

## Review article

## Recent advances in flame retardant epoxy systems containing non-reactive DOPO based phosphorus additives

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## ABSTRACT

Epoxy resins are widely used in the manufacturing of fire safety products in the industry. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is a commercially available non-toxic reactive flame retardant and its incorporation improves the fire behavior of epoxy systems by releasing active phosphorus species to the gas phase. The reaction between DOPO and oxirane moieties negatively affects the glass transition temperature of epoxy-based composites and thus to overcome this drawback, it is usually modified to obtain non-reactive derivatives (i.e. mono- and multi DOPO derivatives). Besides, DOPO can also interact with the surface of silica- and carbon based nanostructures, leading to hybrid DOPO additives ("hybrid" term is referred to the organic-inorganic structure of such derivatives, which do not react directly with the polymer matrix). Non-reactive DOPO derivatives allow effective hybrid flame retardant mechanism and, in some hybrid DOPO derivatives, good mechanical performances for the resin can be realized. This review focuses primarily on the technological advances in the last ten years (2011 onwards) on non-reactive DOPO derivatives for epoxy systems. Though DOPO is quite a common flame retardant additive in the polymer industry, for commercial exploitation of its derivatives, there is a need to develop economical alternative synthesis methodologies.

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**Abbreviations:** APTS, (3-aminopropyl)triethoxysilane; DGEBA, bisphenol A diglycidyl ether; DDM, 4,4'-diaminodiphenylmethane; DDS, diamino-diphenyl sulfone; DMA, dynamic mechanical analysis; DOPO, 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide; DP-MS, direct pyrolysis/mass spectrometry; DSC, differential scanning calorimetry; EHC, effective heat of combustion; FGI, fire growth index; FIGRA, fire growth rate; FPEI, fire performance index; FPI, flame propagation index; FRI, flame-retardancy index; FTIR, Fourier transform infrared spectroscopy; GPTMS, 3 glycidoxypropyltrimethoxysilane; <sup>1</sup>H NMR, <sup>1</sup>H nuclear magnetic resonance; HRR, average heat release rate; IDA, isophorone diamine; LOI, limiting oxygen index; MCC, micro cone calorimetry; MLR, mass loss rate; PHRR, peak of heat release rate; PY-GC-MS, pyrolysis gas chromatography mass spectrometry; SEM-EDX, scanning electron microscopy coupled with energy dispersive X-ray; TTI, time to ignition; T<sub>d</sub>5%, Initial degradation temperature (the temperature at weight loss of 5 wt%); TEM, transmission electron microscopy; TEOS, tetraethyl orthosilicate; T<sub>g</sub>, glass transition temperature; TGA, thermogravimetric analysis; THE, total heat release measured at the end of cone calorimeter test; THR, total heat release; TML, total mass loss; tp, time at peak of heat release rate; TSR, total smoke release; TTF, time to flashover; VTES, vinyltriethoxysilane - XPS, X-ray photoelectron spectroscopy.

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## 1. Introduction

Epoxy resins are widely used in many industrial applications, for example as castables, adhesives, molding materials, components for wires and cables, owing to their excellent mechanical properties, and suitable chemical and thermal resistance [1]. However, epoxy resins are very flammable and cause the release of high heat and smoke, therefore can be contributors of fire risk when used in aircraft, trains and ships [2]. Consequently, it is crucial to enhance the flame retardancy of epoxy resins without negatively affecting other properties [3]. In this context, different types of flame retardants have been developed for epoxy resins, which can be incorporated through a structural modification of polymer matrix or as reactive or non-reactive additives during the manufacturing process [4]. In the market, the most common flame retardants for epoxy resins are based on halogen- [5], nitrogen [6], phosphorus [7] and metal-containing compounds [8]. The decomposition of halogen-based flame retardants produces toxic dioxin and other pollutants [9]. This poses serious limitations on the exploitation of halogen flame retardants, as their impact on the envi-

ronment and human health is coming under the scrutiny of regulatory authorities [10]. The scientific community is focusing its attention on finding alternative solutions, which offer a good compromise between the costs of ecological health and the fire safety benefits of using flame retardants. For this reason, currently, researchers are developing environmentally friendly flame retardants for epoxy resins, which include phosphorus-based flame retardants, carbon-based materials, silicon-containing compounds and nanocomposites [11]. For instance, the phosphorous-based compound DOPO and its derivatives are important intermediates for the developments of organophosphorus flame retardants. They offer high thermal stability and flame-retardant efficiency [12]. However, DOPO and some of its derivatives (e.g. bis-(9,10-dihydro-9-oxa-10-oxide-10-phosphaphenanthrene-10-yl)-substituted methylene), have been shown to have a detrimental impact on the crosslinking of epoxy resins and thus adversely affecting their mechanical properties [13]. To overcome this issue, non-reactive DOPO-based flame retardants with different architecture (bridged, polymeric, hyperbranched, etc) have been developed [14]. Besides, DOPO can be used as a functionalization agent involving hybrid chemical strategies to produce modified silica- and carbon based nanostructures which can work as flame retardants and coupling agents at the interphase of composites, hence improving their mechanical performances [15].

DOPO and its derivatives have been shown to function in gas and condensed phases, trapping oxygen radicals in the flame (i.e. phosphorous radicals can terminate oxygen radicals, leading to a flame inhibition mechanism) and boosting the char production during combustion [16]. This char may work as a thermal shield and oxygen barrier, slowing down the heat transmission to the underlying polymer matrix. Non-reactive DOPO-based flame retardants have been widely used in aviation where a relatively lower loading is required to achieve improved fire behavior and allow a good compromise between flame retardancy and mechanical performances in epoxy systems [17–20]. The incorporation of mono- and multi DOPO derivatives into DGEBA resin, especially cured with aromatic hardener (e.g. DDM), improves its fire and mechanical properties. The DOPO moiety can release phosphorus species which trap free radicals of oxygen and catalyzes the dehydration of the polymer matrix leading to UL-94 V0 rating and increase (e.g. from 21.8 to 32.2%) of LOI with low phosphorous contents (e.g. 1, 2 wt%) [21–23]. Also, DOPO-based flame retardants containing triazine moiety can be useful in epoxy systems to obtain self-extinguishing composites with a longer time to ignition and delayed peak of heat release rate, even with small amounts of additive (e.g. 6, 12 wt%) [24]. Such types of derivatives, when used in combination with an aromatic curing agent (e.g. DDS), can significantly delay the thermal degradation and improve the thermal stability of composites [24]. DOPO has been exploited for the synthesis of functionalized hybrid (organic/inorganic) systems acting as a compatibilizer for the epoxy matrix with another flame retardant filler or a charring agent. A small addition (e.g. 1, 5 wt%) of these hybrid species in DGEBA resin allows for the manufacturing of aliphatic/aromatic epoxy composites with self-extinguishing capability, highly insulating char, low THR and good mechanical properties [25].

The willingness to move toward a diversified market and the increasing demand for safer high-performance materials have boosted the production and development of DOPO-based flame retardants suitable for epoxy systems. Despite a growing interest in DOPO derivatives as flame retardants there exist no comprehensive review, which summarizes in detail their synthesis and application in epoxy systems since 2011 (last decade) [26–31]. This review focuses on recent advances in non-reactive DOPO derivatives, including mono- and multi DOPO derivatives and nanomaterials containing DOPO as a functional component. Furthermore, the aspects re-

lated to fire retardant mechanisms of the DOPO derivatives as well as thermal and mechanical features of the epoxy systems are also considered in this review. DOPO is a reactive molecule where the P-H bond is converted into different types of bonds such as P-O, P-C, P-N, P-S to form derivatives with varying fire and thermal properties. Therefore, the conversion of the P-H bond also allows for the preparation of organophosphorus heteroaromatic compounds, which can establish physical crosslinking points with the matrix and trigger synergistic flame retardant effects, hence improving the fire and mechanical behaviors of epoxy thermostets [26–31]. For simplicity, in this review, the different DOPO derivatives are broadly classified and mono DOPO derivative (compound containing only one DOPO unit) and multi-DOPO derivative (compound containing multiple DOPO units). Further, such derivatives are categorized into subgroups based on the conversion of their P-H bond to P-O, P-C, P-N, P-S bonds.

## 2. Mono-DOPO derivatives as flame retardants for epoxy systems

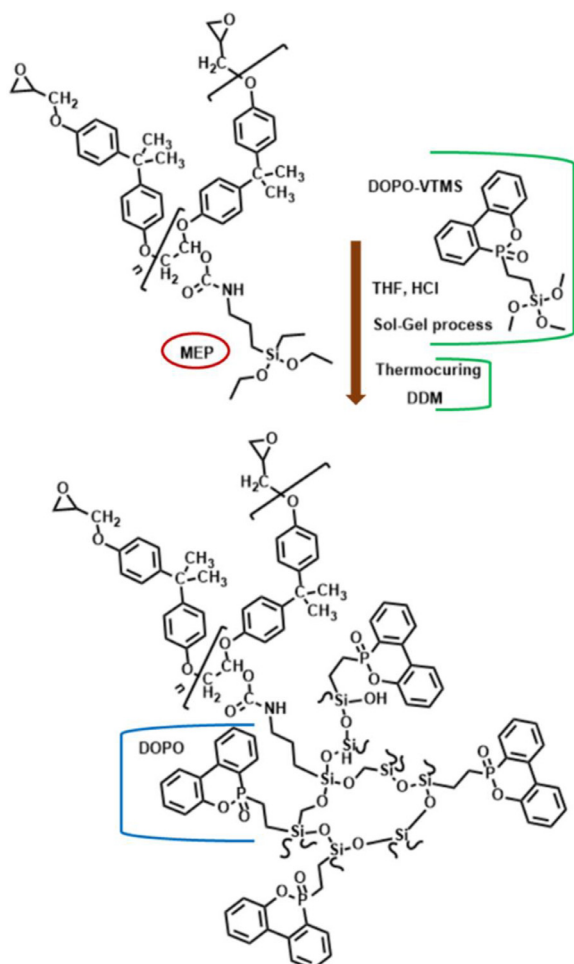
### 2.1. P-C bonded mono-DOPO derivatives

The modification of DOPO with silicon- and nitrogen containing species may influence the charring process, allowing for both higher production of char and lower flammability in the gas phase. Qian et al. [32] modified DGEBA epoxy (EP) resin through reaction with (3-isocyanatopropyl)-triethoxysilane. Therefore, modified-DGEBA was reacted with DOPO-vinyl trimethoxy silane (DOPO-VTMS) and cured with DDM as a hardener, resulting in the formation of organic/inorganic epoxy hybrids (Scheme 1). The LOI of the EP/DOPO-VTMS hybrids increased from 22.5 to 32% and the hybrids with 15 wt% DOPO-VTMS could reach the V0 rate in UL-94 vertical test.

The strong influence of DOPO-VTMS on PHRR reduction (~50%) was attributed to the presence of organophosphorus-modified oligosiloxane (organic/inorganic network) boosting the formation of a silicon-rich char, with honeycomb structure, working as an efficient thermal shield [32] (Fig. 1).

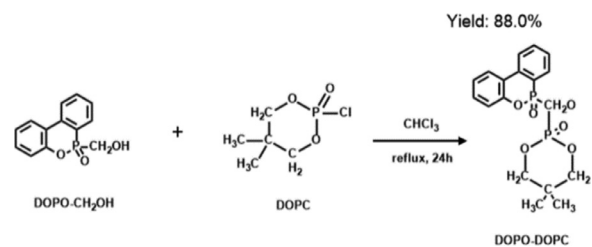
The modification of DOPO with a carbon source molecule may increase the yield of char without any addition of oligosiloxanes. Fang et al. [35] prepared a DOPO derivative flame retardant DOPO-DOPC through a reaction under reflux between 6H-dibenz[c,e][1,2]oxaphosphorin-6-methanol, 6-oxide (DOPO-CH<sub>2</sub>OH) and 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (DOPC) (Scheme 2). The LOI value of EP containing 10 wt% DOPO-DOPC increased up to 31.7% with respect to 24.6% for pure resin, although a load of 15 wt% DOPO-DOPC needed to be added into the DGEBA system to achieve UL-94 V0. It was observed that the morphology of EP containing 10 wt% DOPO-DOPC was a continuous, smooth, and compact surface, which reduced the heat transmission from the outside and the combustible gas diffusion from the inside. DOPO-DOPC showed flame retardant activity in both condensed and gas phases (Scheme 2).

DOPO-VTMS and DOPO-DOPC could only promote the formation of char and a thermal shield effect, mainly acting in the condensed phase. The use of pyrazine may result in a lower production of smoke, because of the nitrogen release which dilutes the gas phase. Tang et al. [36] prepared a DOPO-based pyrazine derivative 6-((2-hydroxyphenyl)(pyrazin-2-ylamino)methyl)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (DHBAP) through a two-step addition reaction between 2-aminopyrazine, 2-hydroxybenzaldehyde and DOPO (Scheme 3). It was used to improve the fire behavior of a DGEBA resin (E-44) cured with DDM agent. At 8 wt% of DHBAP loading in epoxy resin (EP/8% DHBAP), V0 rating, in the UL-94 test, and LOI value up to 34.0% were observed. In addition, cone calorimeter measurements for EP/8% DHBAP showed

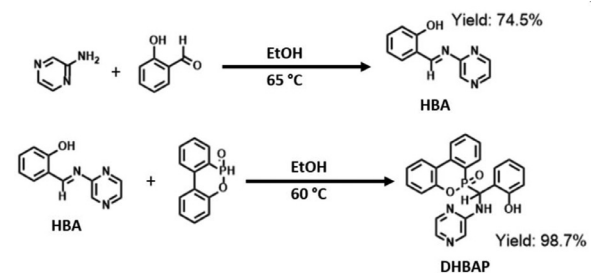


**Scheme 1.** Sol-gel synthesis route of the organic/inorganic epoxy hybrids by using DOPO-vinyl trimethoxy silane (DOPO-VTMS). MEP: modified epoxy resin. THF (tetrahydrofuran) and HCl (hydrogen chloride), reaction solvent and catalyst, respectively.

a strong decrease in PHRR, THR, EHC and TSR by 26.3, 21.3, 16.6 and 60.9% respectively compared to the neat EP (Table 1). DHBAP could show hybrid flame retardant activity in both phases. As can be seen from Table 1, the FIGRA value of EP/8% DHBAP is lower than that of EP, indicating that DHBAP can prevent or reduce the



**Scheme 2.** Synthesis route and chemical structure of DOPO-DOPC flame retardant additive. The chemical structures for both reactants, 6H-dibenz[c,e][1,2]oxaphosphorin-6-methanol, 6-oxide (DOPO-CH<sub>2</sub>OH) and 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (DOPC), are also reported [35].

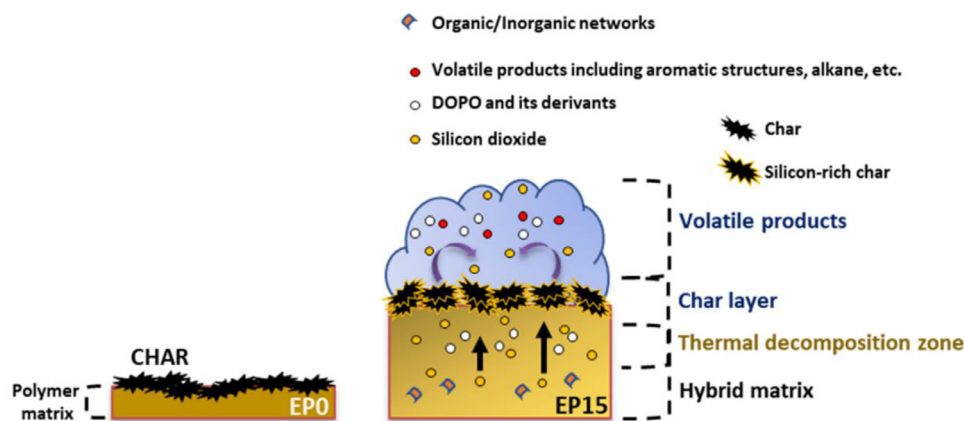


**Scheme 3.** Synthetic route of intermediate 2-((pyrazin-2-ylimino)methyl)phenol (HBA) and DHBAP [36]. DHBAP was synthesized by a two-step addition reaction using 2-aminopyrazine, 2-hydroxybenzaldehyde and DOPO as reactants.

risk of fire. Besides, the TSR value of the EP/8% DHBAP sample was significantly lower than the neat EP.

