Flame Retardants for Epoxy Resins: Application related challenges and solutions

Baljinder K Kandola, Federico Magnoni and John R Ebdon

Institute for Materials Research and Innovation, University of Bolton, Deane Road, Bolton, BL3 5AB, UK

Abstract

Owing to their high versatility from chemical and processing perspectives and hence their capability of being tailored for required properties, epoxy resins are used in a wide range of applications ranging from general use to high performing materials. Most of the applications though also require conformation to certain specified fire safety regulations. The flammability (and other properties) of cured epoxy resins depend on the type of resin, curing agent and curing process used, which have been highlighted in this article. The focus of the review though is on the type of flame retardants required to achieve certain levels of flame retardancy. There are numerous research articles and reviews dealing with flame retardancy of epoxy resins in the open literature and it is beyond the scope of this review to cover them all, hence only selected representative papers are discussed here, while references to previous reviews are provided that cover additional work. Different flame retardants and their chemically modified/synthesized variants developed by various researchers have been critically reviewed in terms of their flame retardant efficiency relative to their commonly used/ commercially available counterparts. The issues related to their suitability in terms of processability and performance in certain applications have also been discussed.

Keywords: epoxy resin, flame retardants, flame retardant additives, flammability

1. Introduction

Epoxy resins are a special class of organic macromolecule capable of being inter- and intra-molecularly crosslinked to form a three-dimensional polymer network, and as such are the most versatile type of thermoset polymer. Although the term 'Epoxy' was first reported in 1934[1], the first epoxy resin (bisphenol A based) was developed in 1943[2] and licenced by Ciba Ltd for commercial use. Since then a number of epoxy resins have been developed, which can be cured (crosslinked) with a number of curing agents. Owing to their high versatility, low cost, high adhesiveness to many substrates, good heat and chemical resistances and excellent mechanical properties, epoxy resins are used in a wide range of applications ranging from low to high end in terms of performance, including as: adhesives[3,4]; protective and decorative coatings[5–7]; encapsulants and circuit boards in electronics[8–10]; components in biomedical systems[11,12] and structural materials, i.e., as composites in construction[13,14] automotive[15,16] and aerospace[17,18] applications. However, in terms of their consumption, the trend is opposite to that above as shown in Figure 1, i.e., the lower performing ones being consumed to a greater extent. The term 'Epoxy' as used today refers to both the resin, the basic liquid monomer component, and the cured end product.[19] The major commercial sources of the monomeric resins at present are the Huntsman Corporation Ltd and Hexion, while the curing agents can be sourced from a variety of chemical companies. There are many commercial formulators supplying complete epoxy resin systems by mixing resins/hardeners, modifiers, additives, fillers, etc.

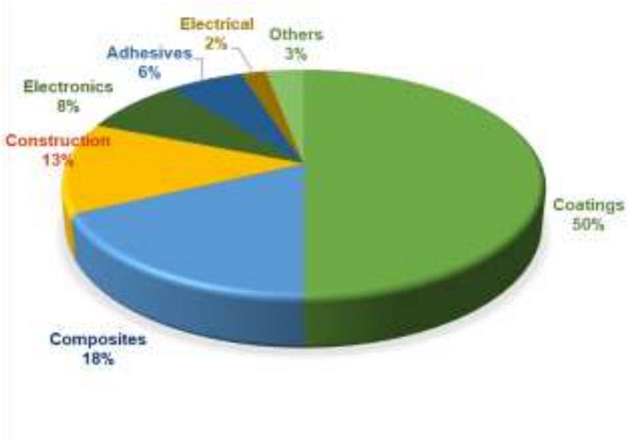
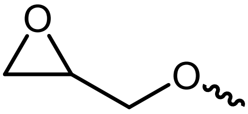


FIGURE 1 Comparison of epoxy market for epoxy resin by demand [20]

Epoxy resins, as the name implies, are a group of reactive liquid, or low melting solid, monomers that contain two or more epoxide or oxirane groups (Scheme I), capable of being cured into a three-dimensional network. The epoxide groups within a monomer usually are terminal, although they can also be present within the chain. The rest of the monomeric part can be aliphatic, cycloaliphatic or aromatic. These monomers can either be homopolymerized using appropriate catalysts, or can react with other monomers, called curing agents, such as polyfunctional amines, acids, acid anhydrides, alcohols or thiols[21–23]. With such a generic structure and so many variables, a large number of cured epoxy resins with required properties can be produced. The quantity of the hardener (curing agent or catalyst) used is calculated from the "*epoxide equivalent weight*", which is the ratio between the molecular weight of the monomer and the number of epoxide groups. Epoxies are typically cured with stoichiometric or near-stoichiometric quantities of hardener to achieve the best physical properties. By appropriate selection of curing agents, epoxies can be cured over a wide temperature range from room temperature to ~230 °C. Since each part of the chemical structure contributes to specific properties, e.g, the number of epoxide groups determines the functionality and hence the cross-linking capacity of the resin, hydroxyl or other polar groups within the monomer structure determine its reactivity, and the choice of curing agent determines its heat stability, etc., desired properties can be easily obtained. Commercial applications are dependent on these properties, hence it is important to consider the basic structures before discussing the properties.



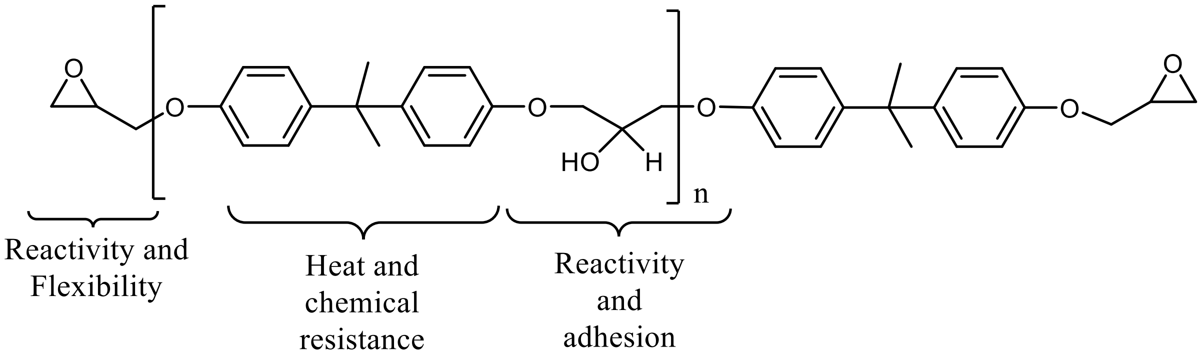
SCHEME 1 Structure of the epoxide group

1.1. Chemistry of epoxy resins

Most of the commercially available epoxy resins are glycidyl-based, produced by reaction of epichlorohydrin with either acidic hydroxyl group (of polyether polyols, aliphatic diols, phenolic or dicarboxylic acids) or nitrogen (of an amine or amide) containing chemicals, followed by dehydrohalogenation. It is beyond the scope of this review to discuss the epoxies produced by other routes as well as all the glycidyl-based epoxies produced from different hydroxyl/nitrogen containing chemicals, so only selected ones, of commercial and/or academic interest and industrial importance are discussed here. For other resin types, the reader is referred to general reviews on epoxy resins.[23–26] The most commonly used reactants for commercial applications are phenols, namely bisphenol A and novolacs, and aromatic amines; hence these are discussed here in more detail.

Bisphenol A based: The most common commercial resin, the diglycidyl ether of bisphenol-A (DGEBA), is formed by the reaction between bisphenol A and epichlorohydrin in the presence of a basic catalyst, and currently commands a 75% share of the epoxy-resin market. [27] Because of its widespread use, the term "DGEBA" has become synonymous for epoxy resin in many spheres. The ratio of epichlorohydrin to bisphenol A determines the epoxide equivalent weight and hence the crosslinking capacity of the resin. Generally, an increase in the relative amount of bisphenol A results in the formation of high molecular weight polyethers with glycidyl end groups and the resin as a consequence becomes closer to being a thermoplastic.[23] Low-molecular-weight molecules tend to be liquids and higher-molecular-weight molecules tend to be more-viscous liquids or solids.[25]

The structure of the DGEBA resin is presented in Scheme 2. As mentioned above, the relative numbers of epoxy and hydroxyl groups depend upon the relative amounts of epichlorohydrin and bisphenol-A used in the preparation of the resin. In Ref[27] the properties contributed by different chemical groups are explained very well. The epoxy groups at the end of the chains and the hydroxyl groups within the chain determine the reactivity towards curing agents. The ether linkages in the main chain provide chemical-resistance and elasticity. The phenylene rings in bisphenol A provide chemical-resistance, adhesiveness, durability, heat-resistance and excellent electrical properties. The coexistence of hydrophilic groups with hydrophobic groups in the molecule significantly increases the adhesion to various adherends.



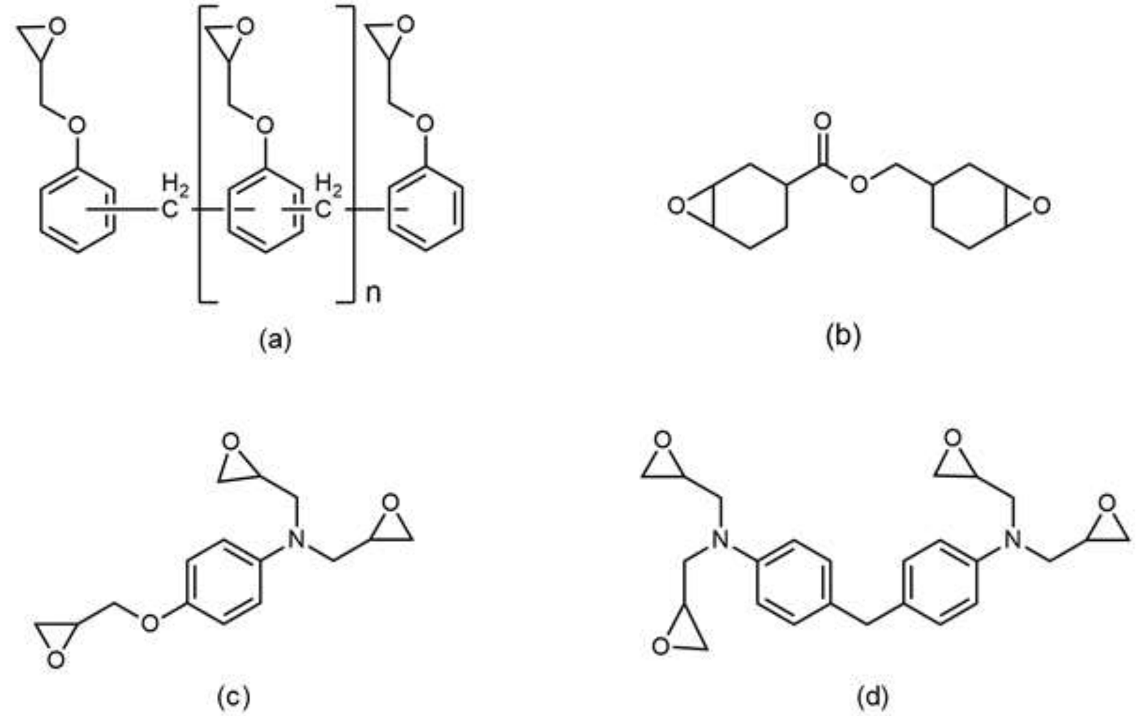
SCHEME 2 Structure and properties of DGEBA based epoxy resin [Adapted from Ref[27]]

DGEBA based epoxies as commonly encountered are low viscosity, room temperature curing resins, and hence are easy to use. Moreover, they have good mechanical properties when cured, and good chemical resistance, making this type of resin very popular.

In addition to bisphenol A, other bisphenols of interest are bisphenol F and halogenated bisphenols. While bisphenol F based resins have similar properties to bisphenol A ones, halogenated bisphenols are inherently flame retardant, and hence are used as co-reactants in epoxy resins for better fire retardancy. Tetrabromobisphenol A (TBBPA) or its diglycidyl ether, 2,2-bis[3,5-dibromo-4-(2,3-epoxypropoxy)phenyl]propane, is commonly used as a reactive flame retardant in epoxy resin circuit boards. Fluorinated epoxy resins are also used for flame retardant applications as well as a wetting agent for glass fibres, but owing to their high cost and low T_g, their commercial use is limited.

Novolac based: The reaction of epichlorohydrin with novolac phenolics of different types produces epoxyphenol novolacs with functionalities ranging from 2.5 to 6.[24] The chemical structure of a typical resin is shown in Scheme 3.

Phenolic resins are known char formers with lower flammability than standard epoxies. However, the thermal stability and flammability of an epoxyphenol novolac depends on the novolac content and the type of curing agent used. When cured with a room temperature-curing system, these resins have similar thermal stability to ordinary bisphenol A type epoxies. However, for resins with higher phenol content and cured with high-temperature hardeners, both thermal degradation stability and heat deflection temperatures are considerably improved.[24] Their main applications are as heat-resistant structural laminates, “electrical” laminates resistant to solder baths, chemically resistant filament-wound pipe, and high-temperature adhesives.[24]



SCHEME 3 General structure of (a) epoxyphenol novolac with *n* usually in the range from 0 to 4, (b) cycloaliphatic epoxy, (c) triglycidyl-*p*-aminophenol (TGPAP) and (d) *N*,*N*,*N*′,*N*′-tetraglycidyl-bis-(4-aminophenyl)-methane (TGAPP)

Aliphatic resins: Aliphatic epoxy resins are produced either by epoxidation of aliphatic compounds containing double bonds (cycloaliphatic epoxides and epoxidized vegetable oils) or by reactions with epichlorohydrin (glycidyl ethers and esters).[28] The cycloaliphatic epoxy resin is the most popular resin (Scheme 3(b)), which with an aliphatic backbone and a fully saturated molecular structure, offers good UV stability, thermal stability and electrical properties.[29] Hence, it is used to fabricate structural components requiring application in high-temperature environments.[29]

Glycidylamine based: Glycidylamine epoxy resins are higher functionality epoxies produced by reacting epichlorohydrin with aromatic amines. Two commonly used commercially available resins are triglycidyl-*p*-aminophenol (TGPAP; functionality 3) and *N*,*N*,*N*′,*N*′-tetraglycidyl-bis-(4-aminophenyl)-methane (TGAPP; functionality 4). The structures are shown in Scheme 3 (c) and (d).

Owing to the higher functionality, these are highly reactive and on curing form highly cross-linked structures. Properties such as high temperature resistance, high T_g, chemical resistance, lower flammability and superior mechanical properties of the resulting cured network make them ideal candidates for aerospace composite applications. Moreover, low viscosity at room temperature and relatively high curing temperatures make them ideal candidates for making prepregs (impregnated reinforcing fibres/fabrics with resin and semi-cured, and stored on release paper), a technique used for fabrication of high performance aerospace composites. The only disadvantage is their brittleness; to reduce this they are blended with thermoplastic resins such as polyether sulfone, polyetherimides, or poly(ether ketones). Flammability of these resins is also lower than other commodity thermoplastic polymers, hence these to do not adversely affect the flammability of the resins.

Biobased: An emerging trend for producing epoxy resins is by epoxidation of precursors from renewable sources, such as carbohydrates, starch, proteins, fats, and oils.[30–32] Amongst these, epoxidized vegetable oils (multi-component mixtures of different triacylglycerols) have a good potential as inexpensive, renewable materials for industrial applications.[25]

1.2. Curing agents

Epoxy curing agents, also referred as hardeners, play a crucial role in the final characteristics of the cured material. Indeed, all the characteristics that are strictly related to the cross-linking density of the polymeric network, such as hardness, chemical resistance, heat resistance, flexibility and brittleness, can be controlled by the hardener. Curing agents can react either with the epoxy groups or the hydroxyl side groups. Curing agents cross-link epoxy resins either by a catalytic mechanism or by bridging across epoxy molecules. Some curing agents may involve both the catalytic and cross-linking mechanisms.[24] Common classes of hardeners for epoxy resins include amines, acid anhydrides, phenols and thiols. For details about different curing agents, the reader is referred to other reviews.[24–26,33] In terms of reactivity these can be ranked as: phenol < anhydride < aromatic amine < cycloaliphatic amine < aliphatic amine < thiol. The most popular choices are amines and acid anhydrides.

Amines are an important class of curing agents. Aliphatic, cycloaliphatic or aromatic amines can be used, which are mainly selected according to the application. In general, the order of reactivity is aliphatic amines > cycloaliphatic amines > aromatic amines. Lower reactivity allows longer working times for processors. Thermal stability of the cured resin also increases in the same order; aromatic amines form much more rigid structures than aliphatic amines, hence more thermally stable and/or less flammable materials. The primarily aliphatic amines provide fast-curing hardeners for use at room temperatures. Amines though are skin irritants.

Acid anhydrides: These are less skin irritant than amines[24] and less reactive, hence the cure exotherm is lower. Some examples include phthalic, hexahydrophthalic, chlorendic, and maleic anhydrides.

Other cross-linkers of interest are amides (e.g., polyamides), and complexes of boron trifluoride and amines, such as monoethylamine. Phenols, such as novolacs, which have already been discussed above under resin systems, also act as curing agents. Thiols, also known as mercaptans, contain a sulfur atom which reacts very readily with the epoxide group owing to its nucleophilicity, even at room temperature. Owing to their very high reactivity, thiols are used where fast cure is required, e.g. for domestic DIY adhesives.

The epoxy curing reaction may be accelerated by addition of small quantities of accelerators; tertiary amines, carboxylic acids and phenols (e.g., bisphenol A) are effective accelerators.

2. Testing procedures and hazard assessments

While there are many techniques for assessing the flammability of polymers, the most commonly used laboratory methods for quantifying their flammability are limiting oxygen index (LOI)[34], UL-94[35] and cone calorimetry.[36] Since these three are mainly used in ranking differently flame-retarded resin samples, these techniques are discussed in more detail here.

LOI is a measure of volume percentage of oxygen in a mixed oxygen-nitrogen gas stream that will just support combustion of a polymer. In this test the upper end of a vertically held specimen in a chimney is ignited by a gas flame and the downward burning behaviour is observed. Since the test is performed at room temperature with top ignition, it is quite often criticised for not representing a realistic fire environment. The correlation of LOI with other fire tests such as cone calorimetry is also poor. [37] The test though is simple to carry out and shows high repeatability and reproducibility, hence is used mainly to rank polymers in order of flammability (or, strictly speaking, ignitability).

