P-Based Flame Retardants In Halogen-Free Laminates

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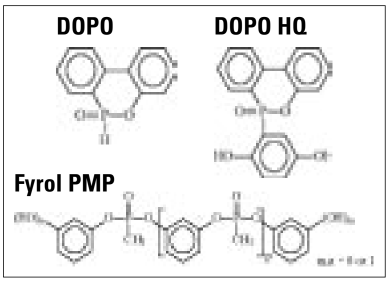
We take a look at the relative performance of two phosphorus-based flame retardants: the recently introduced poly (m-phenylene methyl phosphonate) (Fyrol PMP) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) the basis of many commercial halogen-free laminates. Although DOPO is a reactive flame retardant, it is monofunctional and means must be found to avoid reducing the crosslink density of the cured epoxy. Fyrol PMP on the other hand, is a very effective crosslinker and performs as a curing agent. Comparative study with five types of epoxy resins and four types of co-curing agents showed that both DOPO and Fyrol PMP 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 Fyrol PMP-based laminates are similar. Epoxy resins cured with Fyrol PMP show very high Tg which may satisfy FR-5 type laminates. Slightly higher water absorption of PMP-based laminates can be overcome by appropriate curing which results more complete 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 has performed well. Currently TBBA is undergoing risk assessment in Europe under new REACH legislation. Human health part of the risk assessment has been completed and it is favourable for TBBA. Because TBBA is reacted into the epoxy network, potential exposure to the chemical is very low. At the time of preparation of this article, environmental part of the risk assessment was not completed because additional studies have been commissioned to address the potential degradation of TBBA and the potential risk to sediment and soil.



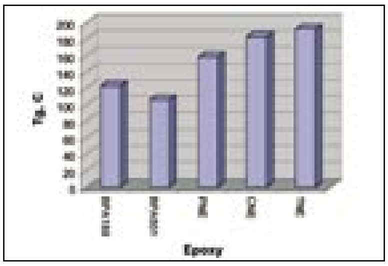
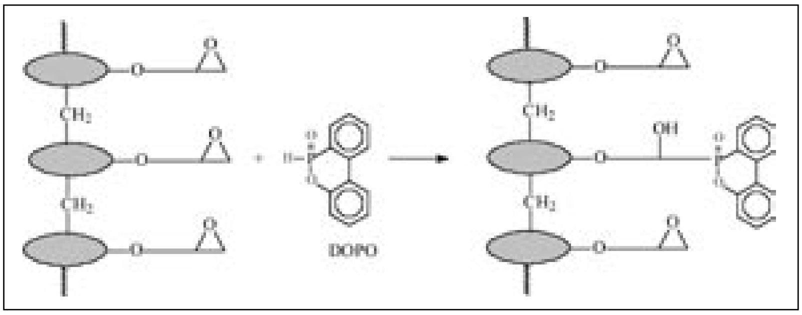


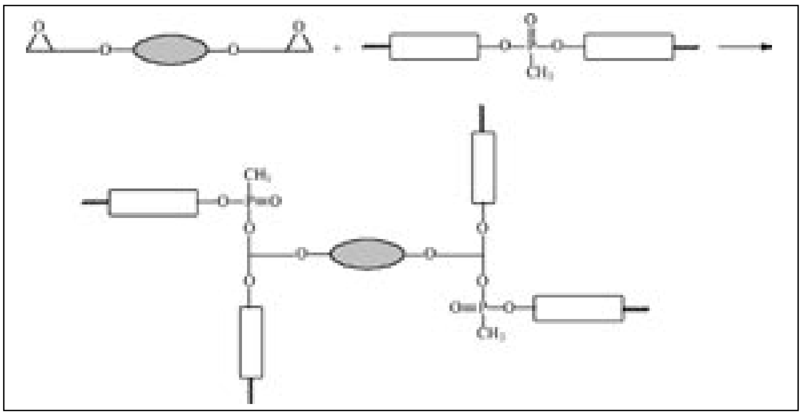
Figure 1 - Glass transition temperatures of various epoxy resins cured with stoichiometric amounts of Fyrol PMP at 200°C for 2 hours

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-phosphaphenanthrene-10-oxide (DOPO). This chemical was originally developed as a heat stabiliser, then it found commercial use as a reacted-in flame retardant in polyester fibres and about 10 years ago it was explored as a flame retardant in epoxies. DOPO is a reactive monofunctional molecule and it can be incorporated into the 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 reacting DOPO with quinone is marketed in Asia Pacific, mostly in Japan as DOPO-HQ. This product has similar



Scheme 1- Reaction of DOPO with multifunctional epoxy



Scheme 2 - Cross-linking of Bisphenol A type epoxy with Fyrol PMP

Property	Fyrol 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
Phsophorus	17.5 %	14.3 %
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	Monofunctional
Solubility	Soluble in MEK and acetone; Insoluble 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

Table 1 - Physical and chemical properties of Fyrol PMP and DOPO

Epoxy Resin		CNE-PMP	CNE-PMP
Complementary Hardener		DICY	PN
PCT (30 min)	Solder test (dips)	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

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

functionality as TBBA and can be used as a chain extender with difunctional epoxies. The 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 as Fyrol PMP. In contrast to DOPO or DOPO-HQ, Fyrol PMP is a multifunctional reactive flame retardant (with higher functionality than the -OH end groups would provide) and therefore it can be used either as a hardener or it can be pre-reacted with epoxy.