Finally, compared to neat EP thermosets, the tensile strength, bending strength and impact strength of EP/8% DHBAP slightly decreased (Table 17) [36].

The addition of silica nanoparticles (NPs) may improve mechanical performances [37]. DOPO-VTMS introduced the presence of silica in the char, which worked as a thermal barrier. Though, the tailoring of DOPO with silica NPs may also positively affect the mechanical properties of the final composite, because an improved interphase between the inorganic filler and the flame retardant. Kim et al. [38] prepared a modified flame retardant 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)-tethered SiO<sub>2</sub> (DOPO-t-SiO<sub>2</sub>), which was then added as hybrid nanoparticles into a DGEBA resin cured with IDA. The DOPO-t-SiO<sub>2</sub> NPs were synthesized through surface treatment of SiO<sub>2</sub> NPs with GPTMS (i.e. oxirane



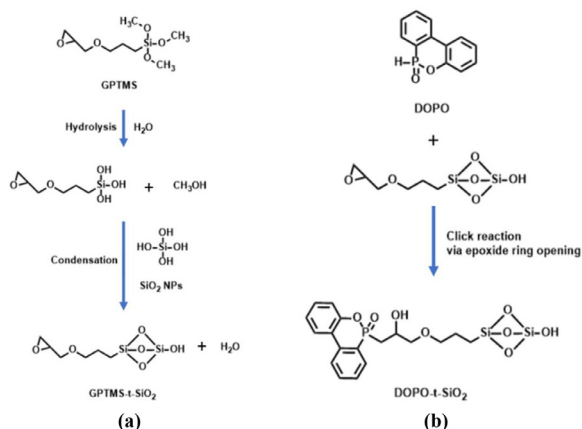
**Fig. 1.** Route of the thermal decomposition mechanism. According to Qian et al. [32], silica could be accumulated or pushed by the bubbles on the surface of burning epoxy [33,34]. Then the bubbles transferred the silica to the surface of the matrix and this ceramic layer provided an enhancement of the thermal stability of the char. EPO represents pure epoxy DGEBA and EP15 indicates modified resin added with 15 wt% DOPO-vinyl trimethoxy silane (DOPO-VTMS).

**Table 1**  
Results from UL-94, LOI and cone calorimetry tests for EP and EP/8% DHBAP [36].

Sample	UL-94 rating	LOI (%)	TTI (s)	PHRR (kW/m <sup>2</sup> )	FIGRA (MJ/kg)	THR (MJ/m <sup>2</sup> )	TSR (m <sup>2</sup> /m <sup>2</sup> )	EHC (MJ/kg)	Char Residue (wt%)
<sup>a</sup> EP	Unrated	25.8	59	1063.1	8.17	76.1	71.4	19.8	11.9
<sup>b</sup> EP/8% DHBAP	V0	34.0	68	783.3	6.52	59.9	27.9	16.5	15.0

<sup>a</sup> DGEBA resin<sup>b</sup> DGEBA resin containing 8 wt% DHBAP**Table 2**Data obtained from cone calorimeter test of pristine epoxy and DOPO-t-SiO<sub>2</sub>/epoxy nanocomposites, respectively [38].

Sample	Additive Content (phr%)	TTI (s)	PHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	EHC (MJ/kg)
Pristine epoxy	0	29	618.3	68.9	20.12
DOPO-t-SiO <sub>2</sub> 1/epoxy	1	23	448.2	43.6	12.23
DOPO-t-SiO <sub>2</sub> 5/epoxy	5	21	431.5	40.4	11.23
DOPO-t-SiO <sub>2</sub> 10/epoxy	10	20	269.8	31.4	8.10

**Scheme 4.** Synthesis mechanism of (a) GPTMS-t-SiO<sub>2</sub> and (b) DOPO-t-SiO<sub>2</sub> [38].

rings) (Scheme 4) [39]. The use of DOPO-t-SiO<sub>2</sub> NPs as flame retardant additives simultaneously improved mechanical properties, thermal stability and the flame retardancy of the epoxy nanocomposites (Table 2). The thermosets exhibited not only higher flexural strength but also fracture toughness, compared to those of pristine resin and nanocomposites with a single additive of SiO<sub>2</sub> or DOPO, respectively.

Kim et al. [38] proposed that the incorporation of DOPO-t-SiO<sub>2</sub> NPs resulted in the synergetic effects of retarding crack propagation as well as a plasticizing epoxy matrix. Besides, the presence of the hybrid nanoparticles in the epoxy matrix promoted an early formation of a continuous char layer, slowing down the penetration of oxygen molecules. In addition, the DOPO-t-SiO<sub>2</sub> NPs system exerted a gas phase inhibition effect (Table 2).

The silicon-rich char produced by DOPO-VTMS during the combustion may be combined with the diluting effect of nitrogen, leading to the formation of an intumescent char. This char shows very low thermal conductivity and may strongly reduce heat transmission [40]. Qian et al. [41] synthesized an organic/inorganic (hybrid) flame retardant DOPO-VTMS/TGIC-KH. They prepared a DOPO derivative through hydrolysis and condensation between DOPO-VTMS and TGIC-KH (Scheme 5) [42].

DOPO-VTMS/TGIC-KH additive was incorporated into a DGEBA system, cured with DDM, at different phosphorus/nitrogen ratios (Table 3).

EP/(DOPO-VTMS/TGIC-KH) composites with a mass ratio of 4/1 (EP-N1 in Table 3) showed the highest char residues in the air atmosphere (3.8 wt%) together with the highest LOI and UL-94 V0 rating. DOPO-VTMS/TGIC-KH derivative exhibited phosphorus-

**Table 3**Chemical composition of composites, phosphorous contents, LOI, UL-94 rating and extinguishing times ( $t_1$  - after first flame application during UL-94 test,  $t_2$  - after second flame application during UL-94 test) [41].

Sample	Phosphorous content (wt%)	LOI (%)	UL-94 rating	Extinguishing Times	
				$t_1$	$t_2$
<sup>a</sup> EP	-	22.0 ± 1.0	Unrated	-	-
<sup>b</sup> EP-N0	1.24	29.0 ± 0.5	V2	3.5	17.3
<sup>c</sup> EP-N1	0.99	29.5 ± 0.5	V0	1.8	6.1
<sup>d</sup> EP-N2	0.74	28.0 ± 0.5	V2	2.7	17.6
<sup>e</sup> EP-N3	0.50	27.0 ± 0.5	Unrated	-	-

<sup>a</sup> DGEBA resin<sup>b</sup> DGEBA resin containing 10 wt% DOPO-VTMS (EP-N0, N0: 5/0)<sup>c</sup> DGEBA resin containing 8 wt% DOPO-VTMS and 2 wt% TGIC-KH (EP-N1, N1: 4/1)<sup>d</sup> DGEBA resin containing 6 wt% DOPO-VTMS and 4 wt% TGIC-KH (EP-N2, N2: 3/2)<sup>e</sup> DGEBA resin containing 4 wt% DOPO-VTMS and 6 wt% TGIC-KH (EP-N3, N3: 2/3)

nitrogen synergism through an inhibition mechanism linked to a strong intumescence. In addition, the presence of an inorganic silica phase in the hybrid epoxy network promoted the production of an abundant and graphitized silicon-rich char (Fig. 2, Table 3) [41,43–46].

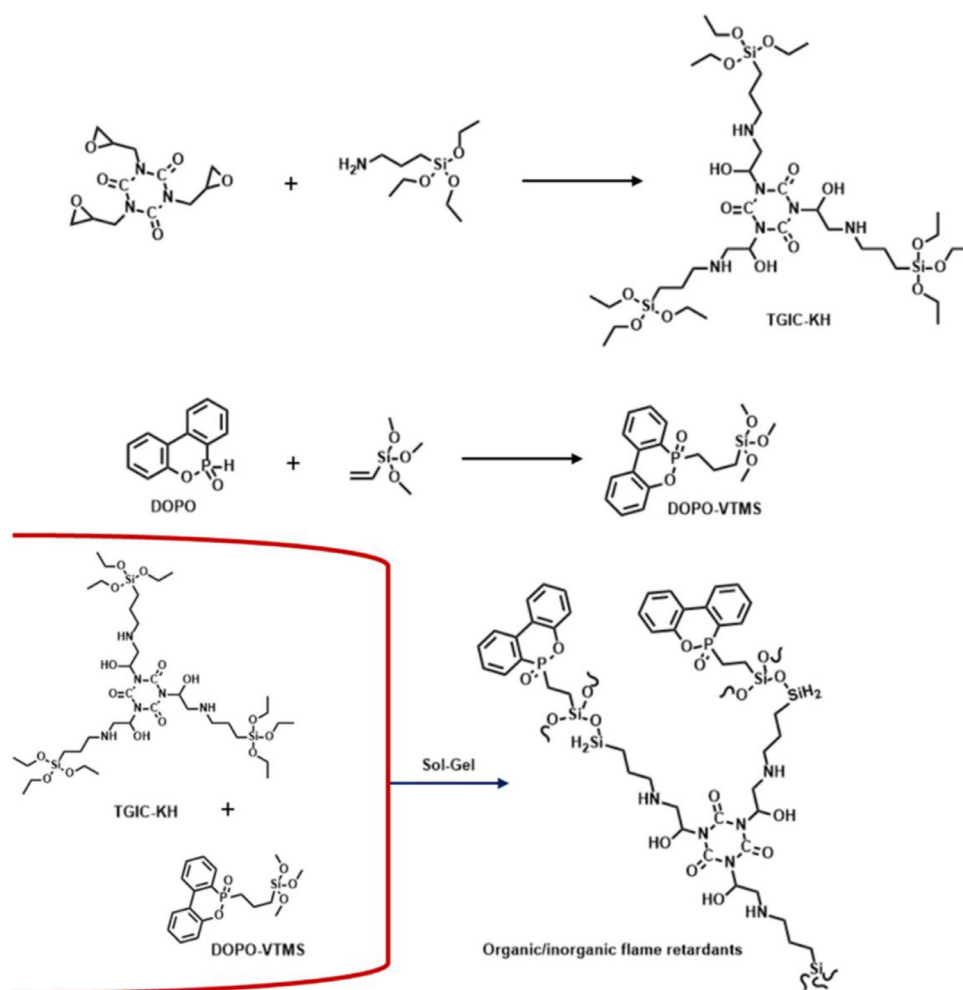
## 2.2. P-O bonded mono-DOPO derivatives

Zhang et al. [47] synthesized a DOPO based flame retardant DOPO-PEPA (DP) through Atherton–Todd reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and 1-oxo-4-hydroxymethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (PEPA) (Scheme 6). DP was used as an additive-type flame retardant in a DGEBA based epoxy resin (E44) cured with DDM [47].

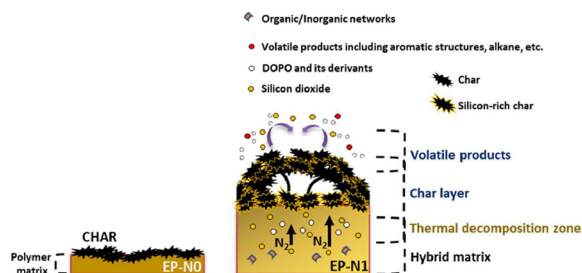
EP matrix containing 9.1 wt% DP achieved a LOI value of 35%, UL-94 V0 rating, and reduced PHRR of ~53.9%. The decomposition of PEPA units produced phosphoric acids during the carbonization process, which strongly boosted the char formation in the condensed phase (Table 17) [40,48]. DOPO part of DP flame retardant was responsible for the release of phosphorus radicals with an inhibition effect in the gas phase [19,49].

DOPO may also be coupled with ammonium to form salts containing nitrogen. This strategy allows for synergism between nitrogen and phosphorus to flame retard an epoxy resin. The presence of the P-O bond in DOPO-PEPA influences the mechanical performances of the final composite [50,51], unlike the DOPO-based salts that only work as flame retardants. Szolnoki et al. [52] improved the flame retardancy of a sorbitol-based epoxy resin. The effect of several flame retardants (i.e. ammonium polyphosphate (APP), re-



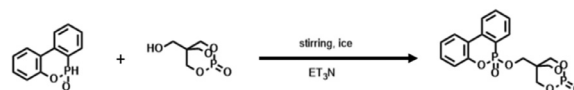


**Scheme 5.** Synthesis route and chemical structure of DOPO-VTMS/TGIC-KH flame retardant additive. DOPO-vinyl trimethoxy silane (DOPO-VTMS) was left to react with a silane modified product (TGIC-KH) based on 1,3,5-triglycidyl isocyanurate and 3-triethoxysilylpropylamine [41].



**Fig. 2.** Route of the thermal decomposition mechanism. Silica could be pushed by the bubbles (pyrolytic gases) rising on the surface of burning epoxy. The presence of a phosphorus-nitrogen synergism system (DOPO-VTMS/TGIC-KH) released decomposition products of DOPO and nitrogen during its thermal decomposition. EP-N0 represents pure epoxy DGEBA and EP-N1 indicates modified resin added with 8 wt% DOPO-VTMS and 2 wt% TGIC-KH [41].

sorcinol bis(diphenyl phosphate) (RDP), red phosphorus (RP) and DOPO-derivatives (DXA and DXM)) added into a bioepoxy resin cured with a cycloaliphatic amine-type hardener (3,3'-dimethyl-4,4'-diaminodicyclohexylmethane (MH3122)) (Fig. 3) was investigated. Thermosets containing RP and ammonium salt of DOPO (DXA) showed self-extinguishing capability at 3 wt% P, whereas the inclusion of melamine salt and DXA (DXM) resulted in HB rating due to lower P-content of the sample. The addition of DXA and DXM into the resin doubled the amount of residue formed



**Scheme 6.** Synthesis route and chemical structure of DOPO-PEPA (DP). DP was synthesized through synthesized via Atherton–Todd reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and 1-oxo-4-hydroxymethyl-2,6,7-trioxo-1-phosphabicyclo[2.2.2]octane (PEPA) [47].

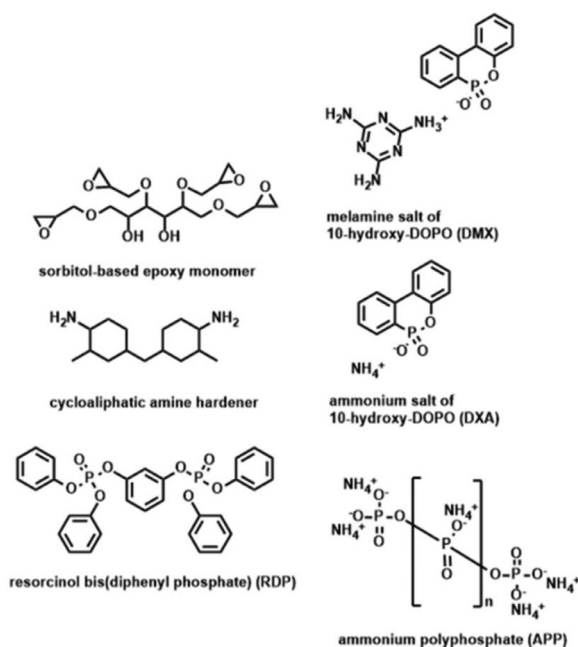
at 800°C compared to the pristine sample. The self-extinguishing compositions containing RP and DXA at 3 wt% P also showed favorable results in cone calorimetry. It is well known that unmodified DOPO mainly works in the gas phase through the radical scavenger mechanism, while DMX and DXM could also act simultaneously in the condensed phase because promoting the formation of a char acting as a thermal shield [52,53].