The UL-94 test, developed by the Underwriters Laboratory of the United States, is another simple test to determine a material's tendency to either extinguish or spread the flame, when exposed to a small flame of 20 mm height. This test also takes into account the dripping of the burning material. The results are provided in terms of a 'vertical classification', ranking from the highest to lowest performance as V0 (burning time <10 s, no flaming drips), V1 (burning time <30 s, no flaming drips), V2 (burning time <30 s, flaming drips igniting the cotton wool present below the sample); there are also a horizontal HB rating (self extinguishes or burning rate is < 76 mm/min for thickness < 3 mm) and a no rating, NR. Both LOI and UL-94 tests are the most important screening and quality control methods used in the plastics industries to characterize both the ignitability and flammability resistance. However, both tests are thickness dependent, with thicker samples more likely to give a higher LOI and a V0 rating.

A cone calorimeter is the most widely used bench-scale instrument to study reaction to fire properties of materials. It provides most of the fundamental combustion characteristics of materials under a wide range of radiant heat and ignition conditions. The radiant heat flux can be varied from 0 to 100 kW/m^2, providing a range of fire scenarios, although 25, 35 and 50 kW/m^2, corresponding to different stages of the fire growth are most commonly used. The choice of heat flux is usually related to end use application as different regulatory standards specify different external heat fluxes. For epoxy resins, researchers use either 35 or 50 kW/m^2, relating the former to requirements of the aviation industry and the latter to compartment (or room) fire scenarios in railway and building industries. It must be emphasized though that the 35 kW/m^2 external heat flux requirement in the US Federal Aviation Regulations (FAR)[38] for the aviation industry are for OSU calorimetry, not cone calorimetry, and that the 35 kW/m^2 heat flux in the former does not relate to a similar heat flux in the latter[39], hence caution should be exercised when relating cone results to the aviation regulations. The important derived parameters from the cone calorimetry include time-to ignition (TTI), time to flame-out (FO), peak heat release rate (PHRR), total heat release (THR), heat of combustion, mass loss, and carbon monoxide, carbon dioxide and smoke concentrations. TTI, PHRR and THR are the most important parameters used to assess fire hazards, e.g., PHRR/TTI can be used as a measure of the severity of the fire. The rationale for using PHRR/TTI as an indicator of flashover is that a short time-to-ignition (TTI) and a high peak heat release rate (PHRR) are considered important prerequisites for flashover to occur, with higher PHRR/TTI values associated with a greater propensity to flashover. The THR value reveals the total amount of heat that can be released by the fuel, i.e., the larger the value of THR, the more heat the material releases as it burns.[40] Amongst the different factors influencing cone results, the external heat flux used is the most important factor. In general, with increasing external heat flux, TTI is reduced and PHRR is increased; total heat release though is related to fuel load or polymer mass, and hence is less affected by heat flux. For detailed effects of external heat flux and other variables, including sample thickness, geometry, etc., on various cone parameters, the reader is referred to a cone calorimeter manual and other literature.[41,42]

In addition to these, during material development/modification stage, researchers use thermal analytical techniques, such as differential thermal analysis (DTA), differential scanning calorimetry (DSC) and thermogravimetry (TGA), from which temperatures at which different physico-chemical changes occur, can be accurately measured. The mass loss measurements from TGA give insight into the thermal stability of the material. These parameters can be used to estimate the flammability of the material, and to establish the mechanisms of thermal degradation and flame retardant action of additives.

In commercial applications, the product has to conform to certain specified regulations for a particular application. Standards vary from one sector to another and depend on the application area within each sector. There are some international (ISO) and EU standards, and in addition some countries have their own standards. It is beyond the scope of this review to collate all the information, though some information on fire standards is provided in a later section; for more details the reader is referred to other literature.[43]

3. Thermal stability and flammability of cured epoxy resins

The thermal stability of epoxy resins, as well as their flammability, depends on the structure of the epoxy monomer, that of the curing agent, and on the cross-link density. Improvements in crosslinking density contribute to improvements in heat-resistance, and thus resins with a short distance between epoxy groups, or multifunctional types of epoxy resin, have higher thermal stability and low flammability, as can be seen from Table 1, where tri (triglycidyl-p-aminophenol) and tetrafunctional resins (tetraglycidyl-4,4 diamino diphenyl methane), are demonstrably less flammable than bifunctional resins. It must though be noted that since the flammability data reported in Table 1 and in the rest of this review have been taken from different sources, tested samples may be of different thicknesses and probably of different dimensions. Since all fire tests are dimension and, in particular, thickness dependent, the comparisons should be treated with care and not used to draw absolute conclusions with regard to trends.

TABLE 1 The flammability performance of epoxy resins of different types and functionalities

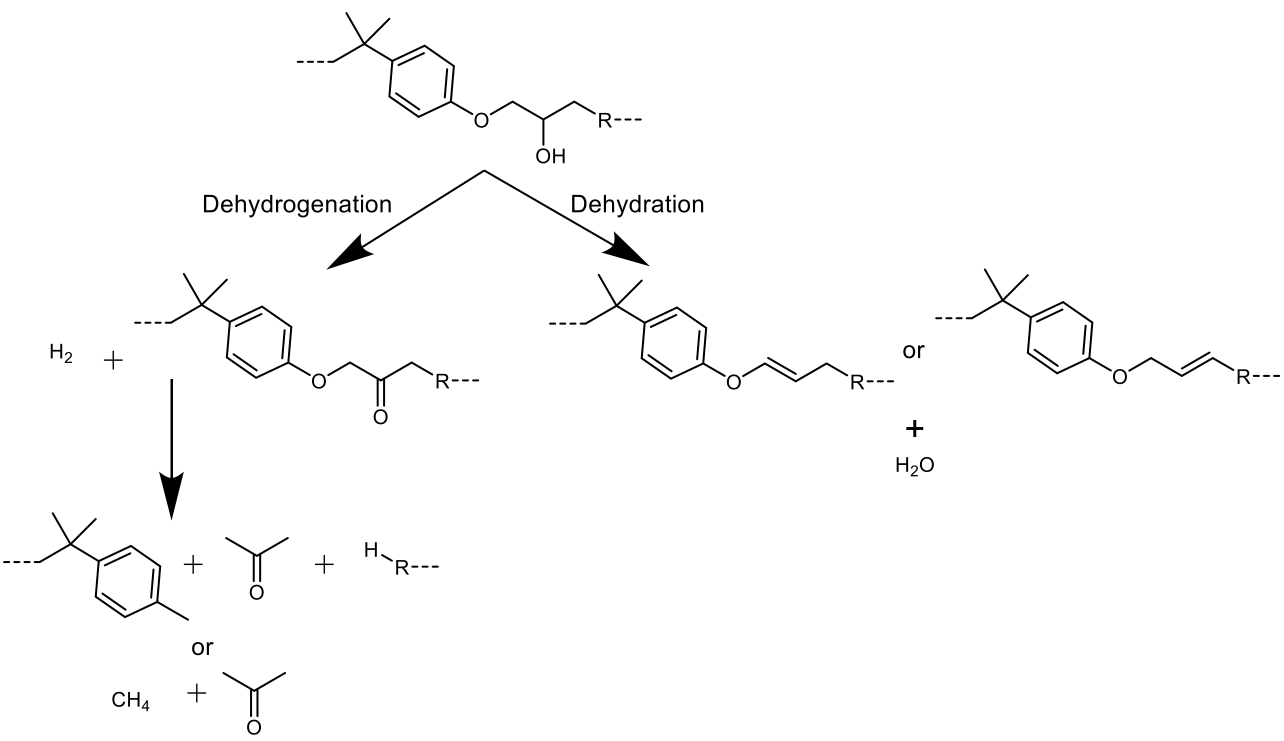
Resin	Curing agent	Thickness (mm)	LOI (%)	UL-94	Cone results at 50kW/m^2			Ref
					TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	
DGEBA	DDM	3	20.2	NR	-	-	-	[44]
DGEBF	DDM	3	20.7	NR	-	-	-	[45]
DGEBA/F	Amine		17.3	NR	45	1863	118	*
Novolac/1,4-butanediol diglycidyl ether	Polyamine	3	16.8	NR	58	1779	109	*
		3	21.5	HB	34	1861	77	[46]
Cresol novolac epoxy	Phenol novolac	-	21	NR	62	688	106	[47]
Epoxy novolac	Dicyandiamide	4	-	NR	51	682	110	[48]

Triglycidyl-p-aminophenol	DDS	3	24	HB/NR	33	1393	44.4	[49]
Tetraglycidyl-4,4 diamino diphenyl methane (MY721)	DDS	3	27.8	HB	24	823	56	[46]
Tetrabromobisphenol A epoxy resin	DDS	3	22.5	-	-	-	-	[50]
Tetraglycidyl methylendianiline (a monocomponent resin)	-	3	25	HB	35	1719	74.2	[51]

Note: DDM = 4,4′-diaminodiphenylmethane; DDS = 4,4'-diaminodiphenyl sulfone
* Unpublished results; ‘-‘ = information not available

Since catalytic curing agents (e.g. BF_3) are not built into the thermoset structure, they do not affect the flammability of the resin. Reactive agents, mostly amines, anhydrides or phenolic resins, on the other hand, are incorporated into the cross-links of these thermosets and hence strongly affect their flammabilities. Epoxy resins cured with amines and phenol-formaldehyde resins tend to produce more char than acid or anhydride-cured resin, hence the flammabilities of the former are lower than those of the latter, as can be seen from Table 2.

Cured epoxy resins undergo two step thermal degradation. The thermal degradation of a typical DGEBA epoxy resin is shown in Scheme 4. The first step (up to 400 ^{o}C) mainly involves dehydration of the material and formation of a polyaromatic structure. The second stage corresponds to a thermo-oxidative reaction which leads to complete degradation of the carbonaceous materials.[52] Early in the first stage of degradation, the reactions are mainly 'non-chain-scission', whereas, at higher temperatures 'chain-scissions' occur.[53] The most important non-scission reactions occurring in these resins are the competing dehydration and dehydrogenation reactions associated with secondary alcohol groups in the cured resin structures[53]:



SCHEME 4 Thermal degradation of DGEBA based epoxy resin

The main products are methane, carbon dioxide, formaldehyde, and hydrogen. Usually a large amount of methane is liberated before the start of scission reactions. During chain scission reactions the aliphatic segments break down into methane and ethylene (and possibly propylene) or acetone, acetaldehyde, and methane (and probably carbon monoxide and formaldehyde), all of which are flammable. From aromatic structures phenol is liberated, which is less flammable. For phthalic anhydride cured resins, phthalic anhydride is regenerated together with CO and CO_2.[53] Aromatic amine cured resins give large amounts of water in the temperature range 300-350 ˚C.[54] Thermal stability of aromatic-amine-cured epoxide resins depends on the aliphatic portion of the network.[55] However, the flammable volatiles outlined above are produced only in relatively small quantities and this, coupled with their cross-linked and related char-forming character, give rise to LOI values in the range 22-23.

The oxidative thermal stability of the polyaromatic structure formed in the first step determines the amount of char that is promoted in a particular cured resin. Char normally acts as a physical barrier for the heat flux coming from the flame to the surface of the thermoset but also as a diffusion barrier to the fuel flux from the polymer to the flame; therefore char formation is an important property of a thermoset, determining its flammability. The charring behaviour of an epoxy is determined by the nature of the aromatic groups in the resin. Moreover, the nitrogen content of the hardener plays a fundamental role, in that resins cured with amines tend to produce more char than anhydride-cured resin, as mentioned above.[53] In Table 2 the effect of hardeners on the combustion properties of a particular type of epoxy resin is shown by compiling results from different literature sources. As can be seen, most of the work has been on DGEBA resin cured with 4,4′-diaminodiphenylmethane (DDM) or 4,4'-diaminodiphenyl sulfone (DDS) hardeners. As can be noticed, there is a variation in results with each type. It must be noted that the flammability test results are always dependent on sample geometry, physical properties such as mass, density etc, environmental factors and operator, hence some variations in results from different laboratories are to be expected. Another factor is that in the literature quite often details of the resins are not provided, instead a generic term such as 'bisphenol A based epoxy resin' is cited, and the resin may have been a modified form of DGEBA. Despite this, in general it can be seen that resins cured with aliphatic amines and polyamides are more flammable than those cured with DDM or DDS.

The only publication available where effects of three hardeners, namely novolac, dicyanamide (DICY) and DDM on the flammability of a cyclolinear cyclotriphosphazene linked epoxy resin are compared, is by Bai et al..[56] Since the resin has been chemically modified with a phosphorus-containing chemical, all three variants had a V-0 rating, but from LOI values it can be seen that the resin cured with DICY is more flame retardant than that cured with DDM followed by that cured with the novolac.

TABLE 2 The flammability performance of epoxy resins cured with different curing agents

Resin	Curing agent	Thickness (mm)	LOI (%)	UL-94	Cone results				Ref
					TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	Tested at heat flux (kW/m^2)	
DGEBA	Polyamine	#	18.7	-	-	-	-	-	[57]
	Diethylenetriamine	3.2	20.6	NR	52	811	114.2	50	[58]
	Isophorone diamine	3	–	HB	50	1068	75.8	50	[59]
	DDM, 4,4′-diaminodiphenyl methane	3 (10^a)	26.4	NR	120	678	157.9	35	[60]
		3	26.4	NR	78	275	56.8	35	[61]
		3	20.2	NR	-	–	–		[44]
		3-3.2	24.7	NR	51	1420	143.6	50	[62]
		3	25.7	NR	71	654	100.3	35	[63]
		3.2	25.8	NR	59	1063	76.1	35	[64]
		3-4	22.8	NR	36	1026	83	50	[65]
		3-3.2	21.5	NR	70	1000	89	35	[66]
		3.2	–	NR	63	1321	157	50	[67]
		3	–	–	85	1653	129.9	35	[68]
		3	–	–	65	1730	113.1	35	[69]
		3-3.2	26.4	NR	56	1420	144	50	[70]
	DDS; 4,4'-diaminodiphenyl sulfone	3.2	32.5	V-1		825	71	50	[56]
		3-3.2	21.7	NR	63	619.8	77.6	50	[71]
		3-3.2	23	NR	61	893	112	50	[72]
		3-3.2	23	NR	50	860	112	50	[73]
	m-phenylenediamine	3	25	NR	45	855	112	50	[74]

	m-Xylylenediamine; triethanolamine catalyst	3	22.2	–	–	–	-		[75]
	Polyamide	3.2 (6[b])	19.6	NR	64	939	179	35	[76]
		3-3.2	19	NR	48	761	112	35	[77]
		3	19.3	HB	15	1334.6	100.1	50	[78]
	Polyethyleneimine+ Imidazol	3.2	23	NR	45	1074	45	35	[79]
	2-Ethyl-**4**-Methyl Imidazole	3.2 (6[b])	21.8	NR	32	781	107	50	[80]
	Phthalic Anhydride	3 (2[b])	21.5	NR	65	900	–	35	[81]
	Methyl hexahydrophthalic anhydride	4	20.2	–	86	1650	213	35	[82]
	Triarylsolfonium hexafluoro-phosphate	3	21	–		–	–		[83]
	bis(4-nitrophenoxy)phenyl phosphine oxide	-	34						[84]
	bis(3-nitrophenoxy)phenyl phosphine oxide	-	35						[84]
	Hyberbranched phosphate ester + triphenyl phosphine (curing accelerator	3	23	–	60	1250	–		[85]
Vinyltriethoxysilane modified DGEBA	DDM	3	22	V-1		–	–		[86]
Cyclolinear cyclotriphosphazene linked resin, CL-CTP	DICY (dicyanamide)	3.2	32.4	V-0		–	–		[56]
	DDM	3.2	31.6	V-0		–	–		[56]
	Novolac	3.2	30.2	V-0		–	–		[56]

Note: ‘-‘ = information not available; [a] = 10 mm thickness for LOI; [b] = 6 or 2mm thickness for cone test.

Rad et al[30] have reviewed the flammability of bio-based epoxy resins cured with different curing agents versus DGEBA based resin where the former are shown have high flammability.

4. Flame retardants for epoxy resins

As demonstrated in the section above, epoxy resins are highly flammable, and require to be flame retarded for applications where the products need to pass stringent fire tests. There could be two approaches to make them flame retardant: (i) structural modification of the resin and/or formulation, and (ii) incorporation of flame retardant chemicals (additives) during preparation of the formulation. Structural modification of the resin involves introducing the elements with flame retardant function into the molecular structure of epoxy resin or hardener, whereas flame retardant additives are added in the resin prior to adding hardener and curing process. The choice of flame retardant element (for structural modification) or compounds (as in additives) is between either one that works by a gas-phase mechanism, such as an halogenated species, or one that operates in the condensed phase, for example a phosphorus-containing species that may react with the polymer during pyrolysis and, in so-doing, catalyse the formation of a protective char. There are many reviews available on using FRs for epoxy resins[30, 87–90] and hundreds of journal articles. A search of the Science Direct and Web of Science databases for publications that addressed additive or reactive flame retardants in the context of epoxy resins, found over 8,000 patents, 1,800 journal articles and over 80 reviews of some relevance, although of these a relatively small number were highly cited. It is beyond the scope of this review to cite every paper in this area, only selected salient ones covering specific properties are included.

For structural modification of the resin, as demonstrated in above section, by using appropriate resin/hardener combinations, reduced flammability can be achieved. The combinations can be further tailored by modifying one component to contain a flame retardant element such as phosphorus and/or nitrogen, halogen or silicon. Phosphorus-containing diamine compounds are generally used in the modification of epoxy resin. Examples include (bis(4-aminophenoxy)phenyl phosphine oxide and bis(3-aminophenyl)phenyl phosphine oxide utilized as curing agents by Liu et al.[84], resulting in an LOI of about 35 vol%. Yang[91] et al. used a polyphosphazene (PBFA), synthesized from N-aminoethyl piperazine and hexachlorocyclotriphosphazonitrile, which helped in reducing flammability and smoke production. Chen[85] et al. synthesized a novel hyperbranched phosphate and used it as a curing agent, which helped in achieving an LOI of 27.5%. Sponton et al.[92] prepared an epoxy based on diglycidyl ether of (2,5-dihydroxyphenyl) diphenyl phosphine oxide, which demonstrated improved flame-retardant performance. Wang's group have synthesized a series of flame-retardant epoxy resins with cyclolinear cyclotriphosphazene-linked structures[56], phenol-substituted cyclotriphosphazene[93] and spirocyclic phosphazene-based structures[94], which gave UL-94 V-0 ratings and LOI values > 30%. Siloxanes are good flame retardants, which can be easily used for modification of epoxy resins. A cycloaliphatic 1,3-bis[3-(4,5-epoxy-1,2,3,6-tetrahydrophthalimido) propyl] tetramethyldisiloxane was synthesized by Tao et al.[95] with better thermal stability than conventional cycloaliphatic epoxies. A siloxane- and imide-modified epoxy was synthesized and cured with siloxane-containing dianhydride by Li et al.[96] for higher thermal stability. While the authors have not studied the flammability of these resins, these are expected to have lower flammability than the unmodified epoxy resin.

