

Polyphenylene Ether Macromolecules. VI. Halogen Free Flame Retardant Epoxy Resins

Edward N. Peters, Scott M. Fisher, Hua Guo, Carolyn Degonzague, Robert Howe
Sabco Innovative Plastics, One Noryl Avenue, Selkirk, NY 12158

Abstract

An important criterion for dielectric materials used in the microelectronics industry is their flammability. Typically, flame retardant epoxy resins use bromine-containing flame-retardants. In the electronics industry, non-halogen flame-retardants are becoming increasingly popular due to environmental pressures in the marketplace and in response to recent regulatory issues. However, there is a perception that halogen-free flame retarded systems are more costly and can have performance issues. For example, phosphorus flame-retardants can be expensive and require high dosages, which can have an adverse effect on some properties. For these reasons, new, more cost effective systems with minimum effect on performance properties are desired. Lowering the needed dosage of flame retardant can have lower cost implications and concurrent improvement in properties. Our approach to lowering the required flame retardant dosage was to react low molecular weight of poly (2,6-dimethyl-1,4-phenylene ether), PPE, macromonomer with epoxy resins. The highly aromatic PPE structure exhibits inherent resistance to burning. Indeed, a unique feature of PPE blends and alloys are their ease of flame retarding with phosphorus-based flame-retardants. Therefore, the reaction of PPE macromonomer with epoxy resins offers the intriguing potential of lowering the needed dosage of flame-retardant. For example, the use of 30 and 50-wt% PPE macromer in epoxy resin resulted in a 25-60% reduction in phosphorus-based flame retardant needed for V-0 flame performance. This in turn improves the odds that physical and mechanical properties of the laminate are not negatively impacted by the flame retardant. Indeed, the use of PPE macromer in halogen-free FR epoxy resins resulted in a single phase networks with increased toughness, lower dielectric properties, lower moisture absorption, and high glass transition temperatures (T_g s).

Introduction

Epoxy resins are commonly used in microelectronics and aircraft industries where flammability and fire behavior are of paramount importance. The use of a variety of compounds to improve the flame retardancy of epoxy resins has been reviewed. [1-4] The two most prominent classes of flame-retardants (FRs) are based on either halogen or phosphorus. The electronics industry is concerned about environmental issues and the demand for environmentally friendly materials is becoming increasingly important for both marketing reasons as well as in response to regulatory mandates. In particular, there is an emphasis on non-halogen flame-retardant epoxy resin systems. Therefore, the use of phosphorus-based FRs is becoming increasingly popular to replace bromine-based flame retardant epoxy resins. This transition has proven to be challenging from both a technical and economic standpoint. In most cases high percentages of flame retardant are needed to achieve adequate flame retardancy, which can significantly influence properties of the polymer matrix. [5] In addition, the use of fillers as a way to reduce overall resin cost may result in performance limitations on laminates.

Three common classifications of non-halogen FRs are reactive phosphorus-based, non-reactive phosphorus-based, and inert fillers. In general, the reactive FRs require chemical reaction with epoxy groups leading to covalent bonding, and can have a pronounced effect on the crosslink density and some properties. The non-reactive phosphorus approach provides a simpler solution, but it has drawbacks as well. Non-reactive FR additives can be soluble or insoluble in the epoxy resin and thermoset matrix. Soluble additives can act as plasticizers and lower the T_g . Furthermore, additives not chemically bonded into the polymer matrix, can lead to the possibility of migration to the surface, loss from the matrix during high temperature processing or secondary operations (extraction by solvents).

Insoluble additives and some inert fillers can be particulate in nature and dispersion issues can lead to processing difficulties. Such particulate additives can behave as defects in the resin matrix that can manifest in the severe degradation of the resulting physical and mechanical properties. [5]

This paper describes the use of PPE materials in epoxy resins as a way to significantly reduce the levels of FR required. PPE is an amorphous, engineering thermoplastic used extensively in blends and alloys. This highly aromatic structure with a fairly stiff backbone has inherent flame resistance and can pass UL 94 flame test with very low levels of phosphorus-based additives. In addition, PPE has no hydrolyzable bonds and no polarizable groups. These structural details result in a polymer with outstanding hydrolytic stability, very low moisture absorption, extremely high T_g , outstanding dielectric properties over a wide temperature range, and low density. [6-9].

A unique low molecular weight PPE telechelic macromonomer (PPE-M) was developed for use in thermoset resins. [10-13] The molecular weight is significantly lower than the PPE used in injection molding thermoplastics and exhibits very high solubility (~50wt%) in toluene and 2-butanone (MEK) at ambient temperatures. Its functionality was tailored for reactivity with epoxy and cyanate ester resins.

Previously we reported that PPE-M was an effective co-reactant to enhance the performance of numerous epoxy resins and appeared unique in its ability to broadly enhance multiple properties. [10, 11] For example, the use of PPE-M in epoxy resins increased the T_g , lowered dielectric properties, increased the toughness and lowered the moisture sensitivity. This lower moisture absorption resulted in more stable dielectric properties in humid conditions. This earlier work used bromine-based FRs.

Materials

PPE macromonomer

The PPE-M telechelic oligomer is available from SABIC Innovative Plastics BV under the MX90 developmental designation (commercial designation Noryl® SA90 trade name). This phenolic-terminated oligomer is designed to react and form covalent bonds with epoxy resins and cyanate ester resins. The general structure of PPE-M is depicted in Figure 1 and properties appear in Table 1.

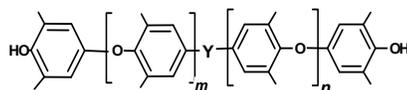


Figure 1. Structure of PPE-M

Table 1. Typical Properties of PPE-M

Property	Value
Hydroxyl equivalent weight	800 g/mol
Number average molecular weight	1700
T_g	150°C
Solubility in toluene	>50%
Solubility in 2-butanone (MEK)	>50%

Epoxy resins

Two different epoxy resins were used in this study. The diglycidyl ether of bisphenol-A will be designated by the DGEBA acronym. It was supplied by Dow Chemical Company under the D.E.R.™ 332 tradename. It was chosen for its low epoxy equivalent weight (EEW). Hexion Specialty Chemicals supplied the cresol novolac epoxy resin under the Epon® 164 tradename. It will be designated by the CNE acronym. The catalyst used to cure the epoxy resins was 2-ethyl-4-methyl imidazole, 2,4-EMI (1.0 phr). Some properties of the epoxy resins are shown in Table 2 and their structures depicted in Figure 2

Table 2. Epoxy Equivalent weights (EEW) of Epoxy Resins

Designation	Chemical Name	EEW, g/equiv.
DGEBA	Diglycidyl ether of bisphenol A	172
CNE	Cresol novolac epoxy	220

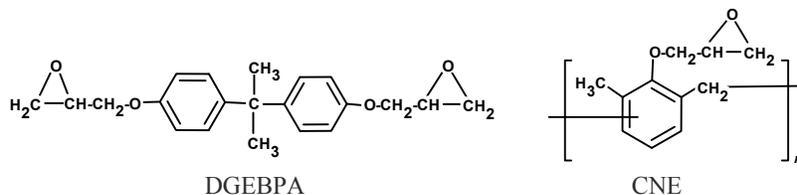


Figure 2. Structure of epoxy resins

Phosphorus-containing flame retardants

There are several options for non-halogen flame retardancy. For these studies, 4 phosphorus-based materials were chosen – both additive and reactive. The choice of these FRs was not intended as an inclusive list, but a small representation of available materials and industry trends. A criterion for phosphorus-based FRs is no hydrolyzable P-O-C bonds – such as phosphate esters. Upon hydrolysis such materials can generate phosphorus acids, which are not tolerable in electronic applications. Two representative reactive FRs were used in this study. The first was 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide obtained from Eastar Chemical Corp. It is commonly called DOPO and will be referred to using this acronym. This cyclic hydrogen-phosphinate contains a P-H bond that can be reacted with epoxy moieties to become covalently bonded to the thermoset matrix. The other reactive FR was 10-(2,5-dihydroxyphenyl)-10H-9-oxa-10-phospha-phenanthrene-10-oxide, which is the reaction product between DOPO and *p*-benzoquinone and was supplied by Sanko Co., Ltd under the HCA-HQ trademark. It will be referred to by the acronym DOPO-HQ. With its two phenolic groups, it can react like a hardener to form covalent bonds with epoxy resins.

Two non-reactive phosphorus-containing FRs were chosen. The first was aluminum diethylphosphinate supplied by Clariant International, Ltd. supplied this material under the Exolit® OP930 trademark. It will be designated by the Al-P acronym. Key aspects of this additive are very low solubility in solvents and epoxy resins and high phosphorus content. Melamine polyphosphate is the salt of polyphosphoric acid and melamine. Hence, it contains both phosphorus and nitrogen. It will be designated by the MPP acronym. This material was supplied by BASF (néé Ciba Specialty Chemicals) under the Melapur® 200 tradename. MPP has very low solubility in solvents and epoxy resins and decomposes endothermically above 350° C. This releases polyphosphoric acid, which can form a barrier layer of polyphosphoric acid on the burning polymer and the melamine may participate in the formation of char. In addition to containing phosphorus, it has a high level of nitrogen and has been suggested as a N-synergist in combination with other phosphorus based flame-retardants. Some attributes of these four FRs are listed in Table 3. Their chemical structures are depicted in Figure 3.

Table 3. Properties of Flame Retardants

Designation	%P	%N	Density	CAS Number
DOPO	14.3	-	1.4	35948-25-5
DOPO-HQ	9.55	-	1.4	99208-50-1
Al-P	23	-	1.35	225789-38-8
MPP	13	43	1.85	218768-84-4

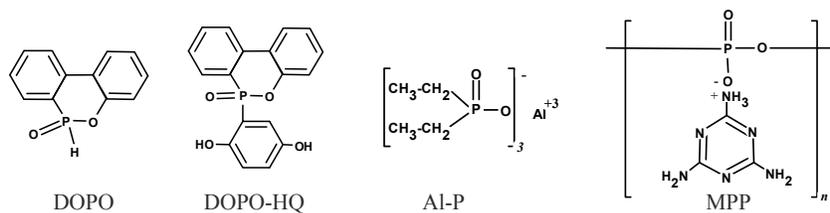


Figure 3. Structure of Flame-retardants

Experimental

The examination of the performance of neat resins provides a unique window to observe the quantifiable effects of various materials used to make the epoxy matrix. Hence, castings were prepared to study the effect of PPE-M and various FRs on the epoxy network. Castings are unfettered by confounding factors from fillers or reinforcement materials. For comparative purposes, the performance of the FRs were reported and compared in terms of total phosphorus content, which was calculated using the phosphorus content of the FRs listed in Table 3 and the amount of flame retardant used in the formulations.

Two tests were used to check flammability – that is, UL94 and Limiting Oxygen Index or LOI. In the UL 94 procedure each specimen is mounted vertical and subjected to a flame from a Bunsen burner under well-defined conditions. For a V-0 rating the specimens may not burn for more than a total of 10 seconds after either application of the test flame. The LOI (ASTM D2863 Test Standard) determines the minimum concentration of oxygen that will just support flaming on a vertical specimen, which has ignited at the top.

Castings were prepared by dissolving the PPE-M, if any, in the epoxy resin at 90-120°C using stirring. FR was then added and allowed to mix thoroughly. After mixing and dissolving the catalyst, the mixture was transferred to a compression mold and cured up to 230°C in a 2-hour cycle. A plaque of the cured composition was removed from the mold and cut into test parts using a tile cutting saw with a diamond-cutting blade.

Results And Discussion

Polymer degradation and combustion are complex processes. Various mechanistic studies have shown that combustion and fire retardance in polymeric materials are closely related to their degradation behavior. [14] In the two-stage combustion model, there are two consecutive chemical processes – decomposition and combustion. Part of the combustion process also involves ignition and thermal feedback. Initially when the polymer is subjected to very high heat the polymer undergoes pyrolysis, which produces volatile low-molecular weight fragments. These volatile decomposition products undergo combustion in the vapor (gas) phase and generate heat. This heat of combustion in part is used to support the further decomposition.

In addition to combustible vapors that are formed during pyrolysis, there can be formed a residue of pyrolysis in the condensed (solid) phase. This carbonaceous residue is referred to as char. Hence, a polymer that contains more groups with a high char-forming tendency will generate smaller amounts of combustible gases and the char can help to form a thermal barrier between the condensed phase and the flame. Indeed, Van Krevelen concluded that increasing char yield could reduce the generation of combustible gases, limit the heat emitted by the pyrolysis reaction, decrease the solid's conductivity of heat, and thus reduce the flammability of materials. [15]

In general, polymeric structures can play an important role in degradation and flame resistance. The strength of the covalent chemical bonds in the polymer is an important factor in determining thermal and thermo-oxidative stability. [16] Aromatic groups are more stable than aliphatic groups. In particular, polymers with aromatic functionalities incorporated into the chain backbone have increased thermal and thermo-oxidative stability and increased charring tendency. The ether linkage of aryl ethers is one of the most stable chemical bonds. [17] Lower hydrogen content or more carbon content can increase flame resistance. Thus, a material with a higher C/H ratio will be less flammable. The composition of PPE and homopolymerized epoxy resins are compared in Table 4 in terms of aromatic, aliphatic, oxygen, hydrogen, and C/H ratio. The PPE has the highest aromatic content and C/H ratio and the lowest aliphatic content. The char yield in air and LOI are higher for the PPE.

Table 4. Composition and thermal characteristics of PPE and epoxy resins

Material	% Aromatic	% Aliphatic	% O	% H	C/H ratio	Char yield in air		LOI
						@ 600°C	@700°C	
PPE	61.7	25.0	13.3	6.7	12.0	37.0	10.1	29
DGEBPA	44.7	36.5	18.8	7.1	10.5	9.0	0	20
CNE	42.1	39.8	18.2	6.8	11.0	17.2	0	21

Epoxy Degradation

In general, the thermal decomposition of cured epoxy resin proceeds in two or more steps depending on the matrix structure. [4] Cured epoxy resins have secondary alcohol groups, which are generated during curing. These alcohol groups undergo dehydration in the first step of degradation of the epoxy networks. This elimination of water occurs around 300°C. [18-27] FTIR shows a decrease in the alcohol functionalities and the appearance of unsaturation. [24-27] In subsequent steps, there is chain scission. Cyclic chain-end structures may also be formed such as benzofuran and benzopyran. [23] This initial epoxy decomposition pathway is shown in Figure 4. At higher temperatures there is the evolution of acetone, carbon dioxide, aliphatic hydrocarbons, etc. The specific decomposition path and the amount of char formation can be a function of the structure of the epoxy network as shown in Table 4.

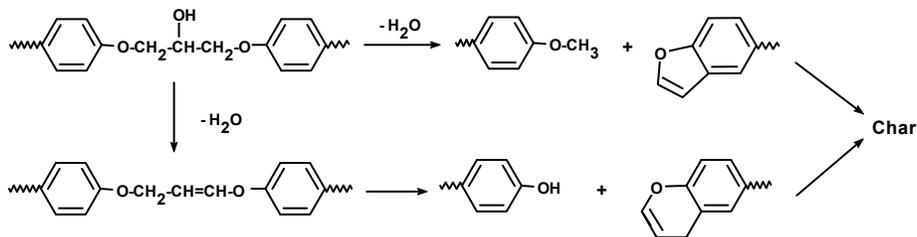


Figure 4. Thermal decomposition of epoxy resins

PPE Degradation

PPE has aromatic functionalities in the chain backbone, which are linked by aryl ethers. These structural details suggest good thermal stability. There have been several studies on the thermal degradation of PPE. [17, 28, 29] In general, it was found that the thermal degradation occurs in two steps. The first degradation step occurs between 430 and 500°C where the polymer undergoes thermal Fries-type rearrangements of the polymer chain. [2] Hence, the methyl diaryl ethers undergo thermal rearrangement in the formation of benzyl phenols. This thermal rearrangement is depicted in Figure 5. FTIR spectrum of the polymer degraded in this way shows the appearance of phenolic OH moieties. The char-forming process occurs at higher temperatures with the formation of a black, highly crosslinked residue and the evolution of phenolic products, and water.

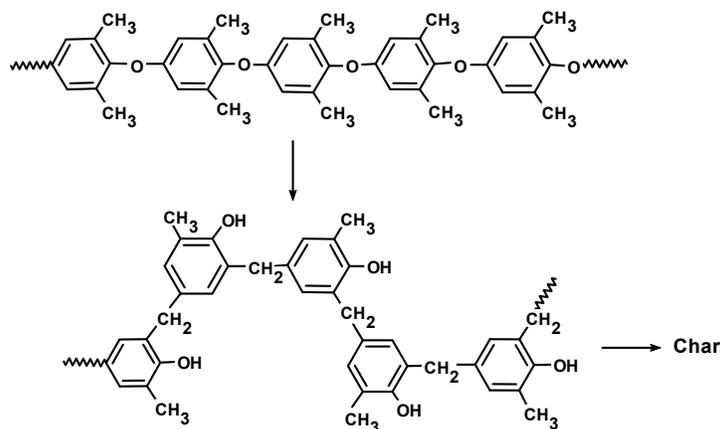
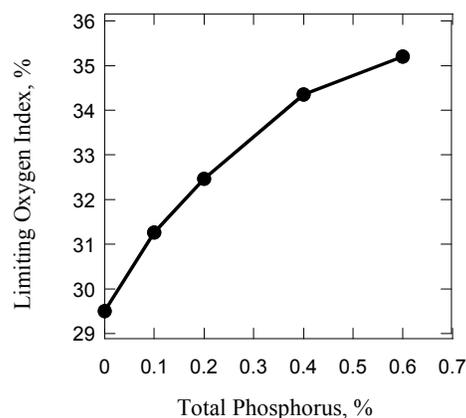


Figure 5. The thermal rearrangement of PPE

PPE Flammability

In addition to being a good char former, PPE has good inherent flame resistance, which can be enhanced with relatively low levels of phosphorus containing additives. For example, a series of PPE materials were prepared which contained very low levels of phosphorus compounds. The effects of phosphorus content on UL94 flame extinguishment times (FET) and LOI are shown in Figures 6 and 7. With 0.1wt% phosphorus the FETs decreased from 31 seconds down to 8 seconds and continued to



decrease with increasing phosphorus content. A similar beneficial effect of very low levels of phosphorus was noted in LOI. With 0.1wt% phosphorus the LOI increased from 29 to 31 and continued to increase with increasing phosphorus content.

