Comparative Study of Phosphorus-based Flame Retardants in Halogen-Free Laminates

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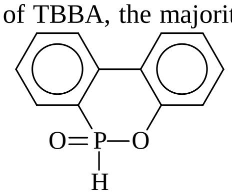
Abstract
This paper compares performance of two phosphorus-based flame retardants: poly-(m-phenylene methyl phosphonate) (PPMP) recently introduced to the market and 9,10-dihydro-9-oxa-10-phosphenanthrene-10-oxide (DOPO) the basis of many commercial halogen-free laminates.

Although DOPO is a reactive flame retardant, it is monofunctional and it can be used only with multifunctional epoxy resins. PPMP on the other hand, is a very effective cross-linker and performs as a curing agent. Comparative study with 5 types of epoxy resins and 4 types of co-curing agents showed that both DOPO and PPMP have very high flame retardant efficiency giving V-0 rating at as low as 1 wt. % phosphorus in the formulation. Electrical properties of DOPO and PPMP based laminates are similar. Epoxy resins cured with PPMP show very high T_g which may satisfy FR-5 type laminates. Slightly higher water absorption of PPMP based laminates can be overcome by appropriate curing and better incorporation of phosphorus in the epoxy network.

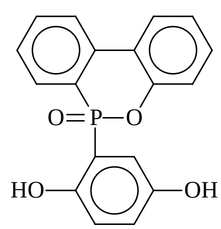
In the current printed wiring board (PWB) technology where flame retardancy is required tetrabromobisphenol A (TBBA) is the product of choice. Industry has been using TBBA for over thirty years and the product performed well. Currently TBBA is undergoing risk assessment in Europe under new REACH legislation. Human health part of the risk assessment has been completed, but at the time of preparation of this paper environmental part of the risk assessment has not been completed yet because additional studies had been commissioned to address the potential degradation of TBBA and the potential risk to sediment and soil. Not waiting for the outcome of risk assessment, many OEMs announced halogen-free policies if technically feasible alternative to TBBA is identified.

Uncertainty over future fate of TBBA has stimulated development of new mainly halogen-free flame retardant systems. Although many chemicals were considered as potential substitution of TBBA, the majority of halogen-free formulations are using 9,10-dihydro-9-oxa-10-phosphenanthrene-10-oxide (DOPO)



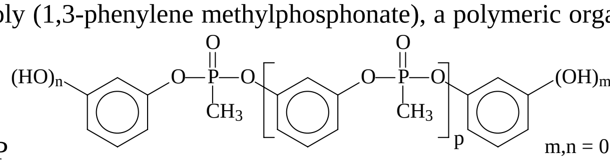
. This chemical was originally developed as a heat stabilizer, then it found commercial use as a flame retardant in polyester fibers and about 10 years ago it was explored as a flame retardant in epoxies. It is manufactured in Europe, Japan and reportedly in China and Taiwan. DOPO is a reactive monofunctional molecule and it incorporates into epoxy network. In order to make effective use of DOPO it needs to be pre-reacted with multifunctional epoxies.

A derivative of DOPO made by reaction DOPO with quinone



is marketed in Asia Pacific, mostly in Japan as DOPO-HQ. This product has similar functionality as TBBA and can be used as a chain extender with difunctional epoxies. Relatively high cost, but low phosphorus content (9.6 wt. %) limits wide application of DOPO-HQ.

The new flame retardant, poly (1,3-phenylene methylphosphonate), a polymeric organophosphorus product is available from Supresta LLC, as Fyrol PMP



m,n = 0 or 1. In contrast to DOPO or DOPO-HQ, PPMP, referred to hereafter as PPMP, is a multifunctional reactive flame retardant and therefore it can be used either as a hardener or it can be pre-reacted with epoxy.

In this paper we will report on flame retardant performance, physical and electrical properties of epoxy resins and laminates formulated with two phosphorus-based reactive flame retardants DOPO and PPMP.

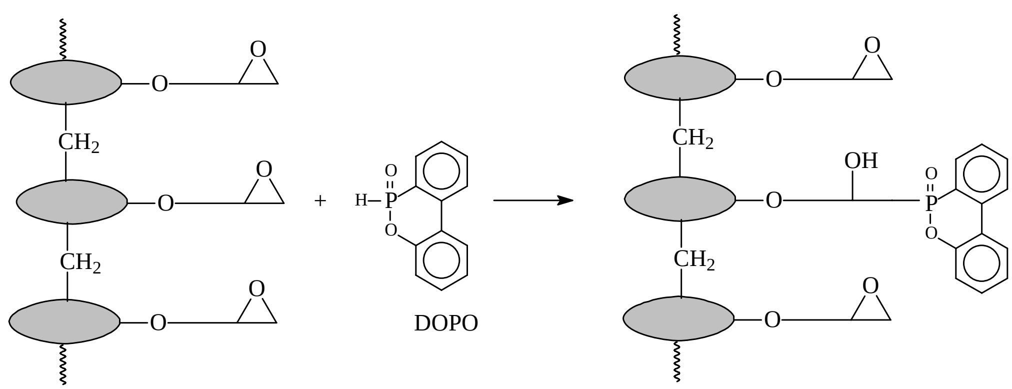
Physical properties of phosphorus flame retardants.
Some physical and chemical properties of PPMP and DOPO are listed in Table 1. PPMP is a colorless or slightly amber glassy low-melting solid. It is a very thermally stable material and it does not show any signs of degradation up to 330ºC. High thermal stability is an indication of the good potential of PPMP in lead-free soldering formulations. It has very high phosphorus content of 17.5 % and is soluble in MEK and acetone, which are most commonly used solvents by the PWB industry.

DOPO is a white hygroscopic powder, which melts at 118°C. DOPO is relatively high in phosphorus (14.3 wt. %), but it is lower than that of PPMP. Since DOPO is not soluble in acetone or MEK, the mixed toluene/MEK or xylene/MEK solvents are used for blending DOPO with epoxy. Pre-reaction of DOPO and epoxy is carried out ether in the melt or in a high boiling solvent. After pre-reaction with epoxy, the resulted resin is soluble in acetone or MEK.

Table 1 - Physical and chemical properties of PPMP and DOPO

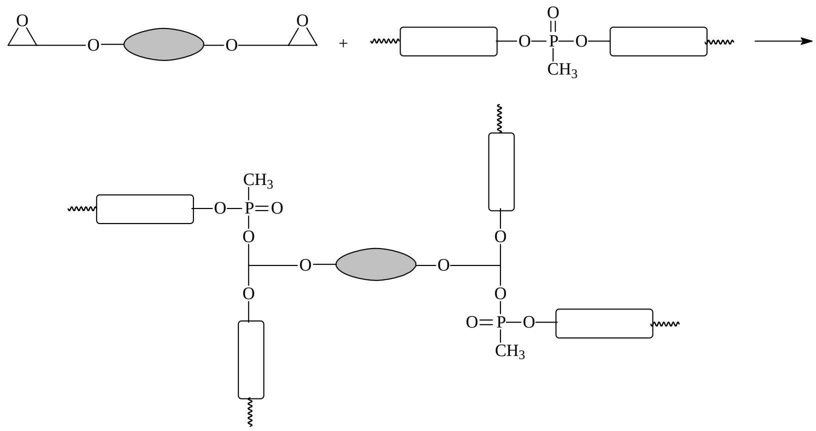
Property	PPMP	DOPO
Chemical name	Poly(1,3-phenylene methylphosphonate)	9,10-dihydro-9-oxa-10-phosphenanthrene-10-oxide
CAS	63747-58-0	35948-25-5
Phosphorus	17.5 %	14.3 %
FR efficiency	V-0 in phenol epoxy resin at 1 – 1.5 wt.% P	V-0 in phenol epoxy resin at 1 – 1.5 wt.% P
Appearance	Transparent semi-solid	White powder
Melting point,	50-60, °C (handled as a melt at 100°C)	118 °C (handled as a powder)
Functionality	Tetrafunctional	Monofunctional
Solubility	Soluble in MEK and acetone Not soluble in toluene or xylene	Soluble in toluene/MEK or xylene/MEK blended solvents.
Application with epoxy	A curing agent with reactive equivalent of 90.	Must be pre-reacted with epoxy

The reaction of DOPO with epoxy is presented on Scheme 1. Because DOPO is a monofunctional reactive product it cannot be used with difunctional epoxy resins like bisphenol A based epoxy. It must be pre-reacted with multifunctional epoxies like phenol novolac epoxy (PNE) or cresol novolac epoxy (CNE). The amount of DOPO incorporated into epoxy is limited because CNE or PNE resin must have on average at least two unreacted epoxy groups in order to effectively cross-link the polymer.