Similarly curing agents can also be modified. Jiao et al.[97] studied the effect of different phosphate esters on the flammability of an epoxy resin (see Table 3), where significant reduction in PHRR with respect to the control (epoxy cured with an amine based curing agent) sample is seen. Xu et al.[98] synthesized the flame-retardant curing agents 1-(diphenylphosphinyl)-1H-imidazole oxide (DPPIO) and diphenyl 1H-imidazol-1-ylphosphonate (DPIPP) for use in epoxy resins. With only 15 wt% addition of DPPIO, the LOI of the cured sample increased to 37-38% compared to 21.0% for the control sample, and gave a UL-94 V-0 rating at 1.6 mm thickness. Dong et al.[99] synthesized a reactive-type flame retardant, 10-(hydroxy(4-hydroxyphenyl)methyl)-5,10-dihydrophenophosphazinine-10-oxide (HB-DPPA) and used it as a co-curing agent with 4,4- diaminodiphenylmethane (DDM) for curing diglycidyl ether of bisphenol A (DGEBA), the cured epoxy achieves UL-94 V-0 rating with an LOI of 29.3%.

TABLE 3 Cone calorimetric results of DGEBA based resins containing different flame retarded curing agents at 50 kW/m^2 heat flux (data taken from[97])

Curing agent	Resin/curing agent ratio (w/w)	TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)
Phenolic modified amine	80/20	67	980	128
Butyl phosphate ester	66.7/33.3	35	203	87
Ethylphosphonate ester	66.7/33.3	76	305	80
Butanediol and butanol mixed phosphate ester	66.7/33.3	76	300	83
Butanediol and octanol mixed phosphate ester	66.7/33.3	79	297	91
Hexanediol and butanol mixed phosphate ester	66.7/33.3	82	283	88

Note: Sample thickness = 3mm

Flame retardant additives, which are the focus of this review, are added to the resin prior to curing and, depending on the additive type, mixing needs to be done at a high shear for good dispersion. With high shear air bubbles can be created, meaning the resin needs degassing before the curing process. Flame retardants usually contain halogen, phosphorus, nitrogen, boron, silicon or metallic elements, either alone or in a combination of two or three elements. Carbon or silicon based nanoparticles are also used for flame retardant applications, mostly in combination with conventional FRs. Quite often two or more FRs are used for synergistic action. While reviewing the literature it was noted that all the available reviews cite all the epoxy resins as one category, i.e., there is no compilation of the type of resin and how flame retardants affect different types, which we have tried to address in this review. Another gap in the literature, apart from our own work, is the study of the effect of the FRs on the crosslinking density of the resin, which would affect both the mechanical properties and the thermal stability of the resin.

4.1 Halogenated flame retardants

Despite all the environmental issues raised regarding usage of halogenated flame retardants, they constitute a major share of the FR market. Halogenated flame retardants operate in the vapour phase through free-radical scavenging mechanisms. The largest single halogenated FR for epoxies, costwise, is tetrabromobisphenol-A (TBBA), used predominantly in printed circuit boards. TBBA is used as a reactive FR since both hydroxyl groups of TBBA can be reacted with epichlorohydrin to form the diglycidyl ether of tetrabromobisphenol-A. This resin is commercially available. Alternatively it can be incorporated into the epoxy resin by ‘chain extension’. Special chain extension catalysts such as triphenylphosphine, or ethyltriphenylphosphonium acetate can be used.[88] The amount of TBBA used is usually such that the finished resin will contain about 18–21% bromine.

While commercial halogenated flame retardants are still being used (as discussed above) and are being further developed by the industrial sector to meet the EU's REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) requirements, owing to environmental issues related to their usage, there is no new academic development in this area. While carrying out the literature search, very few papers dealing with halogenated flame retardants on their own were found; current work tends to concentrate on phosphorus, nitrogen and silicon based flame retardants, which are discussed in more details in the following sections.

4.2 Inorganic flame retardants

Metal hydrates: Aluminium trihydrate (ATH) is the most widely used polymer flame retardant, comprising ~38% of total FR consumption worldwide, due to its versatility and low cost. Since during its endothermic decomposition it produces water vapour, which act as coolant for the decomposing polymer, it is considered as an environmentally safe FR. However, to be effective enough to provide a UL94 V0 rating for the epoxy, it is needs to be used at ≥50 wt%, depending on the resin type and the sample thickness. Our work has shown that for a novolac based epoxy resin plaque of 3.5 mm thickness, 50% ATH is required to achieve a V-0 rating (see Table 4). However, for electrical or electronics application where very thin films are required, ATH at about 120–160 wt.% relative to a phenol-formaldehyde (novolac) resin, would be required.[100] At such high loading levels mechanical properties are seriously impaired as seen from Fig. 2, where even with 30% ATH flexural and tensile properties are significantly reduced compared to those of the control epoxy resin. Magnesium hydroxide (MDH) can be used, but is not preferred over ATH owing to higher cost. This also would require high loadings to be effective. In order to reduce ATH level, other FRs such as red phosphorus can be used; this is very effective in combination with ATH or MDH, as seen from Table 4, where with 25% ATH and 8% red P, a V-0 rating could be achieved. Similar results are reported by Toshiba, where 4% encapsulated red P in a phenolic resin in combination with 25% ATH could achieve a V-0 rating[101] Since ATH is not a reactive FR, it is not cost effective to use a chemically modified or encapsulated version of this as a FR. Pan et al. however, encapsulated ATH with DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) and named it ATH-DOPO, 20 wt% of which produced a V-O rating.[102] They also synthesized a novel honey-comb like mesoporous ATH (pATH) and encapsulated this with DOPO (pATH-DOP), 10 wt% of which could achieve a V-O rating.[102]

TABLE 4 Flame retardancy performance of different inorganic flame retardant additives in an novolac based epoxy resin

Sample	Thickness (mm)	DMTA results		LOI (%)	UL-94	Cone results at 50 kW/m^2		
		Storage modulus at 40°C (MPa)	T_g (°C)			TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)
Epoxy control	3.2-3.4	3487	121	21.8	Failed	45 ±1	3032 ± 394	105.8 ±13.9
Epoxy + ATH 30%	2.0-3.2	4041	101	22.3	Failed	32 ±6	780 ±27	61.7 ±2.5
Epoxy + ATH 50%	5.0	-	-	-	V-0	-	-	-

Epoxy + RP8% + ATH 25%	2.6-2.8	2747	84	27.8	V-0	18 ±5	522 ±56	49.9 ±2.4
Epoxy + APP 25%	2.9-3.0	4069	114	42.5	V-0	19 ±6	215 ±22	39.3 ±6.2

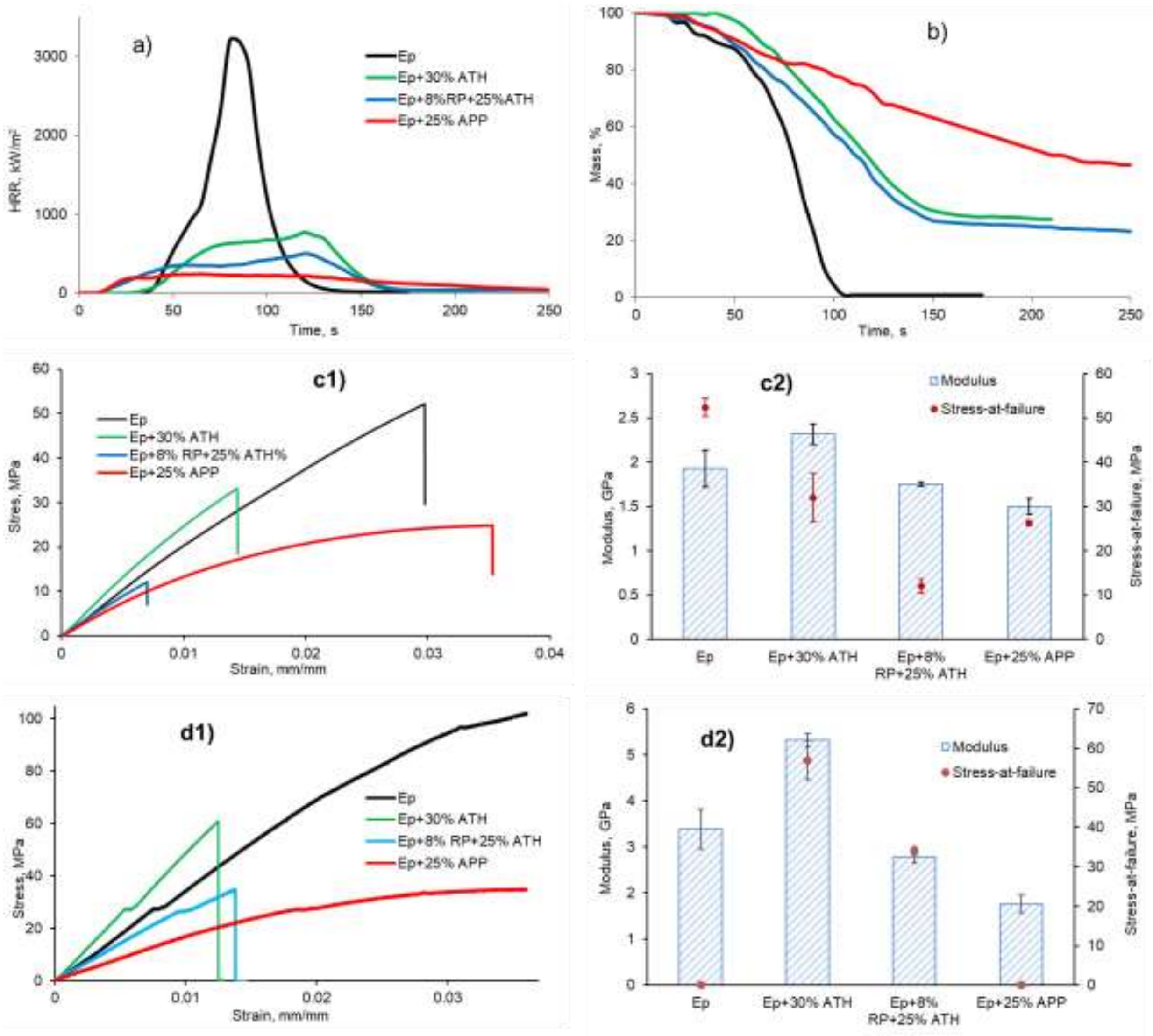


FIGURE 2 Flammability and mechanical performances of epoxy resins containing selected inorganic FRs: Cone calorimetric results at 50 kW/m^2 heat flux, a) HRR vs time, b) mass loss vs time; c) tensile and d) flexural test results for epoxy samples tested using a 50 kN load cell, crosshead speed 3 mm/min

Phosphorus based: Red phosphorus (RP) acts as an effective flame retardant in polymers, including epoxy resin. It works in the vapour phase by producing P_2 molecules, which are active gas phase species.[103] RP powder is difficult to handle as it is flammable, however when

incorporated into a polymer, is safe to use. Commercially masterbatches of RP in epoxy are sold.
We have tried adding RP to a novolac based epoxy resin, and could easily add up to 15% P, however higher concentrations interfered in the curing process. With ~11% P, 5mm thick sample achieved a V-0 rating, whereas with 15% add-on, a 3mm sample failed the test. This is because it is easier to achieve V-0 rating in thicker samples than in thinner ones. However, by using 8% RP with 25% ATH, a V-0 rating could be achieved (see Table 4).

Inorganic phosphates, namely ammonium polyphosphate (APP), melamine phosphate (MP) and melamine pyrophosphate (MPP) are the most commonly used FRs in epoxies, and are very efficient. In general, all phosphorus-based flame retardants (with the exception of RP), including inorganic phosphates, mainly function in the condensed phase by forming phosphoric acid during thermal degradation, phosphoric acid forms polyphosphoric acid. Phosphoric acid and polyphosphoric acid catalyse the dehydration reaction of terminal hydroxyl functions and the released water dilutes the gas phase. The dehydration of the epoxy structure induces cyclization, cross-linking, and aromatization/graphitization resulting in a carbonaceous layer acting as a barrier against oxygen, pyrolysis gases, thermal feedback, smoke, and products of incomplete combustion. Polyphosphoric acid on further heating forms a pyrophosphoric structure, a molten viscous surface layer protecting the polymer substrate against flame and oxygen, and hence acting as a thermal insulator.

The most used phosphate based FR is APP. In the literature there are many examples of using APP, but as can be seen from Table 2, different researchers have reported different additive levels in DGEBA based epoxy resin to achieve UL-94 V-0 rating, which could be due to the different types of resin/hardener as well as the APP used in the different research works. In our work with 25% APP in a novolac based epoxy, a V-0 rating could be achieved. Its high effectiveness compared to ATH with or without RP can be seen from Table 4 and Figure 2.

TABLE 5 Flame retardancy performance of different unmodified and modified ammonium polyphosphates in DGEBA based epoxy resins (adapted from Ref[90])

Flame retardant	Add-on (wt%)	Thickness (mm)	LOI (%)	UL-94	Ref
APP	21	3-3.2	33	NR	[104]
	15	3	36	V-0	[105]
	12	3-3.2	31.9	V-0	[106]
	5	3.2	27.1	V-0	[76]
Modified APP					
Ethanediamine-modified (EDA-APP)	21	3-3.2	33	V-0	[104]
Branched polyethyleneimine- modified (PEI-APP)	15	3.2	29.5	V-0	[79]
Piperazine-modified (PAz-APP)	10	3.2	29	V-0	[107]
Diethylenetriamine-modified (DETA-APP)	10	3.2	28.5	V-0	[108]
Polystyrene encapsulated (PS-APP)	20	3.2	28.7	V-1	[109]
Glycidyl methacrylate microencapsulated (GMA-APP)	15	3	38.5	V-0	[105]
Encapsulated with an inorganic-organic hybrid coating (MAPP)	12	3-3.2	32.5	V-0	[106]
Melamine coated (Mel-APP)	20	2.5	32.6	V-0	[110]

APP and other such inorganic phosphates have poor compatibility with epoxy resin, and although they can be dispersed by mixing at high shear, they will settle down at the bottom, if left for a while. This is not a big issue for fast curing resins bifunctional, e.g., DGEBA and novolac based resins,as the gel time is low and the resin starts curing before the FR particles can start separating. However, the problem is worse for slow curing resins such as tri or tetra functional ones, as shown in our work on a tetrafunctional epoxy resin (tetraglycidyl-4,4 diamino diphenyl methane (MY721, Cytec), where we incorporated different concentrations (4 and 8 wt%) of a variety of inorganic and organic FRs.[49] The inorganic FRs included APP, MP, MPP, phosphorylated pentaerythritol (Int1), phosphorylated pentaerythritol plus melamine (Int2). It was observed that during the curing process, all inorganic FRs settled on the bottom of the resin plaque (see Figure 3[49]], indicating the problem of dispersion in the resin. All organophosphates mixed well with the epoxy resin and did not settle down on the bottom of the plaque indicating better compatibility with the resin. We also studied the effect of FRs on the curing; all FRs affected the curing temperature of the resin slightly, but in each sample >90% curing was achieved.[49]

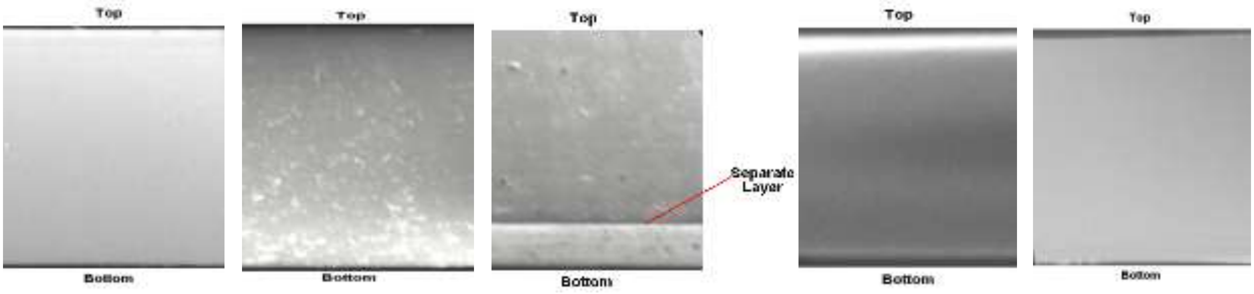
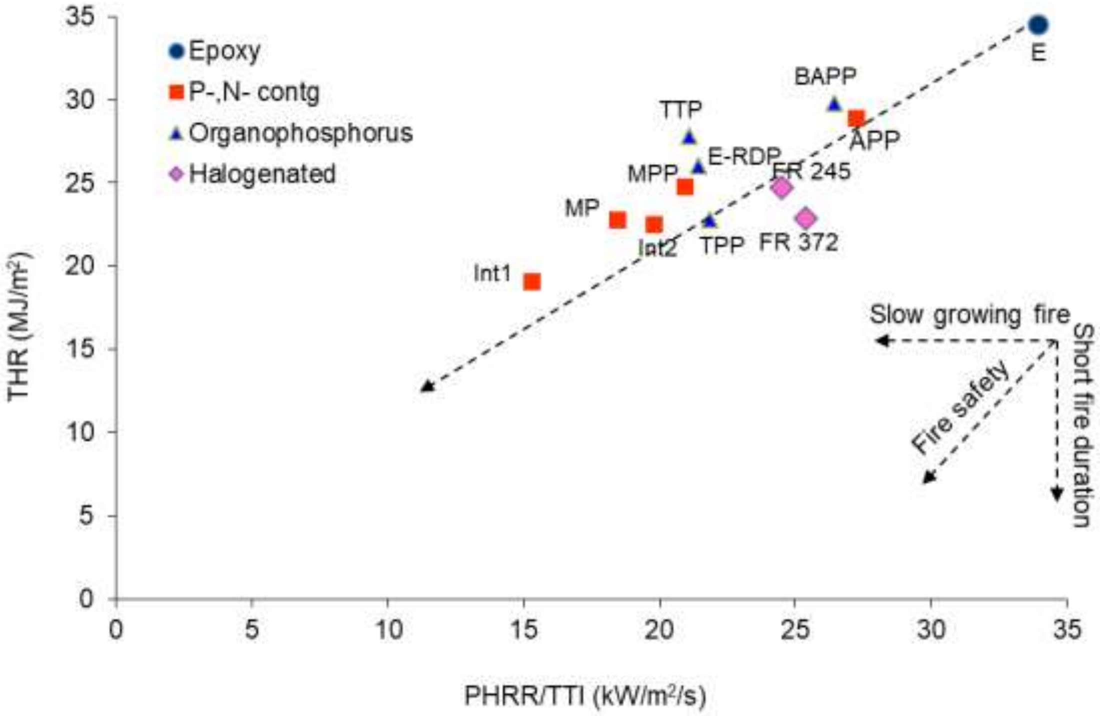


FIGURE 3 SEM images of cross-sections of control and 8% flame retardant containing cast resin plaques: (a) epoxy resin, (b) epoxy + 8% melamine pyrophosphate, (c) epoxy + 8% phosphorylated pentaerythritol, (d) epoxy+ 8% resorcinol bis-(diphenyl phosphate), RDP, and (e) epoxy + 8% tris(tribromophenyl)cyanurate, FR 245 (taken from Ref[49] with permission)

To compare the efficiency of APP with other inorganic phosphorus containing FRs, limiting oxygen index, UL94 tests, and cone calorimetry were conducted. At 4 and 8 % levels, only MPP, gave rise to a V1 UL-94 rating, whereas all other samples failed the test. The cone results at 50 kW/m^2 radiant heating are summarised in Figure 4 where the total heat release (THR) against the fire growth rate values, calculated by dividing peak heat release rate (PHRR) by time-to-ignition (TTI) is plotted. Fire safe materials should have low THR and fire growth rate value (PHRR/TTI), hence the samples with the high fire safety should fall close to the coordinates (0,0) on the 2-D plot. From this it can be seen that it is the intumescent formulation, Int1, that performs the best, with Int2 not far behind, probably because they contain pentaerythritol, a char-forming component.