Recently, Bifulco et al. [54,55] applied an *in situ* sol-gel synthesis of silica nanoparticles to improve the fire behavior of a DGEBA epoxy resin cured with a cycloaliphatic hardener IDA. The presence of silica domains, even at very low loadings (2 wt%), prevented dripping during the UL-94 vertical flame spread test [56], though the samples could not be classified. Bifulco et al. [57,58] further exploited the earlier work with a combination of different hybrid strategies in improving the flame retardancy of DGEBA resin cured with IDA. The flame-retardant epoxy nanocomposites were prepared through the addition into the silica-epoxy matrix of

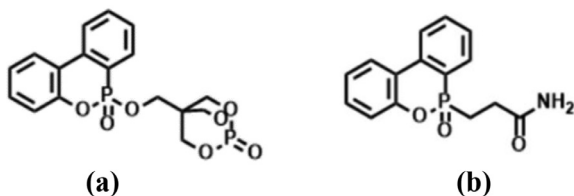
**Table 4**  
Results from UL-94 and cone calorimetry tests for the investigated samples [57,58].

Sample	UL-94 Rating	TTI (s)	HRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	Char Residue (wt%)	FPI (-)	TTF (min)	CO/CO <sub>2</sub> (-)
<sup>a</sup> EPO	Unrated	38 ± 3	532 ± 23	96 ± 3	1	67	-	0.06
<sup>b</sup> EDP	V1	31 ± 1	135 ± 18	61 ± 5	16	24	2.0	0.08
<sup>c</sup> EDA	V0	34 ± 1	160 ± 20	43 ± 3	3	19	3.1	0.15
<sup>d</sup> EPOS	Unrated	40 ± 4	412 ± 10	79 ± 10	4	49	-	0.04
<sup>e</sup> ESDAM	V0	56 ± 4	249 ± 13	59 ± 7	4	14	4.3	0.16
<sup>f</sup> ESDPM	V0	42 ± 5	247 ± 11	57 ± 5	10	22	2.5	0.08

- <sup>a</sup> DGEBA resin  
<sup>b</sup> DGEBA resin containing 17.3 wt% DP  
<sup>c</sup> DGEBA resin containing 23 wt% DA  
<sup>d</sup> DGEBA resin containing 2 wt% of silica  
<sup>e</sup> DGEBA resin containing 22 wt% DA  
<sup>f</sup> DGEBA resin containing 16.3 wt% DP



**Fig. 3.** Chemical structure of the epoxy resin components and the applied flame retardants, adapted from [52].



**Fig. 4.** Chemical structures of DP (a) and DA (b), adapted from [57,58].

3-(6-oxidodibenzo[c,e][1,2]oxaphosphin-6-yl) propanamide (DA) and DP at 2 wt% of P-loading (Fig. 4), together with melamine (M), and subsequently cured with the amine cycloaliphatic hardener (IDA). As previously reported, Zhang et al. [47] disclosed that the incorporation of 9.1 wt% DP into a DGEBA resin cured with DDM allowed to achieve UL-94 V0 rating, together with a significant increase of LOI and a remarkable reduction in PHRR. The sol-gel hybrid strategy applied by Bifulco et al. [57] enabled to obtain self-extinguishing thermosets with the addition of 17.3 wt% DP into a similar DGEBA system and helped to reduce the HRR in cone calorimetry experiments despite the use of a more flammable aliphatic hardener.

DA worked as a plasticizer in the epoxy resin, leading to a lower Tg compared to the neat polymer. Conversely, DSC tests for DP indicated a significant increase (up to 5%) of Tg with respect to the pristine polymer [59].

The epoxy resin containing DA alone could achieve a V0 rating at 2 wt% P, though the presence of silica nanoparticles was fundamental to achieve a V0 non-dripping rating in the UL-94 test (Table 17). Conversely, the incorporation of DP (2 wt% P) alone in the epoxy could already prevent dripping in the fire test. However, when DP was used as a flame-retardant, the combined effects of melamine together with silica-nanoparticles were necessary to achieve a V0 rating (Tables 4 and 17). In addition, a higher char formation and intumescence were observed for samples containing DA and DP with melamine, especially in the case of DP, because of a predominant activity in the condensed phase [29]. Conversely, DA showed a remarkable gas phase activity from the early stage of decomposition of composite.

Bifulco et al. [57] proposed a flame retardant mechanism of ESDPM in an oxygen atmosphere (Fig. 5).

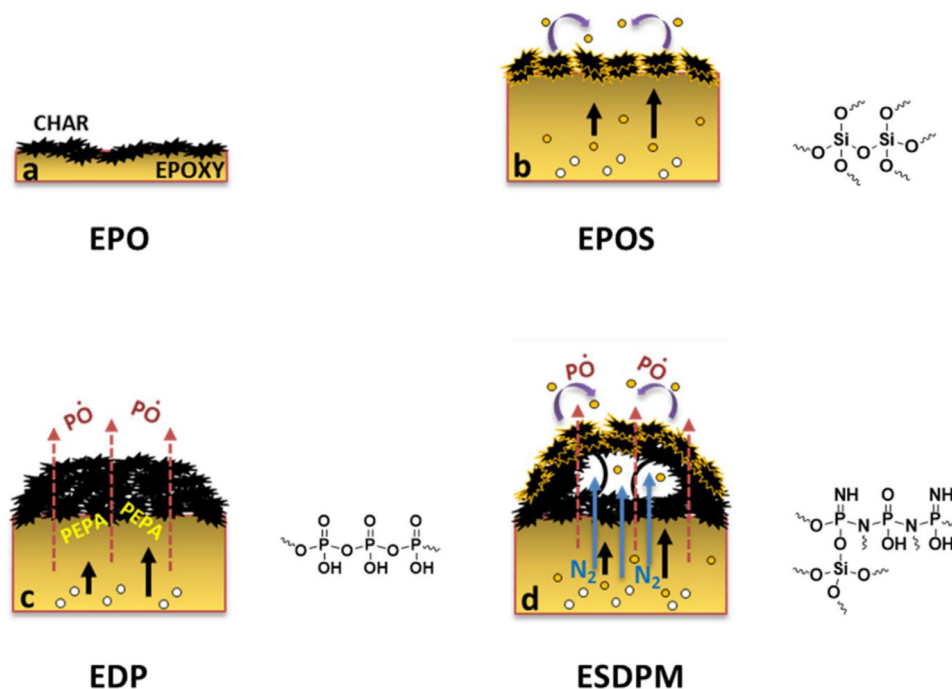
Tensile and three-point bending flexural tests showed that the addition of DA and DP enhanced the rigidity of the resin, resulting in a strong increase in Young's modulus (up to 34%) and a slight reduction in fracture strength, elongation at break and toughness [57,58].

### 2.3. P-S bonded mono-DOPO derivatives

Jian et al. [60] synthesized an organophosphorus heteroaromatic compound (DMBT) derived from DOPO and 2-mercaptobenzothiazole (MBT) and incorporated it into a DGEBA based resin cured with DDM hardener (Scheme 7). The idea to use MBT in the modification of DOPO came out from some recent works, which used this compound to improve the adhesion, toughness and curing behavior of epoxy resins [61,62].

DMBT molecules acted as physical crosslinking points (i.e.  $\pi$ - $\pi$  interactions and hydrogen bonds) like bridges to connect the epoxy macromolecular chains, leading to the strengthening of epoxy thermosets (Fig. 6). Due to this strengthening effect of the DMBT additive, epoxy composites containing 10 wt% of the DOPO derivative resulted in an increase in the tensile strength, flexural strength and modulus compared to pure EP [60].

The epoxy composite containing 10 wt% DMBT (EP-2) passed UL-94 V1 rating, possessed a LOI value of 33.5% and had reduced PHRR and THE values during combustion (Tables 5 and 17). Jian et al. [60] also calculated the FIGRA value of the sample. It is defined as the ratio of "PHRR" to "tp" and is recognized as an important parameter to assess the hazard of developing fire [63]. FIGRA value of EP-2 was much lower than that of EP, because of its lower fire-spreading rate in the developing fire.



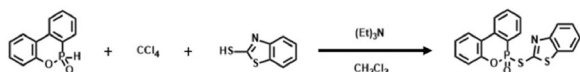
**Fig. 5.** Proposed mechanism of ESDPM in an oxygen atmosphere. (a) EPO, (b) EPOS, (c) EDP, (d) ESDPM. The black arrows indicate the direction of the rising bubbles (white balls) from the hot bulk polymer matrix (pink region). The yellow circles represent the *in situ* generated silica nanoparticles in the epoxy resin. The yellow border line around the black char designates a ceramic silica layer lying on the carbonaceous residue. The chemical formulas represent the polymeric substructures formed in the respective residue surface. The Figure was adapted from [57,58].

**Table 5**  
LOI, UL-94 rating, cone calorimeter test results of the cured epoxy resins [60].

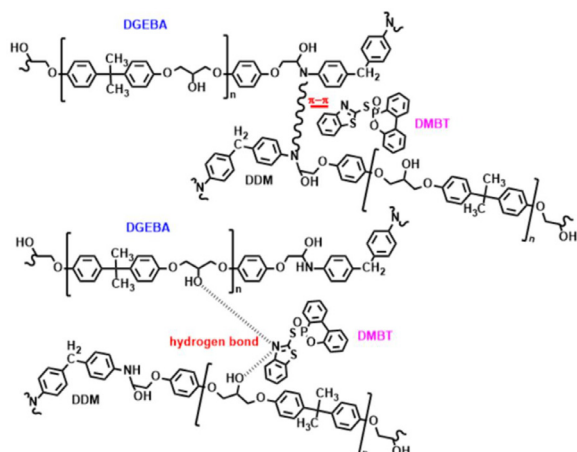
Sample	UL-94 rating	LOI (%)	PHRR (kW/m <sup>2</sup> )	Tp (s)	THE (MJ/m <sup>2</sup> )	FIGRA (MJ/kg)	EHC (MJ/kg)	MLR (g/s)
<sup>a</sup> EP	Unrated	25.2	1140 ± 2	130 ± 2	76 ± 3	8.8	22.3	0.071
<sup>b</sup> EP-2	V1	33.5	524 ± 16	125 ± 2	71 ± 2	4.2	18.9	0.068

<sup>a</sup> DGEBA resin

<sup>b</sup> DGEBA resin containing 10 wt% DMBT



**Scheme 7.** Synthesis route of the organophosphorus heteroaromatic compound (DMBT). DMBT was designed and synthesized derived from DOPO and 2-mercaptobenzothiazole (MBT) [60].



**Fig. 6.** The proposed mechanism of DMBT to reinforce epoxy resin, adapted from [60].

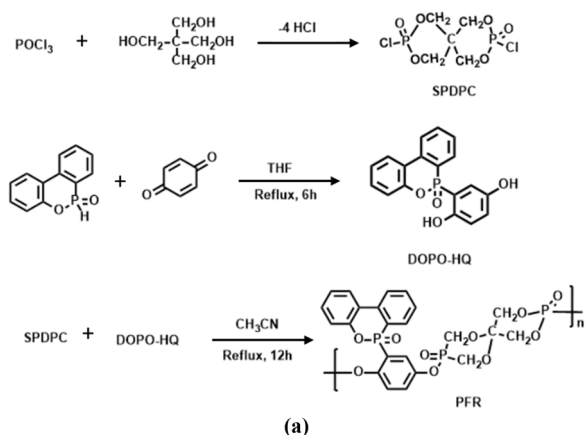
Table 5 shows that DMBT also decreased EHC and MLR values, which revealed a simultaneous activity of the flame retardant in both gas phase and condensed phases [60].

### 3. Multi-DOPO derivatives as flame retardants for epoxy systems

#### 3.1. P-C bonded multi-DOPO derivatives

Wang et al. [64] prepared a series of flame-retardant epoxy resins (EP) with different content of poly(DOPO substituted dihydroxyl phenyl pentaerythritol diphosphonate) (PFR). The PFR was synthesized via the polycondensation reaction between 10-(2,5-dihydroxyl phenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-HQ) and pentaerythritol diphosphonate dichloride (SPDPC) (Scheme 8a). The synthesis route was confirmed through FTIR and <sup>1</sup>H NMR.

The same research group synthesized another PFR compound, from the polycondensation of DOPO-disubstituted benzenedimethanol (TDCA-DOPO) with pentaerythritol diphosphonate dichloride (SPDPC) (Scheme 8b) and confirmed its structure [65]. Both PFR additives were added as flame retardant additives in DGEBA epoxy resin and cured with polyamide (651) and DDM hardener, respectively. The incorporation of PFRs into EP significantly improved its thermal stability, although the mechanical results demonstrated that PFRs slightly enhanced failure strain accompanied by a decrease in tensile strength. The degradation of

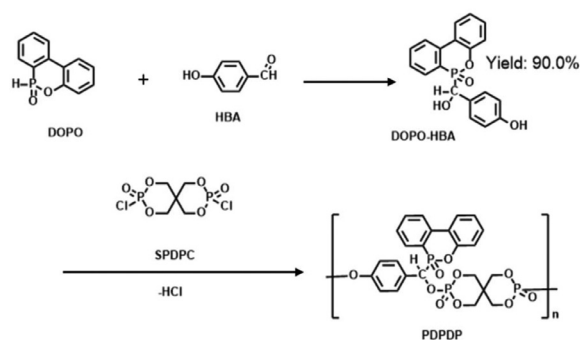


**Scheme 8.** Synthesis routes and structure of poly(DOPO substituted dihydroxyl phenyl pentaerythritol diphosphonate) (PFR) flame retardant additives. Regarding DOPO-HQ, it was named DOPO-BQ in the references [64,65].

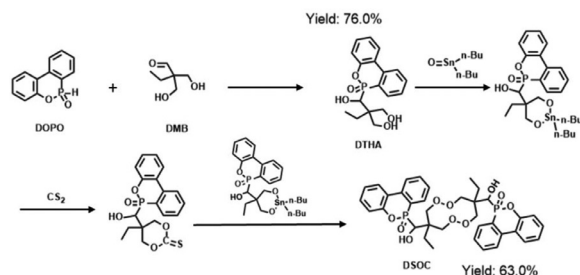
EP/PFR hybrids resulted in the formation of an intumescent char layer at high temperatures, protecting the inner polymer matrix (pure EP) from further burning [46,66,67]. LOI values increased from 21.5% for pure EP to 36.0% for resins containing PFR, and UL-94 V0 (self-extinguishing) materials were obtained with the 15 wt% PFR [64,65]. EP/PFR composites possessed higher glass transition temperatures than phosphorus-free EP. PFR additives worked as hybrid flame retardants, also working in the gas phase by poisoning the flame through the release of PO· radicals. Finally, MCC data showed that the PHRR and THR of the EP/PFR composites were significantly reduced compared to pure EP (Table 17).

Wang et al. [68] also synthesized a phosphorus-containing oligomeric flame retardant poly(DOPO substituted hydroxyphenyl methanol pentaerythritol diphosphonate) (PDPDP) through the reaction of 4-hydroxybenzaldehyde (HBA) with DOPO (Scheme 9). This DOPO derivative was used as a flame retardant additive in DGEBA epoxy resin cured with DDM. During the combustion process, PDPDP could reduce the release of combustible gas and induced the formation of a char layer. The addition of 20 wt% PDPDP into pure EP significantly increased LOI value from 21.5 to 34.5%, although already the 15 wt% of PFR content was enough to achieve UL-94 V0 rating [43,68,69].

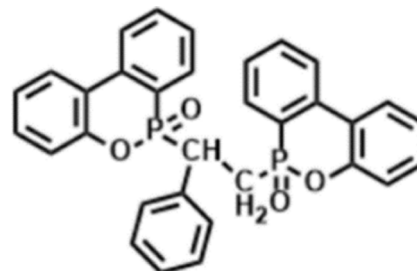
Xu et al. [70] synthesized a DOPO-based spiroorthocarbonate (DSOC) through a reaction between DOPO and 2,2-dimethyl-1-butanol (DMB) (Scheme 10). It was used as a flame retardant additive in the cationic polymerization of a DGEBA-based epoxy resin (E-51) [71]. DSOC increased LOI values of composites from 19.9%



**Scheme 9.** Chemical structure of poly(DOPO substituted hydroxyphenyl methanol pentaerythritol diphosphonate) (PDPDP) flame retardant additive and its synthesis procedure [68].



**Scheme 10.** Synthesis route and chemical structure of 6,6'-(3,9-diethyl-1,5,7,11-tetraoxaspiro[5.5]undecane-3,9-diyl)bis(hydroxymethylene)bis(6H-dibenzo[c,e][1,2]oxaphosphine 6-oxide) (DSOC). DMB: 2,2-dimethyl-1-butanol. DTHA: DOPO based trihydroxy alcohol. CS<sub>2</sub>: carbon disulfide [70].