Scheme 1 - Reaction of DOPO with multifunctional epoxy

Although PPMP contains some terminal OH functional groups, its main reactive functionalities are phosphonate groups, where epoxy inserts in the presence of strong base catalyst. Schematic curing mechanism is shown in Scheme 2. The detailed curing mechanism has been published elsewhere [1]. Every reaction of the phosphonate (P-O-C) with epoxy produces a branch in the polymer chain, which eventually becomes a cross-link. This is usually not the case with other phosphorus based products and conventional curing agents. Since each phosphonate group creates two branching points (potentially two cross-links each) PPMP should be regarded as a tetrafunctional. No aliphatic OH groups are formed in the course of reaction of PPMP with epoxy. This is very beneficial for epoxy resin thermal stability the thermal decomposition of cured epoxy usually begins with elimination of water from aliphatic OH groups, which further results break of polymer chains [2].



Scheme 2 - Cross-linking of Bisphenol A type epoxy with PPMP.

Epoxy Resins Cured with PPMP

PPMP is a curing agent with reactive equivalent of 90. Normally it cures epoxy resins at 170 – 200 °C in the presence of base catalyst, like 2-methyl imidazole (2-MI). Figure 1 shows glass transition temperatures of various epoxy resin cured with a stoichiometric amount of PPMP. As expected, the multifunctional epoxies (PNE, CNE and TNE (tetrafunctional)) showed higher T_g compare to difunctional bisphenol A type epoxies (BPA188 (EEW=188) and BPA510 (solid epoxy, EEW=445)). The values of T_g for multifunctional epoxies can easily accommodate requirements for lead-free soldering.

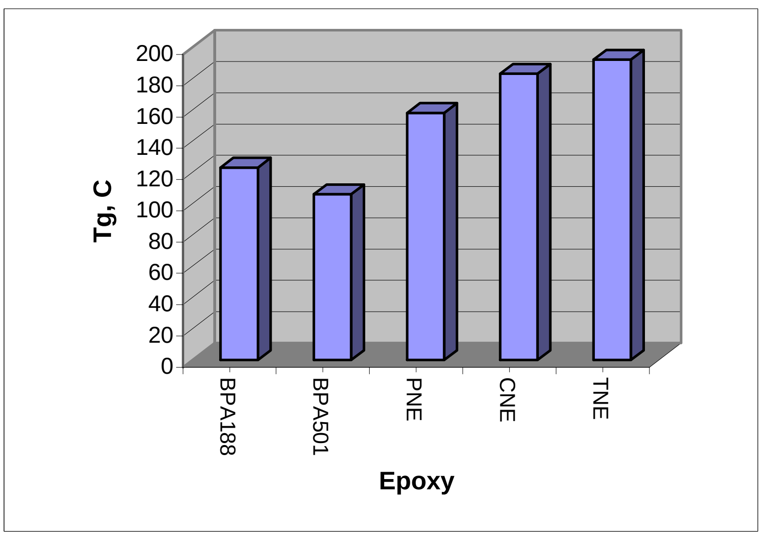


Figure 1 - Glass transition temperatures of various epoxy resins cured with stoichiometric amount of PPMP at 200 °C for 2 hours

Figure 2 shows glass transition temperatures of CNE epoxy resin cured with the blend of DICY and PPMP. The T_g decreases upon progressive replacement of DICY with PPMP. This phenomenon is mostly related to the different reactivity of PPMP and DICY. Because DICY is more reactive than PPMP, DICY reacts first and gels epoxy resin relatively fast. Because of restrained mobility of polymer chains, PPMP can only partially participates in the curing process. In order to overcome this discrepancy in the reactivity PPMP can be pre-reacted with epoxy first, prior to cure with DICY.

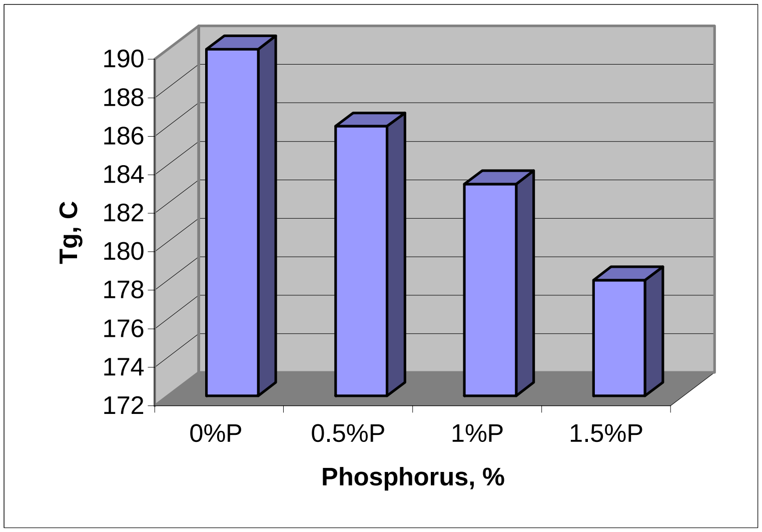


Figure 2 - Glass transition temperatures of CNE cured with DICY/PPMP at 185 °C for 2 hours.

CNE pre-reacted with DOPO and PMP.
Since PPMP is a multifunctional reagent, pre-reaction of PPMP and epoxy should be carried out with great caution. Prolonged heating at high temperature can result in cross-linking. Figure 3 shows kinetic curves of pre-reaction of CNE epoxy resin with PPMP at phosphorus content 3 wt. %. At 190 °C reaction proceeds very fast and the resin approaches gelling point (viscosity > 600 cp) within only 20 min. The process is much better controllable at 150 °C.

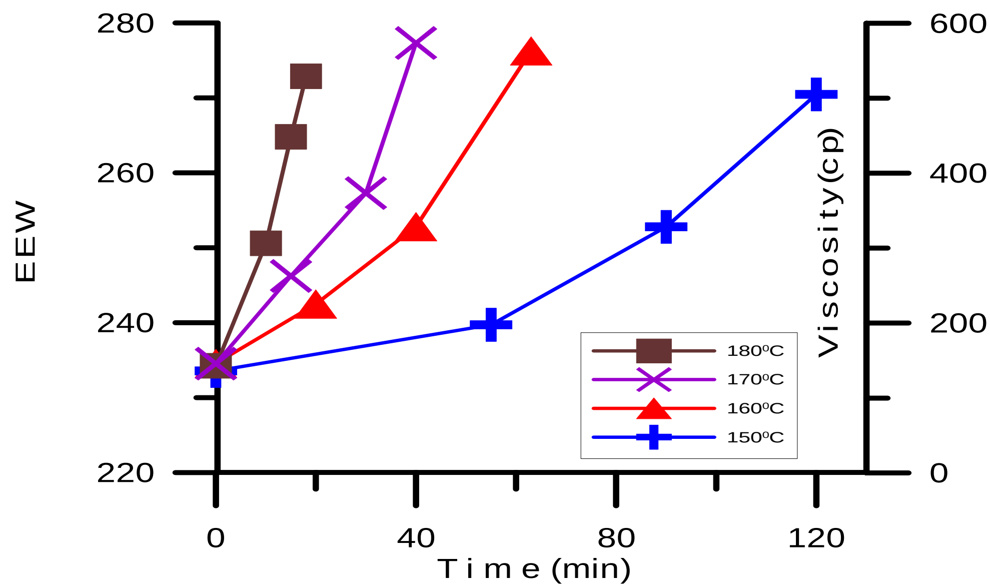


Figure 3 - Kinetics of pre-reaction of CNE with PPMP at 3 wt. % P content.