Note: APP= ammonium polyphosphate, MP = melamine phosphate, MPP = melamine pyrophosphate, Int1= phosphorylated pentaerythritol, Int2 = phosphorylated pentaerythritol plus melamine, TPP = triphenyl phosphate, TTO = tritolyl phosphate, RDP = resorcinol bis-(diphenyl phosphate), BAPP= bisphenol A bis(diphenyl phosphate), FR372 = tris(tribromoneopentyl) phosphate, FR245 = tris(tribromophenyl) cyanurate.

FIGURE 4 Fire safety diagram, i.e. plot of total heat released (THR) vs. peak heat release rate (PHRR) divided by time to ignition (TTI), for epoxies containing 8 wt% of various fire retardants based on cone calorimetric data recorded with 50 kW/m^2 radiant heating [adapted from Ref[49]]

In order to improve the compatibility of inorganic phosphates with epoxy resin, they can be surface modified chemically or can be microencapsulated. An example in the literature of surface modification is treatment of APP with branched polyethyleneimine (PEI)[79], which enhanced compatibility between APP and the resin. The modified resin at 15 wt% level of FR had an increased LOI of 29.5%, achieved a UL-94 V-0 rating and THR was decreased by 76% compared to that of the neat epoxy resin. Microencapsualtion of APP, both for improved flame retardancy and hydrophobicity, has been reported in literature. An example is microencapsulation by ethanediamine[104], whereby adding 18% microencapsulated APP and 2% Cu_2O to an epoxy resin, a 35% LOI and a V-0 UL-94 rating could be achieved. Other examples include microencapsulation with polystyrene[109] and poly(glycidyl methacrylate) [105], mainly for making it more hydrophobic. The flame retardant efficiencies of these different modified APPs are given in Table 5.

Researchers have also used boron phosphate as an FR[111,112], although even with 15% only a V-1 rating could be achieved (Table 6). Another flame retardant of interest is zirconium phosphate; a cardanol-derived zirconium phosphate has been synthesized by Fu et al., which at 6% level showed better dispersion and reduction in flammability of the epoxy resin compared to that of pristine zirconium phosphate.[113] To allow comparison of the efficiencies of different phosphates, the data taken from ref[90] has been presented in Table 6. Since cone results vary depending upon the resin types, sample geometry, external heat flux, etc., it is difficult to compare the results from different references. To address this, Vahabi et al. introduced a dimensionless parameter, Flame Retardancy Index (FRI), that reflects improvement in fire retardancy of the flame retarded sample with respect to that of the control resin sample [90,114].

$$Flame\ Retardancy\ Index\ (FRI) = \frac{[\mathrm{THR} * (\frac{\mathrm{pHRR}}{\mathrm{TTI}})]_{\mathrm{Control\ sample}}}{\left[\mathrm{THR} * (\frac{\mathrm{pHRR}}{\mathrm{TTI}})\right]_{\mathrm{FR\ Sample}}} \qquad \mathbf{(1)}$$

Where PHRR = peak heat release rate, THR= total heat release, and TTI = time-to-ignition. The higher the FR1 value, the better is the fire performance.[90] FRI has been used to rank the flammability performances of differently flame retarded resins, when the data is taken from multiple sources, here as well as in the rest of the document.

As can be seen from the FRI values in Table 6, both boron phosphate and zirconium phosphate are less effective than APP.

TABLE 6 Flame retardancy performance of different inorganic phosphates in DGEBA based epoxy resins (adapted from Ref[90])

Flame retardant	Add-on (wt %)	Thickness (mm)	LOI (%)	UL-94	Cone results at 50 kW/m^2				Ref
					TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	FRI	
Ammonium polyphosphate	21	3-3.2	33	NR	57	594	53	3.9	[104]
Ammonium polyphosphate	15	3	36	V-0	63	398	35	15.46	[105]
Boron phosphate	15	3-3.2	31.5	V-1	46	602	84	2.58	[111]
Boron phosphate	5	3	29.6	—	53	652	31	2.8	[112]
Zirconium phosphate	6	3	—	—	51	1248	85.5	1.15	[113]
Cardanol-derived zirconium phosphate (CZrP)	6	3	—	—	54	858	67.8	2.24	[113]

Another inorganic phosphate of interest is melamine polyphosphate (MPP). Since it contains both phosphorus and nitrogen based groups, it is an effective flame retardant. Variants of MPP include melamine poly(metal phosphates), which are commercially available under the trade name Safire®. Müller and Schartel[59] have studied the effectiveness of MPP and different melamine poly(metal phosphates) in a DGEBA based epoxy resin compared with use of diethyl aluminium phosphinate (AlPi-Et), another effective FR. All FRs were added at 20% level, The results in terms of FRI vs UL-94 results are shown in Table 7, where it can be seen that with both MPP and AlPi-Et UL-94, a V-0 rating could be achieved. While all melamine poly(metal phosphates) were effective in reducing cone calorimetric parameters, melamine poly(magnesium phosphate) (MPMgP) was more effective and led to a V-2 rating, whereas use of melamine poly(aluminium phosphate) (MPAlP) and melamine poly(zinc phosphate) (MPZnP), gave only an HB rating.

TABLE 4 Flame retardancy performance of melamine polyphosphate variants in DGEBA based epoxy resins (adapted from ref[59]). All FRs were added at 20wt% level

Flame retardant	UL-94	Cone results at 50 kW/m^2			
		TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	FRI
Melamine polyphosphate (MPP)	V-0	38	244	26.6	8.77
Melamine poly(aluminium phosphate) (MPAlP)	HB	40	540	60	1.85
Melamine poly(zinc phosphate) (MPZnP)	HB	43	312	60	3.44
Melamine poly(magnesium phosphate) (MPMgP)	V-1	44	298	57.3	3.86
Aluminium diethyl phosphinate (AlPi-Et)	V-0	41	492	55.8	2.23
Melamine polyphosphate (MPP)	V-0	38	244	26.6	8.77

Note: Sample thickness = 3mm

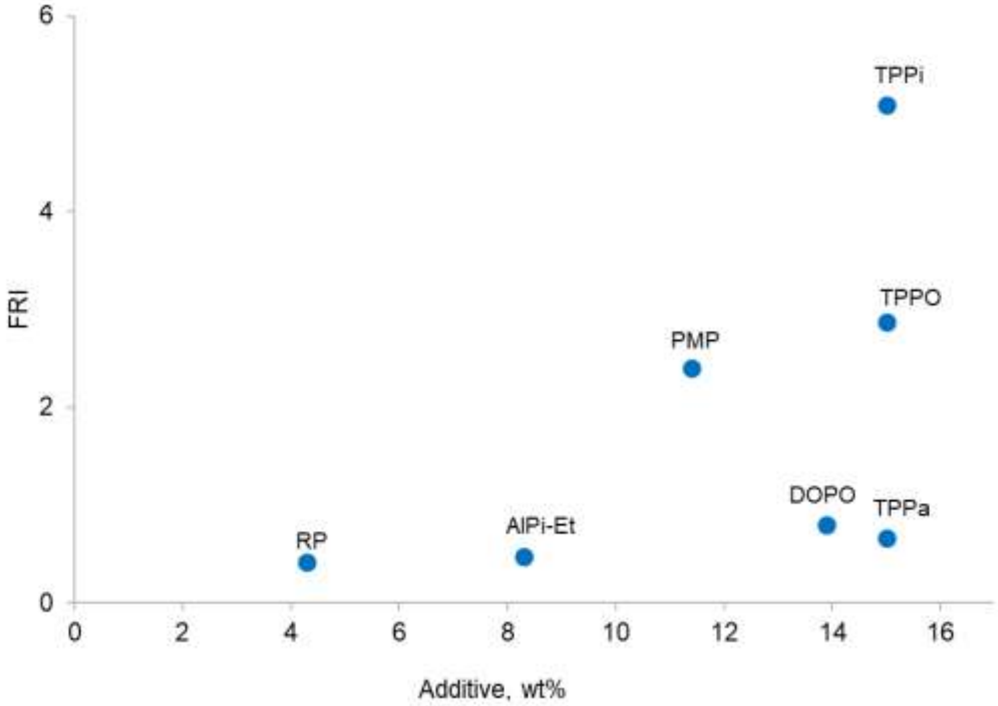
Inorganic phosphates are key ingredients of intumescent flame retardants. While the main application of intumescent chemicals is in intumescent coatings, these are also used as flame retardant additives in polymers, including in epoxy resins. The basic components of an intumescent formulation are an acid source (e.g., ammonium polyphosphate), char former (e.g., pentaerythritol) and a blowing agent (e.g., melamine). Sometimes two components are replaced by one, e.g., melamine phosphate and melamine polyphosphate where the melamine derivative acts as a blowing agent and as an acid source; or pentaerythritol phosphate incorporating both acid source and a char former. In the case of an epoxy resin, the resin can act as a char former and hence, APP, MP, MPP also act as intumescent chemicals. We have explored the use of different intumescent chemicals in epoxy resins (Figure 4) as well as in glass fibre-reinforced composites, which will be discussed in a later section. Jiao et al. have studied the effects of a single component intumescent FR, the melamine salt of pentaethytritol phosphate, 30 wt% of which effectively reduced PHRR and THR in cone experiments.[115]

4.3 Organophosphorus flame retardants

Organophosphorus flame retardants include phosphates, phosphonates phosphines, phosphine oxides and phosphinates. The mode of action depends on the phosphorus species as well as on other additives. While predominantly they function in the condensed phase by char promotion, some FRs may also act in the gas phase by flame inhibition. The gas-phase activity of phosphorus-containing flame retardants can be described in a similar way as for halogen-containing flame retardants[116] where PO$^{\cdot}$ radicals act as free radical quenchers. The efficiency of phosphorus in the gas phase is nearly the same as that of HBr.[117] A good example of gas phase active FRs is DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) and its derivatives, discussed later in this section.

Mariappan et al. have studied the effect of the oxidation state of phosphorus in different flame retardants, on the flammability of an epoxy resin. Flame retardants included triphenylphosphite

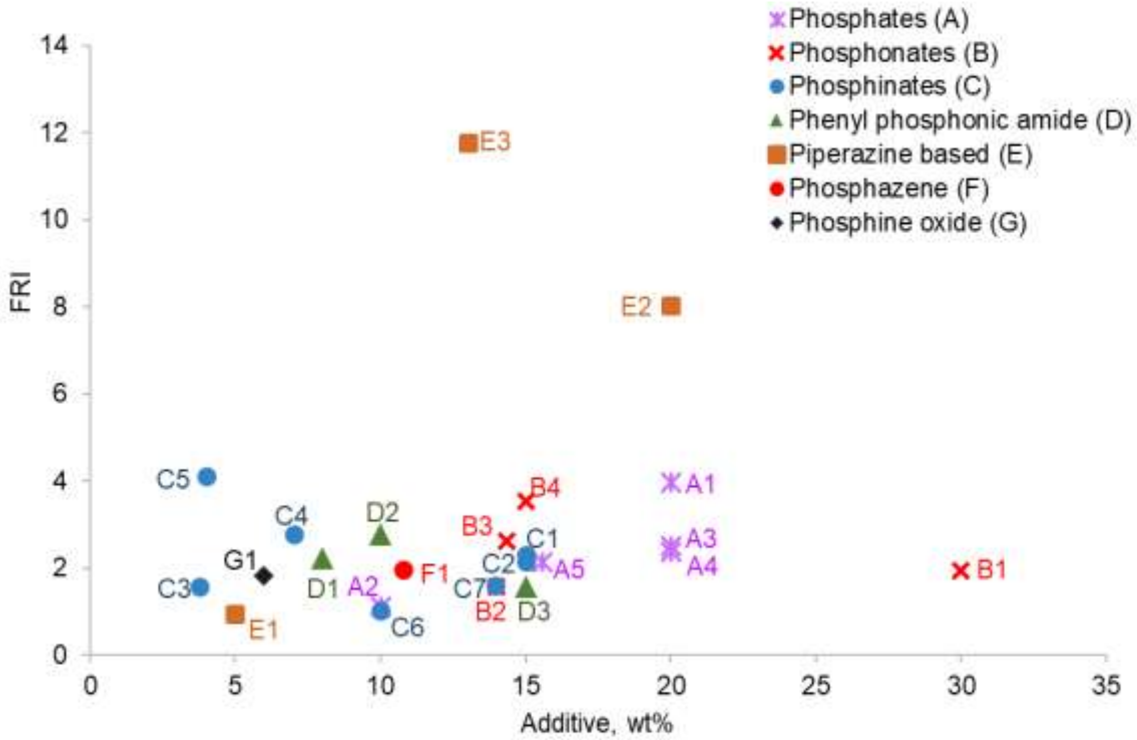
(TPPi), triphenylphosphate (TPPa), triphenylphosphine oxide (TPPo), all at 15 wt% (1.5 wt% phosphorus content) [118]; red phosphorus (RP), aluminium diethylphosphinate (AlPi-Et), poly(m-phenylene methyl-1-phosphonate) (PMP) and DOPO with wt% values of 4.3 8.3, 11.4 and 13.9% (all with 2 wt% phosphorus content).[119] As can be seen from Figure 5, TPP is the most effective FR followed by TTPO, whereas TPPo is the least effective.



Note: TPPi = triphenylphosphite , TPPa = triphenylphosphate , TPPo = triphenylphosphine oxide[118]*; RP = red phosphorus, AlPi-Et = aluminium diethylphosphinate, PMP = poly(m-phenylene methyl-1-phosphonate), DOPO = 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide.*[119]

FIGURE 5 Flame retardancy evaluation versus additive levels of different phosphorus based FRs in a DGEBA based epoxy resin

Organic phosphates include triphenyl phosphate (TPP), tritolyl phosphate (TTO), tris(tribromoneopentyl) phosphate, resorcinol bis-(diphenyl phosphate) (RDP), bisphenol A bis(diphenyl phosphate), (BAPP). FRs such as triphenyl phosphate (TPP), tert-butylphenyl diphenyl phosphate and cresyl diphenyl phosphate, have a high volatility resulting in a relatively low fire retardant efficiency, whereas oligomeric derivatives of resorcinol bis(diphenyl phosphate) (RDP), bisphenol A bis(diphenyl phosphate) (BDP), and the biphosphate resorcinol bis(dixylenyl phosphate) (RXP) are less volatile and have a higher thermal stability than TPP.[120] The effectiveness of different phosphates reported in the literature are given in Figure 6.