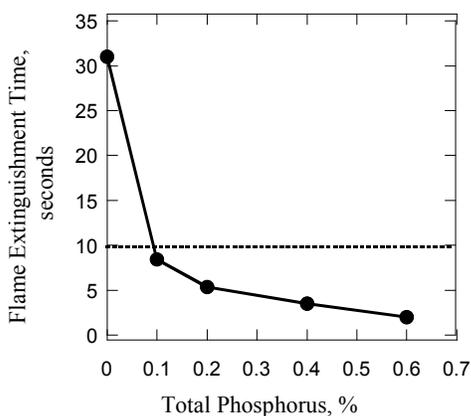


Figure 6. Effect of P on FET of PPE

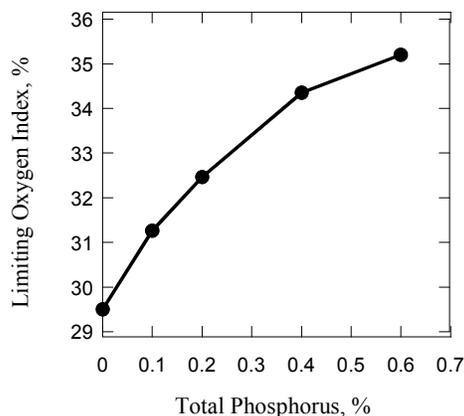


Figure 7. Effect of P on LOI of PPE

FR Mechanism

The two-stage theory of polymer combustion suggests the possibility of different modes of action for a FR in the condensed and vapor phase. The FR may act in the vapor phase by inhibiting exothermic oxidation reactions in the flame, thus reducing the energy feedback to the polymer surface, which in turn, decreases the amount of volatile degradation fragments. In general, condensed phase flame retardancy is characterized by the formation of visible carbon char layer on the polymer surface, which can help to form a thermal barrier between the condensed and gaseous phase that prevents heat transfer back to the pyrolyzing polymer and inhibits the generation of volatile fuel. Another possible condensed phase activity of a flame retardant is in modifying the pathway of pyrolytic decomposition of the polymer and hence decrease the rate of formation of volatile decomposition fragments. [30, 31]

Phosphorus-based FRs have been used extensively in flame retarding numerous polymeric materials. [1, 3, 32] They have been incorporated in polymers as additive or reactive comonomers. They are known to impart fire retardation by condensed phase and vapor phase mechanisms [33]. The types of phosphorus FRs and types polymers they are used in are extensive.

In a vapor-phase mechanism, thermal breakdown products phosphorus-based FR can be vaporized at the temperature of the pyrolyzing surface. These phosphorus-containing materials can break down further in the flame to give smaller molecular species such as PO, PO₂, P₂O₃, HPO₂, etc. Hastie and McBee have studied the mechanism of phosphorus containing FRs and found that phosphorus monoxide to be the most significant phosphorus-containing species present in the flame. [34, 35] The presence of PO resulted in a dramatic reduction in the flame. For example, a concentration of several hundred ppms PO in the flame was sufficient to markedly reduce the radical population and concomitantly the burning velocity or flame strength. Thus, phosphorus oxides can act as a poison with PO species participating in a kinetic mechanism analogous to halogens in flames [34, 36].

In the solid phase two mechanisms have been proposed to account for the condensed phase behavior of phosphorus-based FRs. They are the formation of a barrier layer of polyphosphoric acid on the burning polymer (especially in non-charring polymers such as polystyrene) and in the formation of char.

The formation of char can be an important part of the flame retarding process. Various mechanisms have been proposed in the formation of char. For example, the phosphorus species can act as a catalyst in the formation of char via a series of dehydrating, cyclization, and crosslinking reactions. The phosphorus species can become part of the char, increase the aromatic nature of the char, and facilitate in the formation of a coherent char. [31, 37-39] Thus, choosing resins that have inherent ability to form char or can form char in the presence of phosphorus compounds can increase the relative effectiveness of the flame retardant and minimize the amount of flame retardant required.

The high char yield, inherent flame resistance, and positive effect of very low levels of phosphorus compounds suggest that PPE could have utility in non-halogen epoxy resins. The lower molecular weight PPE-M should also have these attributes. Zhu and Weil have studied the effect of wide range of molecular weights of the PPE resin on char formation. [40] They concluded that PPE resin was the best char-forming polymer among those investigated in their study. They also noted minor differences in decomposition temperatures and performance based on molecular weight.

The effectiveness of PPE-M in char formation of CNE was shown in Figure 8 using thermo gravimetric analysis (TGA) in air. At 600°C the char increased from 17 to 23 and 29% as the PPE-M is increase from 0 to 30 and 50%, respectively. The effect of phosphorus FR (Al-P) on char in PPE-M/CNE 50/50 resins is shown by TGA in air in Figure 9. As the %P goes from 0 to 1.5 and 2.5% the char at 600°C increases from 29 to 32 and 36%, respectively. Clearly, the FR is facilitating char formation. Thus, meaningful levels of char can be formed with the combination of epoxy, PPE-M, and phosphorus FR.

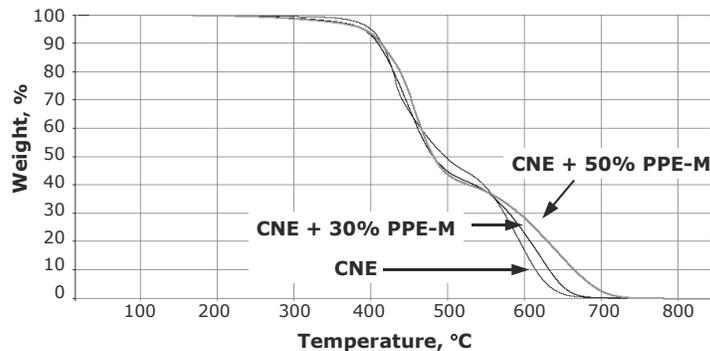


Figure 8. Effect on PPE-M on char in CNE

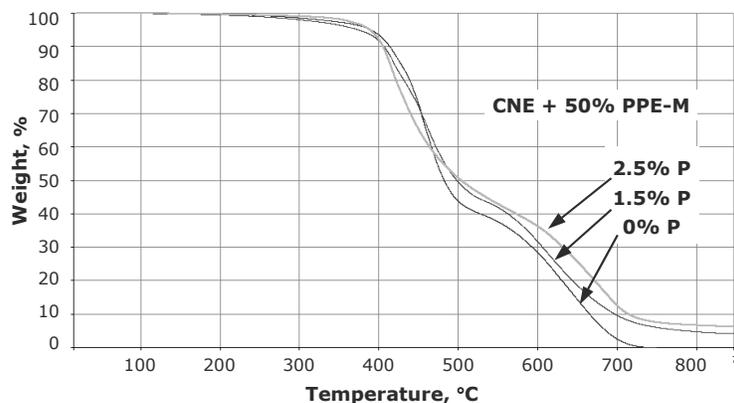


Figure 9. Effect on % P on char in CNE/PPE-M (50/50)

Flame Extinguishment Times

The performance of PPE-M on FR epoxy resins was studied by FETs versus weight % PPE-M and % phosphorus from the FR. For comparative purposes, the performance of the various FRs was compared in terms of % total phosphorus. Since UL94 FET below 10 second is a requirement for V-0 performance, the key target in these studies was to determine the amount of phosphorus necessary for lowering the FETs to below 10 seconds. The PPE-M levels were 0, 30 and 50wt% of the resin. The amount of the different FRs was varied until the FETs were below 10 seconds. The FETs of FR epoxy and FR epoxy/PPE-M resins versus total phosphorus content are shown graphically.

CNE and CNE/PPE-M castings with DOPO, Al-P and a mixture of Al-P and MPP were studied. The CNE resins with DOPO were prepared by pre-reacting the DOPO with the CNE resin. The FETs showed two general trends. They decreased with increased levels of total phosphorus and decreased with increased levels of PPE-M (at similar phosphorus levels). Thus, in CNE-DOPO castings, increased PPE-M levels resulted in a notable enhancement in FR performance. Increasing PPE-M levels from 0 to 30 and 50wt% decreased the %P loadings required for 10 sec FETs from 2.4 to 1.6, and 1.1%, respectively. The FETs versus %P for CNE-DOPO and CNE-DOPO/PPE-M appear in Figure 10.

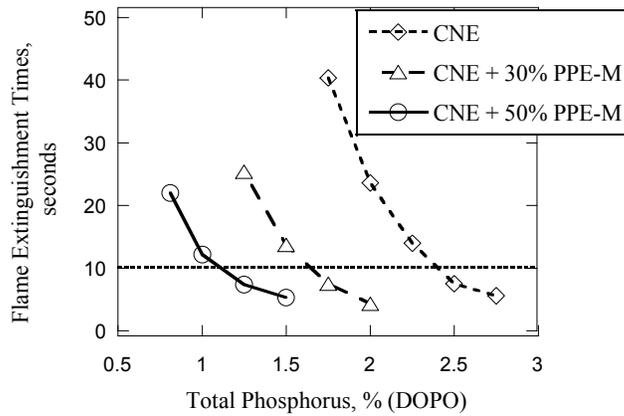


Figure 10. FETs of CNE with DOPO and PPE-M

Castings were prepared from CNE, Al-P, and PPE-M. The FETs decreased with increasing total phosphorus as shown in Figure 11. Moreover, PPE-M was very effective in lowering the amount of FR needed. As the addition of PPE-M was increased from 0 to 30 and 50wt%, there was a meaningful reduction in the %P loadings required for 10 sec FETs from 2.4 to 1.7, and 1.3%, respectively.

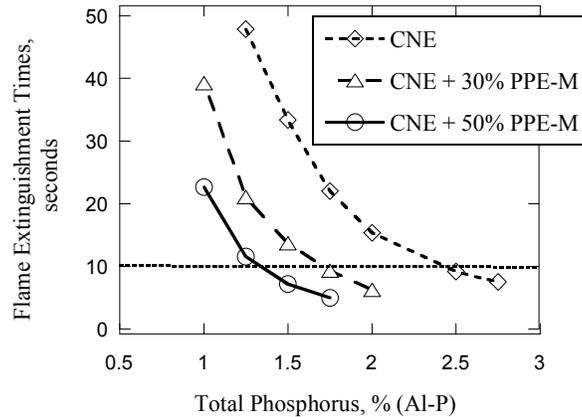


Figure 11. FETs of CNE with Al-P and PPE-M

Certain nitrogen containing materials can act as a synergist with phosphorus based FRs. In particular, the use of MPP with Al-P in a 1:1 ratio has been suggested to be effective. [41] In CNE the FETs are lowered with increasing loading of Al-P and MPP. The combined total % P was 2.75 for FET of 10 seconds. The addition of 30 and 50wt% PPE-M into the CNE resulted in a remarkable decline in the combined %P necessary for 10 sec FETs – that is, 1.95, and 1.1%, respectively. The FETs versus %P and PPE-M appears in Figure 12.

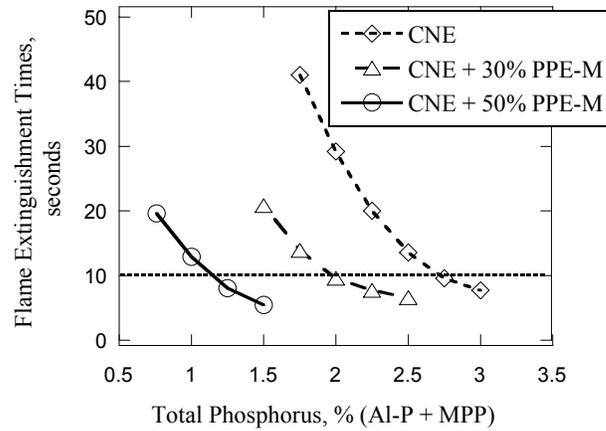


Figure 12. FETs of CNE with Al-P, MPP, and PPE-M

The flammability of DGEBA and DGEBA/PPE-M castings were evaluated with DOPO, DOPO-HQ, and Al-P FRs. The DOPO FR castings were prepared by pre-reacting the DOPO with the DGEBA. The DGEBA-DOPO casting requires about 2.6% P for FET of 10 seconds. The addition of PPE-M to DGEBA-DOPO resulted in significantly lower FETs. Thus, 30 and 50wt% PPE-M required 1.95 and 1.36% P, respectively, for 10 sec. FETs. The FETs for DGEBA-DOPO/PPE-M versus %P are shown in Figure 13.

Castings were prepared from DGEBA, DOPO-HQ, and PPE-M. The FETs decreased with increasing %P. In addition, as the PPE-M increased from 0 to 30 and 50wt% there was meaningful reduction in the %P loadings required. Indeed, for 10 sec FETs, the %P decreased from 2.8 to 2.2, and 1.6%, respectively. The data appear in Figure 14

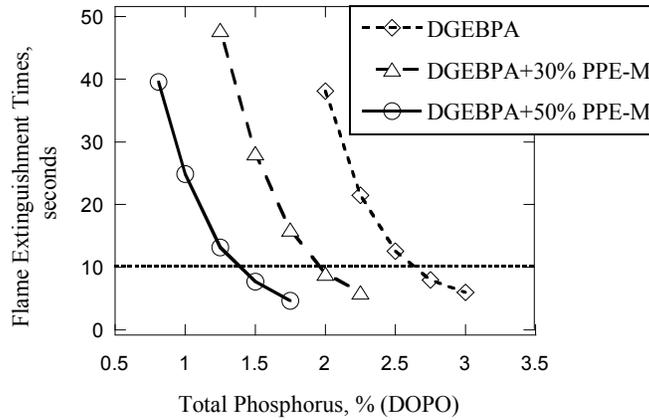


Figure 13. FETs of DGEBA with DOPO and PPE-M

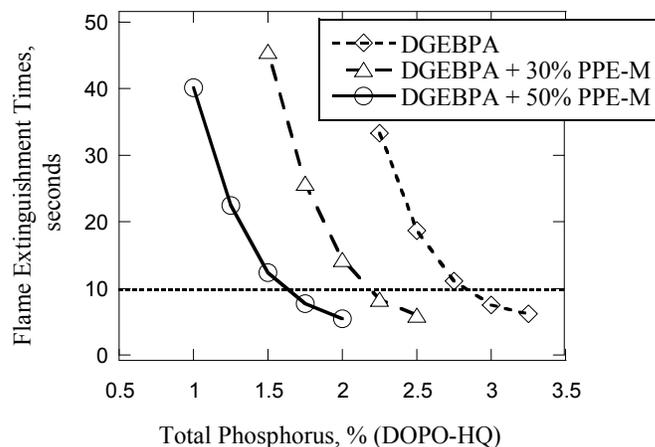


Figure 14. FETs of DGEBA with DOPO-HQ and PPE-M

The results for flame retarding DGEBA with Al-P appear in Figure 15. The %P required for 10 sec. FETs decreased with increased loadings of Al-P. The addition 0, 30 and 50wt% PPE-M in the resin had a beneficial effect in lowering the %P needed for 10 sec FETs to 2.65, 1.9, and 1.5%, respectively.

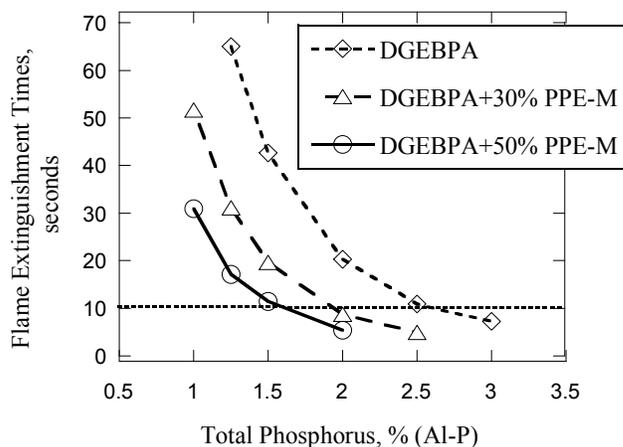


Figure 15. FETs of DGEBA with Al-P and PPE-M

Based on the epoxy resins and the phosphorus based FRs used in these evaluations, the data from Figures 10-15 demonstrate that the use of PPE-M in epoxy resins can significantly reduce the amount of non-halogen FR needed to get low FETs. Compared to the base resins with no PPE-M, 30% PPE-M with the epoxy resins resulted in a 25-32% decrease in needed flame retardant. Moreover, 50% PPE-M with the epoxy resins resulted in a 43-59% decrease in needed flame retardant.

Property Comparisons

To quantify the effects on properties of using PPE-M and the subsequent need for less flame retardant, compositions were chosen with approximately 7-second FETs. The 7-second time was chosen arbitrarily as flame performance below the 10-second threshold for FETs to satisfy UL94 V0 performance. The level of FR to achieve this UL94 behavior was determined from the respective graphs of FETs versus Total Phosphorus, %.

FR CNE Properties

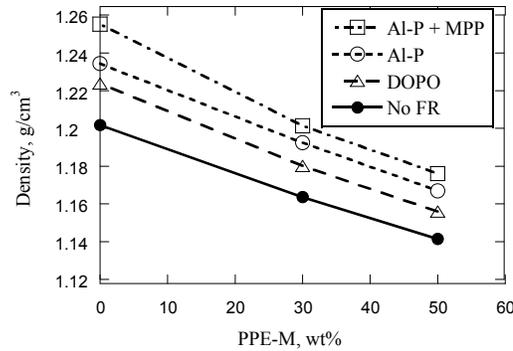
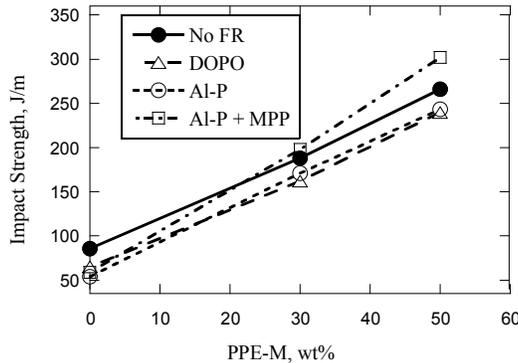
The formulations of the CNE resins appear in Table 5. Castings were made from these formulations and properties determined. All flame retardant castings exhibited FETs between 6.6 and 7.7 seconds. Comparative castings with 0, 30, and 50% PPE-M and no FRs were prepared as part of this comparison of properties (Formulations A, B, and C).