Both PPMP and DOPO were pre-reacted with CNE epoxy resin at 3 wt. % P content and then for some experiments CNE-DOPO and CNE-PMP resins were diluted with plain CNE to achieve 1.0 or 2.0 wt. % P content. These epoxy resins were cured with DICY. Figure 4 shows glass transition temperatures for CNE-DOPO and CNE-PMP. Apparently, PPMP provides higher T_g which is in agreement with its multifunctionality.

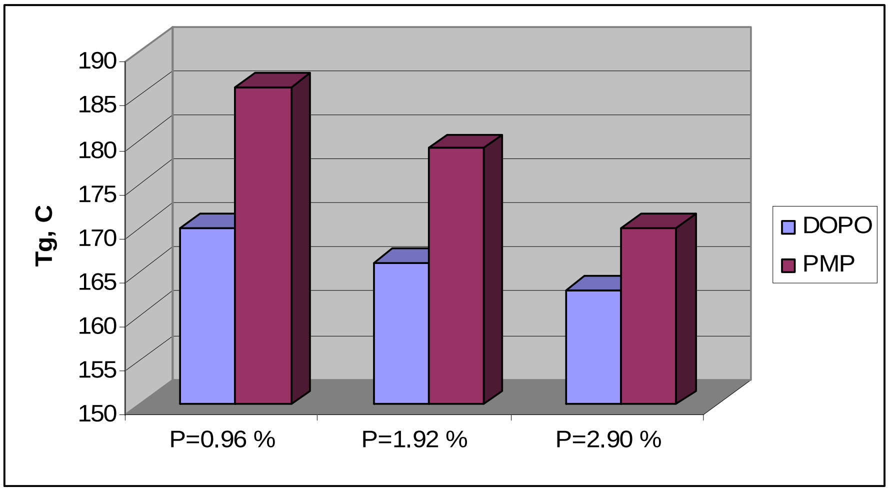


Figure 4 - Glass transition temperatures of CNE-DOPO and CNE-PMP cured with DICY at 185 °C for 2 hours.

The water absorption of the same CNE-DOPO and CNE-PMP formulations is shown in Figure 5. As expected the water absorption increases with increase of phosphorus content. Although at acceptable level, PPMP shows higher water absorption than DOPO. We believe this can be explained by incomplete reaction of PPMP with epoxy due to competition with more reactive DICY (see above).

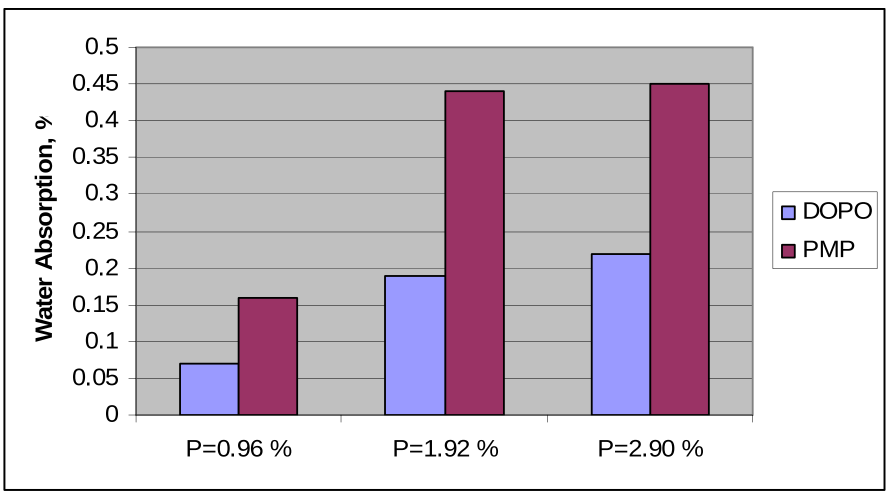


Figure 5 - Water absorption of CNE-DOPO and CNE-PMP cured with DICY.

Glass transition temperatures of CNE-PMP and CNE-DOPO cured with phenol novolac (PN) are ranging from 160°C to 185°C depending on phosphorus content and are very similar for PPMP and DOPO. Water absorption of CNE-PMP and CNE-DOPO cured with PN is shown in Figure 6. Although DOPO shows slightly lower absorption both CNE-DOPO and CNE-PMP have low acceptable values. Because the reactivity of PN is lower than the reactivity DICY, there is less competition in curing reactions with PPMP, therefore incorporation of PPMP in epoxy is more complete and water absorption is lower.

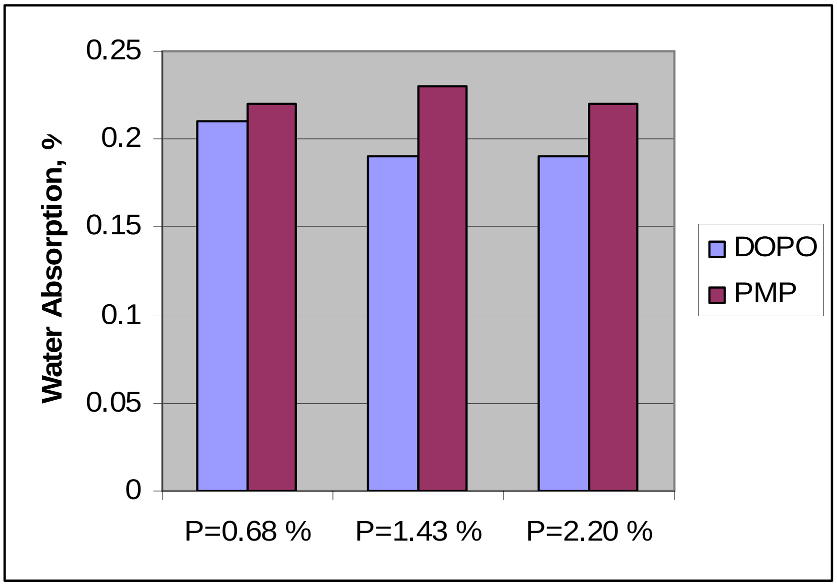


Figure 6 - Water absorption of CNE-DOPO and CNE-PMP cured with PN.

Electrical properties of CNE-PMP and CNE-DOPO cured with DICY are shown in Figures 7 and 8. The dielectric constant (D_k) and loss factor (D_f) were measured in formulations with different phosphorus content at 1 and 100 MHz. It is important to note that increase of phosphorus concentration independently of source (DOPO or PPMP) is beneficial for the epoxy resin because of decrease of D_k and D_f. Although both CNE-PMP and CNE-DOPO show comparable values of D_k and D_f, the values for CNE-PMP tend to be lower.

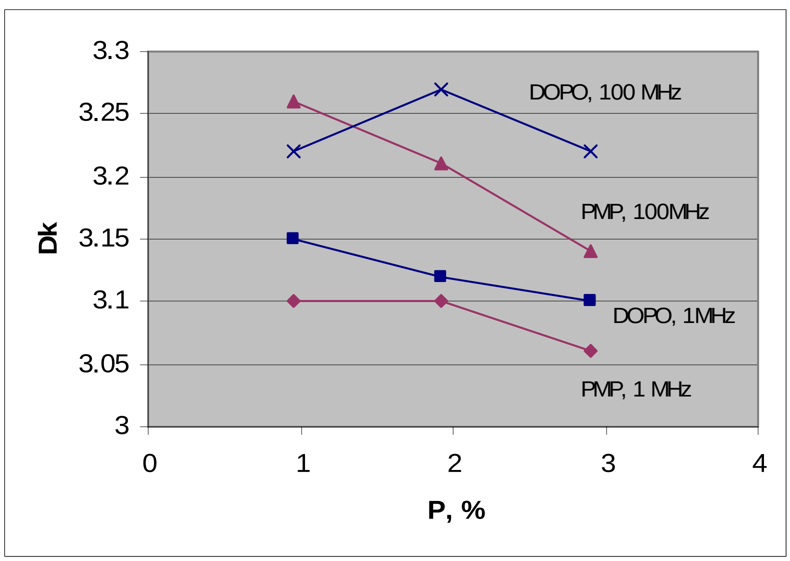


Figure 7 - D_k of CNE-DOPO and CNE-PMP cured with DICY.