Note:

A1 = melamine phenylphosphate[121]*, A2 = bisphenol-A bis(diphenyl phosphate)*[122]*, A3 = isopropylphenyl phosphate*[123]*, A4 = tertbutylphenyl phosphate*[123]*, A5 = poly(bisphenol sulfone phenoxy phosphate)*[124]*;*

B1 = α,ω-dicarboxyl aromatic polyphosphonate[125]*, B2 = bis(2,6-dimethyphenyl) phenylphosphonate*[126]*, B3 = poly(bisphenol sulfone phenoxy phosphate)*[124]*, B4 = [4-(2,4,6-Tris[24] dioxaphosphinan-2-yl) hydroxymety] phenoxy]-(1,3,5)-triazine* [127]*;*

C1 = aluminium ethylphenylphosphinate[128]*, C2 = Aluminium diisobutylphosphinate*[129]*, C3 = melamine-organophosphinic acid salt*[130]*; C4 = aluminium diethyl phosphinate*[131]*, C5, C6 = aluminium poly-hexamethylenephosphinate*[122,132]*, C7 = DOPO*[133]*;*

D1 = N, N^0-diallyl-p-phenylphosphonicdiamide[134]*, D2 = phenylphosphonic di-benzothiazolyl amide*[135]*, D3 = poly(4,4^0-diamino diphenyl sulfone phenyl phosphonamide)*[124]*;*

E1 = polyphosphoric acid piperazine[136]*, E2 = poly(pentaerythritol phosphate phosphinic acyl piperazine)*[137]*, E3 = poly (piperazine phosphaphenanthrene)*[138]*;*

F1 = Phosphazene[48]*;*

G1 = 6-(((1H-tetrazol-5-yl)amino)(4hydroxyphenyl)methyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide[63]

FIGURE 6 Flame retardancy evaluation of different organophosphate FRs in epoxy resins

In the study mentioned in Section 4.2 (Figures 3 and 4), along with inorganic phosphates, we also investigated the flame retardant efficiency of some organophosphorus FRs, namely resorcinol bis-(diphenyl phosphate) (RDP), bis phenol a bis(-diphenyl phosphate), (BAPP), triphenyl phosphate (TPP), tritolyl phosphate (TTO), tris(tribromoneopentyl) phosphate (FR 372), and tris(tribromophenyl) cyanurate (FR 245) in a tetrafunctional epoxy resin (tetraglycidyl-4,4 diamino diphenyl methane (MY721, Cytec) at 4 and 8 wt% level.[49] All FRs were compatible, hence showed good dispersion in the resin (Figure 3). Even at 4% levels, RDP, BAPP and FR372 gave rise to a V1 UL-94 rating (the control sample failed) and at 8%, use of FR372 gave rise to a V0 rating. The FR efficiency from cone results can be seen from

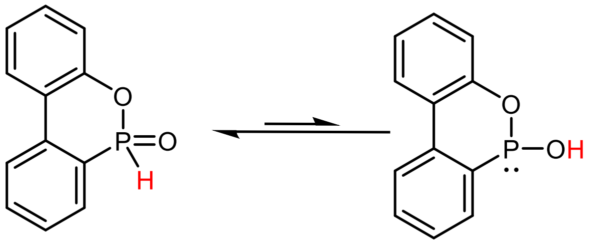
Figure 4, where TTP, TPP and FR 372 show better results than other organophosphorus FRs. Relatively low char yields were seen with TTP, TPP and FR 245, indicating that in these cases fire retardance probably proceeds mainly via a gas-phase mechanism. On comparing the FR efficiencies of inorganic vs organic phosphates in Figure 4, mixed results are seen. The FR efficiency depends on the phosphorus content and phosphorus-nitrogen ratio, as well as on whether that particular molecule exhibits condensed-phase or vapour-phase FR activity.

Amongst phosphonates, polymeric methylphosphonates are commercially available; one example is poly(1,3-phenylene methylphosphonate), 20–30% of which is needed to give a V-0 rating at 1.6 mm thickness.[139] Examples of others are presented in Figure 6.

Metal salts of dialkylphosphinic acid, such as aluminium or zinc diethyl phosphinate are effective FRs for epoxy resins. Liu et al.[44] have reported that with 15% aluminium diethylphosphinate and aluminium methylphosphinate in DGEBA based epoxy resin, a UL-94 V-0 rating and an LOI value ≥ 30.0% could be obtained. Both additives enhanced the flexural modulus of the EP, but affected the flexural strength. Yang et al. synthesized aluminium ethylphenyl phosphinate and achieved a V-0 rating with 15% add-on.[128] Results for other phosphinates are presented in Figure 6.

Among phosphinates, the cyclic hydrogenphosphinate, 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) made from o-phenylphenol and phosphorus trichloride, is the most promising FR for epoxies. This is also the most researched FR, and hence is discussed below in more detail.

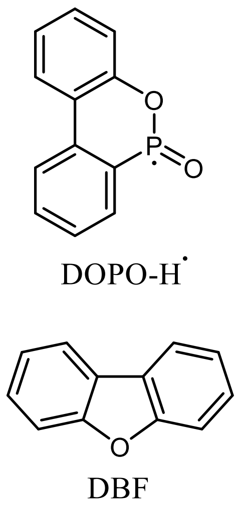
DOPO is one of the most promising organophosphorus FRs, and owing to its versatile flame extinguishing behaviour it has been widely investigated as an FR for epoxy resins. DOPO is incorporated in the epoxy resin network through reaction of the P-H group with the epoxide ring. It is classified as an H-phosphinate compound, characterised by two tautomeric forms, represented in Scheme 5.



SCHEME 5 9,10-Dihydro-9-oxa-10-phosphaphenantrene-10-oxide (DOPO) structure

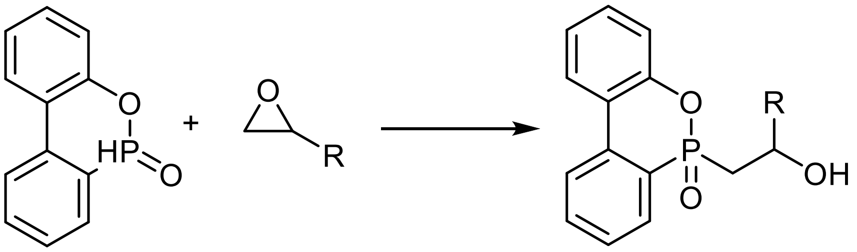
DOPO has been very effective in DGEBA and novolac epoxy resins, leading to a UL-94 V-0 rating with 1.6-2.2% P-loading (11-15% DOPO)[103] The proposed mechanism of action is:

$$\begin{aligned}
\mathrm{HPO} &\longrightarrow \mathrm{H}^{\bullet} + \mathrm{PO}^{\bullet}\\
\mathrm{DOPO\text{-}H}^{\bullet} &\longrightarrow \mathrm{DBF} + \mathrm{PO}^{\bullet}\\
\mathrm{DOPO} &\longrightarrow \mathrm{DBF} + \mathrm{HPO}\\
\mathrm{DOPO} &\longrightarrow \mathrm{H}^{\bullet} + \mathrm{DOPO\text{-}H}^{\bullet}\\
\mathrm{DOPO} + \mathrm{H}^{\bullet} &\longrightarrow \mathrm{H_2} + \mathrm{DOPO\text{-}H}^{\bullet}\\
\mathrm{DOPO} + \mathrm{OH}^{\bullet} &\longrightarrow \mathrm{H_2O} + \mathrm{DOPO\text{-}H}^{\bullet}\\
\mathrm{DOPO} + \mathrm{H}^{\bullet} &\longrightarrow \mathrm{H_2} + \mathrm{DBF} + \mathrm{PO}^{\bullet}\\
\mathrm{DOPO} + \mathrm{OH}^{\bullet} &\longrightarrow \mathrm{H_2O} + \mathrm{DBF} + \mathrm{PO}^{\bullet}
\end{aligned}$$

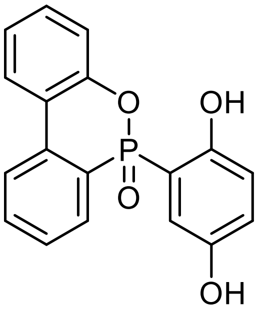


SCHEME 6 Proposed mechanism of flame retardant activity of DOPO in the gas phase[103])

Since DOPO reacts with the epoxy backbone, it can impair the cross-linking and hence the mechanical properties of the cured resin. To address that, the reactive functionality needs to be enhanced, and consequently many DOPO derivatives have been developed commercially as well as by researchers publishing in the open literature. Commercially available derivatives include bifunctional DOPO-HQ (10 (2,5-dihydroxypheny)-10h-9-oxa-10-phospha-phenanthrene-10-oxide), the polymeric HFC-X and tetrakis(DOPO-methyl)bisphenol A.[140] Roughly 10–15% of DOPO or DOPO derivative, corresponding to a 1.5–2% phosphorus content, are required to achieve a UL 94 V-0 rating, depending on the epoxy resin and the hardener.[141]



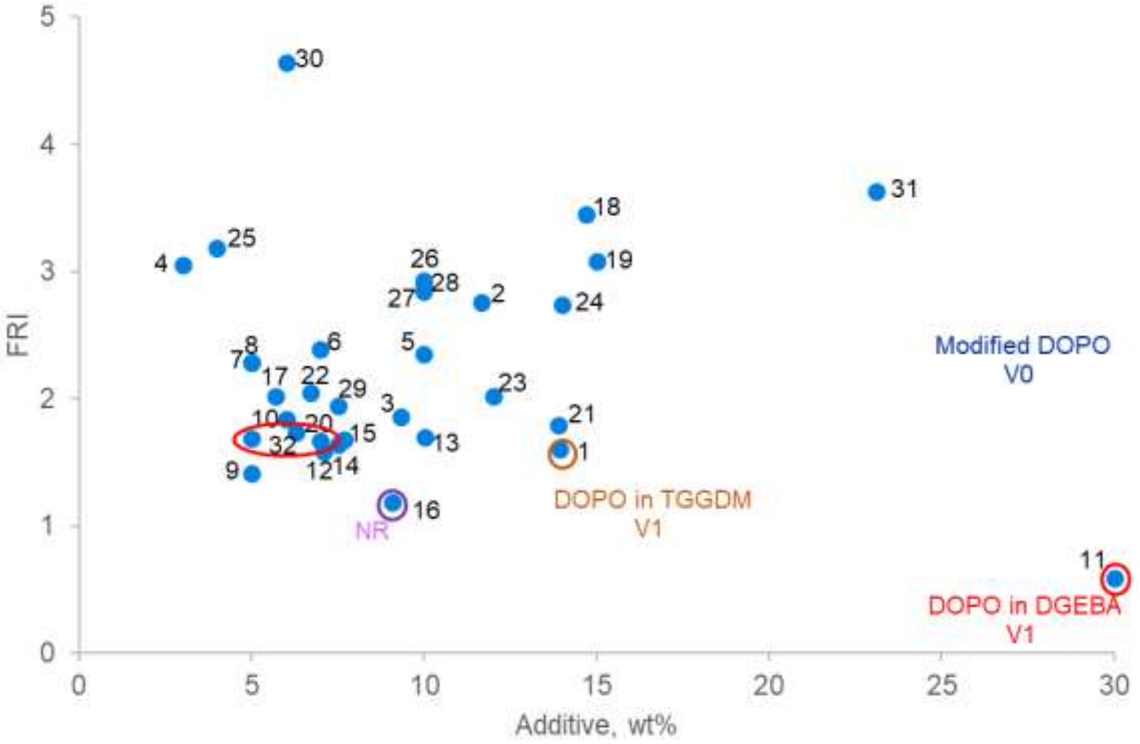
SCHEME 7 Reaction of DOPO with epoxy functionality



SCHEME 8 Chemical structure of DOPO-HQ

Many derivatives of the DOPO have been synthesized. It is beyond the scope of this review to capture all the citing, for which the reader is referred to other reviews.[89,90,103] Some important examples are:

Perret et al. modified DOPO by linking it to the star-shaped aliphatic ground body tetra-[(acryloyloxy)ethyl] pentarythritol (DOPP), or heterocyclic tris- [(acryloyloxy)ethyl] isocyanurate (DOPI).[51] DOPP and DOPI increased the LOI of a tetrafunctional epoxy resin from 25 to 37.9 and 34.2%, respectively, and improved the UL-94 HB rating of base resin to V-1 and V-0. Other modifiers of DOPO include pyrazine (DHBAP[64], achieving a UL-94 V-0 rating with 8% in the epoxy resin; tetrazole ring (ATZ)[63], achieving a V-0 rating at 9 wt% level; acrolein[62] achieving a V-0 rating at 4 wt%; phenethyl-bridged (DiDOPO), achieving V-0 at a 3% level[142], and bismaleimide in a DOPO modified resin[143], increasing a V-1 rating of the DOPO modified resin to V-0 with 7% bismaleimide addition. The effectiveness of DOPO and its derivatives in an epoxy resin is summarised in Figure 7, where it can be seen that use of unmodified DOPO could only produce V-1 ratings whereas all modified DOPO resins had V-0 ratings.



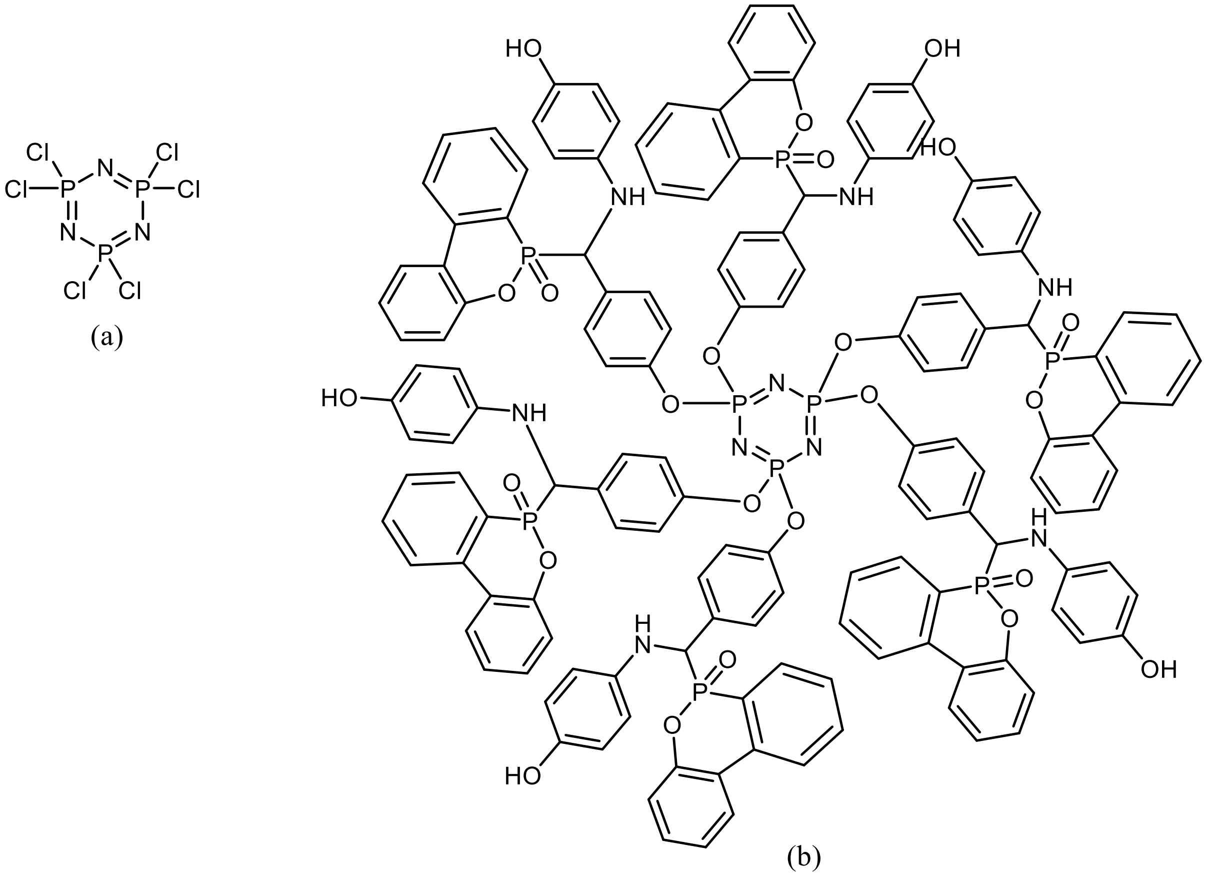
Note;
1, 11, 12, 14, 16, 20, 32, 33 = DOPO[133,144–150]*;*
2 = DOPO-PHE (PHE = bis(4- hydroxyphenyl) methyl) diphenylphosphine oxide)[151]
3 = DOPO-T (T=cyanuric chloride)[152]
4,5,6,7,8 = DiDOPO (phenethyl-bridged DOPO derivative) [80,153–155]*;*
9 = DOPO-MPL (MPL = 6-morpholino-6Hdibenzo[c,e][1,2]oxaphosphinine 6-oxide)[156]*;*
10 = DOPO- ATZ (ATZ = 6-(((1H-tetrazol-5-yl)amino)(4hydroxyphenyl)methyl)dibenzo[c,e] [1,2] oxaphosphinine 6-oxide)[63]*;*
13 = DOPO- BPD (BPD= 1,4-Phthalaldehyde & 2-benzothiazolamine)[145]*;*
15 = DOPO-TPMP (TPMP = reaction between 4-(hydroxymethyl)-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane 1-oxide & 6-(2,5-dihydroxyphenyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide)[157]*;*
17 = DOPO-PEPA (PEPA = 1-oxo-4 -hydroxymethyl-2,6,7-trioxa-l phosphabicyclo[2.2.2] octane)[147]*;*
18 = DOPO-BNP (BNP = phenylboronic acid)[158]*;*
19 = DOPO-DTB (DTB = reaction between triglycidyl isocyanurate & DOPO & boric acid)[159]*;*
21 = DOPO-TMT (TMT = tri(phosphaphenanthrene-maleimide-phenoxyl)-triazine)[148]*;*
22 = D-bp (bp = reacted 4,4'-diaminodiphenyl methane & 4-hydroxybenzaldehyde)[160]*;*
23 = DOPO = TAD (TAD = triallyl isocyanurate)[161]*;*
24 = DOPO-trif (trif = tri-(phosphaphenanthrene-(hydroxyl-methylene)-phenoxyl)-1, 3, 5-triazine)[162]*;*
25 = DOPO-TOD (TOD = reacted with 1,3,5-triglycidyl isocyanurate & 10-(2,5-dihydroxyphenyl)-10-H-9-oxa-10-phosphaphenanthrene10-oxide)[163]
26 = DOPO-DDM (DDM = 4,4diaminodiphenyl methane)[164]
27 = DOPO-DDE (DDE =4,4diaminodiphenyl ether)[164]
28 = DOPO-DDS (DDS =4,4diaminodiphenyl sulfone)[164]
29 = DOPO-ABZ (ABZ =2-aminobenzothiazole)[165]
30 = DOPO-MMT (MMT = montmorillonite)[166]
31 = DOPI (linked to the star-shaped aliphatic heterocyclic tris-[(acryloyloxy)ethyl] isocyanurate[51]

FIGURE 7 Flame retardancy evaluation of DOPO and its derivatives in DGEBA based epoxy resins (otherwise stated in the caption) in terms of FRI values as a function of additive wt%. All achieved UL-94 V0 ratings, except for the marked ones

In addition, phosphine oxide[130], phosphonamides[124,134,167] and piperazine[127,136] based FRs have also been reported, their efficiencies as compared to those of other FRs are reported in Figure 6.