Table 5. Formulations of CNE castings with 7 sec FETs

Formulation	CNE wt%	PPE-M wt%	DOPO phr	Al-P phr	MPP phr	P %	Thickness mm	FET sec	T_g °C
A	100	0	-	-	-	-	1.43	-	180
B	70	30	-	-	-	-	1.44	-	176
C	50	50	-	-	-	-	1.43	-	178
D	100	0	21.54	-	-	2.54	1.45	7.4	153
E	70	30	14.27	-	-	1.79	1.44	6.6	158
F	50	50	9.98	-	-	1.30	1.46	7.2	166
G	100	0	-	14.31	-	2.88	1.46	7.3	179
H	70	30	-	9.00	-	1.90	1.45	7.6	180
I	50	50	-	7.23	-	1.55	1.44	7.1	179
J	100	0	-	11.52	11.52	3.37	1.44	6.8	178
K	70	30	-	7.62	7.62	2.38	1.45	6.6	179
L	50	50	-	3.99	3.99	1.33	1.45	7.7	179

All the T_g s were between 176 and 180°C, except the DOPO containing resins (Formulations D, E, and F). A possible explanation is that the DOPO is pre-reacted with epoxy groups and, hence, there are fewer epoxy groups available for crosslinking. This results in lower crosslink densities and lower T_g s. The T_g s do increase when PPE-M is part of the CNE-DOPO formulations.

The toughness was measured by pendulum impact. Impact strength for non-FR and FR CNE castings appear in Figure 15. The CNE castings without any FR showed an increase in impact strength as the amount of PPE-M was increased. Indeed, the incorporation of 30 and 50wt% PPE-M increased the impact strength by 120 and 210%, respectively. Addition of the FRs to CNE castings with no PPE-M, resulted in a 24-37% decrease in impact strength. However, the combination of PPE-M and less FR in CNE materials resulted in major increases in toughness. For example, 30 and 50wt% PPE-M in FR CNE increase impact strength of 150-230 and 270-400%, respectively.

**Figure 15. The effect of PPE-M on the Impact Strength of FR CNE****Figure 16. The effect of PPE-M on the Density of FR CNE**

A comparison of the CNE densities as a function of type of FR the amount of PPE-M appears in Figure 16. The graphical data indicates that the more PPE-M in the castings, the lower the density. There are two phenomena working together to lower the densities. PPE-M has a lower density than the cured epoxy resins. Hence the more PPE-M in the resin, the lower the density. In addition, the FRs used in this study have higher densities than the cured epoxy resins and PPE-M. Therefore, the more PPE-M, the lower the required flame retardant, and hence, the lower the density. Compared to the formulations without any PPE-M, the use of 30 and 50wt% PPE-M in CNE achieved 3.2-4.3 and 5.0-6.3% decrease in density, respectively. These density reductions suggest that less resin and FR would be used to make molded parts. This magnitude of change may have some economic benefits.

PPE has excellent dielectric properties and the addition of PPE-M to FR CNE resins resulted in decreases in dielectric constants (relative permittivity, D_k) and dissipation factors (loss tangent, D_f). As shown in Figures 17 and 18, the D_k and D_f for non-FR and FR CNE resins decreased as the amount of PPE-M was increased.

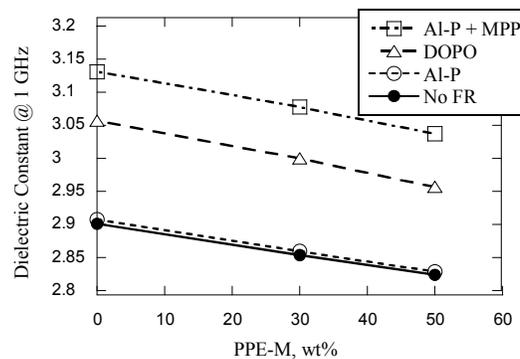


Figure 17. The effect of PPE-M on the D_k of FR CNE

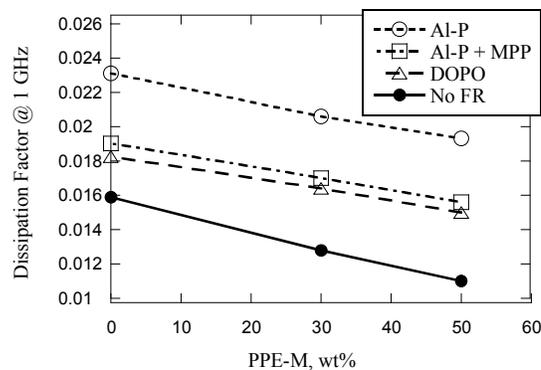


Figure 18. The effect of PPE-M on the D_f of FR CNE

FR DGEBA Properties

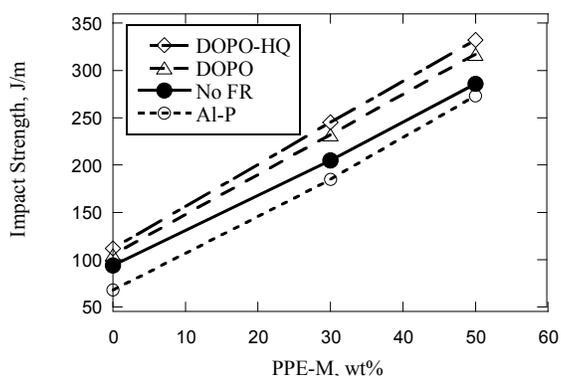
The properties of FR DGEBA and the effects of PPE-M and the subsequent need for less FR on properties were evaluated. Hence, compositions with approximately 7-second FETs were arbitrarily chosen for use in the property evaluations. This choice leads to formulations that satisfy the 10-second FET threshold for UL94 V0 performance. The %P and hence the level of FR to achieve 7-second FET behavior was determined from the respective graphs of FETs versus Total Phosphorus, %. For DGEBA, the formulations appear in Table 6. Castings were made from these formulations and properties determined. All flame retardant castings exhibited flame extinguishment times between 6.8 and 7.7 seconds. Comparative DGEBA castings with 0, 30, and 50% PPE-M and no FR were prepared as part of this comparison of properties (Formulations M, N, and O).

Table 6. Formulations of DGEBA castings with 7 sec FETs

Formulation	DGEBA wt%	PPE-M wt%	DOPO phr	DOPO-HQ phr	Al-P phr	P %	Thickness mm	FET sec	T_g °C
M	100	0	-	-	-	-	-	-	138
N	70	30	-	-	-	-	-	-	158
O	50	50	-	-	-	-	-	-	165
P	100	0	24.93	-	-	2.86	1.44	7.6	100
Q	70	30	17.65	-	-	2.15	1.45	6.8	117
R	50	50	12.13	-	-	1.55	1.45	7.2	125
S	100	0	-	47.6	-	3.08	1.46	7.1	173
T	70	30	-	32.64	-	2.35	1.43	6.9	167
U	50	50	-	23.54	-	1.82	1.44	7.2	163
V	100	0	-	-	15.58	3.10	1.44	7.0	140
W	70	30	-	-	10.42	2.17	1.46	7.7	156
X	50	50	-	-	8.54	1.81	1.43	6.7	163

The effects of the various FRs and PPE-M on the T_g s of DGEBA castings are compared to DGEBA castings with no FR. In the series with no FR, the T_g s increased with increasing levels PPE-M. The series with Al-P as the FR, the T_g s were similar to the non-FR series and increased with increasing levels PPE-M. However, with the reactive FR DOPO, the T_g s were lower than DGEBA by itself. This lower T_g may be attributed to the decrease in crosslink density from the DOPO reacting with epoxy groups as noted above for CNE-DOPO castings. The lower crosslink density can decrease the T_g . The addition of PPE-M to the formulation increased the T_g s.

Impact strength as determined by pendulum impact on non-FR and FR DGEBA castings appear in Figure 19. The impact strength of non-FR DGEBA castings increased with increasing levels of PPE-M. Hence, the use of 30 and 50wt% PPE-M in DGEBA increased the impact strength by 118 and 200%, respectively. The addition of Al-P to DGEBA resulted in a 27% decrease in impact strength. However, the combination of Al-P and 30 and 50wt% PPE-M in DGEBA resulted in the impact increasing 95 and 190%, respectively, over the impact of DGEBA by itself. Compared to DGEBA, DGEBA-DOPO and DGEBA-DOPO-HQ showed a minor increase in impact strength of 11 and 19%, respectively. This could be the result of a decrease in crosslink density. DOPO-HQ is bifunctional and would not be a crosslinking agent but would react to form linear chains. Thus, the molecular weight between crosslink sites will increase and give lower the crosslink densities. Significant increases in toughness were achieved by the addition of 30 and 50wt% PPE-M that resulted in 145-160 and 230-250% increase in impact strength, respectively.

**Figure 19. The effect of PPE-M on the Impact Strength of FR DGEBA**

As a consequence of the FRs having higher densities than the cured DGEBA there was a corresponding increase in densities in the FR formulations. On the other hand, PPE-M, which has a lower density than both DGEBA and the FRs, would decrease the densities. In general, 30 and 50wt% PPE-M in the DGEBA FR formulations lowers the density by 3 and 5%, respectively. The effect of type of FR and PPE-M on densities is shown graphically in Figure 20.

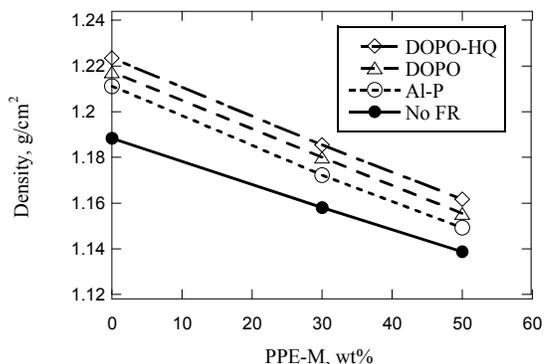


Figure 20. The effect of PPE-M on the Density of FR DGEBA

In general, there can be a slight increase in dielectric properties of DGEBA resins with the addition of FRs. The use of PPE-M with DGEBA lowered the dielectric properties. The effect of the combination of PPE-M and FRs is shown in Figures 21 and 22. Clearly, PPE-M was effective in decreasing D_k and D_f of FR DGEBA resins.

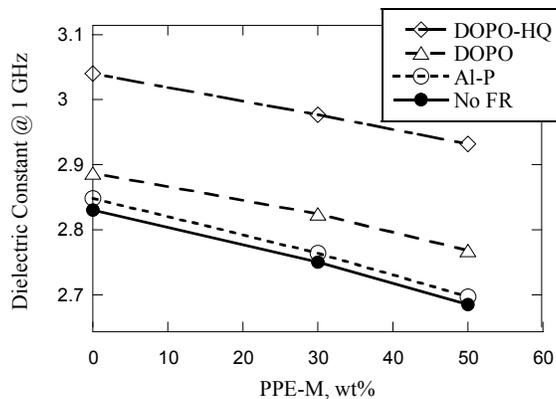


Figure 21. The effect of PPE-M on D_k of FR DGEBA

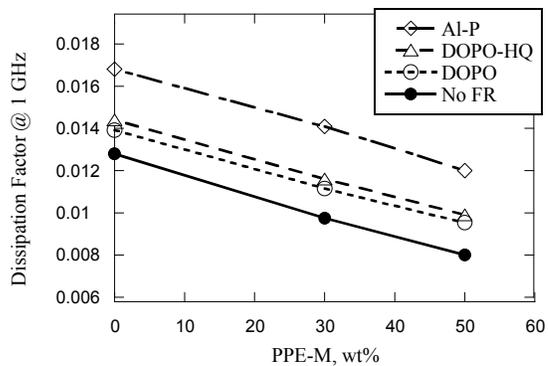


Figure 22. The effect of PPE-M on D_f of FR DGEBA

Effect of Moisture

In many instances when a material is selected for use as an insulator, moisture absorption is a significant consideration because for a dielectric material, the insulation capability is reduced due to the absorption of moisture. [42] Epoxy resins can absorb water from immersion in water or from humidity in the atmosphere, which has important effects upon their properties. [43, 44] Water sorption is essentially governed by hydrogen bonding interactions between water and hydrophilic moieties in the cured resin. [45, 46] In addition, the FRs contain moieties which in principle could hydrogen bond with water.

The effect of the type FR and PPE-M on moisture uptake and the corresponding effect on dielectric properties were examined by immersion of test specimens in water at 80°C. The higher temperature was chosen to accelerate the water absorption and shorten the test time. The water absorption over time for epoxy resins with and without FRs appears graphically in Figure 23 and 24. All the materials showed an increase in water absorption as immersion times increased. Cured epoxy resins can contain alcohol groups, which will strongly hydrogen bond with water and ether groups, which will weakly hydrogen bond with water. Interestingly, soluble reactive FRs increased the moisture uptake compared to the epoxy with no FR. On the other hand, the insoluble, non-reactive FRs only had a minor effect. This suggests that it is more difficult for the water molecule to penetrate into these particulate additives.

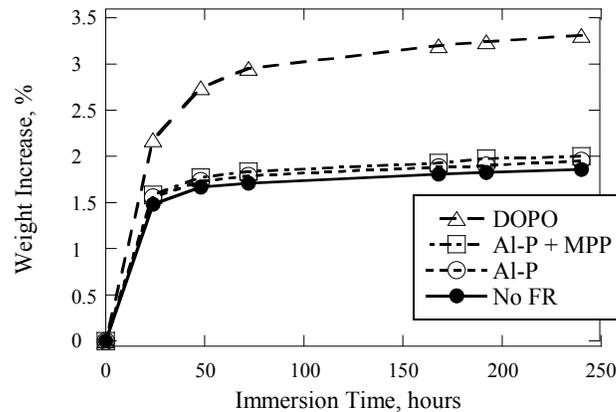


Figure 23. Moisture absorption in FR CNE resins

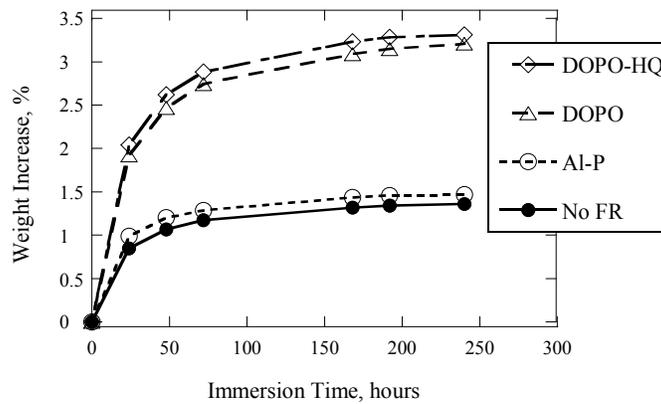


Figure 24. Moisture absorption in FR DGEBA resins

A unique feature of PPE is its very low moisture absorption. Hence, the effect of 30 and 50wt% PPE-M was evaluated in these FR epoxy resins. For simplicity, the moisture uptake after 168 hours (1 week) immersion in water at 80°C are shown in Figures 25 and 26. The moisture absorption decreased as the level of PPE-M is increased. Clearly, PPE-M is effective in lowering the water absorption in FR DGEBA and CNE.

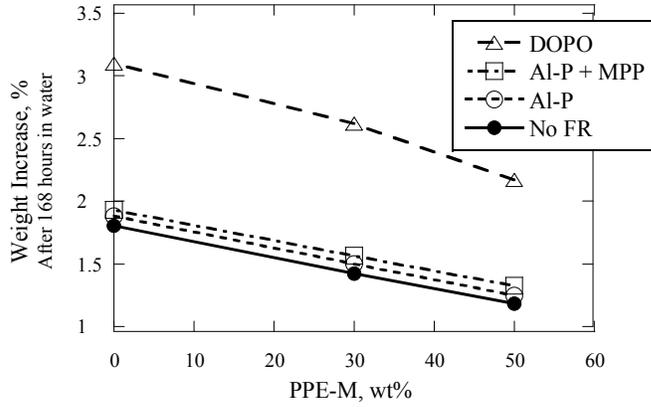


Figure 25. The effect of PPE-M on moisture uptake of FR CNE

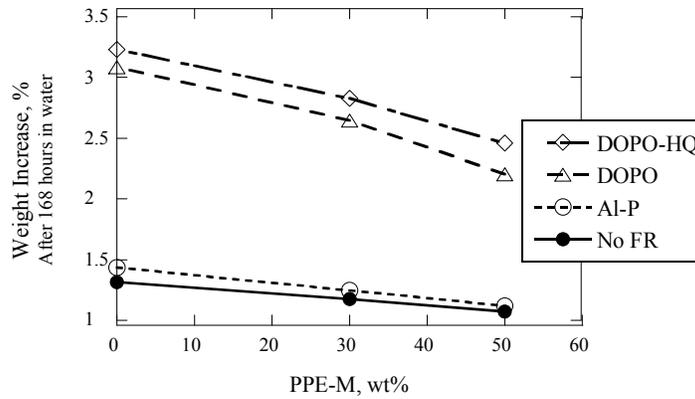


Figure 26. The effect of PPE-M on moisture uptake of FR DGEBA

Even a small amount of moisture in a dielectric material can drastically increase both D_k and D_f . Thus, low moisture absorption would be a key criterion for dielectric materials. The effects of increased moisture over time on dielectric properties of epoxy resins with and without FRs appear in Figures 27 –30. For all the resins, D_k and D_f increased with increased immersion time, which corresponds to increased moisture absorption. Compared to DGEBA and CNE with no FR, the resins prepared with reactive FRs exhibited greater increases in D_k and D_f .