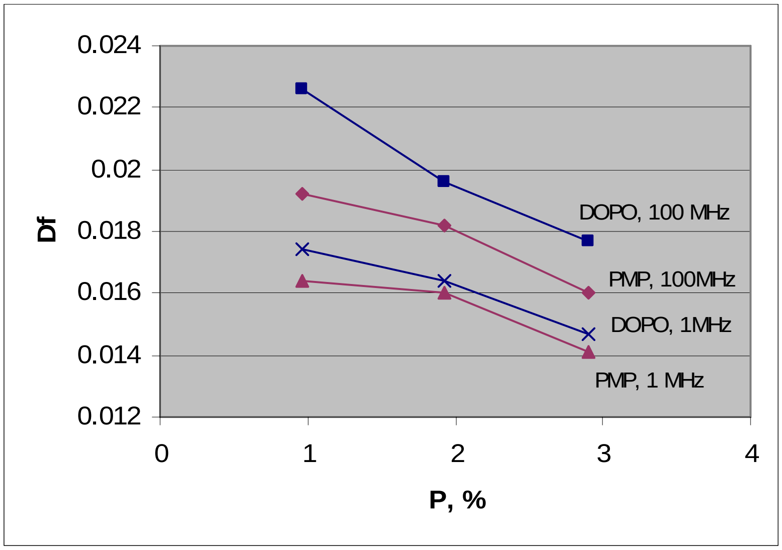


Figure 6 - D_f of CNE-DOPO and CNE-PMP cured with DICY.

Laminates Containing PPMP

Finally, eight layers glass cloth laminates were manufactured using CNE-PMP epoxy resin. Phosphorus content was adjusted to 2 wt. %. Table 2 lists physical properties of the laminates cured with DICY and PN respectively. Both laminates show strong V-0 UL-94 rating, good heat resistance in lead-free soldering (288°C) and excellent chemical resistance. PN cured formulation has lower water absorption and as result better performance in lead-free soldering, however glass transition temperature of PN –cued formulation is lower.

Table 2 - Physical properties of laminates based on CNE-PMP (2 wt. % P)

Epoxy Resin		CNE-PMP	CNE-PMP
Complementary Hardener		DICY	PN
PCT (30 min)	Solder test (times)	7	>10
	Moisture abs., %	0.63	0.23
PCT (60 min)	Solder test (times)	6	>10
	Moisture abs., %	0.86	0.36
Flammability	UL-94	V-0	V-0
T_g (DSC),	°C	195	165
Chemical Resistance	MEK	Ok	Ok
	DMF	Ok	Ok
	10% HCl	Ok	Ok
	10% NaOH	Ok	Ok

Conclusions

A new halogen-free flame retardant curing agent, PPMP, is a polymeric phosphonate which is reactive with epoxy resins. PPMP cross-links resin via insertion of epoxy group into the phosphonate linkage, which effectively cross-links the resin and ensures its high thermal stability. PPMP can be applied as a curing agent either alone or in combination with co-curing agent. PMP can be pre-reacted with epoxy resin similar to DOPO, however special precautions are needed in order to avoid gelation.

On the other hand, DOPO is a monofunctional reagent and it must be pre-reacted with a multifunctional epoxy resin. Both PPMP and DOPO are efficient flame retardants and provide V-0 rating at similar P content (1-2 wt. %) depending on the type of epoxy resin and auxiliary curing agent. Because the phosphorus content of PPMP (17.5 wt. %) is higher than that of DOPO (14.3 wt. %), PPMP is effectively used at lower loading level than DOPO. Both PPMP and DOPO show very good thermal properties and are suitable for lead-free soldering. Because PPMP is a multifunctional cross-linker, it allows to achieve higher glass transition temperature than DOPO, which may satisfy even FR-5 type laminates. Electrical properties of both PPMP and DOPO epoxy formulations are in the range of common FR-4 laminates. Water absorption of PPMP is marginally higher than water absorption of DOPO, which is due to incomplete reaction of PPMP and can be improved by proper formulation.

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1 T. Wu, A.M. Piotrowski, Q. Yao and S.V. Levchik, *J. Appl. Polym. Sci.* **101**(2006)4011-4022.
2 S.V. Levchik and E.D. Weil, *Polym. Int.*, **53**(2006)1901-1920.

Comparative Study of Phosphorus-based Flame Retardants in Halogen-Free Laminates

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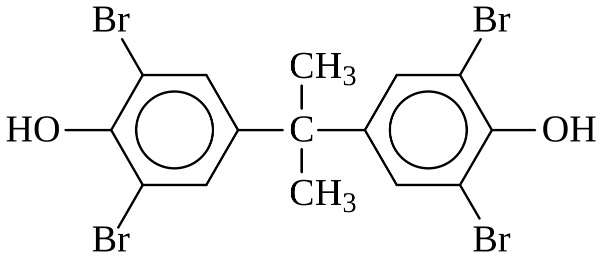
supresTA™ BUILT-IN DEFENSE

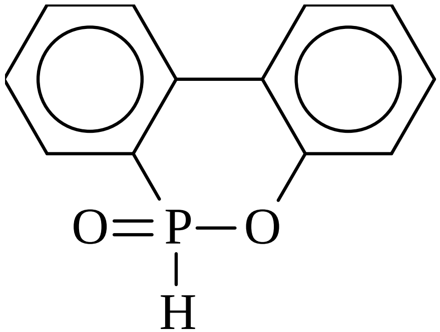
Introduction - TBBA

- Industry has been using TBBA for over thirty years
- Currently TBBA is undergoing risk assessment in Europe under new REACH legislation.
- Human health part of the risk assessment has been completed
- The environmental part is in progress
  - additional studies had been commissioned for
    - degradation of TBBA
    - risk to sediment and soil.
- Many OEMs announced halogen-free policies if technically feasible alternative to TBBA is identified.



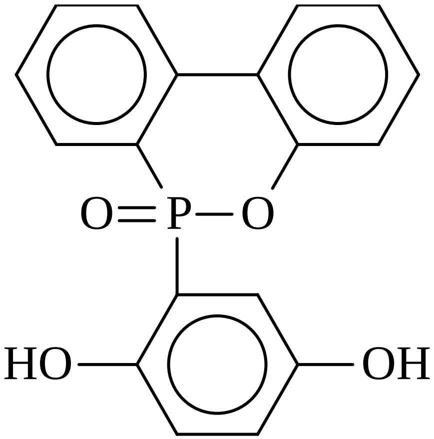
Introduction - DOPO

- Uncertainty over future of TBBA has stimulated development of halogen-free flame retardant systems
- Majority of halogen-free formulations are using DOPO
  - DOPO has been originally developed as a heat stabilizer
  - later it found use as a flame retardant in polyester fibers
  - about 10 years ago it was explored as a flame retardant in epoxies.
- DOPO is manufactured in Europe, Japan and reportedly in China and Taiwan.
- DOPO is a reactive monofunctional product



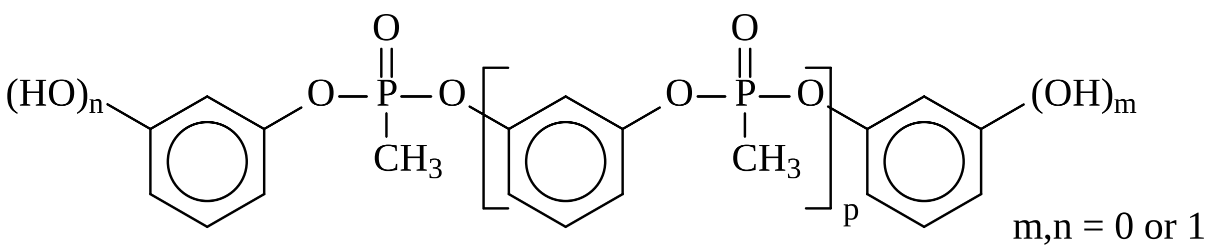
Introduction – DOPO-HQ

- DOPO-HQ is made by reaction of DOPO with quinone.
- It is marketed in Asia Pacific, mostly in Japan.
- This product has similar functionality as TBBA and can be used as a chain extender with epoxies.
- Relatively high cost, but low phosphorus content (9.6 wt. %) limits wide application of DOPO-HQ.