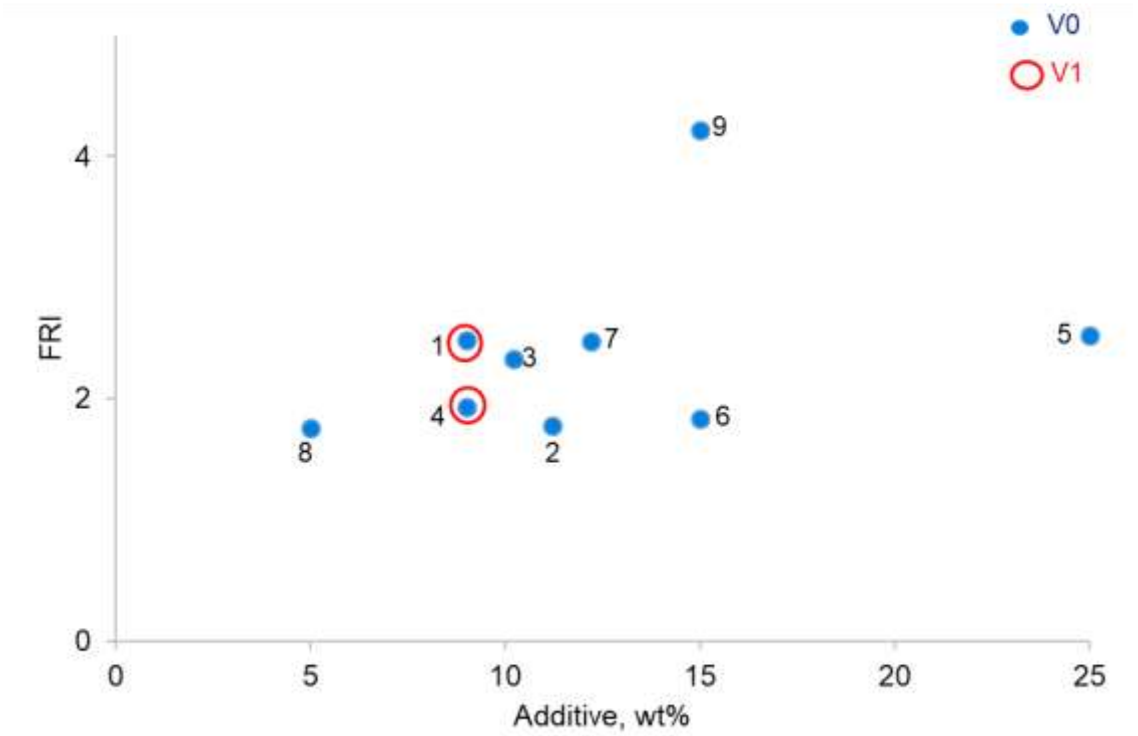
In order to avoid the blooming out or leaching of low molecular weight organophosphorus FRs, polymeric hyperbranched FRs can be used. Batting et al.[168] demonstrated that using *hb*-organophosphates, such as *hb*-polyphosphoramide, *hb*-polyphosphate, *hb*-polyphosphoramidate and *hb*-polyphosphordiamidate, the flammability of an epoxy resin is marginally reduced (max 5% LOI improvement with 10 wt% of hb-FR). Later the same group developed hyberbranched sulfur containing[169] and poly(phosphoester)[170] FRs, which showed improved flame retardant properties. Zhang et al.[60] however, developed novel *hb*-FRs using an itaconic anhydride hb-polymer with DOPO and diisopropanolamine (ITA-HBP). The results showed that 4 wt% of ITA-HBP improved the LOI of the epoxy resin by 10% and that increasing the concentration of hb-FR to 14 wt% led to an LOI improvement of 16%, maintaining a V-0 classification. Besides demonstrating the flame retardant efficiency of the ITA-HBP hyperbranched system, Zhang et al. reported also a bio-based alternative to the hb-FRs that are normally derived from petroleum.

Another family of organophosphorus FRs that has shown efficient flame retardancy in epoxy resin is derivatives of cyclophosphazene (CP). These organophosphorus compounds are derived from the chemical modification of hexachlorocyclotriphosphazene (HCCP), the central group of which is alternately connected by single and double bonds between phosphorus and nitrogen atoms, and in which the side chain Cl is replaced by organic groups. P-N synergism is responsible for their flame retardant efficiency.



SCHEME 9 (a) HCCP and (b) Modified HCCP

Cyclophosphazene derivatives include hexakis (4-boronic acid-phenoxy)-cyclophosphazene[65] providing a UL-94 V-0 rating at 10 wt%; cyclolinear cyclotriphosphazene linked structure[56] also giving a V-0 rating; bisphenol s-bridged penta (anilino) cyclotriphosphazene (BPS-BPP)[66,171] with V-1 rating at 9 wt%; DOPO substituted[71] giving a V-0 rating at 10.6 wt%; hexaphenoxycyclotriphosphazene[133] giving V-0 at 11.2% loading in a tetrafunctional epoxy resin; hexa(4-maleimido-phenoxyl) cyclotriphosphazene[172] and amine-terminated cyclophosphazene[173] obtaining V-0 at 15 wt%. Their effectivenesses are compared in Figure 8.



Note:
1 = bisphenol A bridged penta(anilino) cyclotriphosphazene (BPA-BPP)[171]*;*
2, 8,9 = hexaphenoxycyclotriphosphazene (HPCTP)[133,174]*,*
3 = hexa(4-maleimido-phenoxyl) cyclotriphosphazene (HMCP)[172]
4 = bisphenol-S bridged penta(anilino)cyclotriphosphazene (BPS-BPP)[66]
5 = [(1,1,3,3-tetramethyl-1,3-disiloxanediyl)-di-2,1-ethanediyl]bis(diphenylphosphine oxide) (PSi)[47]
6 = amine-terminated cyclophosphazene (ATCP)[173]
7 = 1,3,5-triglycidyl isocyanurate &9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (TGIC-DOPO)[175]

FIGURE 8 Flame retardancy evaluation of cyclophosphazene based FRs in DGEBA based epoxy resins in terms of FRI values as a function of wt% FR. All achieved modified resins gave UL-94 ratings, except the marked ones

Phenoxyphosphazene compounds (mixtures of poly- and cyclobisphenoxyphosphazenes) are also used in epoxy resins, mainly in printed circuit boards. These are thermally and hydrolytically stable compounds. The flame retardant mechanism of the phosphazene compound depends on the phosphazene substituent and occurs in the gas phase as well as in the condensed phase.[176]

4.4 Silicon based flame retardants

Silicon-based flame retardants mainly include siloxanes, polysiloxanes, silicates, silsesquioxanes and silica. The latter three are mostly used at nanoscales. They function in the condensed phase by physical means, forming an oxidation resistant thermal barrier surface layer on the burning polymer. In the presence of other flame retardant elements, e.g., phosphorus, they act synergistically, where the phosphorus based FR helps in char formation and the silicon based part consolidates the char and provides oxidation resistance.

Siloxanes, containing Si-O-Si bond in the main chain, are considered non-toxic and environmentally friendly flame retardants, hence gaining in popularity. Most researchers have used siloxanes and polysiloxanes as reactive FRs to chemically modify epoxy resins.[95,177] An example of their use as additives is by Qiu et al.[70] where they synthesized different phosphaphenanthrene/phenylsiloxane macromolecules (DDSi-n, with n= 1, 2, 5) and used these as additives in a DEGBA epoxy resin. With 8 wt% of DDSi-1, a V-1 UL-94 rating and 35.9% LOI could be obtained. Li et al.[45] prepared an epoxy-functionalised polysiloxane, 10 wt% of which in a DGEBA resin while it could raise the LOI of the resin from 20.7% to 24.8%, could not achieve any UL-94 rating. However, when used at 5 wt% in presence of 5 wt% of a phosphoric triamide, an LOI of 30.2% and a V-1 rating was obtained.

One form of silsesquioxane, polyhedral oligomeric silsesquioxane (POSS), is a well known flame retardant for different polymers, including epoxy resins. This is discussed in detail in the following section.

Silica is one of the commonly used fillers for epoxy resins. Its variants include spherical silica, mesoporous silica (m-SiO_2) and nano silicas, which because of their larger surface-to-volume ratios, have been of great interest. Since these are of nanoscale, these are discussed in the next section. Another form of silica are layered silicates, or nanoclays, which are also discussed in the next section.

4.5 Nanoparticles as flame retardants

Nanoparticles have attracted considerable attention over the last three decades by offering good mechanical, thermal and fire retardant properties to polymers at low loading levels of 2-5 wt % as opposed to > 15% with conventional FRs. Nanoparticles can be one (1D), two (2D) or three dimensional (3D). 1D nanoparticles have one dimension (i.e. thickness) on the nanoscale and the other two (i.e. width and length) measuring hundreds to thousands of nanometers, e.g., layered silicate nanoclays, such as montmorillonite (MMT) and layered double hydoxides (LDH). Two dimensional (2D) have two dimensions on a nanoscale and the third larger, e.g. carbon nanotubes, graphene, carbon nanofibres and sepiolite; whilst species with three nanoscale dimensions (3D), are true nanoparticles with an aspect ratio of 1, e.g., polyhedral oligomeric silsesquioxanes (POSS) and nanometallic oxides (silica, titania, alumina) and carbides. 1D and 2D nanoparticles with high aspect ratios are capable of acting as reinforcing elements and hence capable of forming nanocomposites. The term “nanocomposite”, which became very popular when Toyota researchers [178] reported the unique flame retardant and mechanical properties of 5-wt% montmorillonite dispersed in polyamide 6, is applicable to those polymer formulations in which the polymer conformation is changed in proximity to a nano-sized filler: the polymer can be absorbed by the filler surface or be trapped between filler particles. This can give rise to intrinsically new properties that are not displayed by the pure components, mainly due to unique interfacial effects resulting from the dispersion of nanoparticles of high specific surface area and high aspect ratio.[179] Strong nanoparticle-polymer interactions however, increase the viscosity of the polymer, which increases with increasing nanoparticle concentration. It is difficult to process above 10 wt % nanoparticle concentration. The use of nanoparticles in epoxy resins is widely reported in the literature, and it is beyond the scope of this review to cover all relevant papers, for which reader is referred to previous reviews [180–184] so only selected examples are provided here. The main mechanism of FR action of a nanoparticle is believed to be by physical means whereby during combustions nanoparticles aggregate on the polymer surface, forming a thermally insulative layer, which slows down the diffusion of pyrolysis gases and hence slows down flame propagation.

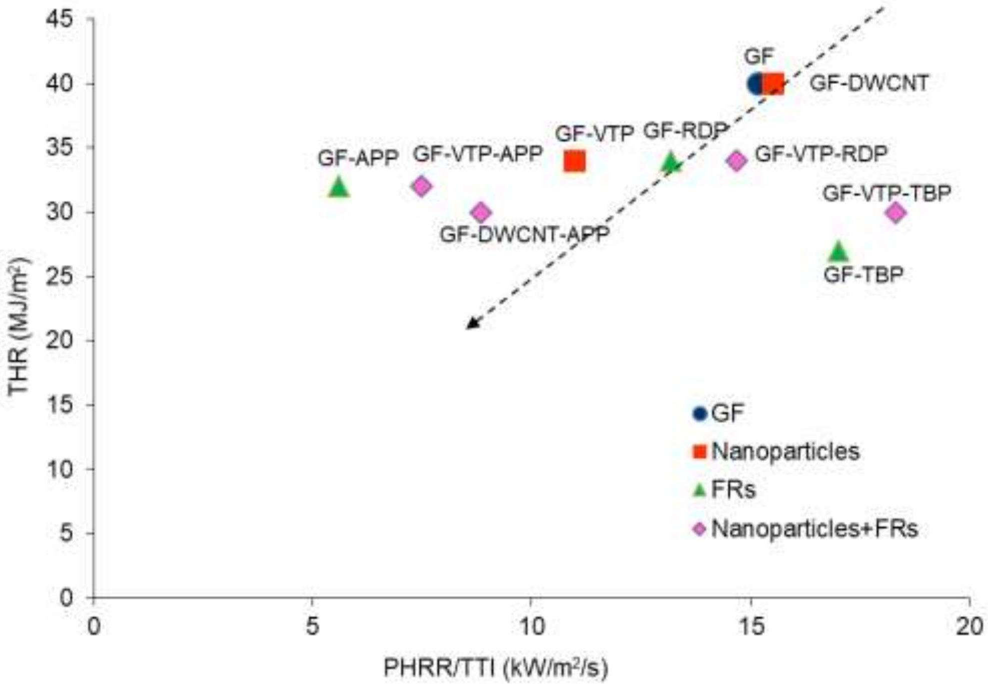
Layered silicates, also called nanoclays, can be cationic (e.g., montmorillonite (MMT)) or anionic (e.g., layered double hydroxides (LDH)). Both types of clays have been used in epoxy resins. While MMT clays enhance the thermal stability of the resin in terms of reducing the rate of mass loss as a function of temperature in thermogravimetric tests and reducing flammability in terms of reductions in peak heat release rate (PHRR) and total heat release (THR) in cone calorimetric test, their overall effect in improving flammability ratings (LOI, UL-94 and flame spread tests) is marginal[46,181,185] as can be seen from Table 7, where the effects of three different organically modified nanoclays (5wt%) on two types of epoxy resins, a bi-functional epoxy resin, 1,4-butanediol diglycidylether, (Nov-Ep)) with a modified cycloaliphatic amine-based hardener (HY5052) and a tetra-functional epoxy resin, tetraglycidyl-4,4’ diaminodiphenylmethane (TGDDM) with 4,4’-diaminodiphenyl sulphone (Aradur 976-1) used as a curing agent, have been reported.[46] All samples with nanoclay alone had HB UL-94 ratings. In terms of limiting oxygen index, a typical increase between 1 to 3 % in the LOI values is obtained with 5 wt % organoclay. As can be seen from Table 7, highly the cross-linked TGDDM resin has a high LOI value compared to that of the less cross-linked resin, Nov-Ep. In both cases the presence of nanoclays increased the LOI compared to that of the neat resin, although the effect is more pronounced in TGDDM. In both cases VTP clay has shown the best result, achieving V-1 rating in TGDDM resin, which is due to the presence of phosphorus in the organic modifier. The FRI index obtained from cone calorimetric results shows that the effect of each nanoclay is similar in both resin types with marginal reduction in the flammability. These results are similar to those reported by other researchers.[181,185]

TABLE 7 Effect of nanoparticles on flame retardancy performance of a bi-functional, novolac epoxy resin (Nov-Ep) and a tetrafunctional, tetraglycidyl-4,4’ diaminodiphenylmethane (TGDDM) epoxy resin (data taken from[46])

Nanoparticles and concentration (wt%)	LOI (%)		UL-94		FRI from cone results at 50 kW/m^2	
	Nov-Ep	TGDDM	Nov-Ep	TGDDM	Nov-Ep	TGDDM
-	21.5	27.8	HB	HB	-	-
MMT, 30B (5wt%)	21.9	30.8	HB	HB	1.14	1.06
MMT, VTP (5wt%)	23.1	31.7	HB	V-1	1.28	1.78
MMT, 1.30 E (5 wt%)	20.5	30.0	HB	HB	1.14	1.16
DWCNT (0.5 wt%)	20.1	29.6	HB	V-1	1.02	1.05
Nanosilica (30 wt%)	-	29.4	-	V-1	-	1.85

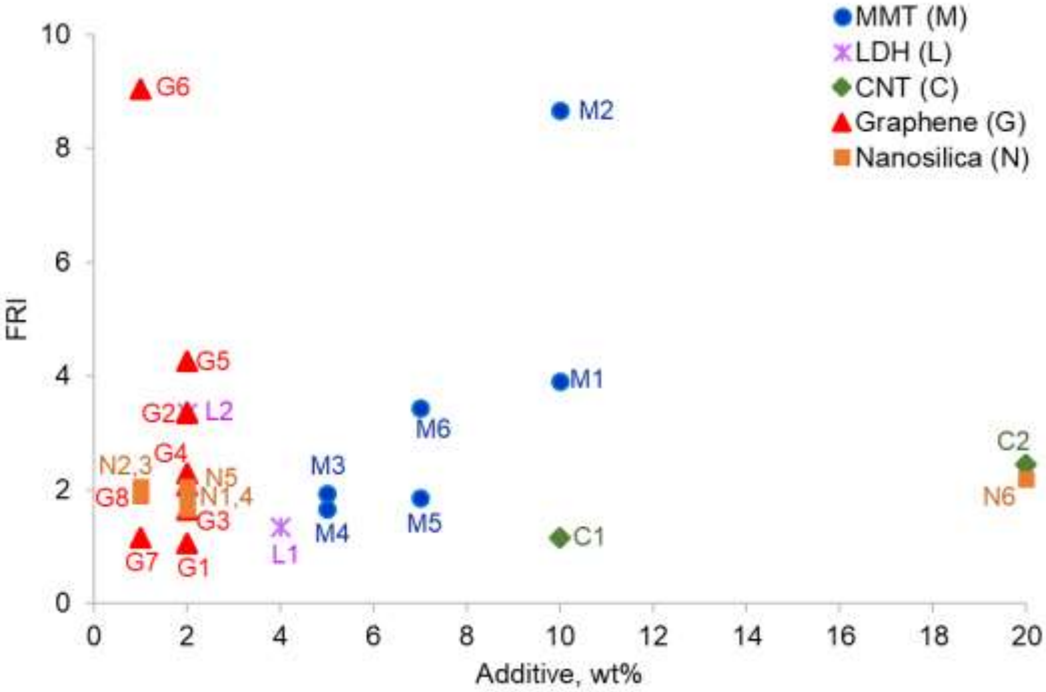
Note: 1.30E= Octadecyl ammonium ion-modified montmorillonite clay;
30B= Alkyl quaternary ammonium modified montmorillonite clay;
VTP= Vinyl triphenyl phosphonium bromide modified montmorillonite clay;
DWCNT= double walled carbon nanotubes.
Sample thickness = 3mm

To improve the flame retardant efficiency of MMT nanoclays, researchers have used organic modifiers containing fire retardant groups or grafted on them, or have added conventional FRs to the polymer while forming polymer nanocomposites. Katsoulis et al.[46], (see results of VTP clay in Table 7) and Schartel et al.[186] have shown that by using a phosphorus containing organic modifier for the MMT clay, its flame retardant efficiency can be enhanced. When used with additional organophosphorus flame retardants, the effects of MMTs can be antagonistic[186–189] or synergistic.[190] This can be seen from Fig. 9, where fire risk assessments based on cone calorimetry data taken from ref[189] have been plotted for glass fibre-reinforced epoxy composites from the TGDDM resin (GF) from Table 7 with selected clays (VTP) and nanotubes, different FRs (ammonium polyphosphate (APP); resorcinol bis-(diphenyl phosphate), (RDP); and tris (tribromoneopentyl) phosphate (TBP), and combinations of nanoparticles and FRs. The addition of VTP together with RDP, APP, and TBP produced worse fire performance than those with individual components. Hussain et al.[187] and Liu et al.[188] also reported an antagonistic FR effect of nanoclay on DGEBA and TGDDM epoxy resins, containing chemically reactive flame retardants DOPO (9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide) and bis(4-aminophenoxy)phenyl phosphonate (BAPP), respectively. The antagonistic effects could be due to the effect of FRs and nanoclays (or other nanoparticles) on the cross-linking density of the resin.[189,191,192] However, Torre et al. have reported that the nanoclays and additional FRs do not adversely affect the cross-linking of the resin.[193] Yan et al.[80] however, reported a synergistic effect between MMT and phenethyl bridged DOPO derivative (DiDOPO), with 3.5wt% of rendering an epoxy flame retardant with 32.2% LOI value and a UL-94 V-0 rating. He et al.[194] prepared an epoxy containing an APP-MMT nanocompound, 10% of which led to a UL-94 V-0 rating; these results were similar though to those obtained by using a physical mixture of APP and MMT. The effectiveness of some of these modified MMTs is compared in terms of the FRI values their use produces in Figure 10.