**Fig. 7.** The chemical structure of phenethyl-bridged DOPO derivative DiDOPO, adapted from [76].

for pure E-51 to 30.9% for modified systems, in addition, UL-94 V0 rating was achieved when 15 wt% of additive was incorporated into the epoxy network (Table 6). The incorporation of DSOC not only significantly enhanced the char yield but also the toughness and adhesive strength of the EP (Table 6) [70]. The significant presence of aliphatic carbon chains in DSOC makes this flame retardant more flexible compared to PFR additives [72,73], therefore it does not negatively affect the normal packing in the polymer matrix, even leading to an improvement of mechanical properties with respect to pristine epoxy (Table 6).

Recently, the use of multi-walled carbon nanotubes as flame retardants is rising great attention [1,74,75], because they decrease the thermal conductivity of the final composite and in combination with DOPO may allow for a hybrid activity, where more heat-resistant char is produced together with a flame inhibition action. Yan et al. [76] combined the use of a phenethyl-bridged DOPO derivative (DiDOPO, Fig. 7) with multi-walled carbon nanotubes (MWNT) in DGEBA epoxy resin cured with 2-ethyl-4-methylimidazole (EMI-2,4) to improve its flame retardancy. The introduction of 10 wt% DiDOPO/0.8 wt% MWNT into EP (EP/DiDOPO10/MWNT0.8) increased the LOI from 21.8 to 38.6% and



**Table 6**  
Chemical composition of epoxy composites, flame retardant contents, LOI, UL-94 rating and mechanical properties of cured samples [70].

Sample	DSOC content (wt%)	UL-94 rating, drip	LOI (%)	Tensile strength (MPa)	Adhesive strength (MPa)	Impact strength (kJ/m <sup>2</sup> )
EP-0	0	Unrated, Yes	19.9	56.7	15.8	8.1
EP-5	5	Unrated, Yes	21.5	55.1	17.1	8.9
EP-10	10	V1, No	26.7	53.4	18.7	9.6
EP-15	15	V0, No	28.6	49.9	19.4	11.3
EP-20	20	V0, No	30.9	47.3	20.6	14.1

<sup>a</sup>E-51 (DGEBA-based resin)

<sup>b</sup>E-51 (DGEBA-based resin) containing 5 wt% DSOC

<sup>c</sup>E-51 (DGEBA-based resin) containing 10 wt% DSOC

<sup>d</sup>E-51 (DGEBA-based resin) containing 15 wt% DSOC

<sup>e</sup>E-51 (DGEBA-based resin) containing 20 wt% DSOC

**Table 7**  
Quantitative assessment of the three flame-retardant effects [76].

Sample	Flame inhibition effect (%)	Barrier and protective effect (%)	Charring effect (%)
<sup>a</sup> EP/MWNT0.8	15.1	33.2	-0.2
<sup>b</sup> EP/DiDOPO10	31.8	16.1	5.3
<sup>c</sup> EP/DiDOPO10/MWNT0.8	36.5	33.0	7.9

<sup>a</sup> DGEBA resin containing 0.8 wt% MWNT

<sup>b</sup> DGEBA resin containing 10 wt% DiDOPO

<sup>c</sup> DGEBA resin containing 0.8 wt% MWNT and 10 wt% DiDOPO

helped to achieve the UL-94 V0 rating. MWNT could act as an efficient thermal shield in the condensed phase to emit much of the incident radiation back into the gas phase [44]. To get a better understanding of the flame-retardant mechanism exerted by the DiDOPO/MWNT system, Yan et al. [76] carried out a quantitative analysis of the cone calorimeter data according to a method proposed in the literature [77,78]. The flame retardant effects during combustion were divided into three parts: the (1) flame inhibition effect, (2) barrier and protective effect from char layer, and (3) charring effect (decrease fuel). The first effect occurred in the gaseous phase and the last two effects occurred in the condensed phase. All the effects were quantitatively calculated by using the results obtained in the cone calorimeter experiment (Table 7) and the following equations Eqs. (1)–(3):

$$\text{Flame inhibition effect} = 1 - \text{EHC}_{\text{FR-EP}} / \text{EHC}_{\text{EP}} \quad (1)$$

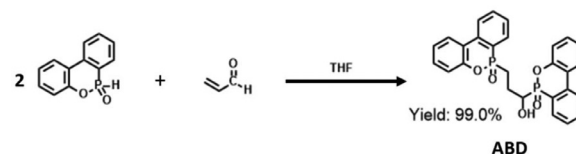
$$\text{Barrier and protective effect} = 1 - (\text{PHRR}_{\text{FR-EP}} / \text{PHRR}_{\text{EP}}) / (\text{THR}_{\text{FR-EP}} / \text{THR}_{\text{EP}}) \quad (2)$$

$$\text{Charring effect} = 1 - \text{TML}_{\text{FR-EP}} / \text{TML}_{\text{EP}} \quad (3)$$

Where FR-EP subscript represents the parameter calculated in the case of flame retardant modified epoxy resin and EP is blank polymer, respectively.

The results which are reported in Table 7 additionally confirmed the increased synergistic effect of DiDOPO/MWNT in the gaseous phase, where the fire-resistance property of MWNT enhanced both the protective and the inhibition effects exerted by DiDOPO during its degradation [76]. Yan et al. also investigated the use of DiDOPO in combination with organo-modified aluminum hydroxide (OATH) [76,79,80]. This combined flame retardant system was added into a DGEBA resin cured with EMI-2,4, where 10 wt% DiDOPO/60 wt% OATH increased the limited oxygen index of the resin from 21.8% (blank) to 39.2% (modified) and allowed for UL-94 V0 rating. The strong sink effect exerted by OATH together with a strong flame inhibition due to the presence of DiDOPO resulted in the self-extinguishing capability of the polymer matrix [80,81] (Table 17).

Wang et al. [82] prepared a flame retardant system combining the use of phenethyl-bridged DiDOPO with acidified silica nanopar-



**Scheme 11.** Synthesis route of ABD. ABD owning relatively short bridged bonds and a hydroxyl group was synthesized via an addition reaction between acrolein and DOPO [21].

ticles (Nps) (DiDOPO/SiO<sub>2</sub>). DiDOPO/SiO<sub>2</sub> was added as flame retardant into epoxy nanocomposites (i.e. EP/DiDOPO/SiO<sub>2</sub>) cured with D-230 polyether amine. LOI and UL-94 tests performed on EP/DiDOPO/SiO<sub>2</sub> samples showed that the introduction of 15 wt% SiO<sub>2</sub> and 5 wt% DiDOPO in EP lead to an increase in the limiting oxygen index from 21.8 to 30.2%, and the nanocomposites resulted in V-0 rating (Table 8). TGA and SEM investigations supported that the acid character of silica Nps promoted the formation of a protective silicon-rich char (Table 8). Based on the cone calorimeter test results, the “FRI” of pristine resin and all prepared nanocomposites was calculated by the procedure reported in the literature. In this work samples having FRI index falling within 1–10 were classified as good.[83]. The FRI index of four composites (DiDOPO/SiO<sub>2</sub>) are presented in Table 8. As the FRI of these composites are in the range of 1.05 to 1.86, they can be classified as good.

Jin et al. [21] synthesized a flame retardant named ABD, which was obtained through a reaction between acrolein and DOPO and then, applied into flame retardant DGEBA epoxy resin cured by DDM (Scheme 11). When the mass fraction of ABD in epoxy resin was 3 wt%, the thermoset acquired a higher LOI value of 36.2%, whereas for pure EP it was 24.7%. The sample also achieved a UL-94 V0 rating. ABD containing epoxy resin exhibited a reduced PHRR, THR, TML, EHC, average CO<sub>2</sub> yield and showed increased residue (Table 17). The superior flame retardant performance of ABD, with respect to a system containing unmodified DOPO, was mainly due to the quenching action of the phosphorus phenanthrene groups and the presence of hydroxyl group which promoted the formation of insulating char [84,85]. A higher amount of DiDOPO compared to ABD is necessary to self-extinguish the resin.

**Table 8**

Results from UL-94, LOI and cone calorimetry tests for all the samples. In addition, char residue, from TGA measurement under nitrogen atmosphere, and FRI are also reported [82].

Sample	UL-94 rating	LOI (%)	TTI (s)	PHRR (kW/m <sup>2</sup> )	TSR (m <sup>2</sup> /m <sup>2</sup> )	EHC(MJ/kg)	Char Residue (wt%)	FRI (-)
<sup>a</sup> EP	Unrated	21.8	43	1101.7	5793.9	23.4	6.70	/
<sup>b</sup> EP/DiDOPO/SiO <sub>2</sub> 2	V1	25.6	43	1093.6	6345.1	21.7	8.72	1.05
<sup>c</sup> EP/DiDOPO/SiO <sub>2</sub> 5	V0	27.7	47	1059.1	6544.3	22.2	10.37	1.16
<sup>d</sup> EP/DiDOPO/SiO <sub>2</sub> 10	V0	28.1	42	801.5	6796.9	21.9	13.48	1.42
<sup>e</sup> EP/DiDOPO/SiO <sub>2</sub> 15	V0	30.2	47	644.1	6568.9	21.7	16.11	1.86

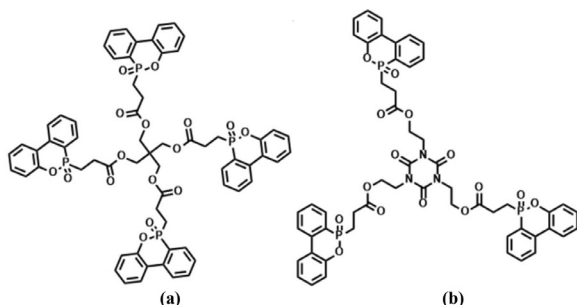
<sup>a</sup> DGEBA resin

<sup>b</sup> DGEBA resin containing 2 wt% SiO<sub>2</sub> nanoparticles (Nps) and 5 wt% DiDOPO

<sup>c</sup> DGEBA resin containing 5 wt% SiO<sub>2</sub> Nps and 5 wt% DiDOPO

<sup>d</sup> DGEBA resin containing 10 wt% SiO<sub>2</sub> Nps and 5 wt% DiDOPO

<sup>e</sup> DGEBA resin containing 15 wt% SiO<sub>2</sub> Nps and 5 wt% DiDOPO



**Fig. 8.** Structures of two phosphorus-containing flame retardants: (a) tetra-[(acryloyloxy)ethyl] pentaerythritol (DOPP) and (b) heterocyclic tris-[(acryloyloxy)ethyl] isocyanurate (DOPI), adapted from [19].

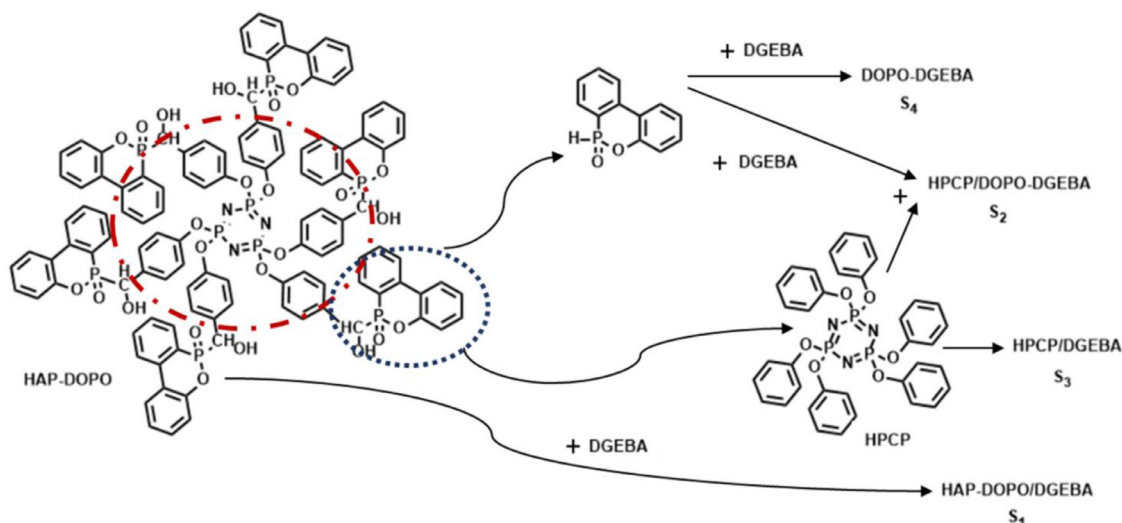
Moreover, DiDOPO contains more aromatic moieties and thus may release more smoke during the combustion of material [86].

Perret et al. [19] synthesized two phosphorus-containing flame retardants, based on DOPO units linked to the star-shaped aliphatic templates i.e. tetra-[(acryloyloxy)ethyl] pentaerythritol (DOPP), or heterocyclic tris-[(acryloyloxy)ethyl] isocyanurate (DOPI) (Fig. 8). They were then incorporated in a commercial epoxy resin RTM6 (a premixed epoxy-amine system composed by a tetra-functional epoxy resin, i.e. tetraglycidyl methylene dianiline (TGMDA) and 70 wt% carbon fibre (CF) RTM6 composites (RTM6-CF) cured with methylene-bis-(2,6-diethylaniline) (MEA) and methylene-bis-(2,6-diisopropylaniline) (MIA) as aromatic hardeners.

DOPP and DOPI worked in the gas phase by suppressing the flame and charring in the condensed phase because a part of phosphorus was bound to the char network [57,87]. Flame-retardant systems containing 0.6 wt% P content, exhibited a LOI of 45.3% (DOPI) and 47.7% (DOPP), respectively, and both systems achieved self-extinguishing capability (UL-94 V0). DOPI and DOPP strongly affected PHRR and THR parameters, resulting in their decrease by 50% compared to the values of the pristine resin RTM6 [19,88]. These two star-shaped DOPO-based flame retardants improve the fire behavior of epoxy without affecting the mechanical properties and the packing of polymer chains, though both compounds show a larger volume than ABD and DiDOPO.

The connection of DOPO with a phosphazene core may confer higher fire retardancy performances, resulting in very low PHRR values through a synergism between nitrogen and phosphorus in the condensed phase. This occurs by branching DOPO to phosphazene, where phosphorus and nitrogen are directly bonded, unlike DOPP and DOPI flame retardants. Qian et al. [89,90] synthesized a flame retardant additive hexa-(phosphaphenanthrene-hydroxyl-methyl-phenoxy)-cyclotriphosphazene (HAP-DOPO) with phosphazene core and DOPO moieties as branches. HAP-DOPO was incorporated in epoxy DGEBA systems, and cured with DDS. In addition, the fire behavior of hexa-phenoxy-cyclotriphosphazene (HPCP) in DOPO pre-reacted DGEBA resin was also studied. Scheme 12 shows the chemical structures of each compound and composition of the final products.