Introduction – Fyrol PMP

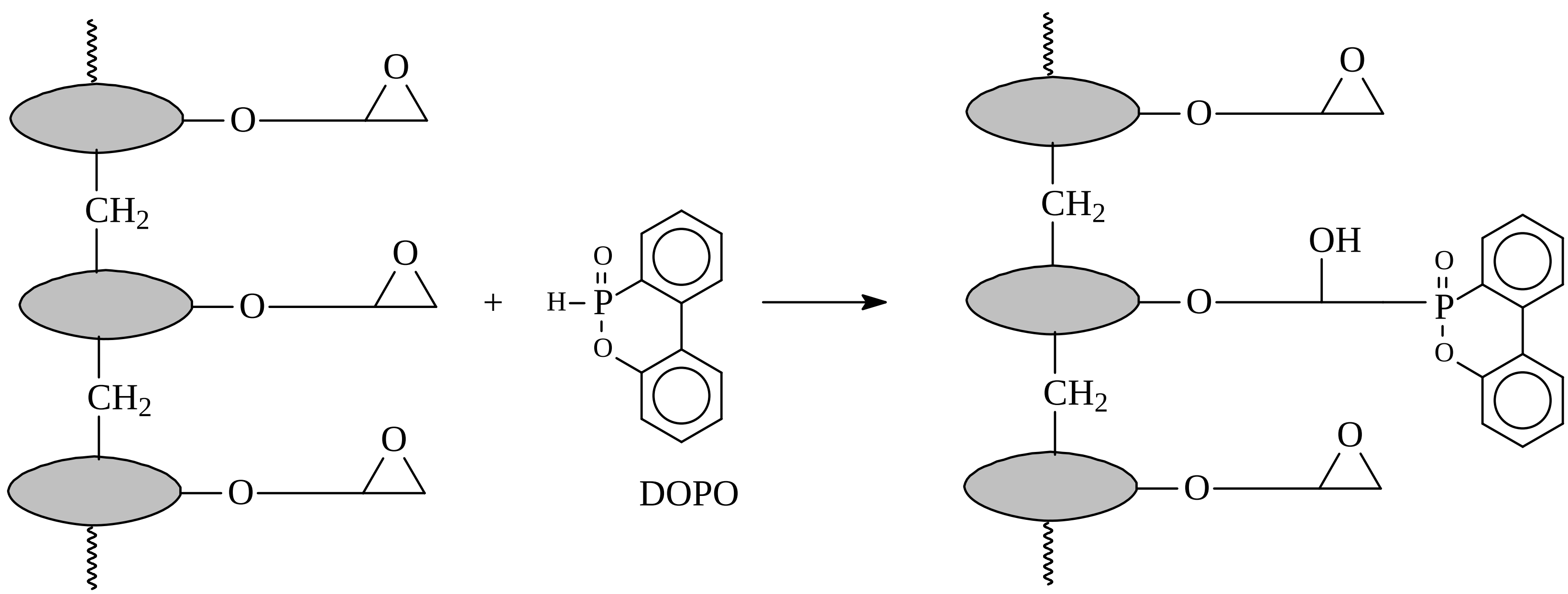
- The new flame retardant, poly (1,3-phenylene methylphosphonate), Fyrol PMP (PMP) is available from Supresta LLC..
- In contrast to DOPO or DOPO-HQ, PMP is a multifunctional reactive flame retardant
- It can be used either as a hardener or it can be pre-reacted with epoxy.
- In this paper we will compare performance of DOPO and PMP.



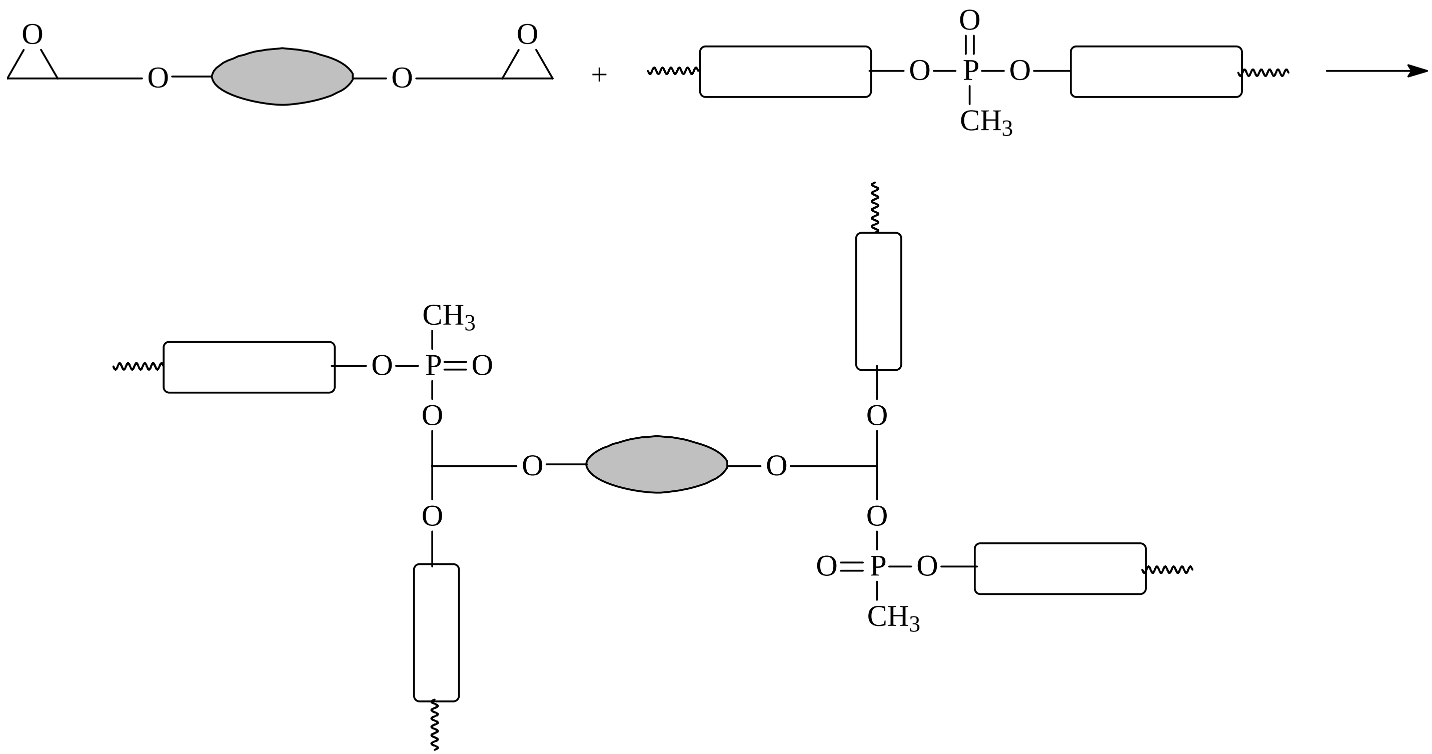
Properties of DOPO and PMP

Property	PMP	DOPO
Chemical name	Poly(1,3-phenylene methylphosphonate)	9,10-dihydro-9-oxa-10-phosphenanthrene-10-oxide
CAS	63747-58-0	35948-25-5
Phosphorus	17.5 %	14.3 %
FR efficiency	V-0 in phenol epoxy resin at 1 – 1.5 wt.% P	V-0 in phenol epoxy resin at 1 – 1.5 wt.% P
Appearance	Transparent semi-solid	White powder
Melting point,	50-60, °C (handled as a melt at 100°C)	118 °C (handled as a powder)
Functionality	Multifunctional (tetrafunctional)	Monofunctional
Solubility	Soluble in MEK and acetone Not soluble in toluene or xylene	Soluble in toluene/MEK or xylene/MEK blended solvents.
Application with epoxy	A curing agent with reactive equivalent of 90.	Must be pre-reacted with epoxy