Note: GF = glass fibre-reinforced epoxy composites; VTP= Vinyl triphenyl phosphonium bromide modified montmorillonite clay; DWCNT= double walled carbon nanotubes; APP= ammonium polyphosphate; RDP = resorcinol bis-(diphenyl phosphate); TBP = tris(tribromoneopentyl) phosphate

FIGURE9 Fire safety diagram, i.e., a plot of total heat released (THR) vs. peak heat release rate (PHRR) divided by time to ignition (TTI), for glass fibre-reinforced epoxy composites containing nanoparticles, various fire retardants and combinations of both based on cone calorimetric data recorded with 50 kW/m^2 radiant heating (adapted from Ref[189])



Note:

M1= MMT+APP[73]*, M2 = APP-MMT*[73]*, M3 = tetraphenylphosphonium modified montmorillonite (TPP-MMT)*[195]*, M4 = phosphorylated chitosan modified montmorillonite intercalation iron compounds (PCTS-Fe-OMMT)*[196]*, M5 =MMT*[80]*, M6 = MMT + DiDOPO*[80]*;*

L1 = ((1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(propane-3,1-diyl))bis (2-methoxy-4,1-phenylene)bis(phenylphosphonochloridate) modified magnesium-aluminium layered double hydroxide (SIEPDP-Mg-Al LDH)[197]*; L2 = Ni-Fe LDH (Ni– Fe layered double hydroxide*[69]

C1 = PPMS-CNT (PPMS= pentaerylthritol phosphate melamine salt[78]*, C2 = dimethyl methylphosphonate loaded halloysite nanotube (DMMP-HNT)*[198]*;*

G1, G3, G5 = GNS (graphene sheets)[68,69,199] *, G2 = Ce-MnO$_2$-GNS (Ce-doped MnO$_2$–graphene hybrid sheets)*[68]*, G4 = MoS$_2$-GNS (molybdenum disulphide - modified graphene)*[199]*, G6 = Ni-Fe LDH/GNS (Ni–Fe layered double hydroxide/graphene hybrids)*[69]*, G7 = phosphorus and nitrogen-containing FR treated graphene* [200]*, G8 = DOPO-phosphonamidate functionalized reduced graphene*[201]*;*

N1 = HPPA-SH-mSiO$_2$ (a hybrid material with different FR elements)[202]*, N2 = SiO2@PZM (silica-polyphosphazene nanospheres)*[203]*, N3 = SiO2@PZM@Cu (ciprous oxide nanoparticles on silica-polyphosphazene nanospheres)*[203]*, N4 = HM-SiO$_2$ (hollow mesoporous silica)*[204]*, N5 = HM-SiO$_2$@CS@PCL; Chitosan/phosphorylated cellulose coated mesoporous silica*[204]*, N6 = RH-SiO$_2$ (rice husk extracted silica)*[58]

FIGURE 10 Flame retardancy evaluation of different modified nanoparticles in epoxy resins in terms of FRI values as a function of additive wt%

The anionic clays, layered double hydroxide (LDHs), function in a different manner than the cationic MMT clays. When subjected to heat, LDHs first release adsorbed and intercalated water, followed by endothermic decomposition of hydroxyl layers and decomposition of organic anions[181]; both the endothermic reactions and the released water contribute to a cooling effect and the residual oxide acts as a thermal barrier, similar to that produced from MMTs. On comparing LDHs with MMT, Zammarano's[181] work has shown that in UL-94 tests epoxy-LDH samples could achieve an HB rating had reduced burning rates and self extinguished, whereas epoxy-MMT samples burned completely. Zammarano et al.[205] also observed that LDH clays are more effective in thin samples as compared to thick samples, which is contrary to the action of MMT based cationic clays. This is due to their different mechanisms of action, i.e., with DHs, the cooling effect due to release of water vapour is more effective when the polymer mass is less, whereas MMTs function by physical means i.e., by aggregating on the surface the chance of which is greater when the samples are thick.

Carbon nanotubes (CNTs), have also been used extensively in epoxy resins; however, the effectiveness of them depends on whether these are single walled, double walled or multiwalled, although there is no single study in which different types have been compared. We have studied the effects of double-walled carbon nanotubes (DWCNTs, 0.5wt%) in DGEBA versus TGDDM resins and the results are given in Table 7. It can be seen that DWCNTs are more effective in the |TGDDM resin giving an increased LOI compared to that of the control resin and a V-1 UL-94 rating. DWCNTs though did not have a significant effect on the cone calorimetric parameters of either epoxy resin. However, when DWCNTs were used with APP, there was a significant reduction in flammability as can be seen from Fig.9. In a similar manner to that used with MMTs, researchers have tried to modify carbon nanotubes with flame retardant groups. Im et al.[83] have used fluorinated MMTs and multi-walled carbon nanotubes, MWCNTs, mainly to enhance their dispersion in the resin, but which also helped in increasing thermal stability and reducing flammability of the resin. Yu et al.[81] grafted molybdenum-phenolic resin (Mo-PR) onto the surface MWCNTs, and used 3 wt% of the modified MWCNTs with 8 wt% melamine in an epoxy resin to achieve a UL-94 V-0 rating.

Researchers have also used CNTs in novel ways. For example, Kuan et al.[86] functionalized CNTs with vinyl triethoxysilane (VTES-CNT) and prepared EP composites by a sol-gel reaction. With 9 wt% VTES-CNTs content, a UL-94 V-0 rating was obtained.

Wu et al.[206] have used SWCNTs and MWCNTs to fabricate membranes, called buckypaper, and have used these on the surface of epoxy carbon fiber composites as potential fire shields. While SWCNT buckypaper did not produce a notable improvement in fire retardancy in cone calorimetric tests, MWCNT buckypaper acted as an effective flame-retardant shield, reducing the peak heat release rate by more than 60% and reducing smoke generation by 50% during combustion.

Graphene, because of its larger specific surface area and layered barrier effect, has reinforcing and flame retardant properties, but flame-retardant efficiency of neat graphene is marginal. Guo et al.[207] have reported a 44% reduction in PHRR of an epoxy resin containing 5 wt%

graphene compared to that of the unmodified resin. In our own work, the effects of graphene in the presence of the flame retardants DOPO and MP on the flammability of glass fibre-reinforced epoxy composites was studied[208] and are reported here in Table 8. It can be seen that when graphene is added with MP or DOPO, the flammability of the resin is reduced compared to that when the FR is used alone, but the effect is marginal. It can also be seen that the inclusion of 10 wt% FR slightly impaired the mechanical performance, which was attributed to the poor interfacial interactions in case of MP and the decreased cross-linking density in case of DOPO flame retarded resin. The addition of graphene however improved flexural and impact properties, but slightly decreased tensile performance.

TABLE 8 Mechanical and flame retardant properties of fibre –reinforced epoxy-graphene-flame retardant composites [208]

Sample	Composition of the resin (50 wt% of the composite*)			Modulus			Cone calorimetry at 50 kW/m^2			
	Epoxy	FR	Graphene	Flexural (GPa)	Tensile (GPa)	Impact (GPa)	TTI (s)	PHRR (kW/m^2)	THR (MJ/kg)	EHC (MJ/kg)
EP	100	0	0	13.2 ± 0.4	10.1 ± 0.1	8.1 ± 0.4	44	853	51.9	25.7
EP-MP	90	10	0	10.3 ± 0.3	9.5 ± 0.2	7.8 ± 0.6	38	528	48.8	22.2
EP-MP-G	90	9	1	12.6 ± 0.3	9.3 ± 0.0	9.1 ± 0.7	36	483	47.9	21.7
EP-DOPO	90	10	0	11.7 ± 0.5	10.4 ± 0.2	7.7 ± 0.3	34	624	41.3	20.5
EP-DOPO-G	90	9	1	13.4 ± 0.2	9.2 ± 0.1	8.4 ± 0.5	32	538	36.5	20.0

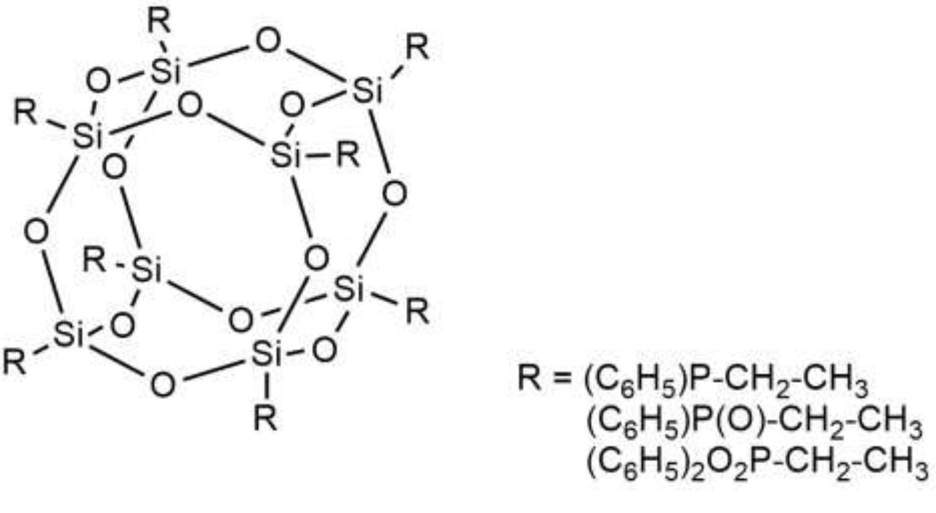
Note: EP=epoxy resin, MP=melamine phosphate, G=graphene, DOPO=9,10-Dihydro-9-oxa-10-phosphaphenanthrene- 10-oxide; FR = flame retardant (MP or DOPO)
Sample thickness = 3mm

In order to improve the flame retardant effect of graphene, researchers have carried out surface modification with FR elements.[200,209] Modification of graphene sheets with a Ce-doped MnO_2[68]; layered molybdenum disulfide (MoS_2)[199]; nickel-iron layered double hydroxide (Ni-Fe LDH)[69] have all been reported in the literature and their FRI values are included in Figure 10, where it can be seen that at 2 wt% level, these modified graphenes are quite effective. Although in these research citations UL-94 test results are not reported, it is envisaged that all samples with FRI values > 3 should achieve a V-0 rating.

Nanosilica: Among 3D nanoparticles, nanosilica is commonly used in epoxy resins. Spherical silica at 30 wt%[210] has been shown to increase the thermal stability of the epoxy resin, without having a detrimental effect on the mechanical properties. In our work, with 30wt% nanosilica in TGGDM resin, significant reduction in cone calorimetric data and a UL-94 V-1 rating were obtained (see Table 7). Afzal et al. produced epoxy-silicon nanocomposites by a sol-gel process[211]; with 20 wt% silica content, the thermal stability of the resin was significantly improved. Using a similar sol gel process, Shree and Sen[212] incorporated different phosphorus compounds during the sol-gel process to produce epoxy-phosphorus-silicon nanocomposites with improved thermal stability and reduced flammability.

Hu’s group have reported using unmodified hollow mesporous silica and mesoporous silica coated with chitosan/phosphorylated cellulose[204], or modified with P/N hyperbranched molecules[202] in epoxy resin at 2 wt%, all of which significantly reduced PHRR and smoke emission in a cone calorimetric test and increased char formation. In a separate study silica nanospheres were modified with oganic-inorganic polyphosphazene nanoshells and cuprous oxide nanoparticles to produce 3D nanostructures, 2 wt% of which in an epoxy resin significantly reduced the flammability of the resin.[203] The effectiveness of surface modified silica compared to that of unmodified silica nanoparticles can be seen from Figure 10.

Polyhedral oligomeric silsesquioxane (POSS) and its derivatives are hybrid inorganic/organic chemical composites with the general formula $Si_nO_{3n/2}R_n$. The structure (Scheme 10) possesses an inner inorganic silicon and oxygen core $(SiO_{1.5})_n$ and external organic substituents (R_n) that can feature a range of polar or non-polar functional groups, including those containing flame retardant elements. The organic substituents on their outer surfaces make them compatible or miscible with most polymers, and also determine its flame retardant efficiency. POSS nanostructures having diameters ranging from 1 to 3 nm can be considered as the smallest possible particles of silica, i.e., as molecular silica. They combine the advantages of siloxanes/silicates, such as thermal stability, good mechanical properties, low toxicity and solubility with functional groups, R, which impart flame retardancy. While some derivatives of POSS are commercially available, researchers have synthesized many variants, most of those being DOPO based (Scheme 10).



SCHEME 10 Polyhedrical oligomeric silsesquioxane (POSS) general structure. The R groups define the different variants of POSS

The effect of octa(aminopropyl)silsesquioxane, POSS-NH_2 on the thermal stability and mechanical properties of an epoxy resin was demonstrated by Zhang et al.[213], who tested the flexural and impact properties of epoxy_POSS composites before and after placing them in a muffle furnace in air at 500°C for 5 min. The retention of flexural and impact strengths illustrated in Fig. 11 indicate that the incorporation of POSS into epoxy networks enhances the thermo-oxidative resistance of the epoxy. It was postulated that incorporation of POSS leads to the formation of an inert layer on the surface of the material which can protect the internal structure from decomposition.

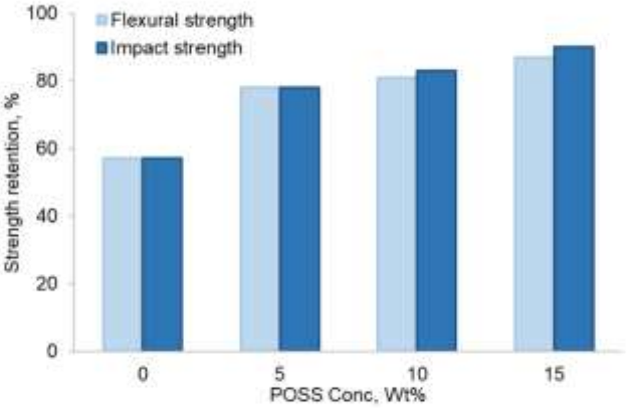


FIGURE 11 Mechanical property retention after thermo-oxidation (performed by heating in a muffle furnace at 500˚C for 5 min) of Epoxy-POSS composites (adapted from[213])

Commercially available POSS variants are not very effective flame retardants on their own in terms of achieving a UL-94 rating, hence researchers have used them either in combination with other flame retardants or modified with others, mostly with DOPO. The effects of differently modified POSS from taken from the literature are compiled in Figure 12 in terms of FRI indices.

Wu et al. have demonstrated that the addition of 10 wt% of either a mixture of POSS and triglycidylisocyanurate (TGIC) or a functionalized POSS made by reaction of POSS with TGIC to an epoxy resin, produces a significant improvement in fire retardance of amine-cured resin samples and of glass fibre-reinforced composite laminate samples based on them, when assessed by cone calorimetric experiments.[214,215] When the mixture of POSS and TGIC was used [214], PHRR, THR and CO production were all significantly reduced, albeit with some slight reduction in initial thermal stability, and consequently with shorter times-to-ignition. Nevertheless, thermal stability improved at higher temperatures leading to longer overall burn times. It is suggested that POSS reacts with the epoxy resin chains during later stages in the thermal degradation of the epoxy forming Si-O-C links, thus effectively crosslinking chains, aiding retention of material in the condensed phase, leading to longer burn times, and ultimately to greater char formation (*ca*. 8 wt% in resin plaques without POSS and 19 wt% with POSS). Similar differences in behaviour are seen also with the glass fibre-reinforced composite laminate samples, shown here in Table 9. However, the introduction of POSS reduced slightly both the flexural and the tensile moduli of the composite laminates, possibly owing to some reduction in fibre-resin bonding, although these mechanical properties are better retained in the POSS-containing laminates after exposure to radiant heat in the cone calorimeter. Interestingly, the introduction of the components of the functionalized POSS (POSS and TGIC) separately in the resin produces results little different from those obtained with POSS alone, from which it is concluded that there is no reaction between POSS and the isocyanurate in the resin, either during curing or during thermal degradation.

TABLE 9 Physical, fire and mechanical properties of glass fibre-reinforced epoxy composite (FEP) laminates containing POSS, TGIC or POSS+TGIC[215]

Sample	Composition (Mass %)		Mechanical properties		Fire properties Cone results at 50kW/m^2			
	Carbon fibre	Resin/POSS/ TGIC	Flex. mod (GPa)	Tensile Mod (GPa)	TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	Residual wt
FEP	50	50/0/0	13.9	7.5	125	857	50	54.5
FEP/POSS	50	45/5/0	10.7	6.1	121	420	32	61.5
FEP/TGIC	50	45/0/5	13.5	6.7	108	620	47	53.3
FEP/POSS /TGIC	50	45/2.5/2.5	13.9	5.8	114	385	32	58.1

Note: Sample thickness = 3mm

Zhou et al.[216] reported that by adding 5 wt% POSS to an epoxy, the LOI of the epoxy could be increased from 23% (for the unmodified epoxy) to 27.6% , and the UL-94 rating from NR to V-2. By replacing 1% POSS with with 4 wt% layered phenyl zirconium phosphate (ZrPP), 30.3% LOI and a V-1 UL-94 rating were achieved. Owing to the intercalation of POSS into layers of ZrPP, a nano reinforcing effect of the ZrPP-POSS was observed in terms of increased storage modulus in a DMTA test.