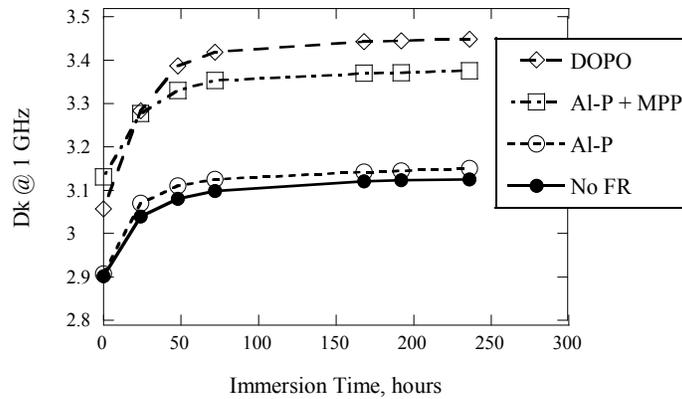


Figure 27. The effect of moisture uptake on D_k of FR CNE

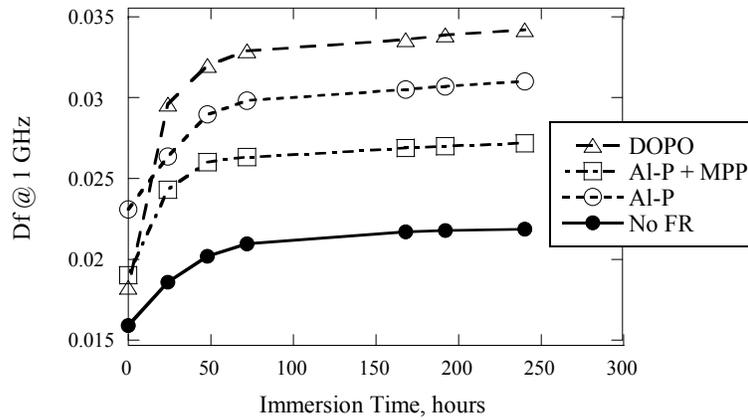


Figure 28. The effect of moisture uptake on D_f of FR CNE

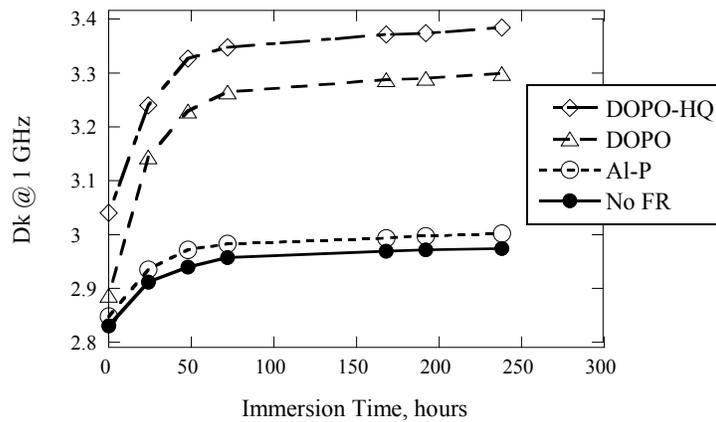


Figure 29. The effect of moisture uptake on D_k of FR DGEBA

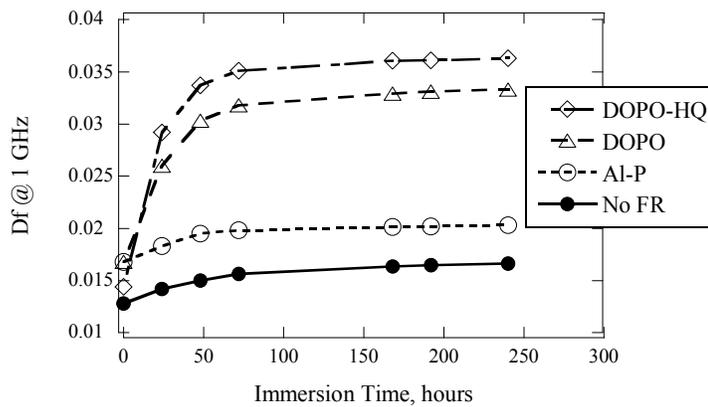
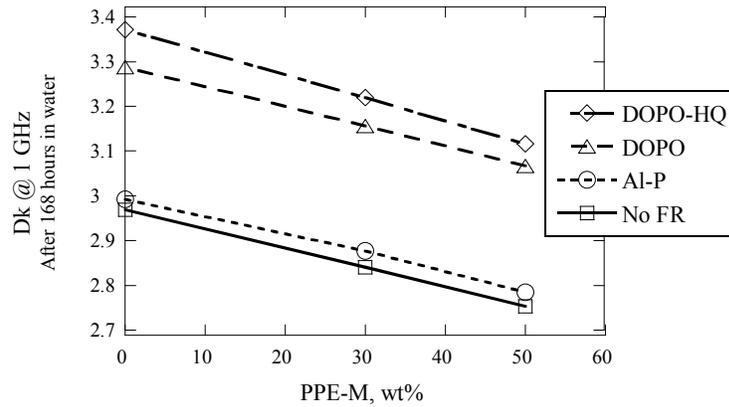


Figure 30. The effect of moisture uptake on D_f of FR DGEBA

The evaluations of the effect of PPE-M on dielectric properties after immersion in water after 168 hours appear in Figures 31-34. Compared to FR DGEBA and CNE with no PPE-M, both D_k and D_f are lowered with increasing levels of PPE-M.



Clearly, PPE-M is an effective way to lower the moisture absorption and diminishing the corresponding effects on dielectric properties.

Figure 31. The effect of PPE-M on D_k of FR CNE

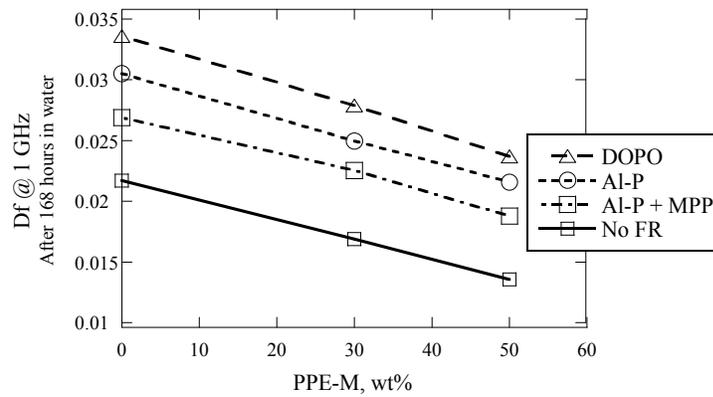


Figure 32. The effect of PPE-M on D_f of FR CNE

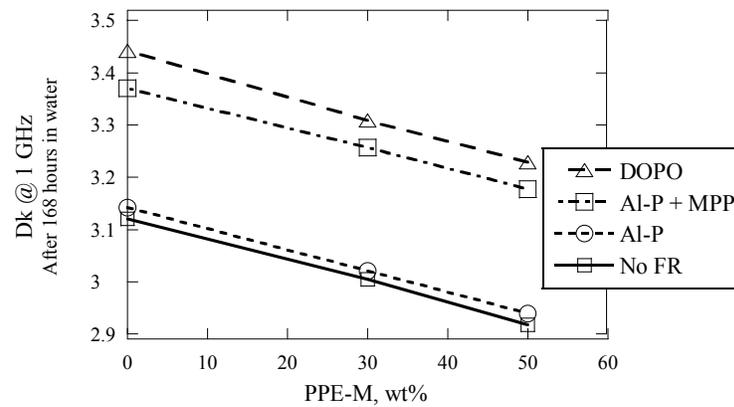


Figure 33. The effect of PPE-M on D_k of FR DGEBA

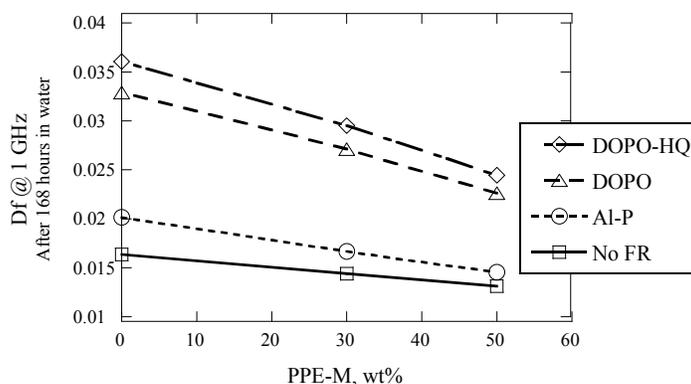


Figure 34. The effect of PPE-M on D_f of FR DGEBA

Conclusions

DGEBA and CNE resins can be flame retarded with a variety of phosphorus-based FRs. However, phosphorus-based FRs can be expensive and require high dosages. The use of PPE-M with epoxy resins significantly lowers the required dosage of non-halogen FRs. Indeed, for V-0 flame performance, the use of 30 and 50-wt% PPE-M in epoxy resin resulted in a 25-60% reduction in phosphorus-based FRs needed. Lowering the needed dosage of FRs can have lower cost implications and concurrent improvement in properties

The higher dosages phosphorus-based FRs can have an adverse effect on some properties. For example, there can be a decrease in impact strength. However, the use of PPE-M resulted in significant increases in impact strength. This increased toughness can have benefits in secondary operations. Compared to the FR formulations with no PPE-M, the combination of lower FRs and PPE-M achieved 3-6% decrease in densities, respectively. These density reductions suggest that less resin and FR would be used to make molded parts. This magnitude of change may have some economic benefits. The use of PPE-M in DGEBA resulted in a general increase in T_g for FR DGEBA resins.

PPE-M is very effective in lowering the moisture absorption of epoxy resins. The advantage of lower water absorption would be more stable dielectric properties and allow for shorter baking times to remove water for secondary operations, which can result in an economic benefit. In addition, the very low moisture absorption suggests better properties and dimensional stability.

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Polyphenylene Ether Macromonomers. VI. Halogen Free Flame Retardant Epoxy Resins

Edward N. Peters, Scott M. Fisher, Hua Guo,
Carolyn Degonzague, Robert Howe



Sabic Innovative Plastics
One Noryl Avenue
Selkirk, NY 12158
USA

Halogen Free Flame Retardant Epoxy Resins

Phosphorus based flame retardants (P-FR)

High loading required

Effect of properties and cost

Polyphenylene Ether Macromonomers (PPE-M)

Reacts with epoxy resins

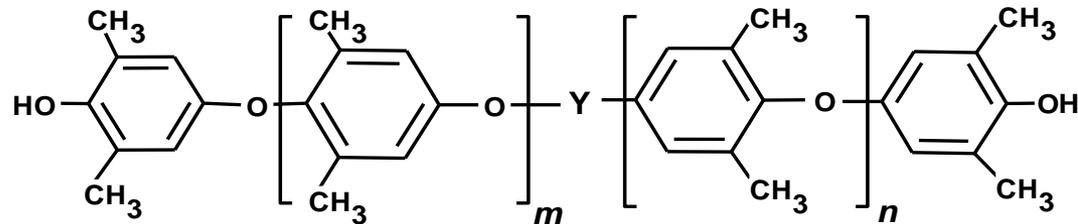
Inherent flame resistance

Use PPE-M to lower in the required loading of P-FR

- **Compare different P-FRs**
Quantify effects on properties
- **Use PPE-M to lower P-FR levels**
Quantify decrease in FR
Quantify effects on properties

Polyphenylene Ether Macromonomer (PPE-M)

Telechelic macromonomer - terminally functional, linear, large monomer



$$m + n = 8-10$$

PPE-M

PPE-M Features

- Bi-functional PPE
- Low molecular weight PPE
- High solubility in MEK and epoxy
- Reacts with epoxy resins

Inherent flame resistance

2009 IPC/APEX Conference

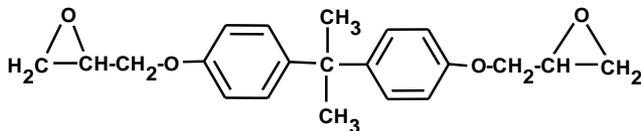
PPE-M in epoxy resins

- **Increased toughness**
- **Higher Tgs**
- **Lower dielectric properties**
- **Lower moisture uptake**

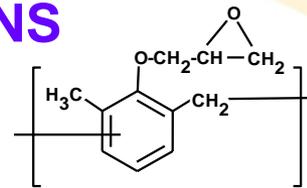
PPE-M in epoxies:

- **Decrease the amount of flame retardant needed**
- **Minimize adverse effects on properties from FRs**

EPOXY RESINS



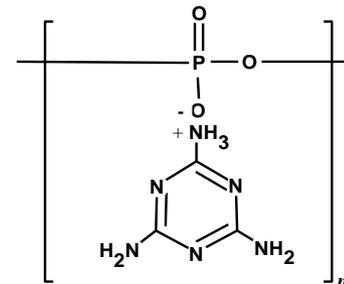
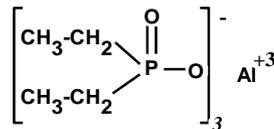
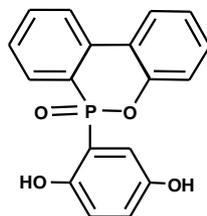
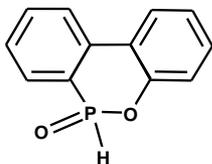
DGEBPA



CNE

Designation	Chemical Name	EEW, g/equiv.
DGEBPA	Diglycidyl ether of bisphenol A	172
CNE	Cresol novolac epoxy	220

PHOSPHORUS-BASED FLAME RETARDANTS (FR)



DOPO

DOPO-HQ

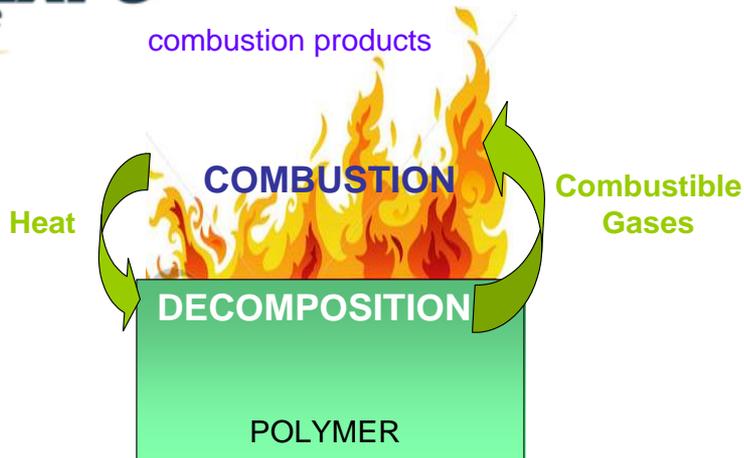
Al-P

MPP

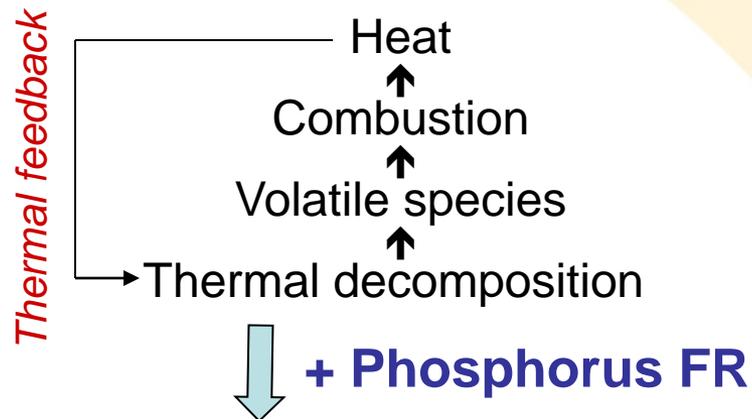
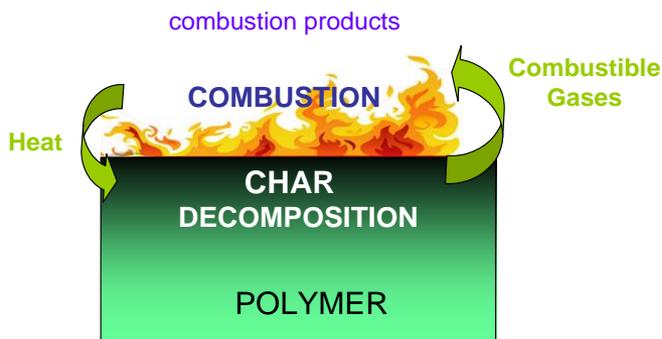
Designation	%P	%N	Density	Type	Solubility
DOPO	14.3	-	1.4	Reactive	+
DOPO-HQ	9.55	-	1.4	Reactive	+
Al-P	23	-	1.35	Non-reactive	-
MPP	13	43	1.85	Non-reactive	-

Reactive and non-reactive P-based FRs

COMBUSTION and FR MECHANISM



↓ + FR



VAPOR PHASE

- PO, PO₂, P₂O₃, quench flame
- Lower heat of combustion

SOLID PHASE

- Char - protective barrier
- Increased char layer
- Improved char stability
- Possible N/P synergy

- Reduce flame strength → less heat → less pyrolysis →
- Increase char → less fuel → less heat →

Increased char → less FR

IMPORTANCE of CHEMICAL STRUCTURES

Ability to form char is very important

- More char, less fuel generation
- Protective barrier from flame
- The use of less FR

Thermal and thermo-oxidative stability

- Aromatic > aliphatic
- Aromatic in backbone → increased char
- Aryl ethers very stable
- High C/H ratio → less flammable

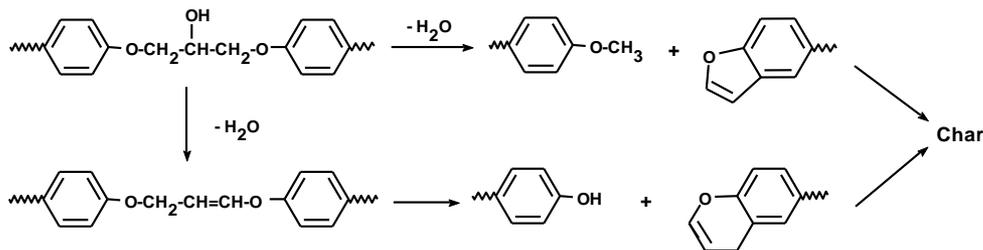
Material	% Aromatic	% Aliphatic	% O	% H	C/H ratio	Char yield in air		LOI
						@ 600°C	@ 700°C	
PPE	61.7	25	13.3	6.7	12	37	10.1	29
DGEBPA	44.7	36.5	18.8	7.1	10.5	9	0	20
CNE	42.1	39.8	18.2	6.8	11	17.2	0	21