Reaction of DOPO with epoxy



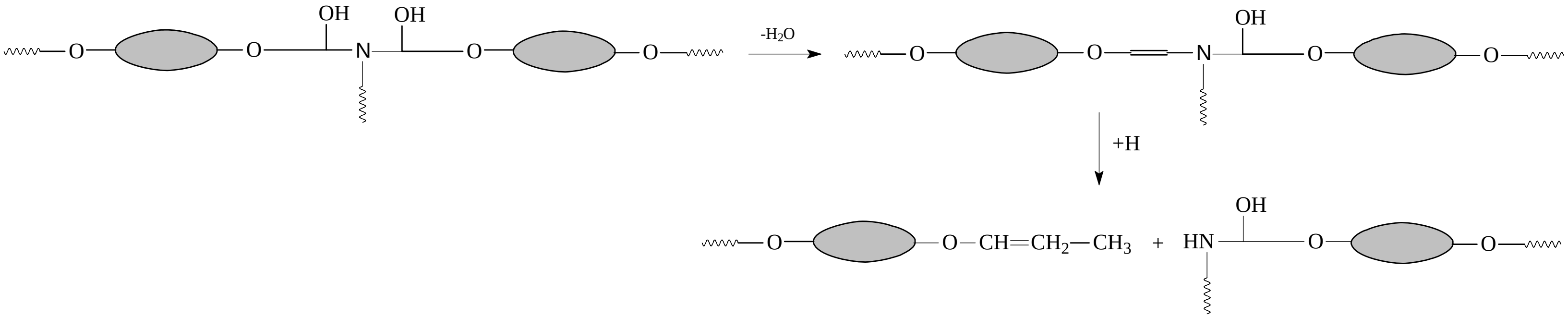
Curing of epoxy with PMP



- PMP is a curing agent with reactive equivalent of 90.
- Normally it cures epoxy resins at 170 – 200 °C

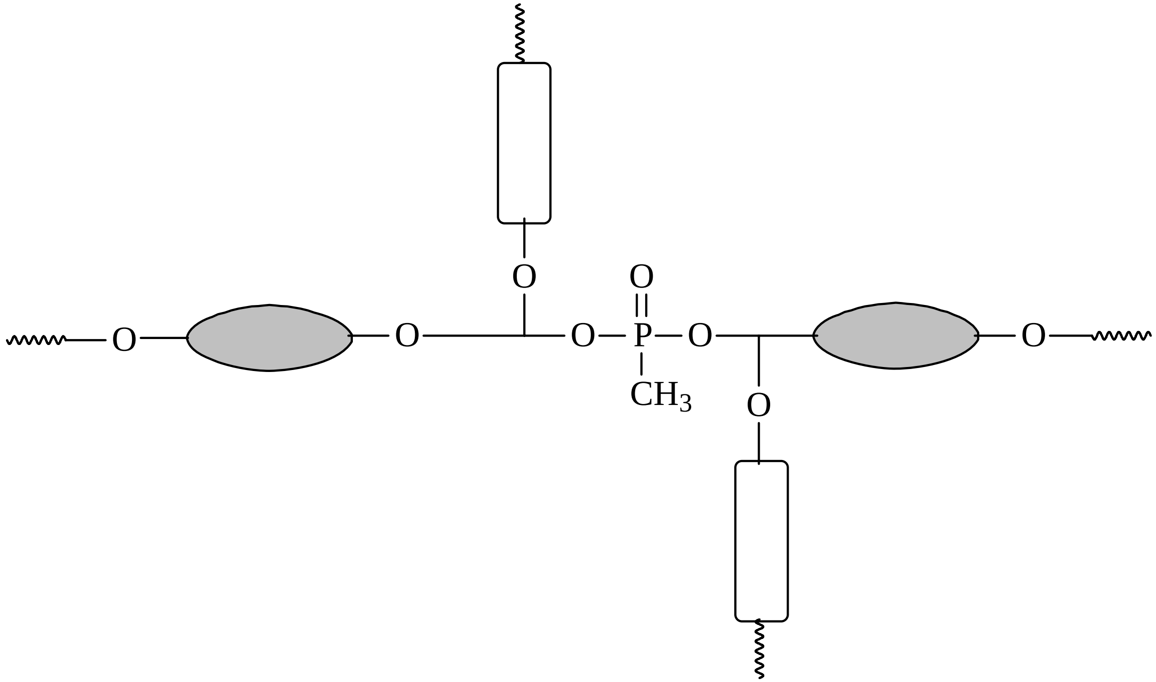
Low thermal stability of amine cured epoxy

- Thermal stability of cured epoxy depends on the presence of OH groups
- At about 300°C, epoxy resin starts losing water from secondary alcohol groups
  - water can cause mechanical failure of the laminates
- The double bonds created after dehydration weaken epoxy network
  - polymer chains start breaking relatively easily



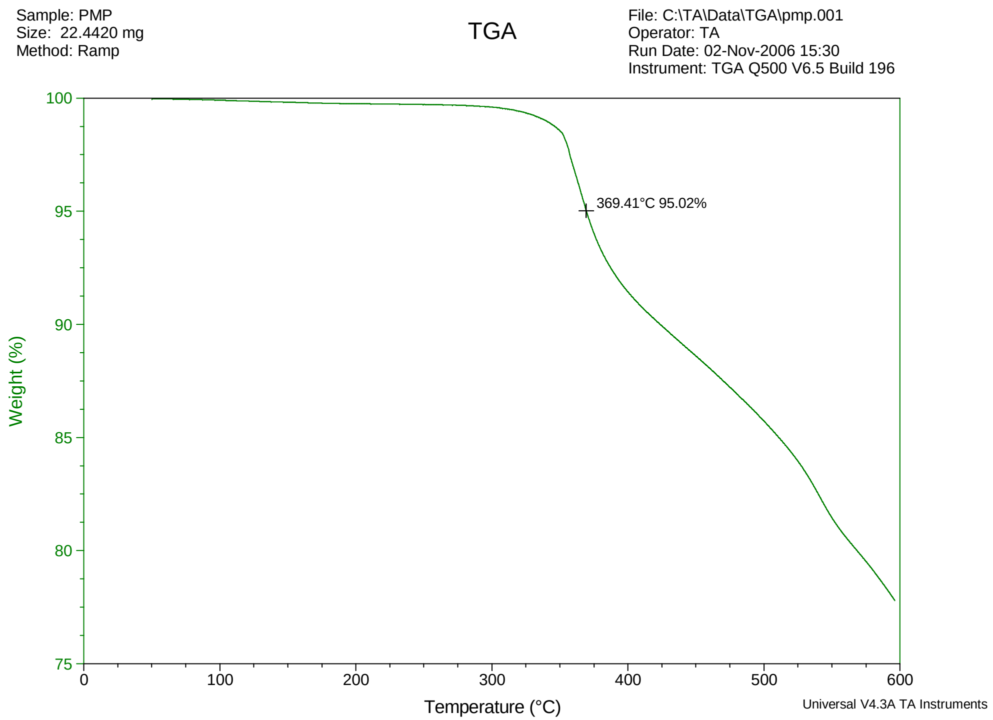
High Thermal Stability of Epoxy Cured with PMP

- PMP <u>does not generate OH groups</u> upon curing
  - intrinsically <u>more thermally stable</u> polymer network is formed