Pan et al.[67] used octapropylglycidylether modified POSS (OGPOSS) with hexaphenoxycyclotriphosphazene (HPCTP) in an epoxy resin in 10 + 5; 7.5 + 7.5 and 5 + 10 wt% ratios in an epoxy and achieved a V-0 rating.

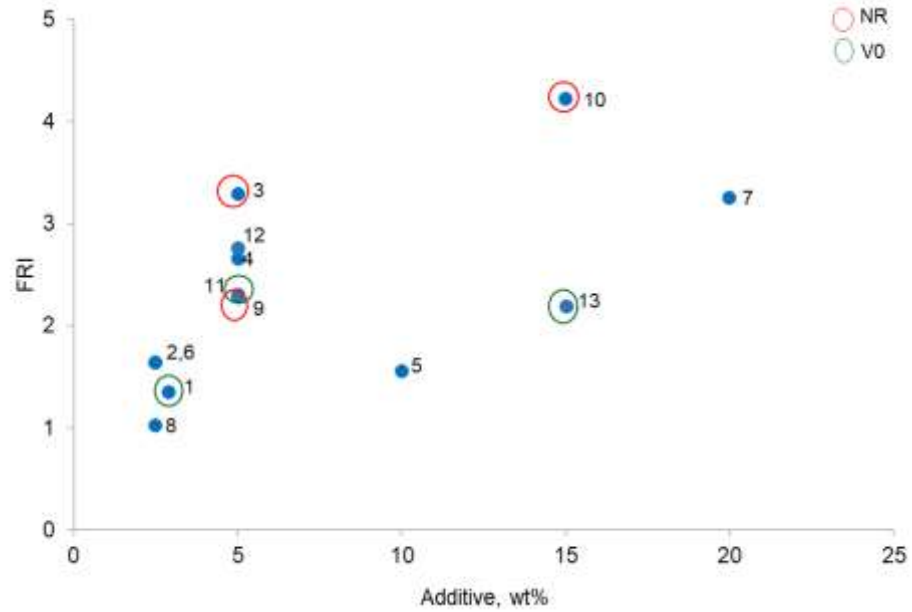
Phosphorus containing POSS: Researchers have prepared phosphorus containing POSS either by complete condensation of phosphorus containing trialkoxysilanes or trichlorosilanes ($RSiX_3$ precursors) or by modification of the POSS cage structures using phosphorus containing compounds.

Using the first approach, Liu et al.[217] synthesized a POSS derivative, namely octa-(N,N-(bis-(9,10-dihydro-9-oxa-10-phosphaphenanthene-10-yl) methyl)aminopropyl) silsesquioxane (ODMAS), which even at 5 wt% level could produce an LOI value of 35.5% and a UL-94 V-0 rating. The mechanical properties of the epoxy were also improved. Using the second approach, the same group later prepared POSS-bisDOPO by reacting aminopropylisobutyl POSS with polyoxymethylene and DOPO.[218] This POSS-bisDOPO had a good affinity with epoxy resin, and by adding 20 wt%, a V-0 UL-94 rating could be achieved; mechanical properties were also enhanced.

Li et al.[219] synthesized a novel cage–ladder-structure, phosphorus-containing polyhedral oligomeric silsesquinoxane (CLEP–DOPO–POSS) via the hydrolytic condensation of DOPO–

vinyl trimethoxysilane (VTMS) with 2-(3,4-epoxycyclohexyl) ethyl trimethoxysilane. At a 2.8 wt% (2.91 phr) level, an LOI of 31.9 % and a V-0 UL-94 rating could be achieved.

Yang's group has done extensive work on modification of POSS. In one study they reacted octa vinyl POSS with diphenylphosphine (DPP-POSS), diphenylphosphine oxide (DPOP-POSS), and DOPO (DOPO-POSS).[72] All three of these at 5 wt % level improved the flame retardancy of the epoxy, with the DPP-POSS being the most effective (33.2% LOI, V-0 rating), followed by DOPO-POSS (30.0 % LOI, V-1 rating) and DPOP-POSS (29.3 % LOI, V-1 rating). Their effectiveness in the cone test is shown in Figure 12. DPP, DPOP and DOPO are known to be vapour phase active flame retardants via release of phopshorus based radicals, hence in this case they worked in the vapour phase, whereas the POSS part worked in the condensed phase. Yang et al. have also synthesized DOPO-POSS by hydrolytic condensation of a modified silane, synthesized by addition reaction between DOPO and vinyl triethoxy silane (VTES)[220] and noticed that by adding 2.5 wt% of this to the epoxy resin a 30.2% LOI and V-1 UL-94 rating could be achieved.[74,221] Increasing the additive levels to 5 and 10 wt%, produced further reductions in cone calorimetric parameters, PHRR and THR (see Figure 12), but the samples could not achieve any UL-94 rating. The authors speculate that the outstanding flame retardancy effect of the DOPO-POSS 2.5 wt% is driven by a "blowing out" effect, in that after the sample was ignited, it showed an unstable flame for several seconds, with the pyrolytic gaseous products jetting outward from the condensed-phase surface. The flame was consequently extinguished such that it looked as though the pyrolysis gases blew out the flame.[221] By FTIR spectroscopy Yang et al. also demonstrated that the hydroxyl group of the DOPO-POSS and epoxy groups of the DGEBA react, which means that DOPO-POSS molecules could easily disperse into the epoxy resin at the molecular level. From TGA-FTIR and TGA-MS studies it was shown that DOPO-POSS changes the decomposition pathways of the epoxy resin and increases the amount of residue at high temperature; moreover, the release of phosphorus products in the gas phase and the presence of Si-O and P-O structures in the residue were noted.[222] Yang et al. also studied the effect of this DOPO-POSS on two different curing systems for DGEBA resin, namely an aromatic 4,4-diaminodiphenylsulphone (DDS) and an aliphatic oligomeric polyamide (PA650). DOPO-POSS is more effective with the DDS system in reducing the flammability of the resin.[223]



Note: 1 = CELP-DOPO-POSS (CELP = cage ladder structure)[219]*; 2,3,4,5,6,7,8,9 = DOPO-POSS*[72,74,221–223]*; 10 = OGPOSS (OG = octapropylglycidylether)*[67]*; 11 = DPP-POSS (DPP = diphenylphosphine)*[72]*, 12 = DPOP-POSS (DPOP=diphenylphosphine oxide)*[72]*; 13 = OGPOSS/HPCTC, 10/5; (HPCTP=hexaphenoxycyclotriphosphazene)*[67]

FIGURE 12 Flame retardancy evaluation of POSS derivatives (mainly DOPO based) in epoxy resins in terms of FRI values as a function of additive wt%

5. Flame retardants for specific applications: challenges

As discussed earlier in the review and shown in Figure 1, epoxy resins are used in a number of applications and that in some of these applications fire regulations are stringent. Issues related only to those fire critical applications are discussed below.

5.1. Composite materials

The use of epoxy resins in fibre-reinforced composites, while being most prevalent in aerospace and automotive sectors, is also of growing importance in the construction sector. In order to use polymer composites as structural materials for these applications, they have to conform to certain specified fire safety regulations. Since this subject is very complex, the reader is directed elsewhere for more detailed regulation and test information[43] and only key international fire performance codes and standards will be highlighted here. In brief, for the aerospace industry all products are required to comply with the US Federal Aviation Regulations (FAR), which govern the requirements for materials used for such applications.[38] The most important test is the Heat Release Rate Test[224], according to which when the sample is tested at 35 kW/m^2 external heat in an Ohio State University calorimeter, both the peak heat release rate and total heat release rates measured over 2 minutes should not exceed 65 kW/m^2. For the automotive sector, in the USA the Federal Motor Vehicle Safety Standard 302 (FMVSS 302)[225] regulates the flammability of materials used in the interiors of cars and trucks. The

FMVSS 302 test is virtually an international standard, as it has been harmonized with many equivalent designations. For the rail industry the rate of fire spread and toxicity of the fumes produced during their combustion are of vital importance. In the USA the Federal Railroad Administration (FRA) has a standard, Federal Register 49:192 (1984), which gives requirements for all materials used in rail carriages. In Europe there is not a common standard across the different countries. Each European country has its own regulations, e.g., DIN 5510 (Germany), BS 6853 (Great Britain), and NF F16-101 (France). There are no international fire safety standards for the construction sector and most countries have their own requirements for fire performance.

The overall burning behaviour of composites depends on the fibre and resin types[226,227] used in a particular structure. Except for some particular fibres (such as UHMW polyethylene or para-aramid), the most commonly used ones (such as glass and carbon) add little to the fuel content of a composite. Glass/carbon fibre-reinforced composites hence are less flammable than cast neat resins of similar thicknesses owing to lower resin contents in the former and also the fibres present acting as inert fillers.

To improve flame retardancy, in principle all flame retardants discussed in Section 4 can be used, but in actual practice it depends on the method of composite preparation. Another important issue when selecting a flame retardant is that it is effective at low concentrations as higher concentrations of FRs (ca. >20 wt%) can affect the mechanical properties of the composite. For the traditional hand lay-up method, where resin is applied on fabrics/fibres with a roller or brush, all types of FRs can be applied as long as these are well dispersed. As previously mentioned, some inorganic FRs do not disperse well and settle down on the bottom of the plaque (see Figure 3). This however is less of a problem in cured glass/carbon fibre composite laminate samples as the fibres help to prevent settling. For example, from our work reported in Figure 4, carbon fibre-reinforced composites were made with epoxy resins containing 8 wt% of flame retardant Int 2 (phosphorylated pentaerythritol plus melamine) or FR 372 (tris(tribromoneopentyl) phosphate). Both flame retarded composites showed good fire retardance with no significant change in physical and mechanical properties compared with those of a control sample containing no FR as shown in Table 10.[49] It can be seen from the results that with 8 wt %, a V-0 UL-94 rating could be obtained, whereas in neat resins, only a V1 rating was obtained.[49] The effectiveness of DOPO[51] and nanoparticles with and without additional flame retardants[208,228] in glass or carbon fibre-reinforced composites has already been discussed in Section 4.

TABLE 10 Physical, fire and mechanical properties of carbon fibre-reinforced composite laminates containing FR additives [49]

Sample	Composition (Mass %)		Thick-ness (mm)	T_g (from DMTA) (°C)	Mechanical properties		Fire properties				
							Cone results at 50 kW/m^2				UL-94 rating
	Carbon fibre	Resin/FR			Flexural mod (GPa)	Tensile Mod (GPa)	TTI (s)	PHRR (kW/m^2)	THR (MJ/m^2)	Smoke (l)	
C	67.1	32.9/0	3.2	61	43.2	85.1	64	224	19.4	1404	NR
C-Int 2	70.8	27.1/2.1	2.9	52	45.1	91.0	61	197	17.3	1399	V0

C-FR 372	70.8	27.1/2.1	2.9	186	43.1	87.3	52	146	11.3	1312	V0

Note: Int 2 = phosphorylated pentaerythritol plus melamine; FR 372 = tris(tribromoneopentyl) phosphate; sample thickness = 3mm

The “prepreg method”, which can be considered as an extension of hand lay-up, involves impregnation of the reinforcing fibres with a resin and partially curing the resin for easy shipment and storage. Any well dispersed FR in the resin can be used with this method.

Other commonly used methods for composite fabrication include resin infusion and resin transfer moulding, where flame retardant additives can affect the viscosity of the resin, particles can agglomerate and may get filtered by the fabrics, causing non-uniform distribution. Hence, many additive FR types cannot be used with these methods

For structural composites, maintenance of their structural integrity during and after fire is also an important issue. On exposure to heat, the resin part of the composite softens before degrading and eventually igniting. With the softening of the resin the fibre-matrix interfacial bonding is weakened and the laminate can lose up to 50% of its original mechanical properties close to its glass transition temperature[229]. Flexural properties being matrix dependent are affected most. The combustion of composite laminate usually is accompanied by delamination, where the resin part of the composite decomposes and the fibres are torn apart from the matrix[229,230], resulting in complete loss of mechanical properties of the laminate. FR additives do not affect the structural integrity of epoxy resin based composites at temperatures below the decomposition temperatures of the cured resin formulations and, in particular at the glass transition temperatures, hence do not add to the safety in the elastic region of the composite. FR additives, however, interact with the resin during thermal decomposition by either quenching the flame (vapour phase active) or promoting char formation (condensed phase active), with the char acting as a physical and thermal barrier slowing down mass and heat transfer to the pyrolysis zone[231,232]. The char thus formed could be structurally more stable when compared to the unmodifed resin, adding to the mechanical integrity of the decomposed composite.

5.2.Electrical and Electronic (EE) Applications

Owing to the excellent insulator, low shrinkage, good thermal, chemical and arc resistant properties of the cured epoxy resins, these are quite popular in the electrical and electronics industry, primarily for printed wiring boards (PWB). The resin is also used for flip chip encapsulation, bonding of leads, die coatings, surface mounting adhesives, encapsulation, and conformal coatings. Usually DGEBA based epoxy resin is used for semiconductor encapsulation and the highly functional phenol novolac epoxy (Scheme 3a) for PWBs.[103] In PWB, glass fibre-reinforced epoxy composites graded as FR-4 by the National Electrical Manufacturers Association (NEMA) are used, which meet the defined flame retardancy standard, UL 94-V0.[88]

Halogenated flame retardants still represent a large portion of the flame retardants market for EE applications. The largest single flame retardant used in PWB is tetrabromobisphenol-A, constituting about 95% of the market share.[88] An alternative method of incorporating bromine into PWB is to use a preformed diglycidyl ether of tetrabromobisphenol-A, which is commercially available. However, owing to environmental issues associated with halogenated FRs, alternative solutions are being explored

ATH is also widely used EE applications, mostly in the presence of other flame retardants such as red phosphorus.[100] The high loading levels of ATH required to achieve a UL-94 V0 rating however affect the mechanical properties and also moisture absorption is increased. While some phosphorus based flame retardants such as aryl phosphates[88], alkyl phosphates and alkyl phosphonates being polar, are subject to hydrolysis under humid conditions.[233] Aluminium diethylphosphinate is as option, because it does not have C–O–P bonds, so it is hydrolysis resistant and has little moisture-absorbing tendency.[88]

DOPO based FRs have shown some promising results for novolac epoxy resins where at a 1.6% phosphorus level a UL 94-V0 rating can be obtained; however, the addition of DOPO to the epoxy resin significantly decreases the T_g of the cured resin, which is problematic for lead-free soldering.[103]

5.3. Paints and coatings

Another area of application for epoxy resins is in anticorrosive paints. Because of the very high surface functionalities such as presence of peripheral hydroxyl (-OH) groups and ether (-O-) bonds, epoxy resins display strong adhesion to various substrates, especially metallic surfaces.[23] Epoxy coatings are also widely used as primers to improve the adhesion of automotive and marine paints on metal surfaces. Hence those resins having peripheral hydroxyl groups, i.e. glycidyl ether based, are preferred for these paints/coatings. Since coatings are thin versions of resin formulations, the types of flame retardant discussed in Section 4 can be used for applications in which greater flame retardancy is required.

Epoxy resins, usually bisphenol A based, are also used as binders for intumescent coatings, where their main function is to adhere the coating to the substrate and keep the components of the intumescent system distributed throughout the coating. Intumescent systems are chemical systems, which by the action of heat melt, bubble, swell and form a foamed char. This char then acts as an insulative barrier to underlying structural material protecting it against fire and heat to certain extent. The basic components of an intumescent formulation are an acid source (e.g., ammonium polyphosphate), char former (e.g., pentaerythritol) and a blowing agent (e.g., melamine). On heating, the acid source produces an acid, which catalyses dehydration reactions of the char former, resulting in the formation of char. In the meantime, the blowing agent produces inert gas(es), which inflate the char. The thickness, coherence and porosity of the char determines its thermal barrier efficiency. The resin binder also has an important role in keeping a skin over the foaming char. Epoxy resin with high molecular weight improves the thermal stability of the coating and enhances the oxidation stability of the char layer at high temperature.[234] Because epoxy-based intumescent coatings provide excellent hydrocarbon fire protection, they are typically used in harsher environments such as in the offshore marine industries or the chemical industry.

6. Conclusions and emerging trends

From the above discussion it can be concluded that by an appropriate choice of the base resin and the curing agent, the flammability of the cured epoxy resin can be tailored to a certain extent. However, for the resin to be used in a particular application and to conform to certain fire safety standards, it needs to be flame retarded. The last decade has seen a significant move away from the use of halogenated flame retardants and more towards phosphorus- based and silicon-containing FRs, and towards nanoparticles and metal salts. There is a vast literature available on phosphorus based inorganic and organic flame retardants, some of which are quite effective. For best results, flame retardants are often used in combinations of two or three to achieve synergistic results, the best being those in which different elements of one flame retardant or different components of a system work both in the gas and condensed phases. Environmental campaigners however keep pushing towards the removal of most of the FRs from products. It seems likely therefore that the use of reactive flame retardants in resins will assume even greater importance, although these may adversely affect the glass transition temperature and crosslinking density of the resin in some cases. For additives, the push is more towards polymeric flame retardants than towards additional small molecule FRs.

The emerging trend is understandably towards using more environmentally acceptable bio-based flame retardants. Recycling of carbon fibre-reinforced composites and EE (electrical and electronic) waste, both of which use epoxy resins, is becoming an emerging societal issue. Given that flame retardants are used in these applications, flame retardants and in particular halogenated ones, are the major impediment to recycling. Major research is underway to develop technologies to recycle flame retarded EE waste.[235] For fibre-reinforced composites, the recent push is towards developing recyclable epoxy resins; one example is by using vitrimers, which introduce dynamic chemical bonds to promote repairability and recyclability. There is also the possibility of developing multifunctional vitrimers, combining recyclability and flame retardant properties. To conclude, despite the availability of many effective flame retardants for epoxy resins, there is a room especially to develop more environmentally friendly, sustainable and multifunctional flame retardants.

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