PPE: Highest aromatic content, lowest aliphatic content, and C/H ratio plus high char yield and LOI

PPE is important in char formation

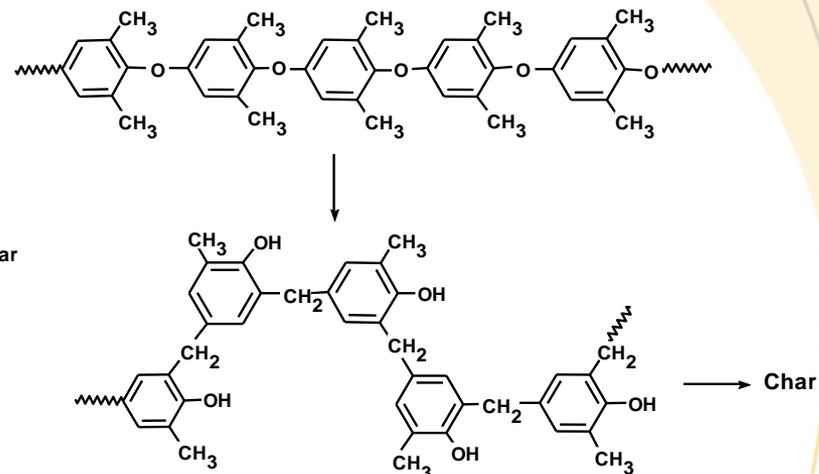
DEGRADATION MECHANISMS

EPOXY DEGRADATION



- Initial decomposition around 300°C
 - Dehydration
 - Chain scission (lower MW)
- Char formation dependant on structure

PPE DEGRADATION



- Thermal rearrangements ~ 430-500°C to phenolic structure
- Char formation at higher temperatures

Chain scission versus phenolic structures

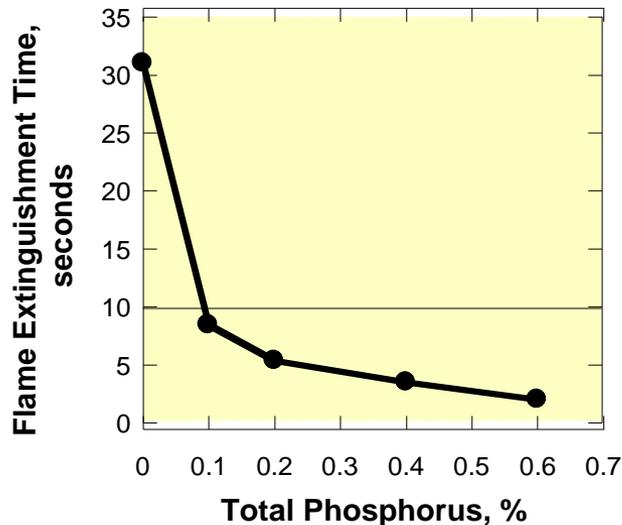
PPE thermal degradations favors char formation

FLAMMABILITY of PPE

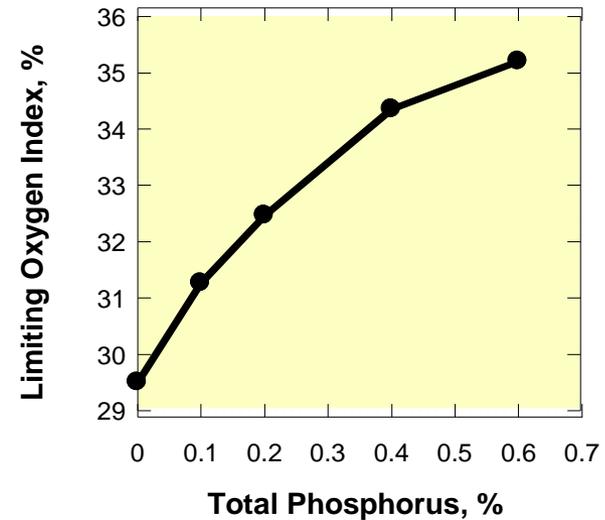
PPE has inherent flame resistance
Enhanced with very low levels of P-FR

The FR content is reported as Total Phosphorus (%)
Calculated from amount of FR used and the P content of FR

UL94 (3.174mm)



LOI



Very low levels of P to enhance FR

With 0.1% P, FET 32 → 8 seconds

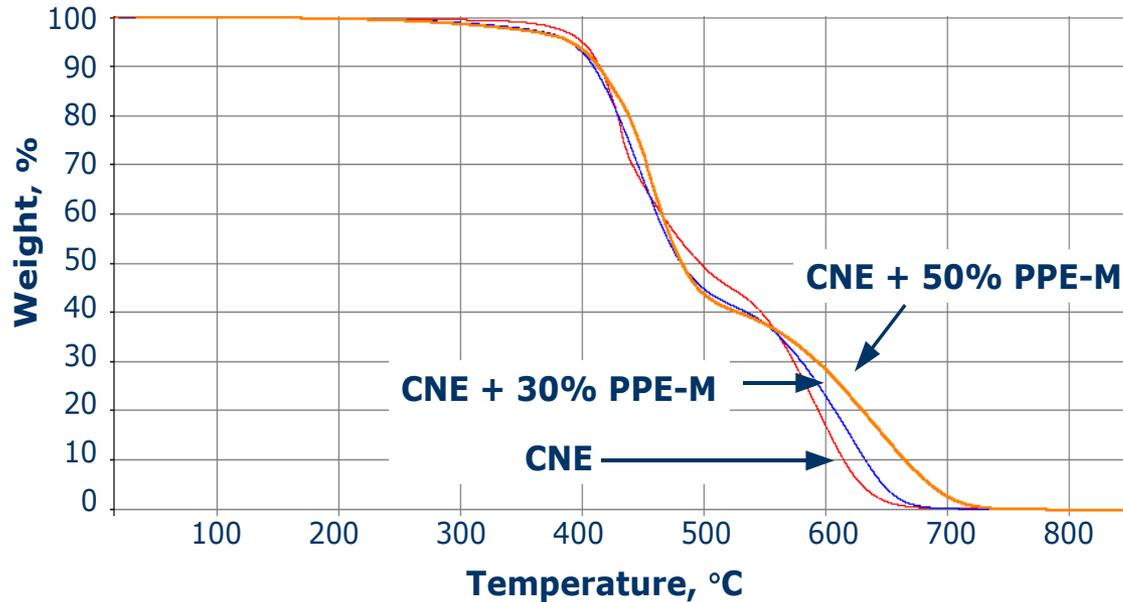
LOI 29 → 31

Inherent flame resistance of PPE → less FR

EFFECT of PPE-M on CHAR of CNE

CNE castings with 0, 30, and 50% PPE-M

Thermogravimetric analysis in air (heating rate 10°C/min)



Char at 600°C increases with increasing PPE-M

% PPE-M	% Char
0	17
30	23
50	29

PPE-M increases char in epoxy

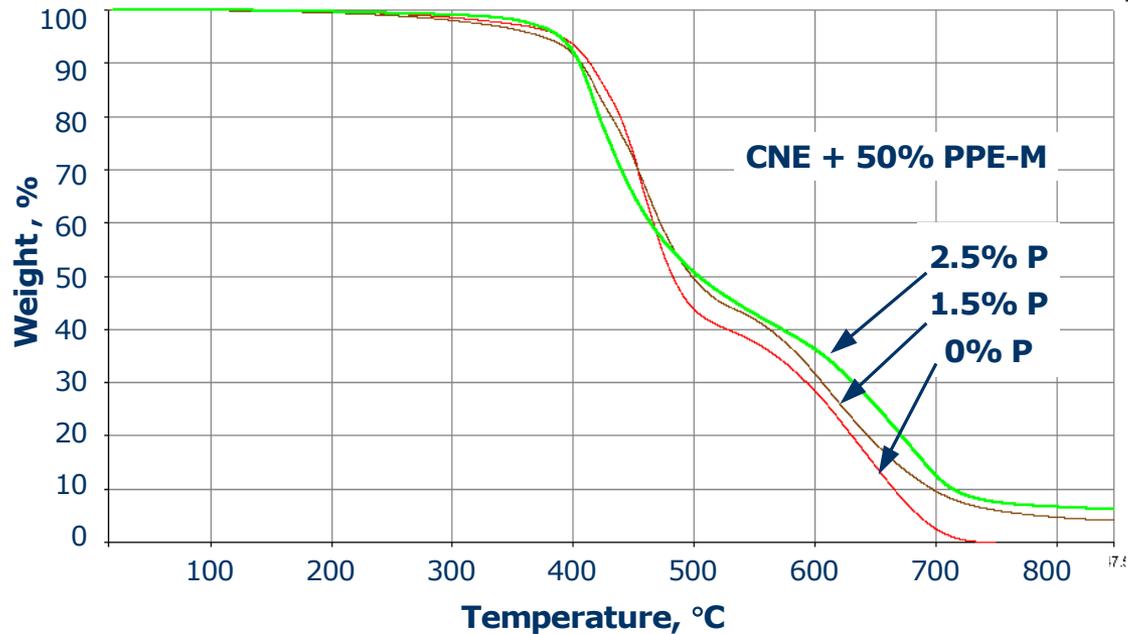
EFFECT of P-FR on CHAR of CNE/PPE-M

CNE/PPE-M (50/50) castings with 0, 1.5, and 2.5% P (Al-P)

The FR content is reported as Total Phosphorus (%)

Calculated from amount of FR used and the P content of FR

Thermogravimetric analysis in air (heating rate 10°C/min)



Char at 600°C increases with increasing P

% P	% Char
0	29
1.5	32
2.5	36

Phosphorus facilitates char formation

FR PERFORMANCE

Evaluation in castings

- Resin only - no glass fiber or filler
- Unfettered by confounding factors from fillers or reinforcement materials

The amount of FR reported as % Phosphorus

- Calculated from wt% FR and P content of FR

UL94 Vertical Flame Test

- Flame Extinguishment Times (FET)
- Sample thickness ~1.44 mm

CNE Evaluations:

CNE + DOPO + PPE-M

CNE + AI-P + PPE-M

CNE + AI-P + MPP + PPE-M

DGEBPA Evaluations:

DGEBPA + DOPO + PPE-M

DGEBPA + DOPO-HQ + PPE-M

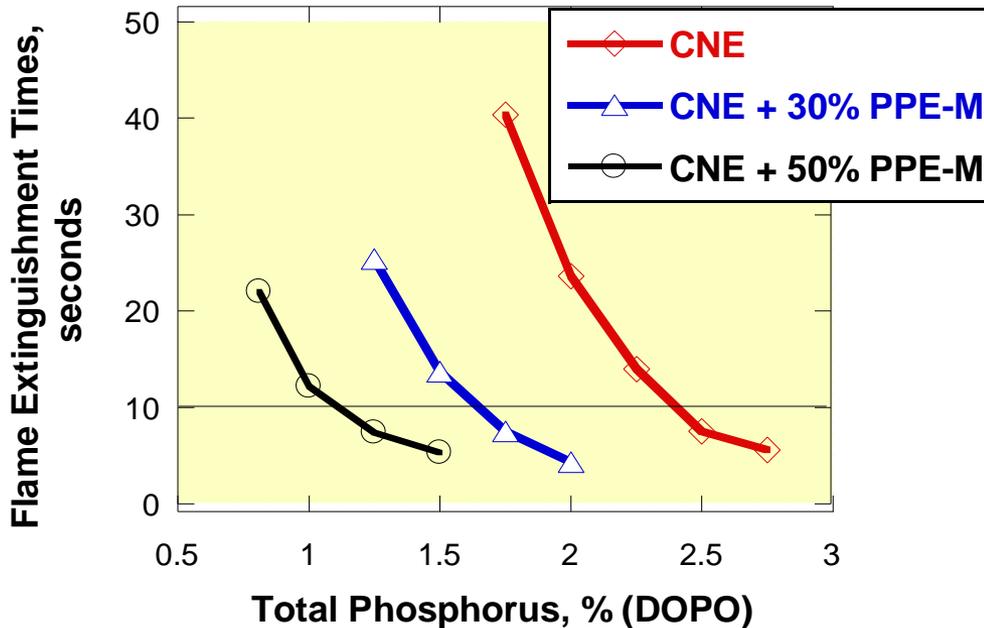
DGEBPA + AI-P + PPE-M

Determine FETs versus Total P%

FETs of CNE + DOPO + PPE-M

Pre-reacted DOPO with CNE

FETs versus %P



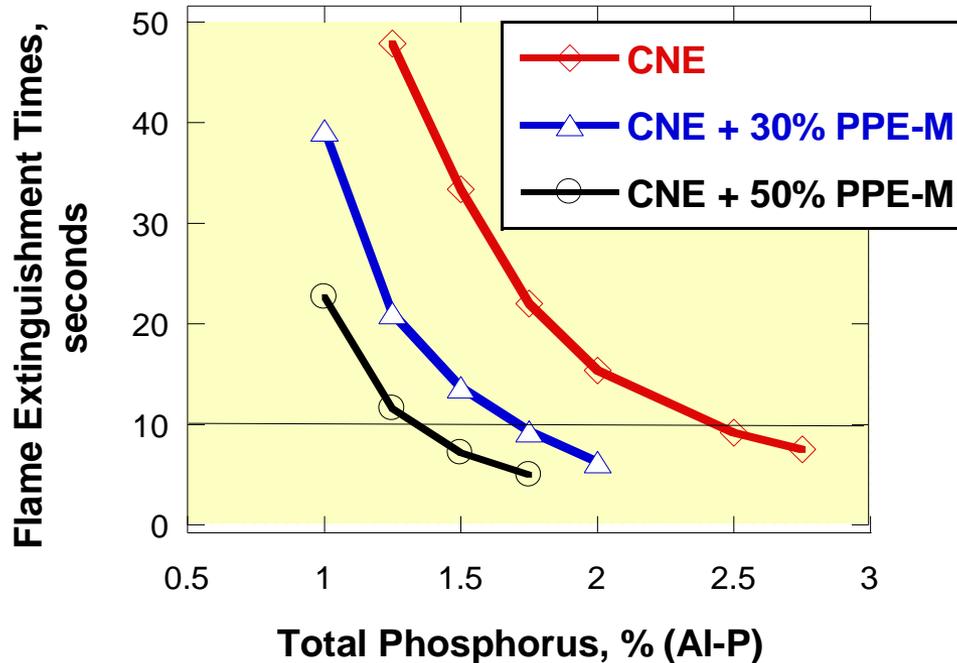
- Increasing %P decreases FETs
- Increasing PPE-M decreases FETs
- For 10 sec FETs:

% PPE-M	0	30	50
%P	2.4	1.6	1.1

PPE-M gives a significant reduction in %P (FR)

FETs of CNE + Al-P + PPE-M

FETs versus %P



- Increasing %P decreases FETs
- Increasing PPE-M decreases FETs
- For 10 sec FETs:

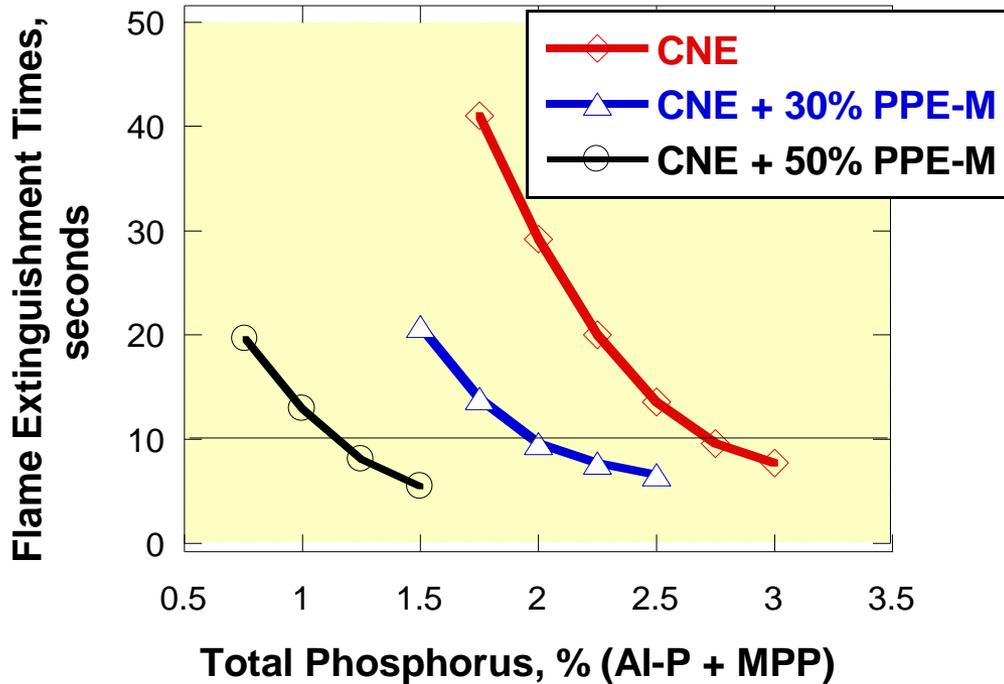
% PPE-M	0	30	50
%P	2.4	1.7	1.3

PPE-M gives a significant reduction in %P (FR)

FETs of CNE + Al-P + MPP

Al-P and MPP using in 1/1 ratio (N-synergy?)