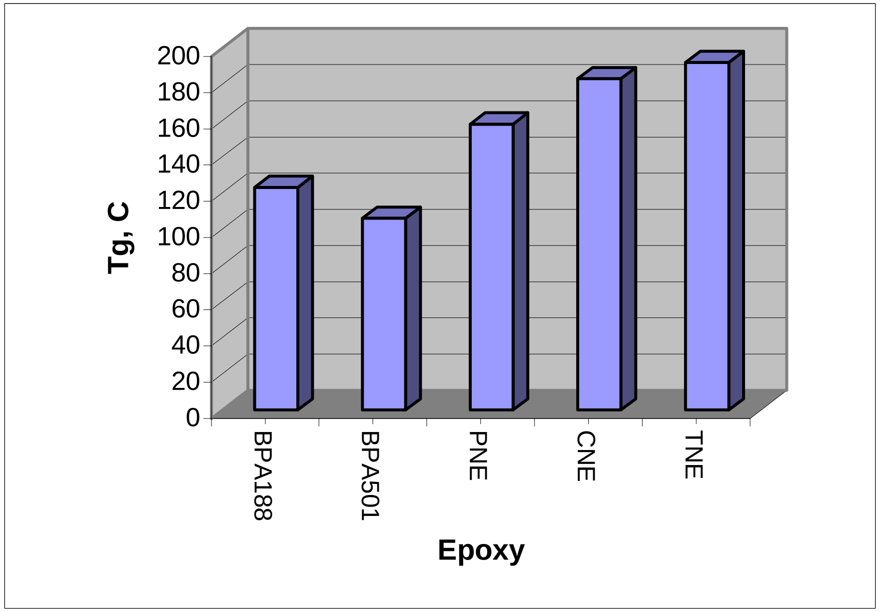
Thermal stability of PMP based laminate

- Formulation containing only PNE, PMP and catalyst
  - shows T_d = 369 C
  - slow weight loss similar to mineral filled systems
- <u>Perfect fit for lead-free soldering</u>



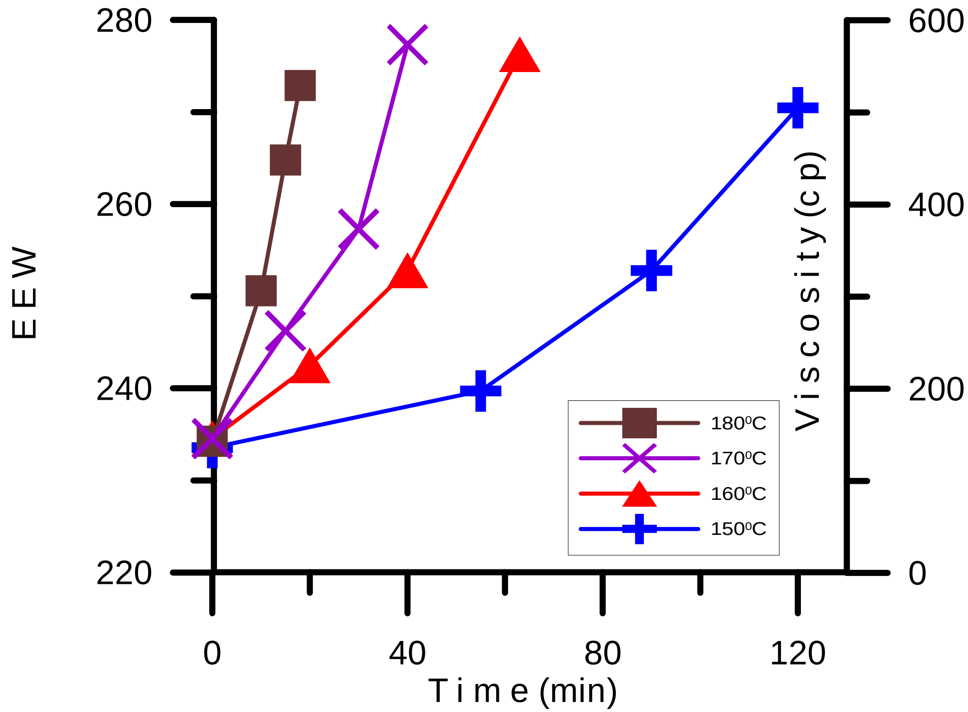
Glass transition temperature

- Tg of various epoxy resin cured with a stoichiometric amount of PMP
- The values of Tg for multifunctional epoxies can easily accommodate requirements for lead-free soldering.



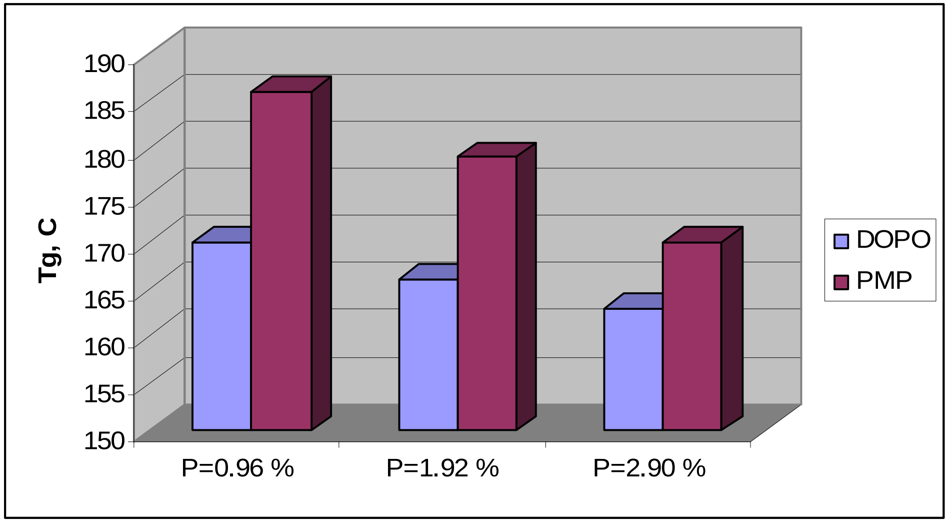
Pre-reaction of PMP with epoxy

- Pre-reaction of CNE with PMP at phosphorus content 3 wt. %.
- Since PMP is a multifunctional reagent, pre-reaction of PMP and epoxy should be carried out with caution.
- At 190 °C reaction proceeds very fast and the resin approaches gelling point within only 20 min.
- The process is much better controllable at 150 °C.



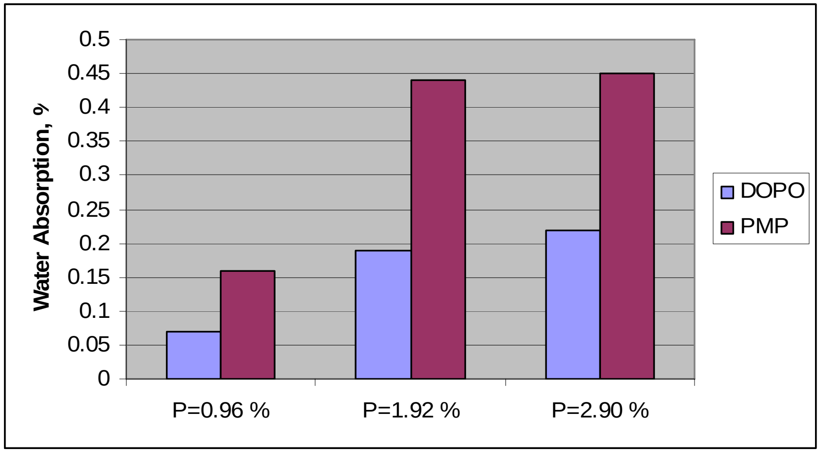
Glass transition temperature of PMP vs. DOPO

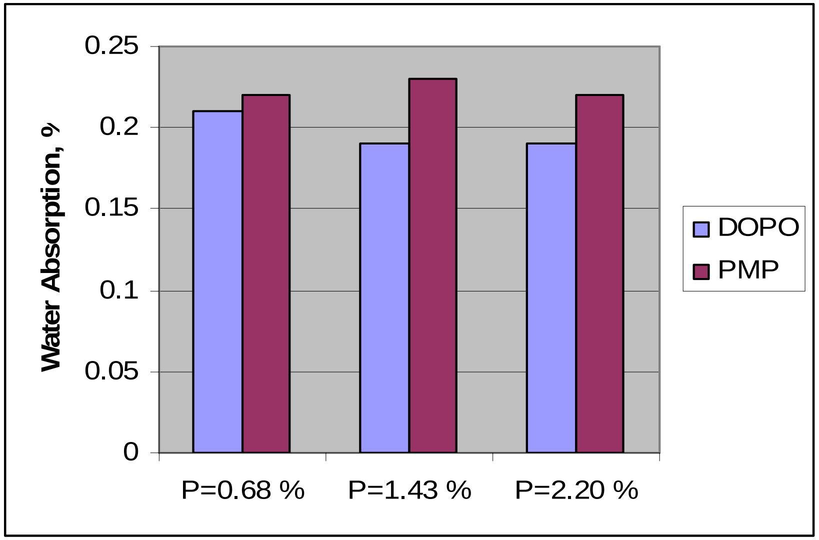
- Both PMP and DOPO were pre-reacted with CNE at 3 wt. % P and then diluted with plain CNE to achieve 1.0 or 2.0 wt. % P content.
- Cured with DICY.
- PMP provides higher Tg which is in agreement with its multifunctionality.



