	DOPO	1.18 ± 0.13 (6.72 ± 0.74)
6	DOPO-Epoxy/ DEN 438	2.50	DOPO+ PFR-1	1.47 ± 0.11 (8.38 ± 0.65)
2	DEN 438	2.75	PFR-1	1.50 ± 0.11 (8.56 ± 0.64)
1	DEN 438	3.00	PFR-1	1.46 ± 0.09 (8.36 ± 0.51)



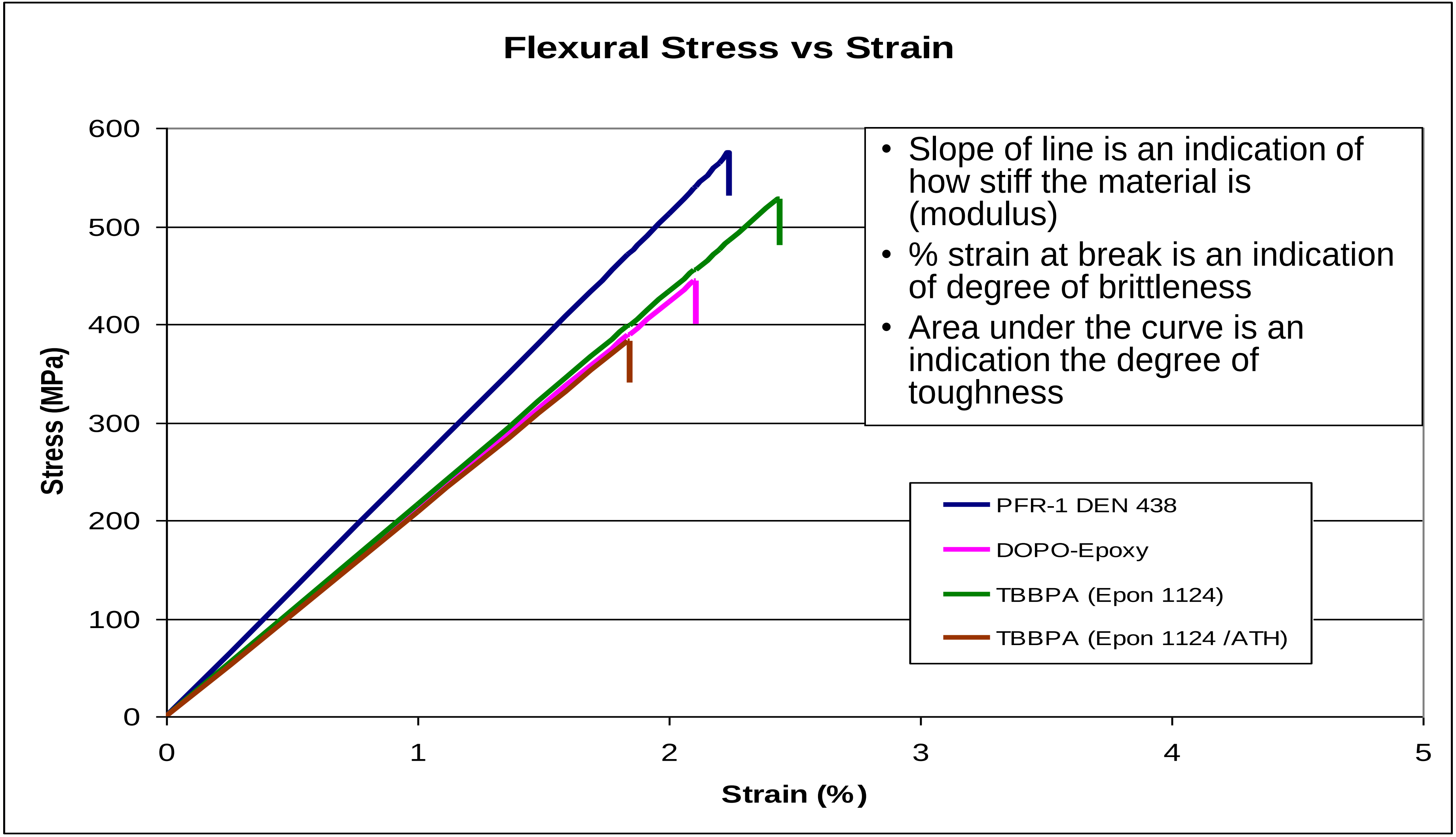
Observe ~27% increase in peel strength for the PFR-1 vs. DOPO-epoxy systems.

Flexural Testing

- Flexural strength indirectly relates to “brittleness” and/or “toughness”.
- Load is applied (stress) to the laminate and the deflection (strain) is measured to the point of failure
- Tested several laminates to determine any differences.
- Made laminates based on TBBPA epoxy resin with and without ATH, all using same novolac curing agent as controls.
- Used data to compare “brittleness” of the different systems.



“Degree of Brittleness”



- Slope of line is an indication of how stiff the material is (modulus)
- % strain at break is an indication of degree of brittleness
- Area under the curve is an indication the degree of toughness

Flexural Testing Data

Run	Epoxy Resin	FR	%P	ATH, %	T_g, °C (TMA)	Modulus, GPa	% Strain at Break
11	Epon 1124	TBBPA	---	23	134	20.8 ± 0.2	1.84 ± 0.05
12	Epon 1124	TBBPA	---	0	131	21.6 ± 0.3	2.44 ± 0.07
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7	Epon SU-8	PFR-1	3.00	23	181	19.2 ± 0.4	1.97 ± 0.04

- ATH decreased the %strain at break vs. no ATH for TBBPA epoxy system.
- PFR-1 system showed slight increase in %strain at break vs. the DOPO-epoxy system.
- Higher modulus combined with higher %strain at break for PFR-1 system.

Conclusions

- Emerald™ 2000 (PFR-1) was shown to be a combination curing agent / flame retardant for epoxy laminates
- Molecule is reactive and meets our “Greener is Better” strategy - not simply a non-halogen material
- Molecule contains phenolic functionality to perform similarly to novolac resin curing
- Data showed:
  - Thermal property improvements (T_d, T-288) vs. DOPO-epoxy systems without diminishing the T_g of the laminates
  - Significantly improved copper adhesion with PFR-1 when compared to the DOPO-epoxy system
  - Improvement in brittleness vs. the DOPO-epoxy system and definite increase in flex modulus. More work is needed in this area to confirm these findings.
- Other formulation approaches should be possible with this curing agent system to optimize properties specific to various market requirements.

Acknowledgements

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Thank You!