FETs versus %P



- Increasing %P decreases FETs
- Increasing PPE-M decreases FETs
- For 10 sec FETs:

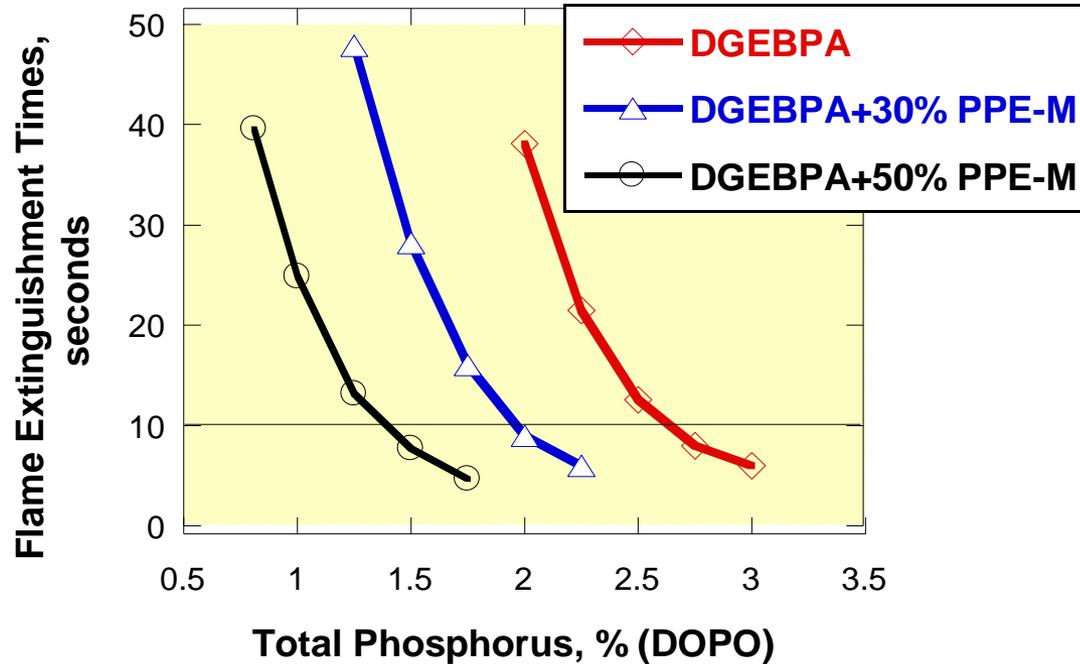
% PPE-M	0	30	50
%P	2.75	1.95	1.1

PPE-M gives a significant reduction in %P (FR)

FETs of DGEBPA + DOPO + PPE-M

Pre-reacted DOPO with DGEBPA

FETs versus %P

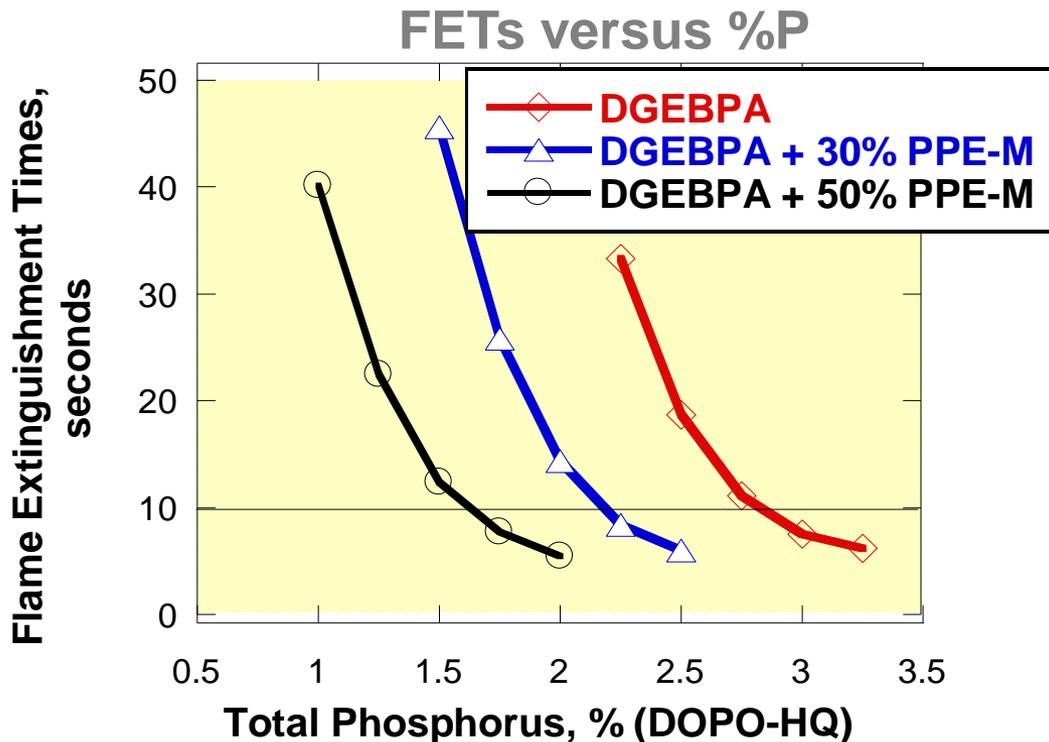


- Increasing %P decreases FETs
- Increasing PPE-M decreases FETs
- For 10 sec FETs:

% PPE-M	0	30	50
%P	2.6	1.95	1.36

PPE-M gives a significant reduction in %P (FR)

FETs of DGEBPA + DOPO-HQ + PPE-M



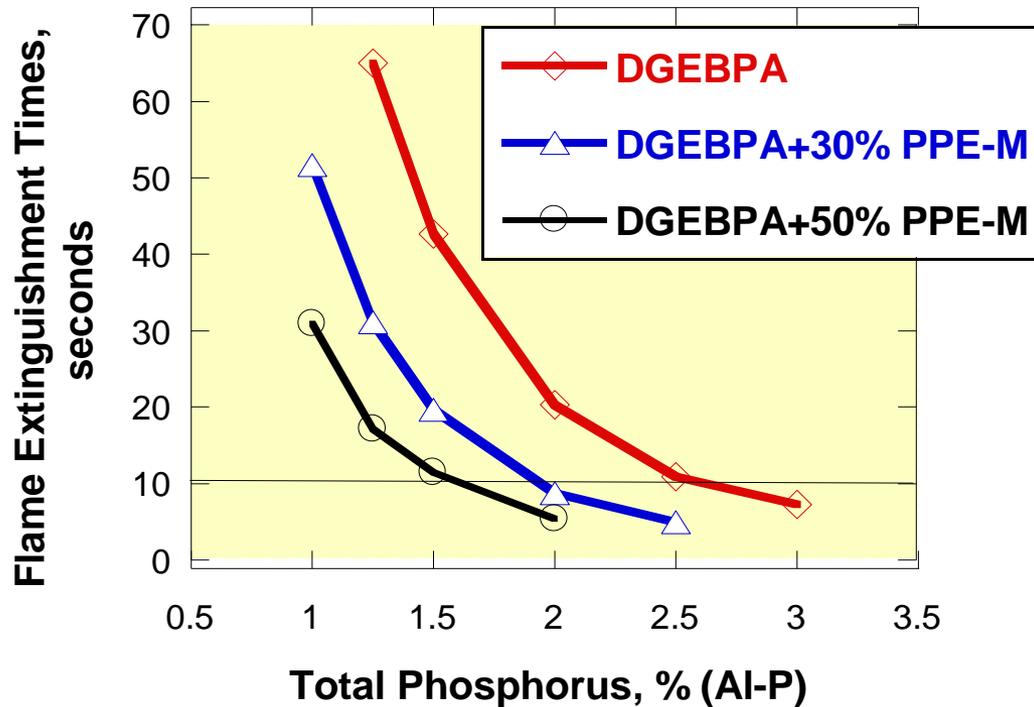
- Increasing %P decreases FETs
- Increasing PPE-M decreases FETs
- For 10 sec FETs:

% PPE-M	0	30	50
%P	2.8	2.2	1.6

PPE-M gives a significant reduction in %P (FR)

FETs of DGEBPA + Al-P + PPE-M

FETs versus %P



- Increasing %P decreases FETs
- Increasing PPE-M decreases FETs
- For 10 sec FETs:

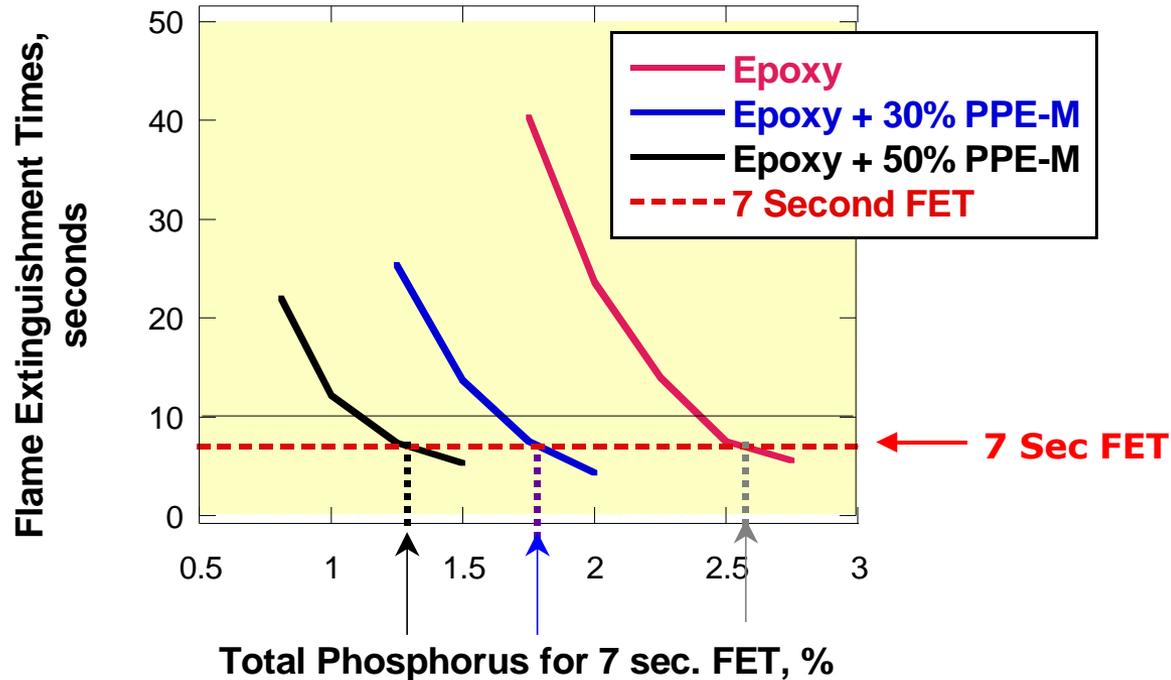
% PPE-M	0	30	50
%P	2.65	1.9	1.5

PPE-M gives a significant reduction in %P (FR)

PROPERTY COMPARISONS

Compare properties with similar FR performance

Chose compositions with 7 sec FETs (below 10 sec for V0 rating)



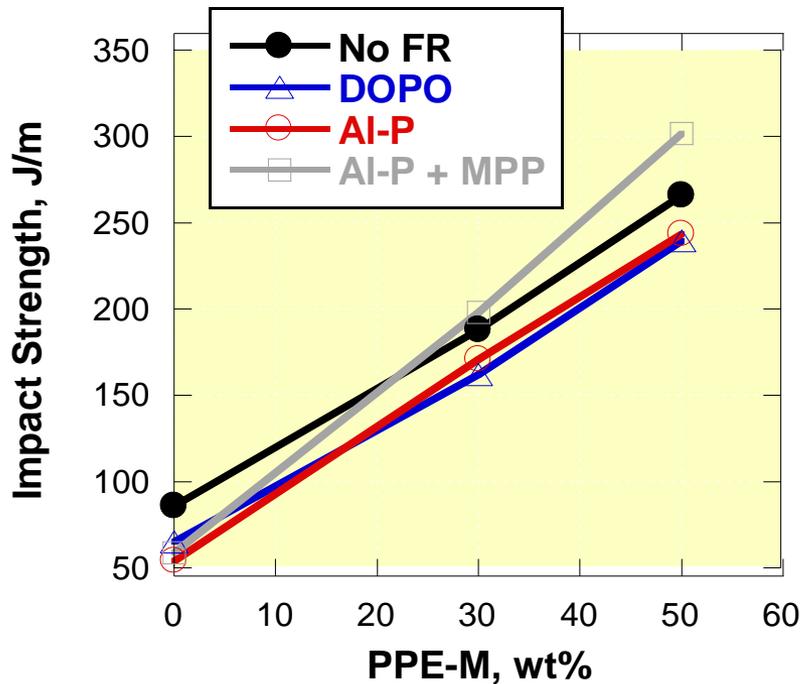
- %P for 7 sec FETs determined graphically
- %FR and formulation calculated
- Castings prepared and tested

Compare properties with similar FETs

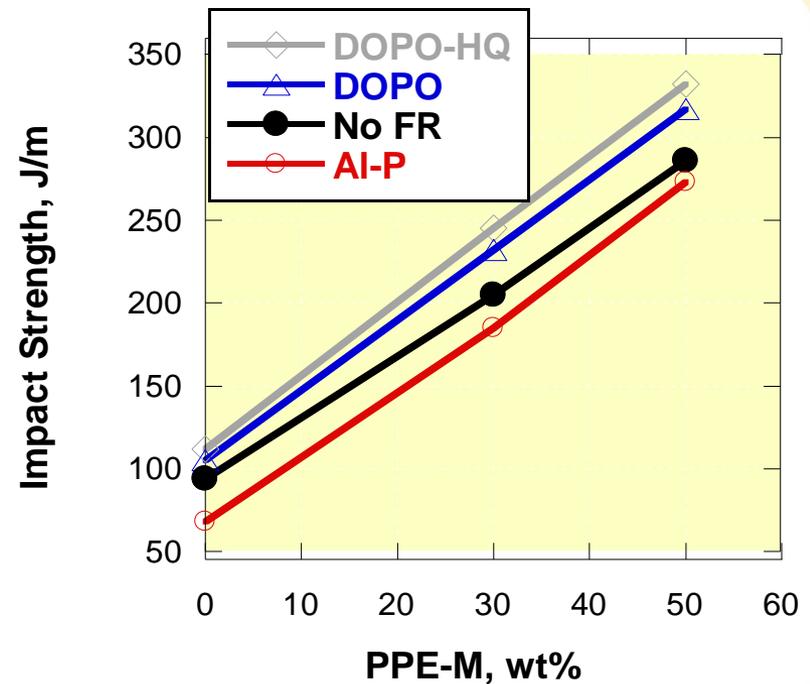
TOUGHNESS

Measured by pendulum impact strength

CNE + FR + PPE-M



DGEBPA + FR + PPE-M



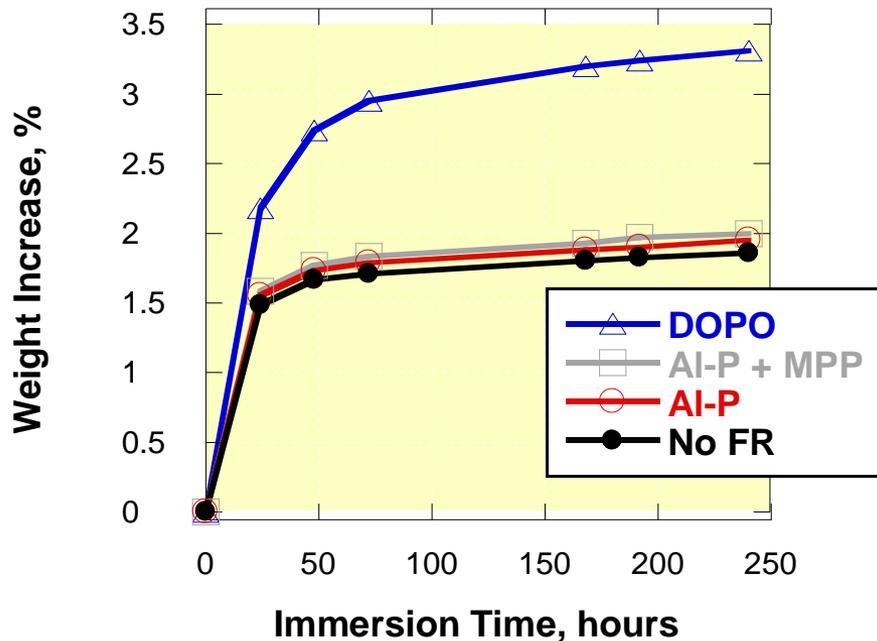
- With no PPE-M, lower or similar impact strength
- Significant increase in toughness as PPE-M increases
 - 150-400% increase in impact strength

PPE-M increases toughness

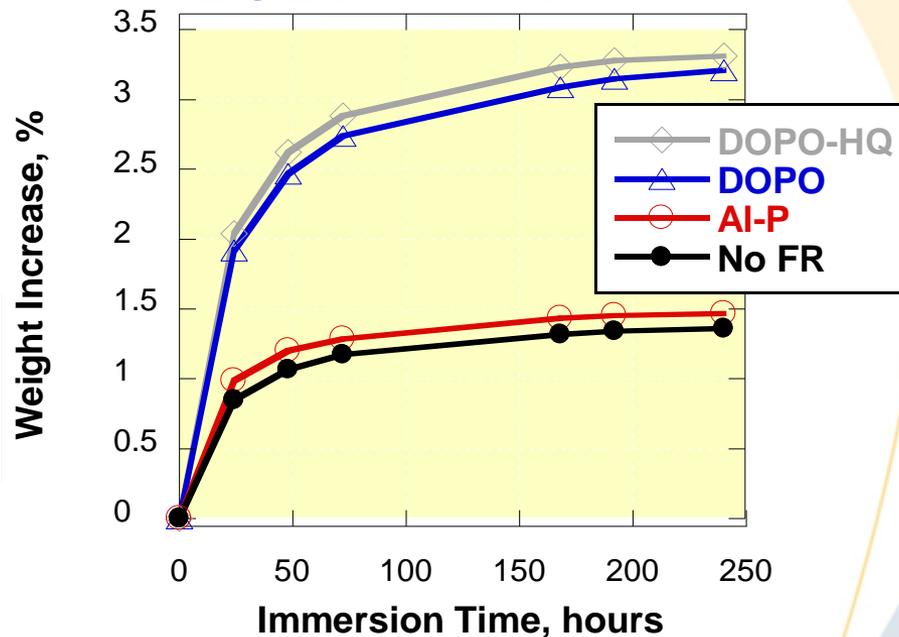
WATER UPTAKE versus TIME

Immersion in water at 80°C
Epoxy + FR (No PPE-M)

CNE + FR



DGEBPA + FR



- Water uptake increases with immersion time
- Larger uptake with reactive FRs
 - Less uptake with non-reactive FRs