Water absorption

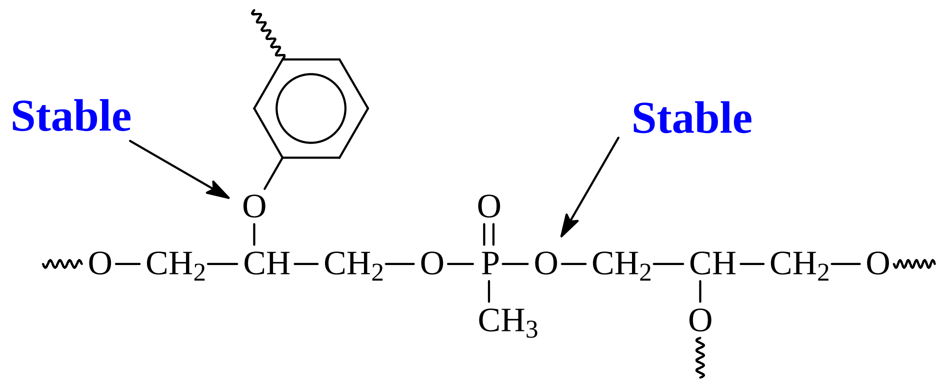
- The water absorption increases with increase of phosphorus content.
- PMP shows higher water absorption than DOPO
  - acceptable level
  - explained by incomplete reaction of PMP
    - competition with more reactive DICY
- Because the reactivity of PN is lower than the reactivity DICY, there is less competition in curing reactions with PMP.
  - incorporation of PMP in epoxy is more complete
  - water absorption is lower



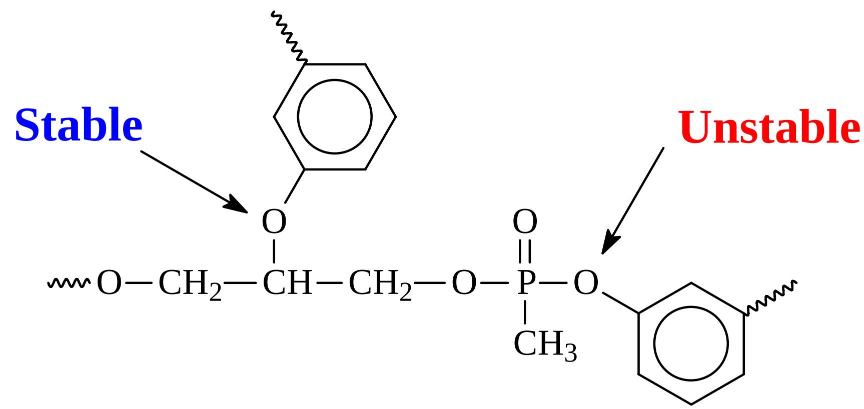


Hydrolytic Stability of Epoxy Cured with PMP

- Fully cured Fyrol®PMP is <u>very hydrolytically stable</u>

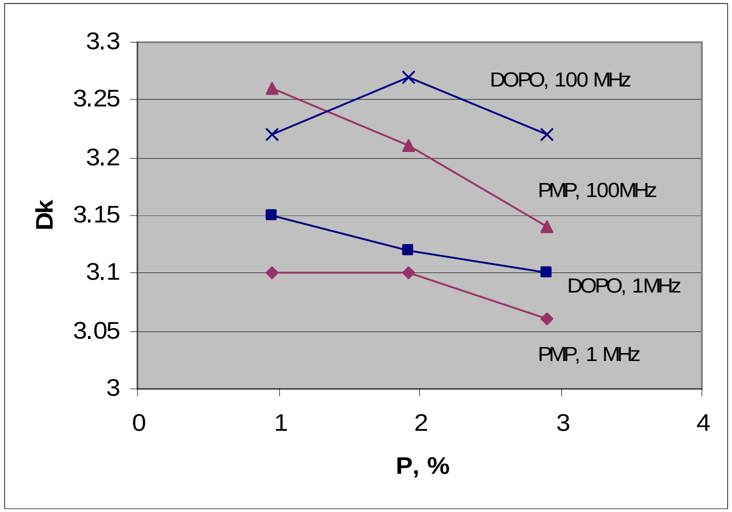


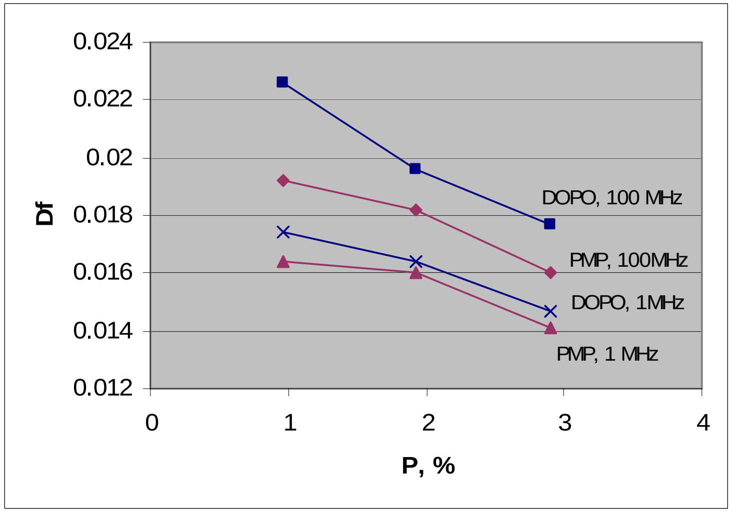
- Partially cured Fyrol®PMP <u>is hydrolytically less stable</u>



Electrical properties, Dk and Df

- Increase of phosphorus concentration independently of source (DOPO or PMP) is beneficial
  - decrease Dk and Df with P content.
- Both Dk and Df for CNE-PMP tend to be lower than for CNE-DOPO.





Conclusions (I)

- A new halogen-free flame retardant curing agent, PMP, is a polymeric phosphonate which is reactive with epoxy resins.
- Because of specific curing mechanism PMP provides exceptional thermal stability, which is important for lead-free soldering
- PMP can be applied either alone or in combination with co-curing agent
- DOPO is a monofunctional reagent and it <u>must be pre-reacted</u> with a multifunctional epoxy resin.
- PMP <u>can be pre-reacted</u> with epoxy resin, but this is not necessary
- Because PMP is a multifunctional cross-linker, it allows achieving very high Tg, which may satisfy even FR-5 type laminates.

Conclusions (II)

- Both PMP and DOPO are efficient flame retardants and provide V-0 rating at similar P content (1-2 wt. %)
  - Because the phosphorus content of PMP (17.5 wt. %) is higher than that of DOPO (14.3 wt. %), PMP is effectively used at lower loading level
- Electrical properties of both PMP and DOPO epoxy formulations are in the range of common FR-4 laminates.
- Water absorption of PMP is marginally higher than water absorption of DOPO, which is due to the incomplete reaction of PMP
  - Can be improved by proper formulation and curing.

Postscript

- "Eventually the development for lead-free and halogen-free will fall together in one multi purpose material."
  - B. Hoevel, New Epoxy Resins for Printed Wiring Board Application, in Proc. Conf., Polymers in Electronics, Munich, January 2007.