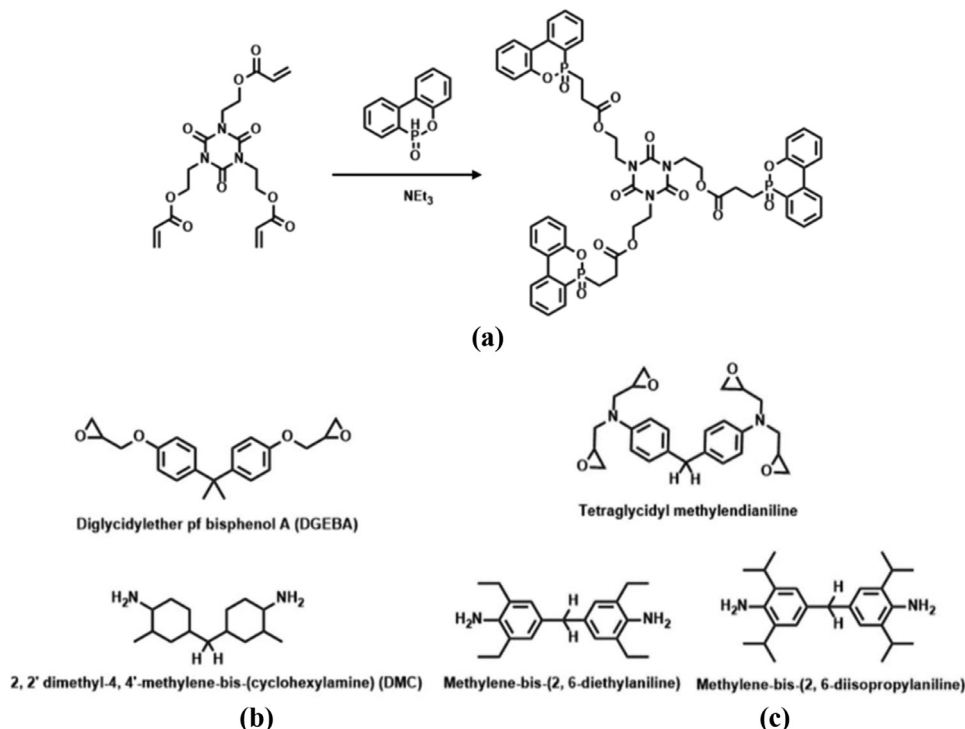
DOPO-based flame retardant additive (HAP-DOPO) showed higher flame retardant efficiency compared to HPCP. HPCP system



**Scheme 12.** Chemical structure of flame retardant additives and synthesis routes of each epoxy system [90].

**Table 9**  
Composition of phosphorous-containing epoxy resins cured with DDS and their flame retardant properties [90].

Sample	HAP-DOPO (g)	HPCP (g)	DOPO (g)	UL-94 rating	Phosphorus content (wt%)	LOI (%)	PHRR (kW/m <sup>2</sup> )
S1	13.5	-	-	V0	1.2	31.0	383
S2	-	4.3	8.1	V0	1.2	31.4	549
S3	-	12.9	-	V2	1.2	32.0	516
S4	-	-	11.7	V1	1.2	31.9	574
S5	-	-	-	Unrated	0	22.5	893



**Scheme 13.** (a) Synthesis procedure of DOPI from DOPO. (b) Components of DGEBA/DMC. (c) Main components of RTM6 [88].

could only achieve a V2 classification, however, when DOPO was used as a reactive co-additive in the HPCP system a V0 classification could be achieved. In contrast, HAP-DOPO system could achieve UL-94 V0 (S1 and S2, Table 9). In addition, the S1 sample (containing HAP-DOPO) exhibited the lowest PHRR. The reason of higher flame retardant efficiency of HAP-DOPO is due to its hybrid activity in the gas phase and condensed phase [90–92].

Perret et al. [88] decided to study the use of DOPI in composites obtained from curing RTM6 and DGEBA with 60 vol% CF by using MEA/MIA and 2,2'-dimethyl-4,4'-methylene-bis-(cyclohexylamine) (DMC) hardeners, respectively. Scheme 13 shows chemical structures of all the compounds and the synthesis procedure for DOPI. DOPI led to a decrease in glass transition temperature in DGEBA/DMC and RTM6 systems. DOPI mainly worked in the gas phase through an inhibition mechanism linked to a charring behavior of DOPI that forms higher phosphorous rich residue [87,93].

When DOPI and CF were added alone in polymer systems, the increase (i.e. 5–9%) in LOI was negligible, although their combination in the epoxy resin improved the LOI to 31.8% and achieved V0 in UL-94 (for DGEBA/DMC system). The same phenomenon was observed for RTM6, where the combined addition of CF and DOPI enhanced the LOI to a value of 47.7% for the DGEBA/DMC system and allowed to achieve V0 classification in the UL-94 test. The combined use of CF and DOPI guaranteed that a strong flame inhibition mechanism occurred simultaneously with a notable char promotion. This synergism positively affected the cone calorimeter data

of the samples containing both additives (CF and DOPI) with respect to pristine systems [88].

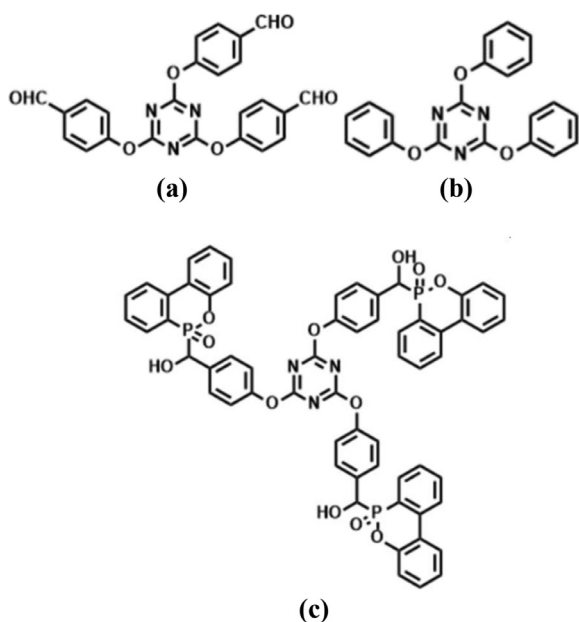
The combined use of inorganic fillers and DOPO derivatives may also lead to a detrimental effect on the mechanical properties of the final composite, though it boosts the thermal shield effect of char during the combustion [54,58]. Triazine containing DOPO derivatives may allow to obtain excellent fire retardant performances, without any addition of inorganic species. Qian et al. [94] synthesized a flame retardant tri-(phosphaphenanthrene-(hydroxyl-methylene)-phenoxy)-1,3,5-triazine (Trif-DOPO) and its control samples (i.e. tri-(4-formacylphenoxy)-1,3,5-triazine (Trif) and triphenoxy-1,3,5-triazine (TPT)) (Fig. 9). Trif-DOPO together with blank compounds were used as flame retardants in DGEBA-thermosetting composites cured with DDS. Trif-DOPO/DGEBA/DDS thermoset containing 1.2 wt% phosphorus showed a LOI value of 36% compared to 22.5% for pristine resin and also achieved V0 classification in the UL-94 test. Further, the addition of Trif-DOPO in resin could strongly decrease the peak of heat release rate of thermosets (Tables 10 and 17) [16,94].

Qian et al. [24] prepared a DOPO derivative tri-(3-DOPO-2-hydroxypropan-1-yl)-1,3,5-triazine-2,4,6-trione (TGIC-DOPO), which was synthesized via a controllable ring-opening addition reaction between 1,3,5-triglycidyl isocyanurate (TGIC) and DOPO (Scheme 14). TGIC-DOPO was added into a DGEBA system cured with DDS. DGEBA thermosets with a 12 wt% of TGIC-DOPO showed a LOI of 33.3%, UL-94 V0 rating, and the lowest PHRR at

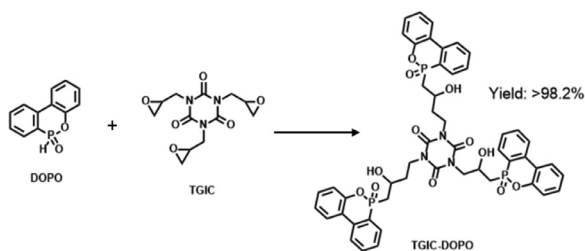
**Table 10**  
Phosphorous content percentage, LOI measurement, PHRR and UL-94 test of the cured epoxy samples [94].

Sample	P (wt%)	UL-94 rating	LOI (%)	PHRR(kW/m <sup>2</sup> )	Dripping
<sup>a</sup> DGEBA/DDS	0	Unrated	22.5	995.0	Yes
<sup>b</sup> Trif-DOPO/DGEBA/DDS-1.0	1.0	Unrated	33.9	390.8	No
<sup>c</sup> Trif-DOPO/DGEBA/DDS-1.2	1.2	V0	36.0	420.7	No
<sup>d</sup> DGEBA-DOPO/DDS	1.2	V1	31.7	437.2	No
<sup>e</sup> TPT/DGEBA/DDS	0	Unrated	24.5	963.5	Yes

<sup>a</sup> DGEBA resin cured with DDS  
<sup>b</sup> DGEBA resin cured with DDS and containing 1 wt% of P (17.5 g of Trif-DOPO)  
<sup>c</sup> DGEBA resin cured with DDS and containing 1.2 wt% of P (21.5 g of Trif-DOPO)  
<sup>d</sup> Modified DGEBA with DOPO (i.e. pre-reacted epoxy with DOPO) and cured with DDS and containing 1.2 wt% of P (12.0 g of DOPO)  
<sup>e</sup> DGEBA resin cured with DDS and containing 21.5 g of TPT



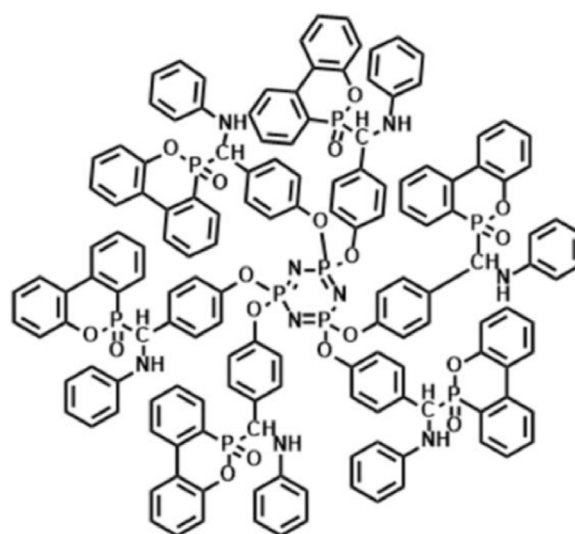
**Fig. 9.** Chemical structure of (a) tri-(4-formacylphenoxy)-1,3,5-triazine (Trif), (b) triphenoxy-1,3,5-triazine (TPT) and (c) tri-(phosphaphenanthrene-(hydroxylmethylene)-phenoxy)-1,3,5-triazine (Trif-DOPO) compounds, adapted from [94].



**Scheme 14.** Synthesis route and chemical structure of TGIC-DOPO flame retardant additive, which was synthesized through a reaction between 1,3,5-triglycidyl isocyanurate (TGIC) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) [24].

481 kW/m<sup>2</sup> (whereas the unmodified DGEBA/DDS system reported a value of 966 kW/m<sup>2</sup>) (Table 11) [16,24].

Xu et al. [95] synthesized a DOPO derivative and used it as a flame retardant for the improvement of fire behavior of DGEBA based epoxy resin thermosets cured with DDS. This flame retardant was named CTP-DOPO in agreement with its chemical structure hexa-[4-(phoxyanilino-phosphaphenanthrene-methyl)-phenoxy]-cyclotriphosphazene (Fig. 10). CTP-DOPO was synthesized from hexachlorocyclotriphosphazene, p-



**Fig. 10.** Chemical structure of hexa-[4-(phoxyanilino-phosphaphenanthrene-methyl)-phenoxy]-cyclotriphosphazene (CTP-DOPO), adapted from [95].

hydroxybenzaldehyde, 4-aminophenol and DOPO [96]. The incorporation of the flame retardant additive into the resin resulted in UL-94 V0 rating and a strong increase of LOI value from 21.7% for cured pure DGEBA to 36.6% when the loading amount of CTP-DOPO was 10.6 wt% (i.e. 1.1 wt% P in thermosets). The incorporation of CTP-DOPO effectively reduced the PHRR and TSR of DGEBA thermosets, lowering the value of both parameters to 45.6% and 54.1%, respectively [95]. The presence of cyclotriphosphazene in the chemical structure of flame retardant reduces the release of smoke, making CTP-DOPO flame retardant very promising in terms of impact on the environment, compared to triazine-containing DOPO derivatives.

Yang et al. [97] prepared a DOPO derivative tri(phosphaphenanthrene-maleimide-phenoxy)-triazine (DOPO-TMT) and its flame retardant effect was studied in a DGEBA resin cured with DDS (Scheme 15). DOPO-TMT exerted a hybrid flame retardant activity because it is composed of multi flame-retardant moieties in one molecule. During thermal decomposition, DOPO-TMT released phosphorus- (such as PO<sup>·</sup> and PO<sub>2</sub><sup>·</sup>) and nitrogen-containing free radicals in the gas phase with a quenching effect. The addition of DOPO-TMT into the epoxy matrix catalysed the production of intumescent and honeycombed structures with a small number of holes on the surfaces [97]. By adding DOPO-TMT up to 1.0 wt% P loading, the LOI value of thermosetting samples increased to 36.2%, and the sample achieves the UL-94 V0 rating.



**Table 11**  
Cone calorimeter data of DGEBA thermosets [24].

Samples	HRR (kW/m <sup>2</sup> )	PHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )
<sup>a</sup> DGEBA/DDS	65	194	966
<sup>b</sup> 6%TGIC-DOPO/DGEBA/DDS	54	135	800
<sup>c</sup> 8%TGIC-DOPO/DGEBA/DDS	54	141	680
<sup>d</sup> 10%TGIC-DOPO/DGEBA/DDS	50	131	520
<sup>e</sup> 12%TGIC-DOPO/DGEBA/DDS	48	113	481

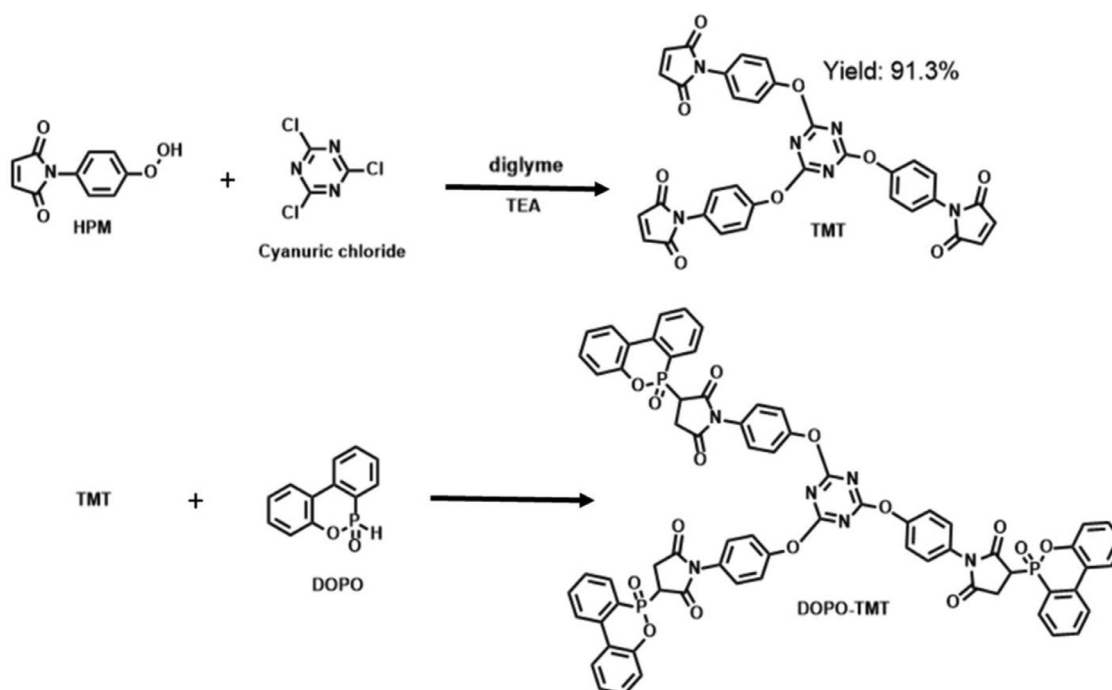
<sup>a</sup> DGEBA resin cured with DDS

<sup>b</sup> DGEBA resin cured with DDS and containing 6 wt% of TGIC-DOPO

<sup>c</sup> DGEBA resin cured with DDS and containing 8 wt% of TGIC-DOPO

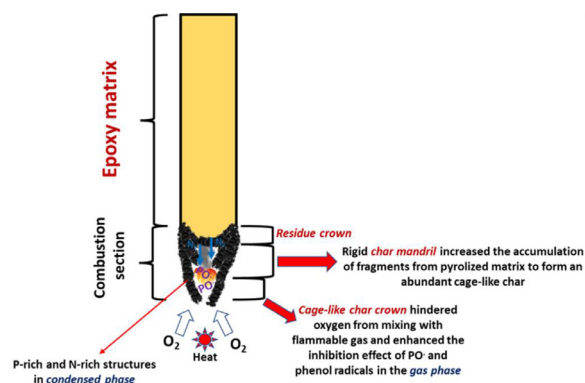
<sup>d</sup> DGEBA resin cured with DDS and containing 10 wt% of TGIC-DOPO

<sup>e</sup> DGEBA resin cured with DDS and containing 12 wt% of TGIC-DOPO



**Scheme 15.** Synthesis route of DOPO-TMT flame retardant additive: maleimido-substituted aromatic s-triazine (TMT) was left to react with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) via addition reaction in presence of diglyme [97]. HPM: N-(4-hydroxyphenyl) maleimide; TEA: triethylamine.