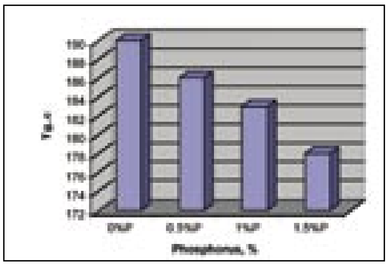


Figure 2 - Glass transition temperatures of CNE cured with DICY/Fyrol PMP at 185°C for 2 hours

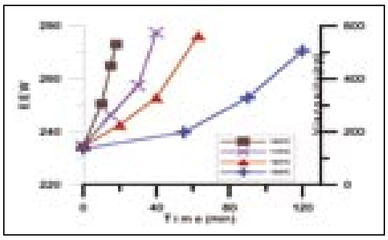


Figure 3 - Kinetics of pre-reaction of CNE with Fyrol PMP at 3 wt. % P content

Physical properties of phosphorus flame retardants

Some physical and chemical properties of Fyrol PMP and DOPO are listed in Table 1. Fyrol PMP is a colourless or slightly amber glassy low-melting (50-60°C) 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 Fyrol PMP 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 lower than that of Fyrol PMP. Since DOPO is insoluble 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 resulting resin is soluble in acetone or MEK.

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.

Although Fyrol PMP contains some terminal OH functional groups, its main reactive functionalities are phosphonate groups, where epoxy inserts in the presence of strong base catalyst. The curing mechanism is shown in Scheme 2. Every reaction of the phosphonate (P-O-C) with epoxy produces a branch in the polymer chain, which eventually becomes a crosslink. 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) Fyrol PMP should be regarded as a multifunctional. No aliphatic OH groups are formed in the course of reaction of Fyrol PMP with epoxy other than possibly from the reaction of the OH end groups with epoxy. This is very beneficial for the epoxy resin's thermal stability, since the thermal decomposition of cured epoxy usually begins with elimination of water from aliphatic OH groups, which further results in breaking of polymer chains.

Cured epoxy resins

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

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

Pre-reaction with CNE epoxy resin

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

Both Fyrol PMP and DOPO were prereacted with CNE epoxy resin at 3 wt. % P content and then for some experiments the 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 Tg temperatures for CNE-DOPO and CNE-PMP. Apparently, Fyrol PMP provides higher Tg.

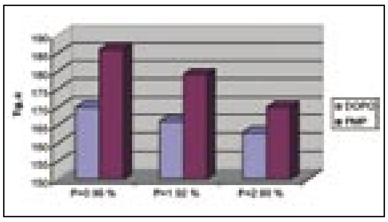


Figure 4 - Glass transition temperatures of CNE-DOPO and CNE-PMP cured with DICY at 185°C for 2 hours

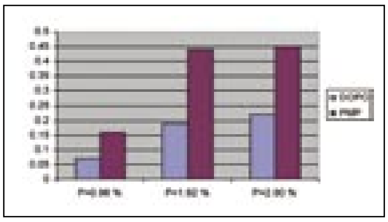


Figure 5 - Water absorption of CNE-DOPO and CNE-PMP cured with DICY

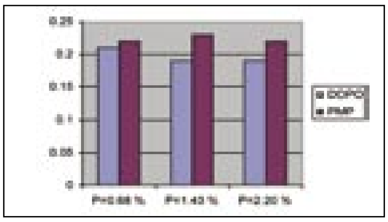


Figure 6 - Water absorption of CNE-DOPO and CNE-PMP cured with PN

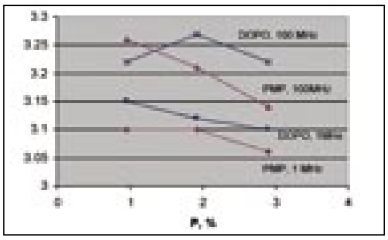


Figure 7 - D_k of CNE-DOPO and CNE-PMP cured with DICY

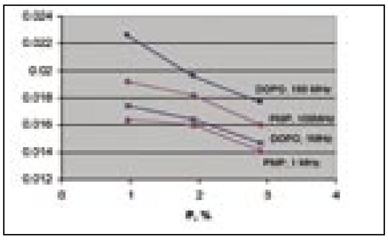


Figure 8 - D_f of CNE-DOPO and CNE-PMP cured with DICY

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. Fyrol PMP shows higher water absorption than DOPO. We believe this can be explained by incomplete reaction of Fyrol PMP with epoxy due to competition with more reactive DICY.

Tg temperatures of CNE-PMP and CNE-DOPO cured with phenol novolac (PN) range from 160-185°C depending on P content and are very similar for Fyrol PMP 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 Fyrol PMP, therefore its incorporation in epoxy is more complete and water absorption is lower.

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

Manufacturing laminates

Eight-layer glass cloth laminates were manufactured using CNE-PMP epoxy resin. P 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. The PN cured formulation has lower water absorption and as a result better performance in lead-free soldering; however, the Tg temperature of the PN-cured formulation is lower.

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