Next: Look at effect of PPE-M after 168 hours

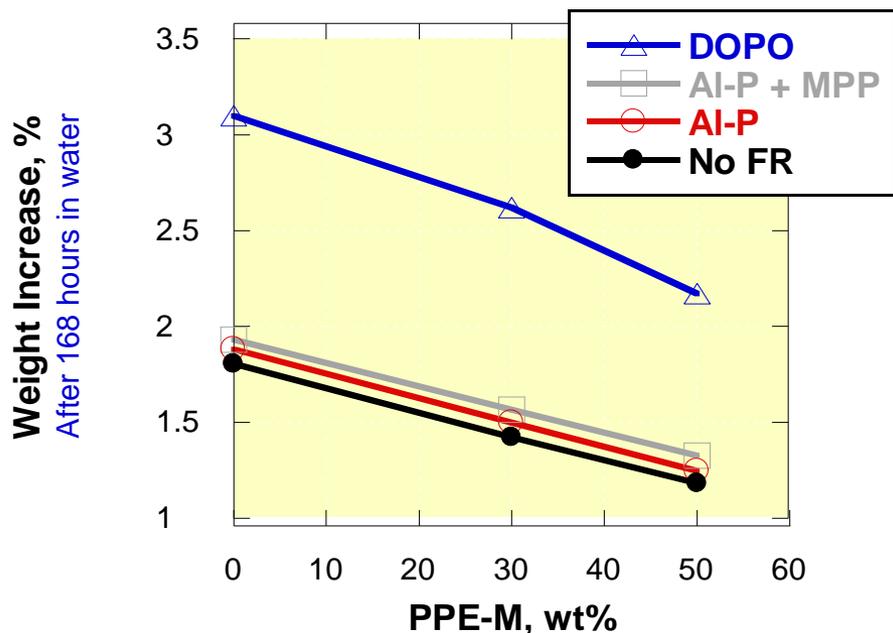
EFFECT of PPE-M on WATER UPTAKE

Immersion in water at 80°C

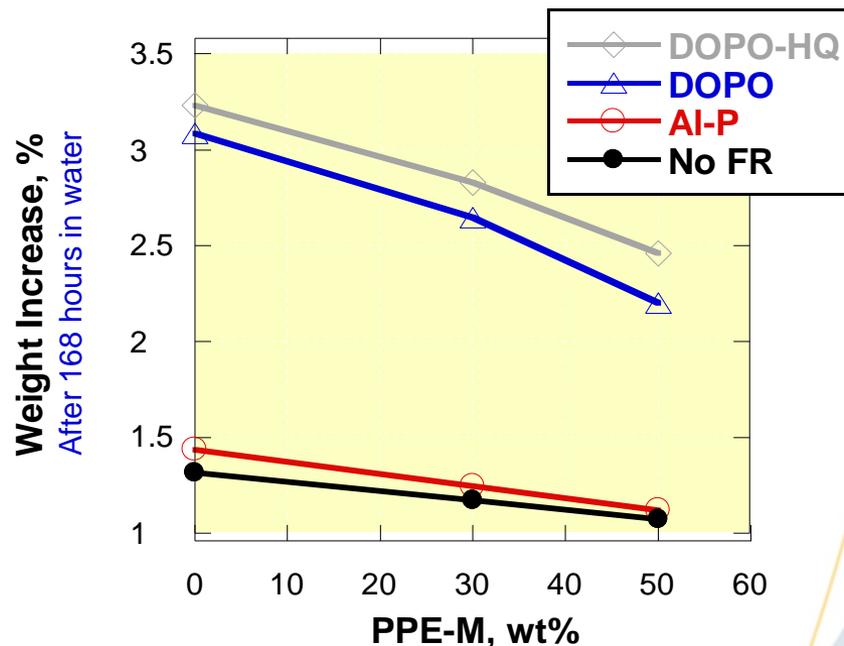
Water uptake compared **after 168 hours** (1 week) immersion

Epoxy + FR + PPE-M

CNE + FR + PPE-M



DGEBPA + FR + PPE-M



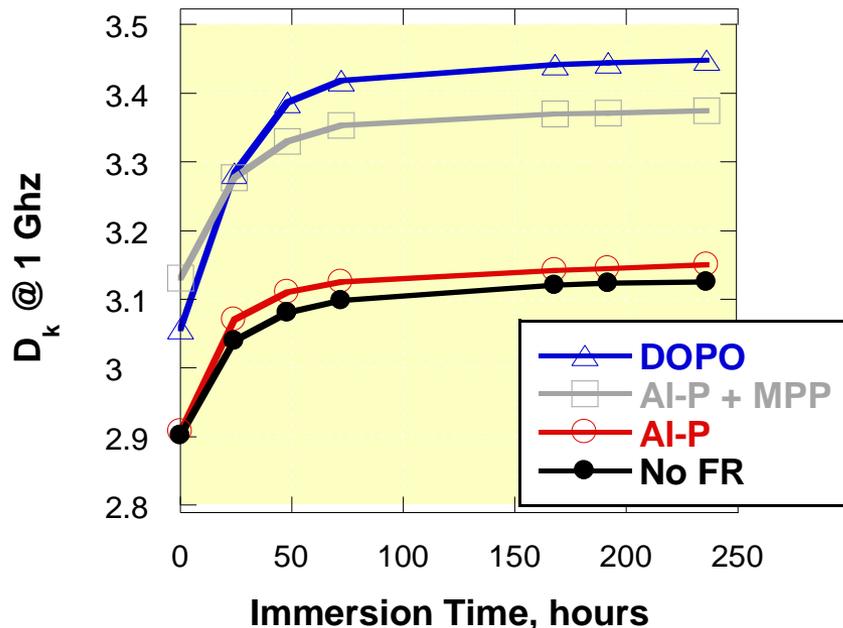
- Larger uptake with reactive FRs
- PPE-M is effective in decreasing water uptake

PPE-M lowers moisture uptake

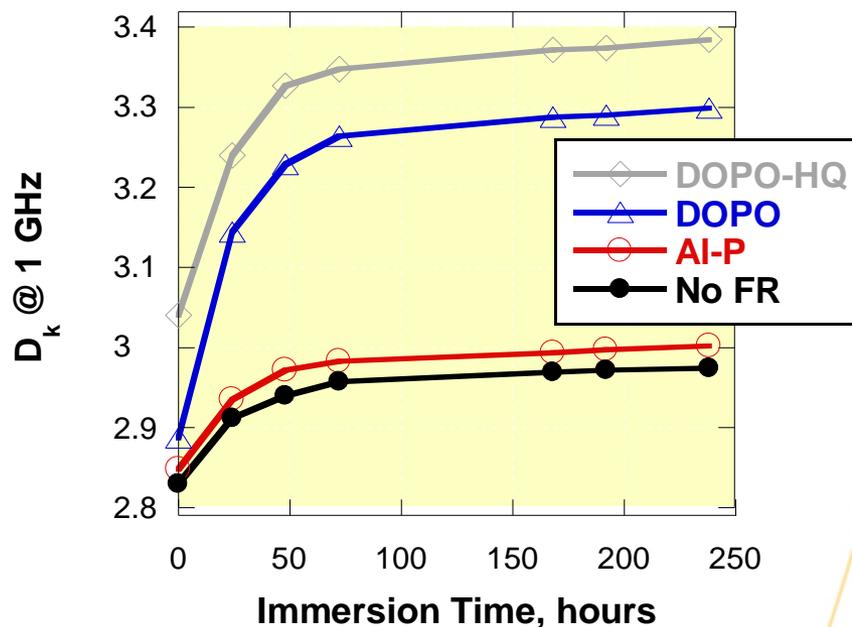
WATER UPTAKE EFFECT on D_k versus TIME

Immersion in water at 80°C
Epoxy + FR (No PPE-M)

CNE + FR



DGEBA + FR



- D_k increases with immersion time
- Larger increase in D_k with reactive FRs

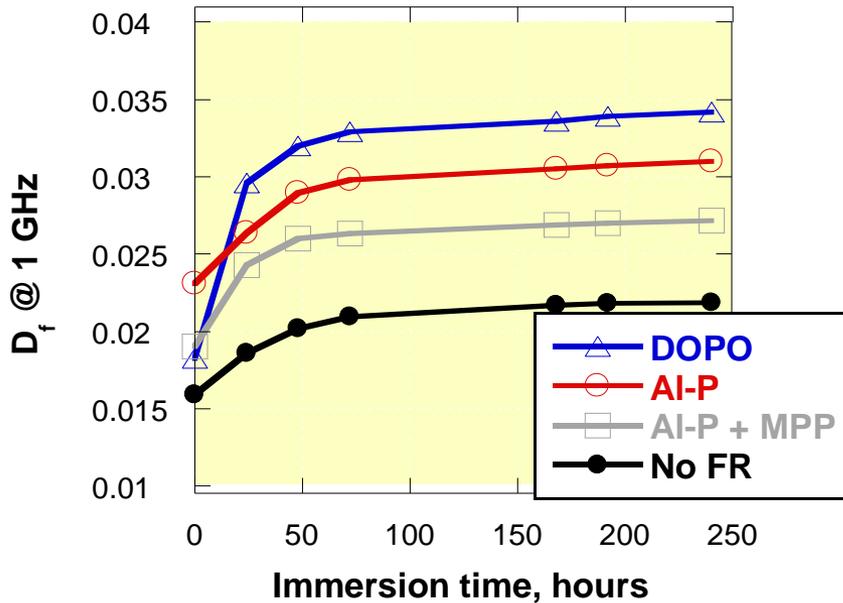
Increased H₂O uptake translates to increased D_k

WATER UPTAKE EFFECT on D_f versus TIME

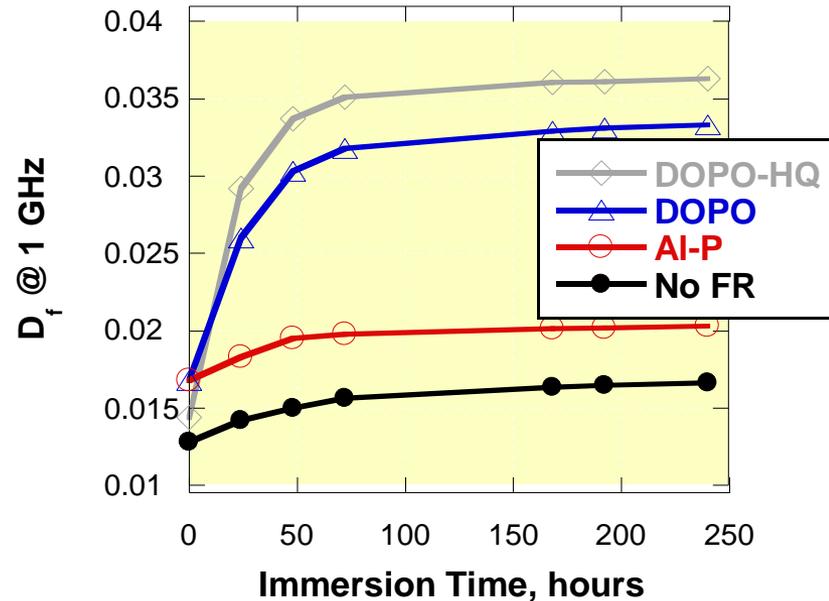
Immersion in water at 80°C

Epoxy + FR (No PPE-M)

CNE + FR



DGEBA + FR



- D_f increases with immersion time
- FRs increase D_f
- Larger increase in D_f with reactive FRs

Next: Look at effect of PPE-M after 168 hours

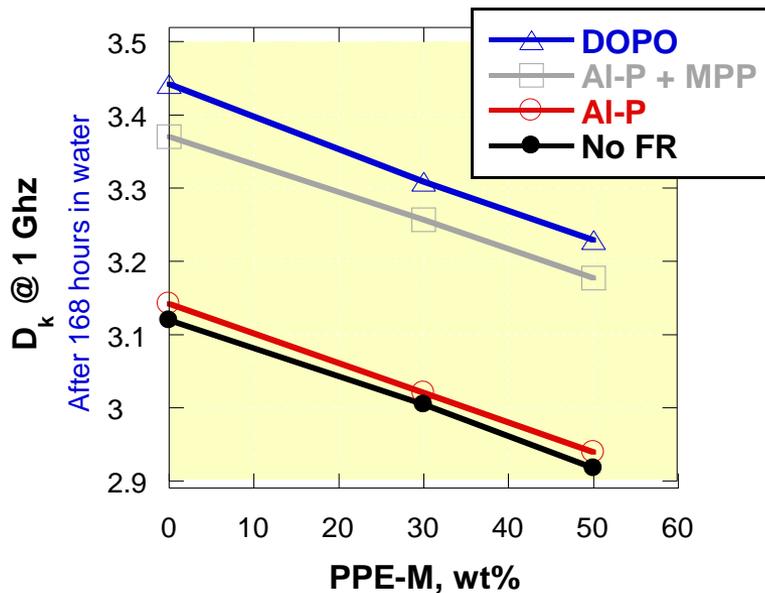
EFFECT of PPE-M on D_k

Immersion in water at 80°C

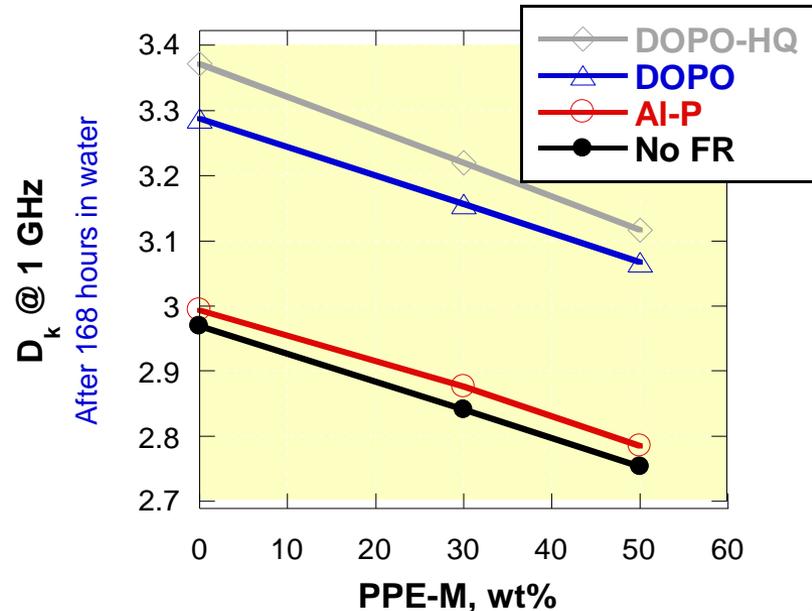
D_k compared **after 168 hours** (1 week) immersion

Epoxy + FR + PPE-M

CNE + FR + PPE-M



DGEBPA + FR + PPE-M



- D_k s higher with reactive FRs
- D_k s decrease with increasing PPE-M levels

Decrease in D_k due to:

- Lower D_k from PPE-M
- Decrease in H₂O uptake from PPE-M

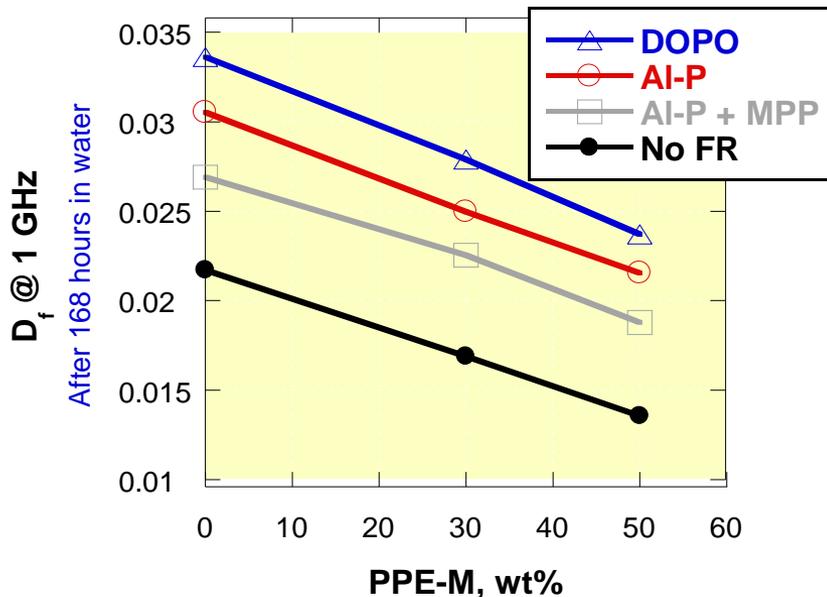
EFFECT of PPE-M on D_f

Immersion in water at 80°C

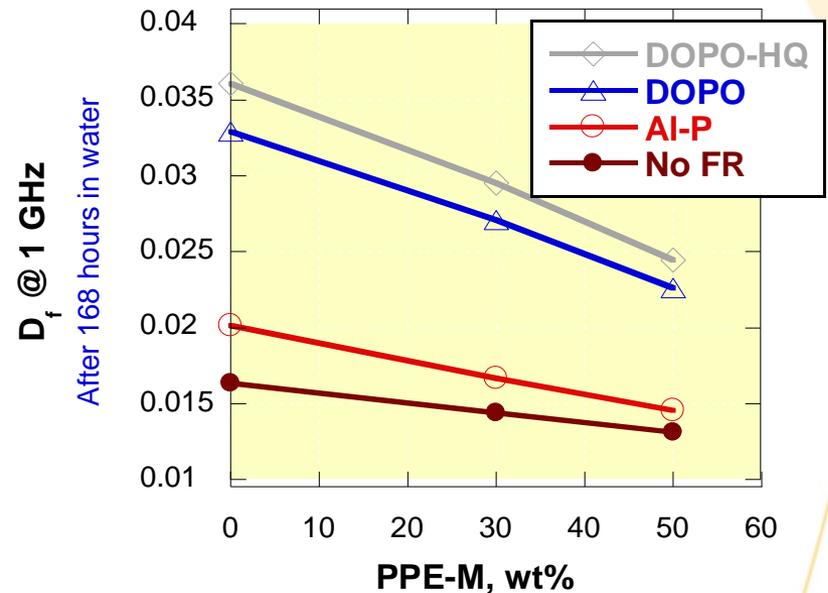
D_f compared **after 168 hours** (1 week) immersion

Epoxy + FR + PPE-M

CNE + FR + PPE-M



DGEBA + FR + PPE-M



- D_f s higher with FRs versus non-FR controls
- D_f s decrease with increasing PPE-M levels

Decrease in D_f due to:

- Lower D_f from PPE-M
- Decrease in H_2O uptake from PPE-M

SUMMARY

PPE-M effectively used in FR CNE and DGEBA

- ✓ **25-60% reduction in the required dosage of FR**

P-FRs can have an adverse effect on some properties

- **Decreased toughness,**
- **Increased D_k , D_f , density, H_2O uptake**

In addition, there are positive effects on properties

- ✓ **3-6% decrease in densities** (lower cost implications)
- ✓ **200-400% increase in toughness** (2ndary operations, more filler)
- ✓ **Lower D_k and D_f** (better performance)
- ✓ **Similar or increased T_g s** (better performance)

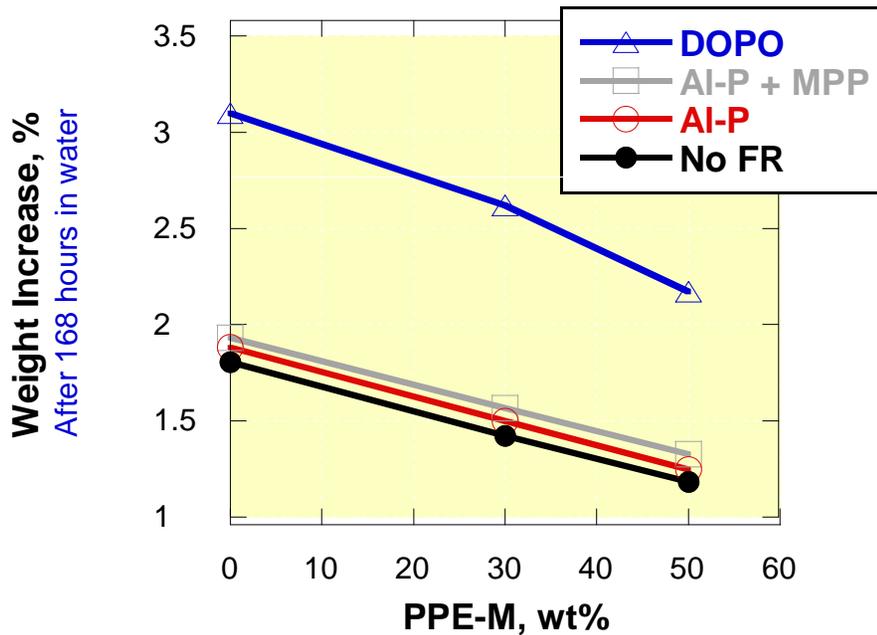
Decrease in moisture absorption

- ✓ **Less change in D_k and D_f** (more stable performance)
- ✓ **Reduced drying time for 2ndary operations** (cost implications)

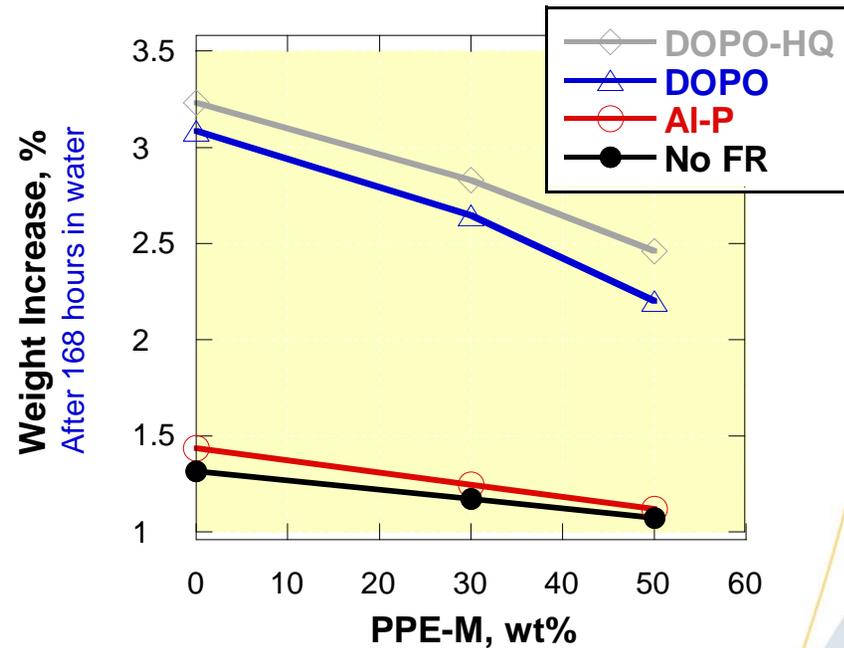
EFFECT of PPE-M on WATER UPTAKE

Immersion in water at 80°C
Water uptake compared **after 168 hours** (1 week) immersion
Epoxy + FR + PPE-M

CNE + FR + PPE-M



DGEBPA + FR + PPE-M



- Larger uptake with reactive FRs
- PPE-M is effective in decreasing water uptake

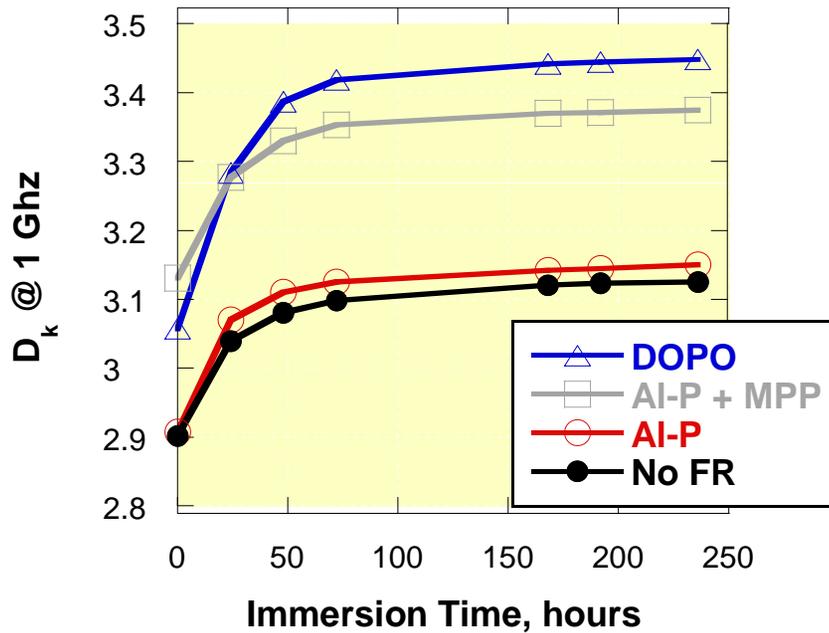
PPE-M lowers moisture uptake

WATER UPTAKE EFFECT on D_k versus TIME

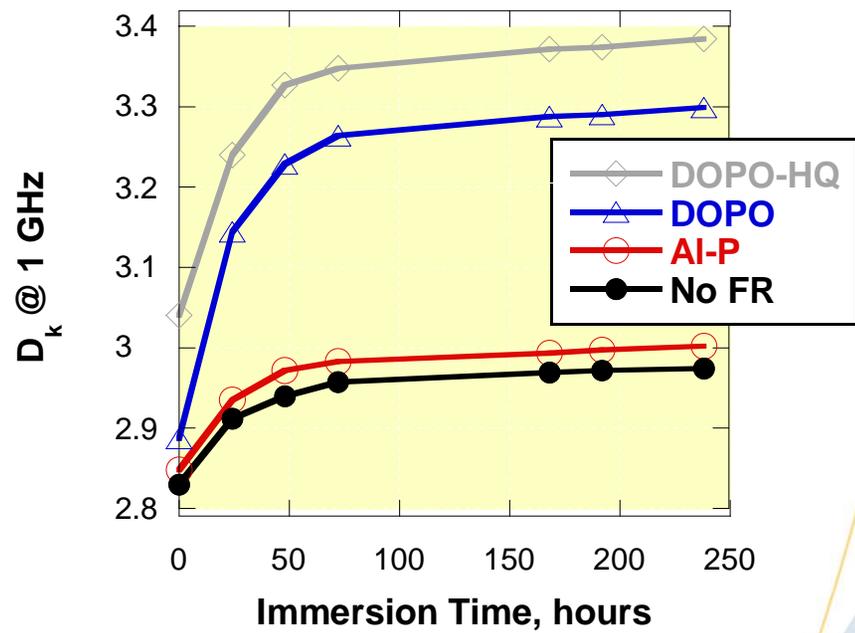
Immersion in water at 80°C

Epoxy + FR (No PPE-M)

CNE + FR



DGEBA + FR



- D_k increases with immersion time
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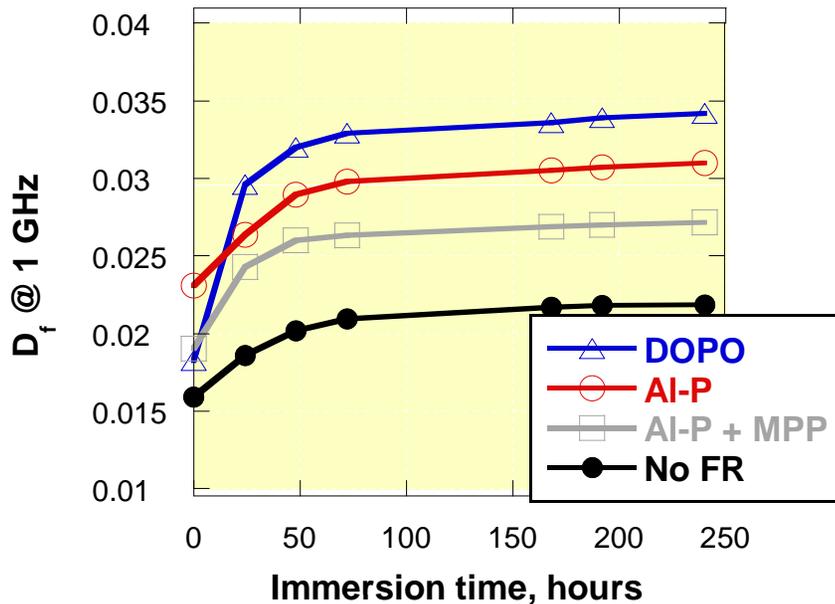
Increased H_2O uptake translates to increased D_k

WATER UPTAKE EFFECT on D_f versus TIME

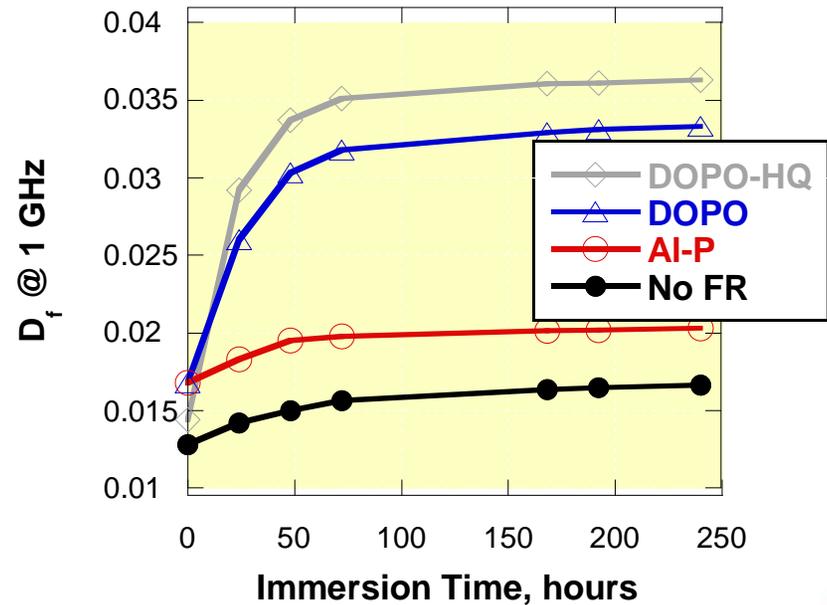
Immersion in water at 80°C

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DGEBA + FR



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- Larger increase in D_f with reactive FRs

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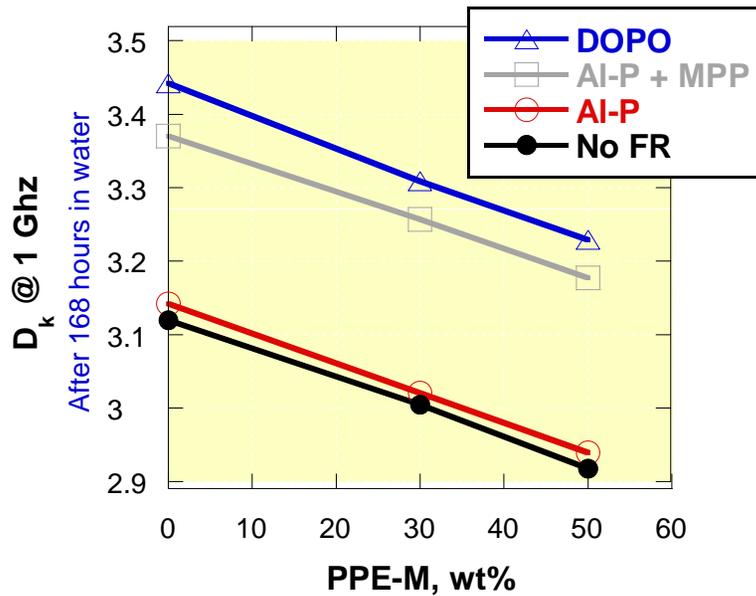
EFFECT of PPE-M on D_k

Immersion in water at 80°C

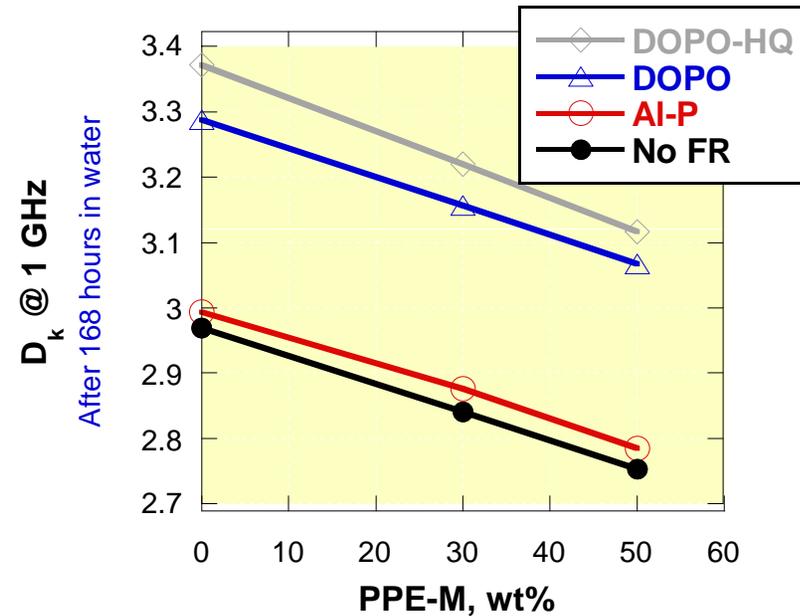
D_k compared **after 168 hours** (1 week) immersion

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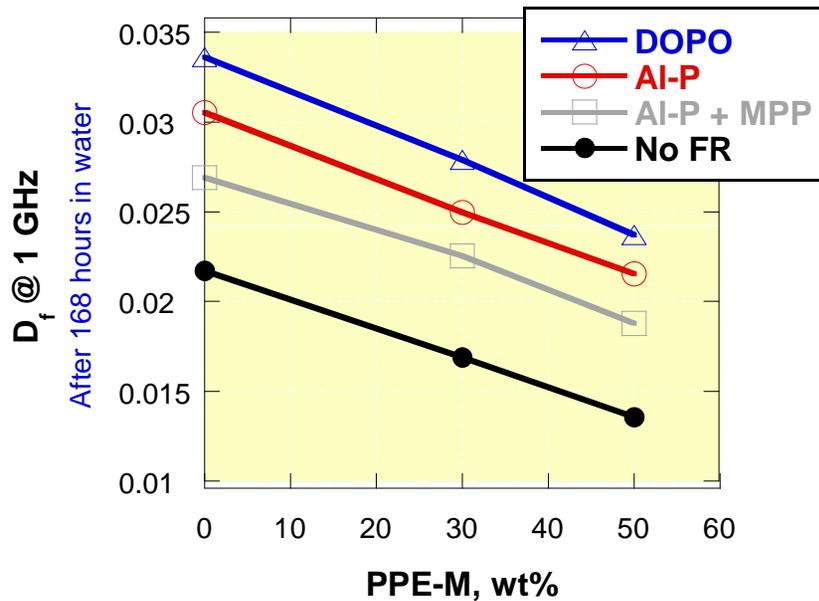
EFFECT of PPE-M on D_f

Immersion in water at 80°C

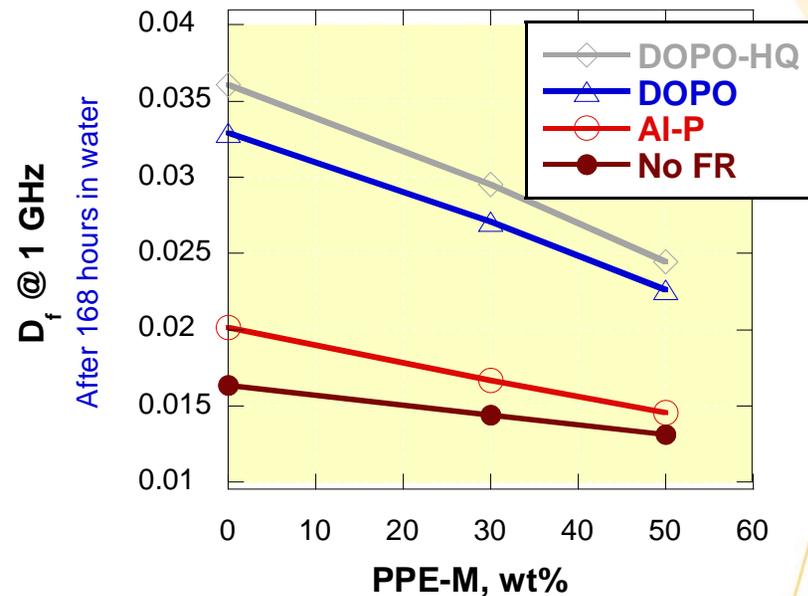
D_f compared **after 168 hours** (1 week) immersion

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