Recently, Qian et al. [98] also investigated the use of TGIC-DOPO (Scheme 14), in DGEBA based epoxy resins cured with DDM and m-PDA respectively. TGIC-DOPO exhibited a better flame retardant effect in EP/DDM compared to in EP/DDS and EP/m-PDA. With 4 wt% TGIC-DOPO (4%TGIC-DOPO/EP/DDM) a UL-94 V0 rating and a LOI value of 35.6% were achieved. In contrast, epoxy composites EP/DDS and EP/m-PDA, containing 4 wt% TGIC-DOPO, could only achieve UL-94 V2 and unrated respectively (Fig. 11). Based on the results of morphology analysis of LOI residues, Qian et al. [98] identified three important aspects of residue (i.e. residue crown, residue mandril, and initial pyrolytic residue) and proposed a flame retardant mechanism of TGIC-DOPO in EP/DDM composites (Fig. 11). TGIC-DOPO/EP/DDM residues formed the biggest char crown among the three samples cured with different hardeners. The separated char crowns were light and soft, but the char crown from TGIC-DOPO/EP/DDM also appeared thicker than the others. In a few words, the presence of phosphaphenanthrene and triazine groups of the flame retardant guaranteed the release of phosphorous and phenol radicals together with nitrogen, which was responsible for an inhibition effect and dilution in the gas phase. In addition, DDM-containing systems promoted the formation of a rigid char mandril and an effective cage-like char crown, enhancing char production and the oxygen barrier effect. In particular, the cage-like char crown enveloped the fire and thus hinder-



**Fig. 11.** Proposal of flame retardant mechanism, based on LOI measurement results, of TGIC-DOPO in DGEBA epoxy resin systems cured with DDM hardener.

ing oxygen from permeating inside and inhibiting the release of PO· and phenol free radicals with an additional quenching effect. The char-cage hindering effect was the main reason for the improved LOI values of 4%TGIC-DOPO/EP/DDM samples. TGIC-DOPO in EP/DDM not only confined more carbon components in the condensed phase but also led to the release of more pyrolyzed PO· and

**Table 12**  
Cone calorimeter data of DGEBA thermosets and results of LOI and UL-94 test measurements [99].

Sample	UL-94 rating	LOI (%)	PHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	CO <sub>2</sub> -yield (kg/kg)	CO <sub>2</sub> -yield (kg/kg)	CO/CO <sub>2</sub> (-)
<sup>a</sup> EP	Unrated	22.5 ± 0.3	966	93.9	0.08	2.25	0.03
<sup>b</sup> TAD/EP-6	Unrated	32.4 ± 0.2	691	60.8	0.15	2.23	0.06
<sup>c</sup> TAD/EP-8	V1	32.6 ± 0.3	590	53.7	0.11	1.82	0.06
<sup>d</sup> TAD/EP-10	V1	34.2 ± 0.2	452	57.7	0.16	2.13	0.07
<sup>e</sup> TAD/EP-12	V0	33.5 ± 0.3	641	55.7	0.14	1.86	0.07

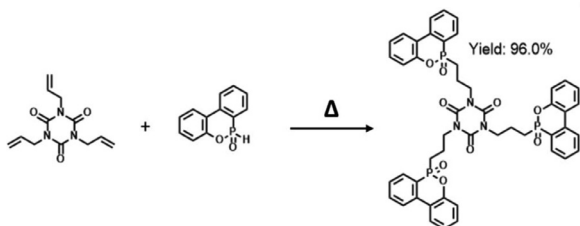
<sup>a</sup> DGEBA resin

<sup>b</sup> DGEBA resin containing 6 wt% TAD

<sup>c</sup> DGEBA resin containing 8 wt% TAD

<sup>d</sup> DGEBA resin containing 10 wt% TAD

<sup>e</sup> DGEBA resin containing 12 wt% TAD



**Scheme 16.** Synthesis route and chemical structure of TAD flame retardant additive. TAD was synthesized through an addition reaction between triallyl isocyanurate (TAIC) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) [99].

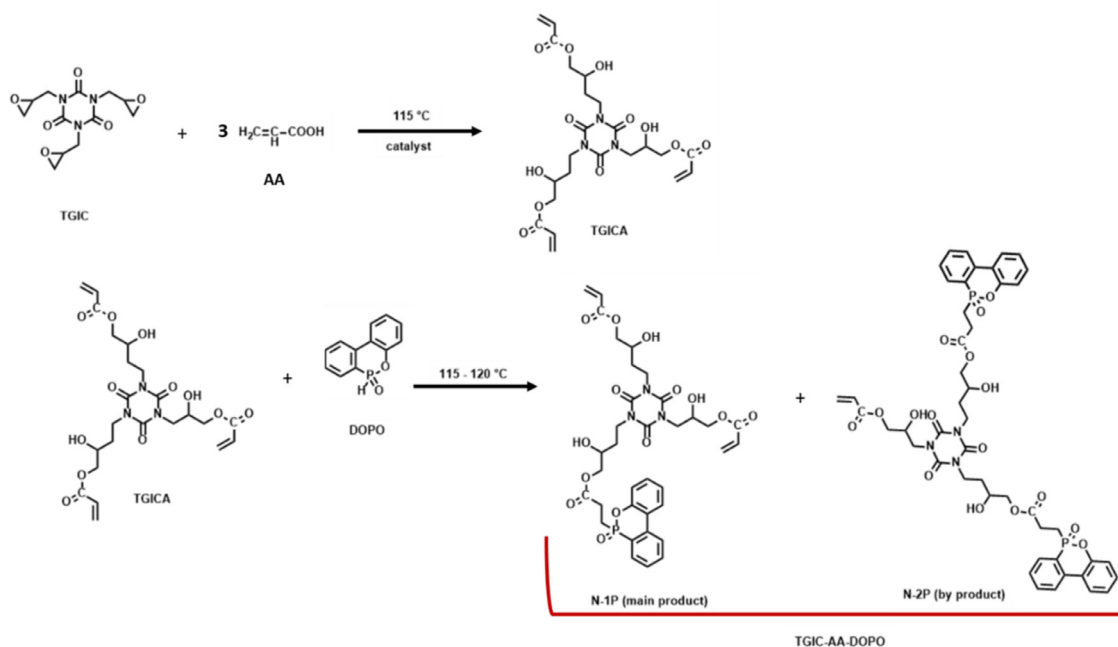
phenol free radicals. The concentrated release of PO· and phenol free radicals allowed the occurrence of an efficient flame inhibition effect, which is the main explanation for the higher flame retardant performance with the addition of a relatively low amount (4 wt%) of TGIC-DOPO [98].

Tang et al. [99] prepared a DOPO derivative TAD through an addition reaction between triallyl isocyanurate (TAIC) and DOPO (Scheme 16). It was incorporated into DGEBA epoxy resin cured with DDS (i.e. a commercial formulation labelled as E-12 containing epoxy matrix and hardener). At 12 wt% TAD loading, the EP system (TAD/EP-12) acquired the highest LOI value of 33.5% and UL-94 V0 rating (Table 12). TAD also reduced the values of PHRR,

THR and average CO<sub>2</sub> and CO yields of epoxy thermosets. TAD acted dominantly in the gas phase and the formation of phosphorus species in the gas phase led to incomplete combustion and formation of CO. Similar flame retardant mechanism was already observed by Qian et al. [24] for TGIC-DOPO derivative, where the same amount (12 wt%) of flame retardant was needed in DGEBA epoxy to accomplish UL-94 V0 rating.

Liu et al. [100] combined the use of TGIC-DOPO with organo-modified montmorillonite (OMMT) to achieve UL-94 V0 rating with the addition of a lower amount of flame retardant into DGEBA epoxy matrix cured with DDM (Scheme 14). With the addition of only 0.5 wt% OMMT and 2.5 wt% TGIC-DOPO, the epoxy thermoset achieved a LOI value of 33.7%, whereas the pure EP reported 26.4%, and passed the UL-94 V0 rating test. Liu et al. [100] also disclosed that this efficiency of the OMMT/TGIC-DOPO system was due to the presence of hydroxyl groups in the chemical structure of TGIC-DOPO which enabled the pyrolysis fragments of TGIC-DOPO and EP matrix to adhere with montmorillonite (MMT) particles, thereby reducing the smoke density and increasing the production of a dense and coherent residual char [101].

Tao et al. [102] prepared a DOPO based flame retardant TGIC-AA-DOPO synthesized from TGIC, acrylic acid (AA) and DOPO (Scheme 17). The intrinsic P-N-containing derivative TGIC-AA-DOPO was incorporated into the vinyl ester resin (901-VER), after dilution with styrene (st) and triallyl isocyanurate (TAIC), and cured with benzoyl peroxide (BPO).



**Scheme 17.** Synthesis route of TGIC-AA-DOPO [102]. TGIC-AA-DOPO was prepared via the reactions between triglycidyl isocyanurate (TGIC), acrylic acid (AA) and DOPO.

**Table 13**  
LOI, UL-94 rating, cone calorimeter test results of the cured epoxy resins [102].

Sample	UL-94 Rating	LOI (%)	Tg (°C)	Dripping	PHRR (kW/m <sup>2</sup> )	HRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )
<sup>a</sup> 901-VER	Unrated	19.8	124.8	Yes	1005.3	314.8	90.1
<sup>b</sup> 40%TAIC	V0	32.0	140.4	No	521.9	127.4	52.9
<sup>c</sup> 10%st-30%TAIC	V1	29.5	122.1	No	721.1	158.9	54.9
<sup>d</sup> 20%st-20%TAIC	V1	29.0	112.3	No	533.6	128.2	53.2
<sup>e</sup> 30%st	Unrated	27.0	113.0	Yes	412.1	129.2	49.5

<sup>a</sup> Vinyl ester resin

<sup>b</sup> Vinyl ester resin containing 40 wt% TAIC

<sup>c</sup> Vinyl ester resin containing 10 wt% st and 30 wt% TAIC

<sup>d</sup> Vinyl ester resin containing 20 wt% st and 20 wt% TAIC

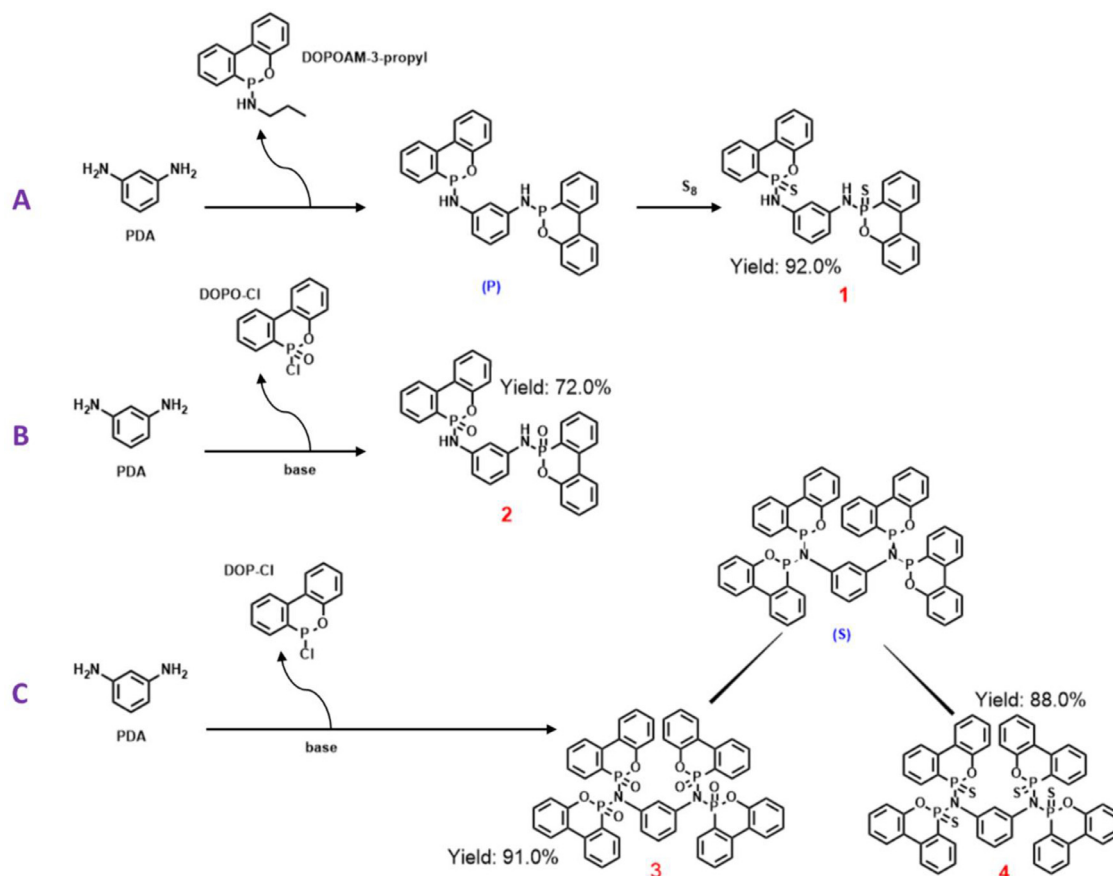
<sup>e</sup> Vinyl ester resin containing 30 wt% st

The flame retarded vinyl ester resin (EP/TGIC-AA-DOPO) with 40 wt% of TAIC loading achieved a LOI value of 31%, and a UL-94 V0 rating. For the 901-VER system containing 40 wt% TAIC, the PHRR, HRR and THR of the composites diluent decreased by 48, 60, and 41% respectively (Table 13). Tao et al. [102] proposed that the flame retardant mechanism of TGIC-AA-DOPO was very similar to the one exerted by TAD [99] in thermosetting composites and suggested the occurrence of both condensed and gas phase flame retardant effects [103]. Table 13 summarizes the Tg values of 901-VER and EP/TGIC-AA-DOPO thermosets diluted by 40%TAIC, the Tg of the latter system was higher than that of 901-VER [102].

### 3.2. P-N bonded multi-DOPO derivatives

Klinkowski et al. [104] synthesized several DOPO derivatives and used them in the improvement of the flame retardancy of a commercial phenol novolac resin (DEN438) cured

with dicyandiamide (DICY) and the crosslinking accelerator 1,1-dimethyl-3-fenilurea (Fenuron). 19-oxa-10-phospha-phenanthrene-10-yl-propylamine (DOPAM-3-propyl), 10-chloro-9,10-dihydro-9-oxa-10-phosphaphenanthrene (DOP-Cl) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-chloride (DOPO-Cl) were prepared and adopted as precursors [104,105]. The thiophosphonamidate 1 was prepared by a two-step procedure (Scheme 18A). First, m-phenylenediamine (PDA) and DOPAM-3-propyl were transformed via a condensation reaction under reduced pressure to form the phosphonamidite (P) [106]. Afterward, (P) was thionated with sulfur to the final thiophosphonamidate 1. The phosphonamidate 2 was obtained in one step via nucleophilic substitution of PDA with DOPO-Cl in the presence of a base (Scheme 18B). The two-step synthesis of the compounds 3 and 4 [104,107] is summarized in Scheme 18C. The first step was the reaction of PDA with DOP-Cl via nucleophilic substitution in the presence of a base to form



**Scheme 18.** Synthesis route and chemical structure of phosphorylated diamines PDA(DOP-S)2 1, PDA(DOP-O)2 2, and tetraphosphorylated compounds PDA(DOP-O)4 3, PDA(DOP-S)4 4. DOP-Cl: 10-chloro-9,10-dihydro-9-oxa-10-phosphaphenanthrene. DOPO-Cl: 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-chloride. DOPAM-3-propyl= 9-oxa-10-phospha-phenanthrene-10-yl-propylamine.

**Table 14**

Chemical composition of epoxy composites, flame retardant contents, char residue after thermal gravimetric analysis (under nitrogen), glass transition temperature, UL-94 rating and temperature for decomposition of 5% mass loss.

Sample	DEN438 (wt%)	Flame retardant (wt%)	P (wt%)	UL-94 rating	Char residue at 850°C(wt%)	T <sub>g</sub> (°C)	<sup>e</sup> T <sub>d5%</sub> (°C)
Neat resin	100.0	-	-	Unrated	28.6	181	337
<sup>b</sup> PDA(DOP-S)2 1	79.31	13.8	1.5	V0	29.7	181	323
<sup>a</sup> PDA(DOP-O)2 2	80.04	12.9	1.5	V1	31.4	186	332
<sup>c</sup> PDA(DOP-O)4 3	81.23	11.6	1.5	V0	32.6	183	318
<sup>d</sup> PDA(DOP-S)4 4	80.50	12.4	1.5	V0	31.7	174	312

<sup>a</sup> DEN438 resin containing PDA(DOP-S)2

<sup>b</sup> DEN438 resin containing PDA(DOP-O)2

<sup>c</sup> DEN438 resin containing PDA(DOP-O)4

<sup>d</sup> DEN438 resin containing PDA(DOP-S)4

<sup>e</sup> Temperature for decomposition of 5% mass loss

**Table 15**

LOI, UL-94 rating, cone calorimeter test results of the cured epoxy resins [109].

Sample	P content (wt%)	UL-94 rating	LOI (%)	PHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	FPEI (m <sup>2</sup> •s/kW)	FGI (kW/m <sup>2</sup> •s)
<sup>a</sup> EP-1	0	Unrated	26	1725	60.2	0.029	17.25
<sup>b</sup> EP-2	0.16	V1	29	1488	56.4	0.025	18.60
<sup>c</sup> EP-3	0.25	V1	29	1450	56.8	0.033	16.47
<sup>d</sup> EP-4	0.33	V0	30	1357	52.4	0.035	15.42
<sup>e</sup> EP-5	0.41	V0	32	1375	49.8	0.036	15.62

<sup>a</sup> DGEBA resin

<sup>b</sup> DGEBA resin containing 1 wt% DOPO-THPO

<sup>c</sup> DGEBA resin containing 1.5 wt% DOPO-THPO

<sup>d</sup> DGEBA resin containing 2 wt% DOPO-THPO

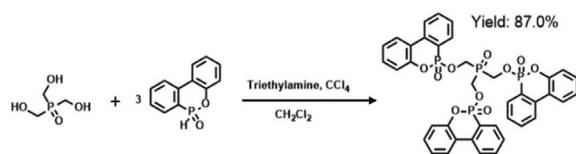
<sup>e</sup> DGEBA resin containing 2.5 wt% DOPO-THPO

the intermediate (S). In a second step, the diphosphonamidite (S) was oxidized with tert-butyl hydroperoxide or thionated with elemental sulfur to the m-phenylene bridged diphosphonamidate 3 or di(thiophosphon)amidate 4, respectively [105]. Finally, 1, 2, 3 and 4 (DOPO derivatives) were incorporated into the epoxy novolac resin system (DEN438/DICY/Fenuron).

TGA analysis showed that the diphosphonamidates 3 and 4 decomposed at much higher temperatures than phosphonamidates 1 and 2. Each DOPS derivative (1 and 4) had a slightly higher decomposition temperature than the corresponding DOPO compounds (3 and 2) (Table 14). The cured epoxy resins containing flame retardant additives 1, 3 and 4 respectively showed V0 classification in the UL-94 test. Also, the cured epoxy resins containing 2 resulted in a good fire behavior accomplishing a V1 classification. DOPO (2 and 3), DOPS (1 and 4) derivatives mainly acted in the gas phase during the combustion of epoxy novolac resin DEN438/DICY/Fenuron composites [14,53,108]. The addition of these DOPO-based flame retardants led to slight changes in the glass transition temperature of the neat epoxy resin (Table 14).

### 3.3. P-O bonded multi-DOPO derivatives

Wang et al. [109] prepared a phosphorus-containing compound (DOPO-THPO) through the Atherton-Todd-reaction between DOPO and trihydroxymethylphosphine oxide (THPO), and then employed this DOPO derivative as a flame retardant in DGEBA epoxy resin cured with DDM (Scheme 19). The EP composite containing DOPO-THPO up to 0.33 wt% of P loading (EP-4 in Table 15) showed self-

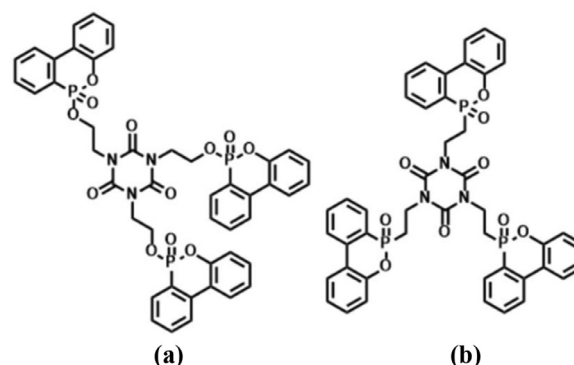


**Scheme 19.** Scheme of the synthesis for DOPO-THPO. DOPO-THPO was synthesized via the Atherton-Todd-reaction between DOPO and trihydroxymethylphosphine oxide (THPO) [109].

extinguishing capability and a LOI value of 30%. Cone calorimeter results showed that the flame retarded EP containing DOPO-THPO resulted in lower values of PHRR and THR than pure EP resin, because of the formation of a protective graphitized char and of phosphorous inhibitors hampering the radical chain reactions (Table 15) [65,87,109,6,83,106].

Wang et al. [109] also calculated from the cone calorimeter experiments the FPEI and FGI to assess the fire hazard of EP composites containing DOPO-THPO flame retardant [110,111]. In particular, a larger value of FPEI is relevant for higher fire safety of materials, because it is linked to an increase in the TTF (i.e. the time available to escape a fire in a confined space) and a lower flammability [112]. In contrast, a higher value of FGI represents a longer time to arrive at PHRR and thus more fire safety of samples. The addition of DOPO-THPO into the epoxy resin guaranteed the suppression of fire hazards, because the flame retardant caused an increase in both FPEI and FGI values (Table 15).

Zang et al. [14] also reported the synthesis of four star-shaped flame retardant derivatives of DOPO for application in epoxy resins. Fig. 12 shows DOPO-based compounds (A and B) synthesized via



**Fig. 12.** Structures of two monomeric DOPO-based flame retardant compounds: (a) phosphonate (A) and (b) phosphinate (B), adapted from [14].



**Table 16**  
Thermogravimetric and fire data of monomeric DOPO-derivative flame retardants [14].

Sample	P (%)	UL-94 ratings	Tg (°C)	<sup>a</sup> T <sub>d</sub> 5% (°C)	<sup>b</sup> T <sub>max</sub> (°C)	Char yield at 900°C (wt%)
Net epoxy resin	-	Unrated	136	350	410	10.5 <sup>c</sup>
Epoxy resin containing only DOPO	<sup>d</sup> N.A.	N.A.	110	N.A.	N.A.	N.A.
A	2.5	V0 in DEN 438/DICY/Fenuron system	135	308	390	12.6
D	2.0	V0 in DGEBA/DICY/Fenuron	129	340	405	12.3

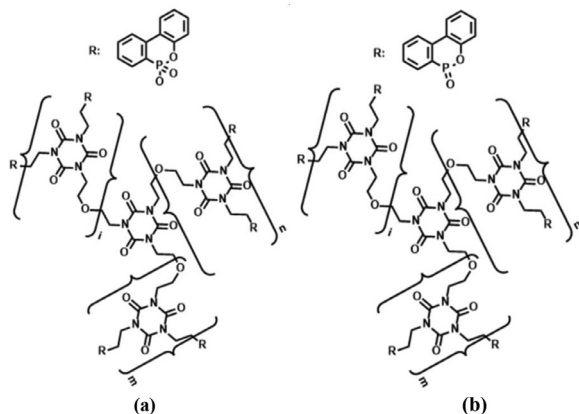
DGEBA, diglycidyl ether of bisphenol A; DICY, dicyandiamide  
DEN 438; DICY, dicyandiamide

<sup>a</sup> Temperature for decomposition of 5% mass loss

<sup>b</sup> Temperature of maximum rate of mass loss

<sup>c</sup> Data for the pure n.c.-rated epoxy sample cured with DICY and Fenuron

<sup>d</sup> Not Available data



**Fig. 13.** Structures of two oligomeric DOPO-based flame retardant compounds: (a) phosphonate (C) and (b) phosphinate (D), adapted from [14].

nucleophilic substitution with 1,3-tris-(2-hydroxyethyl) isocyanurate (THIC) and Fig. 13 represents DOPO derivatives (C and D) obtained by transamination followed by a Michaelis–Arbuzov rearrangement. These products were added into two DEN 438 (novolac resin) and DGEBA epoxy systems, cured with DICY and Fenuron hardeners to obtain flame retardant epoxy systems [14].

All derivatives were thermally more stable than pure DOPO (Table 16). DEN 438/DICY/Fenuron containing derivative A achieved UL-94 V0 rating with 1.0% phosphorus content (9.2 wt% flame retardant). In the case of DGEBA/DICY/Fenuron, the oligomeric DOPO derivative D accomplished the self-extinguishing with about 2% phosphorus content (Table 16). For DEN 438, the addition of phosphinates (B and D) resulted in better flame retardancy compared to the addition of corresponding phosphonates (A and C). The same behavior was observed in the case DGEBA system, where D showed a more efficient flame retardant effect than C [14,86]. These star-shaped flame retardants show very similar behavior to DOPI and DOPP, though they could allow for self-extinguishing capability without the use of fully aromatic hardeners.

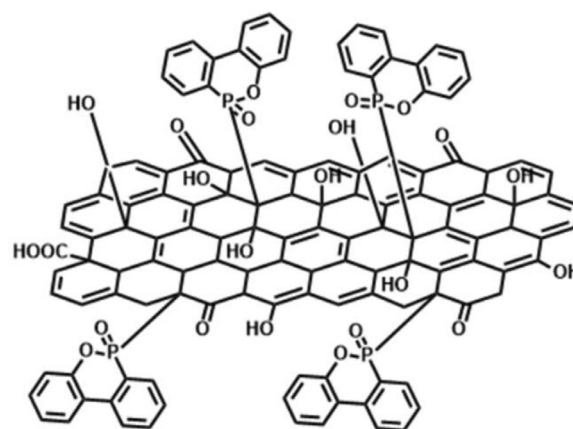
The flame-retardant performance of the most effective mono- and multi DOPO derivatives discussed in this review are summarized in (Sections 2 and 3) in Table 17.

#### 4. Hybrid DOPO derivatives as flame retardants for epoxy resin systems

##### 4.1. DOPO functionalized carbon-based nanostructures

###### 4.1.1. P-C bonded DOPO functionalized carbon-based nanostructures

Liao et al. [113] modified DOPO by grafting its epoxy rings on the surface of graphene oxide (GO). DOPO was not only covalently bonded to the GO, as a functional moiety, but also worked as a reducing agent (Fig. 14). DOPO grafted on the reduced



**Fig. 14.** DOPO-rGO pelletlike structure made of phosphorus and graphene layers. The chemical bond between DOPO and GO was proved through FTIR analysis, where the P-H band ( $2384\text{ cm}^{-1}$ ) disappeared completely because of DOPO-rGO formation. The Figure was adapted from [113,117].

graphene sheets (DOPO-rGO) showed a pellet like structure. Liao et al. [113] performed an investigation of the flame retardancy and the thermal stability of DOPO-rGO/DGEBA-epoxy nanocomposites cured with DDM. The addition of only 10 wt% of the DOPO-rGO hybrid system in epoxy resulted in an increase of char yield and LOI of 81% and 30% respectively compared to the pristine resin [114–116].

Qian et al. [118] prepared DOPO-rGO flame retardant without direct attachment of graphene oxide to the P-H functionality of DOPO, but through an *in situ* sol-gel process. DOPO-rGO was synthesized through reaction between DOPO-VTMS and functionalized rGO (Fig. 15) [119]. Particularly, rGO was functionalized with (3-isocyanatopropyl)triethoxysilane and exfoliated in a solution containing DOPO-VTMS to allow the hydrolysis and condensation between both silanes. Subsequently, the flame retardant DOPO-rGO was incorporated into DGEBA epoxy resin and DDM was used as a hardener [118].

The incorporation of 5 wt% of DOPO-rGO into EP resulted in self-extinguishing composites, where a sample with unmodified DOPO completely burned. In particular, DOPO-rGO/EP nanocomposites showed a LOI value of 29.5% which was higher than 21.0% of the neat DGEBA resin. The char residues of the DOPO-rGO/EP nanocomposites were significantly increased compared to pristine epoxy, due to the condensed phase activity exerted by rGO (Table 18) [118]. In addition, the barrier effects of rGO were enhanced by the char reinforcing effect of silicon. The addition of DOPO-rGO significantly reduced the PHRR by 35% and increased the Tg by 4% [118].

Luo et al. [120] functionalized and reduced GO by grafting DOPO on its surface. They used this functionalized reduced

**Table 17**  
The flame retardancy performance of epoxy containing bridged DOPO derivatives.

Flame retardant (FR)	Polymer matrix	Hardener	FR content (wt%)	Phosphorous content (wt%)	UL-94 rating	Ref.
PFR	DGEBA	DDM, polyamide (651)	15	*NA	V0	[64,65]
PDPDP	DGEBA	DDM	20	NA	V0	[68]
DOPO-VTMS	DGEBA	DDM	15	NA	V0	[32]
PDA(DOP-S)2 1	Phenol novolac resin (DEN438)	DICY	NA	1.5	V0	[104]
PDA(DOP-O)2 2				1.5	V1	
PDA(DOP-O)4 3				1.5	V0	
PDA(DOP-S)4 4				1.5	V0	
DSOC	Cationic polymerization of DGEBA-based epoxy resin (E-51) with boron trifluoride ethylamine as curing accelerator		15	NA	V0	[70]
DOPO-DOPC	DGEBA	DDM	15	NA	V0	[35]
DOPO-PEPA (DP)	DGEBA-based epoxy resin (E44)	DDM	9.1	NA	V0	[47]
DOPO-THPO	DGEBA	DDM	NA	0.33	V0	[109]
DiDOPO	DGEBA	EMI-2,4	10	NA	V0	[76]
MWNT			0.8			
DiDOPO	DGEBA	EMI-2,4	10	NA	V0	[80]
OATH			60			
ABD	DGEBA	DDM	3	NA	V0	[21]
DMBT	DGEBA	DDM	10	NA	V1	[60]
RP	Sorbitol-based epoxy resin	MH3122	NA	3	V0	[52]
DXA						
RP	Sorbitol-based epoxy resin	MH3122	NA	3	HB	[52]
DXM						
DP	DGEBA	IDA	17.3	2	V0	[57]
DOPO-AAM (DA)	DGEBA	IDA	NA	2	V0	[58]
DHBAP	DGEBA-based epoxy resin (E44)	DDM	8	NA	V0	[36]
DiDOPO	DGEBA	D-230 polyether amine	5	NA	V0	[82]
Silica nanoparticles			15			
DOPI	Epoxy resin RTM6	MEA, MIA	*NA	0.6	V0	[19]
Carbon Fibre (CF)			70			
DOPP	Epoxy resin RTM6	MEA, MIA	NA	0.6	V0	[19]
CF			70			
DOPO phosphonate (A)	DEN 438 (novolac resin)	DICY	9.2	1	V0	[14]
DOPO phosphinate (D)	DGEBA	DICY	NA	2	V0	[14]
HAP-DOPO	DGEBA	DDS	NA	1.2	V0	[90]
DOPI	Epoxy resin RTM6	MEA, MIA, DMC	7	NA	V0	[88]
CF			69.6			
DOPI	DGEBA	MEA, MIA, DMC	6.7	NA	V0	[88]
CF			70			
TriF-DOPO	DGEBA	DDS	NA	1.2	V0	[94]
DOPO-VTMS/TGIC-KH	DGEBA	DDM	10	0.99	V0	[41]
CTP-DOPO	DGEBA	DDS	10.6	1.1	V0	[95]
DOPO-TMT	DGEBA	DDS	NA	1	V0	[97]
TGIC-DOPO	DGEBA	DDM, m-PDA	4	NA	V0	[98]
TAD	DGEBA	DDS	12	NA	V0	[99]
TGIC-DOPO	DGEBA	DDM	2.5	NA	V0	[100]
OMMT			0.5			
TGIC-AA-DOPO (TAIC)	Vinyl ester resin (901-VER)	BPO	40	NA	V0	[102]

\*NA= Not Available in the literature

**Table 18**

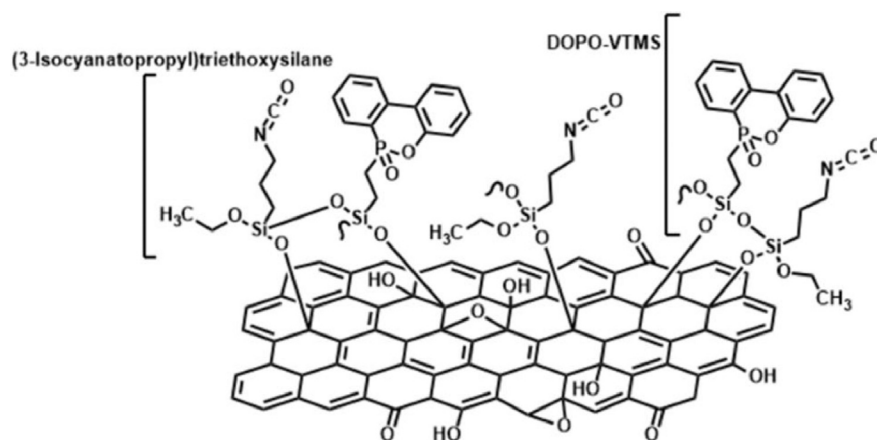
The composition, LOI, UL-94 values and thermogravimetric data pure DGEBA, modified DGEBA with DOPO and DGEBA resin added with DOPO-rGO flame retardant additive.  $T_{max}$  represents the maximum peak of temperature during the degradation.

Sample	FR content (wt%)	UL-94 rating	LOI (%)	$T_{max}$ (°C)		Char at 700°C (wt%)	
				Air	N <sub>2</sub>	Air	N <sub>2</sub>
<sup>a</sup> EPDGEBA	-	Unrated	21.0	396.6	407.2	0.37	14.2
<sup>b</sup> DOPO/EP	5	Unrated	28.5	589.2		1.64	14.9
				396.7	396.4		
<sup>c</sup> DOPO-rGO/EP	5	V0	29.5	585.1		3.16	19.6
				396.5	401.2		
				589.1			

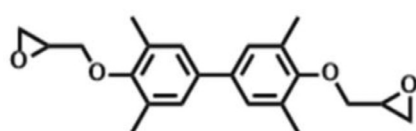
<sup>a</sup> DGEBA resin

<sup>b</sup> DGEBA resin containing only DOPO

<sup>c</sup> DGEBA resin containing DOPO-rGO



**Fig. 15.** Chemical structure of hybrid DOPO-rGO additive. DOPO-rGO was synthesized through a reaction between DOPO-VMMS (DOPO-vinyl trimethoxy silane) and (3-isocyanatopropyl)triethoxysilane functionalized rGO. The Figure was adapted from [32,118].



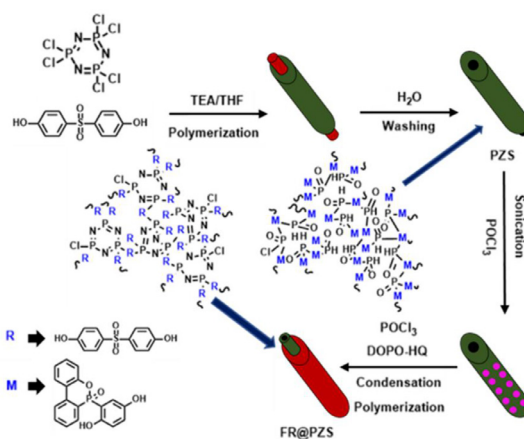
**3, 3', 5, 5'-tetramethyl-4, 4' biphenyl duglycidyl ether**

**Fig. 16.** Chemical structure of mesogenic epoxy (EO) 3, 3', 5, 5'-tetramethyl-4, 4' biphenyl duglycidyl ether, adapted from [120].

graphene oxide (DOPO-rGO) as a nano-filler to improve the flame retardancy, mechanical properties and thermal conductivity of mesogenic epoxy (EO) (Fig. 16) [121]. The DMA results showed that  $E'$  of mesogenic epoxy containing 15 wt% DOPO-rGO (DOPO-rGO/EO-15) achieved a value 26.7% higher than that of EO, which supported a reinforcing effect of DOPO-rGO on EO. The incorporation of 15 wt% DOPO-rGO into EO positively affected the thermal stability of composites resulting in a THR value of  $24.1 \text{ kJ}\cdot\text{g}^{-1}$ , which is  $5.6 \text{ kJ}\cdot\text{g}^{-1}$  lower than that for EO, and a higher char yield with respect to the neat epoxy [120]. DOPO-rGO/EO-15 showed self-extinguishing behavior in the UL-94 test [120,121].

DOPO-HQ is a DOPO derivative that can be synthesized by the reaction of DOPO with 1,4-benzoquinone (BQ) [122]. DOPO-HQ (FR) can work as a nonreactive flame retardant additive through crosslinking and subsequent wrapping on the surface of functionalized polyphosphazene nanotubes (PZS) [123]. PZS can be fabricated via a simple one-pot strategy with controllable morphology (Scheme 20) [124]. Qiu et al. [125] investigated the flame retardant effect of poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) nanotubes modified by DOPO-HQ (FR@PZS) into DGEBA epoxy resin (E-44) cured with DDM (Scheme 20). The nanotube shape was chosen to reinforce the epoxy matrix as a carbon nanotube (CNT) effect [126].

The incorporation of FR@PZS into the EP matrix enhanced its thermal stability, resulting in a strong decrease of the maximum mass loss rate and an increase in the residue at  $800^\circ\text{C}$ . The addition of 3.0 wt% FR@PZS into the thermoset significantly decreased the PHRR and THR values by 46.0% and 27.1%, respectively, compared to those of pure EP. FTIR analysis of evolved gases confirmed that the yield of toxic CO formed from the EP decomposition was significantly suppressed after introducing the FR@PZS hybrids into the matrix. This was mainly due to the flame retardant activity of FR@PZS in the condensed phase [125].



**Scheme 20.** Poly(cyclotriphosphazene-co-4,4'-sulfonyldiphenol) (PZS) were prepared through the polymerization between hexachlorocyclotriphosphazene (HCCP) and 4,4'-sulfonyldiphenol (BPS). The polymerization was carried out in the presence of triethylamine (TEA); the nanocrystals of triethylammonium chloride (TEACl) were produced *in situ* and used as a template. 2-diphenylphosphanyl-1,4 benzenediol (DOPO-HQ) was crosslinked and wrapped on the surface of PZS to form FR@PZS [125].

Wen et al. [127] synthesized an oligomer poly 10-(2,5-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-phospha phenanthrene-10-oxide-1,10-ferrocene dimethyl ester (PFDC HQ) based on DOPO and ferrocene groups to obtain an efficient flame retardant for DGEBA composites cured with m-PDA. PFDC HQ was obtained through the reaction between 1,1'-ferrocenedicarbonyl (FDC) chloride and DOPO-HQ, where FDC was the product of 1,1'-diacetylferrocene (DAF) oxidation [127,128] (Scheme 21). The LOI of EP/PFDC HQ-5 (i.e. 5 wt% PFDC HQ into the epoxy matrix) increased to 30.6%, and a UL-94 V0 rating was achieved compared to unmodified epoxy [129]. The addition of PFDC HQ into the epoxy matrix improved its Young's modulus, and allowed for a strong flame inhibition effect and the production of a coherent and graphitized char [127].

Zhi et al. [130] prepared a phosphorus- and silicon-modified graphene oxide to improve the thermal stability and flame retardancy properties of a DGEBA epoxy resin cured with DDM. DOPO and VTES were successfully grafted onto the surface of GO through the sol-gel methodology. The DOPO and VTES functionalized graphene oxide (DOPO-VTES-GO) was incorporated into the resin (Table 23). The composites containing DOPO-VTES-GO (DOPO-VTES-GO/epoxy) showed increased char residue yield

**Table 19**

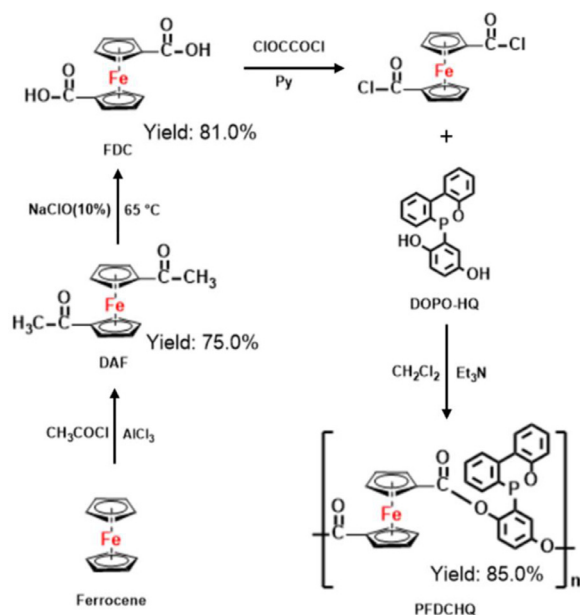
LOI and cone calorimeter test results of the cured epoxy resins. In addition, it is also reported the char yield at 700°C after thermogravimetric analysis under a nitrogen atmosphere [130].

Sample	LOI (%)	PHRR (kW/m <sup>2</sup> )	Tp (s)	THR (MJ/m <sup>2</sup> )	FIGRA (MJ/kg)	Char yield at 700°C (wt%)
<sup>a</sup> Epoxy	19.7	714.7	135	86.1	5.3	17.2
<sup>b</sup> DOPO–GO/epoxy	24.7	384.1	180	59.6	2.1	24.5
<sup>c</sup> DOPO–VTES–GO/epoxy	27.5	390.3	200	50.5	1.9	30.2

<sup>a</sup> DGEBA resin

<sup>b</sup> DGEBA resin containing 3.75 wt% DOPO–GO

<sup>c</sup> DGEBA resin containing 3.75 wt% DOPO–VTES–GO

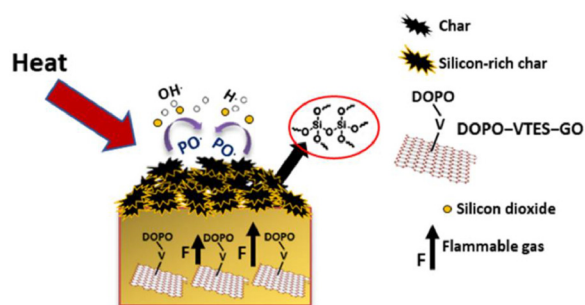


**Scheme 21.** Synthesis route of oligomer PFDCHQ [127].

compared to those of pure resin and resin containing DOPO grafted directly to GO (DOPO–GO/epoxy). DOPO–VTES–GO/epoxy exhibited a lower value of the peak of heat release rate, FIGRA, total heat release as well as a higher LOI value compared to the pure epoxy resin and DOPO–GO/epoxy (Table 19).

From SEM/EDX analysis of char residues it was observed that the thermal degradation of DOPO–VTES–GO/epoxy samples led to the formation of a highly graphitized silicon-rich (i.e. Si–O–Si bridged structures) char [131]. Based on the microscopy analysis of residue and evolved gas analysis, Zhi et al. [130] proposed the flame retardant mechanism of DOPO–VTES–GO. In particular, the activity of DOPO–VTES–GO in the condensed phase was mainly due to a barrier effect of GO and catalytic carbonization of DOPO, though this latter could also act in the gas phase by flame inhibition mechanism (Fig. 17).

Chen et al. [132] synthesized a DOPO derivative, named CCD, by the condensation of cinnamaldehyde and amino group of chitosan, followed by the addition reaction with DOPO. CCD was used as a flame retardant in DGEBA epoxy resin cured with DDM (Scheme 22). Epoxy resin modified with the incorporation of 10 wt% CCD (EP/10%CCD) passed UL-94 V0 rating and showed a LOI value of 31.6%, which is 7.6% higher than that of the neat EP. Cone calorimeter test results showed that the addition of 10 wt% CCD into the epoxy matrix was enough to decrease the THR by 38.8% and decreased the TSR by 72.0%. CCD allowed for the production of a very compact char during the degradation of EP/10%CCD composite, which played a strong flame retardant activity in the con-



**Fig. 17.** Possible flame-retardant mechanism during the combustion in the DOPO–VTES–GO/epoxy composite [130].

densed phase, blocking the exchange of heat and gas during the degradation and slowing down the smoke production [132].

Gu et al. [133] investigated the fire behavior of DGEBA epoxy resin cured with DDM hardener and containing functionalized multi-walled carbon nanotubes (MWCNT) as flame retardant additive. The flame retardant additive was synthesized by the reaction between acylated MWCNT and 10-(2,5-dihydroxyphenyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO–HQ) (Scheme 23). These modified multi-walled carbon nanotubes (MWCNT–(DOPO–HQ)) were incorporated into the resin together with nano-sized aluminum diethylphosphinate (AlPi) to form flame-retardant nanocomposites. The thermosets containing 1 wt% MWCNT–(DOPO–HQ) and 3.67 wt% AlPi (EC-3) exhibited LOI value of 39.5 and self-extinguishing capability. Furthermore, cone calorimeter results showed that PHRR, THR and CO<sub>2</sub> production decreased with increasing phosphorus content in the polymer matrix (Table 20).

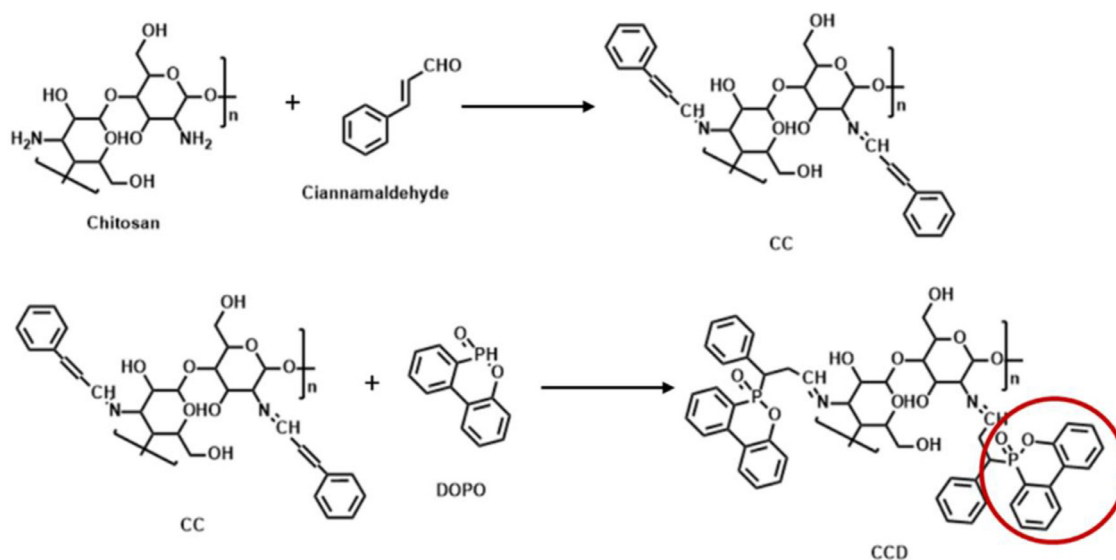
SEM analysis of all the residual char of epoxy nanocomposites containing MWCNT–(DOPO–HQ)/AlPi flame retardant system presented typical morphology of intumescent structure [134]. MWCNT–(DOPO–HQ) and AlPi exerted a synergistic flame retardant effect, which could efficiently impede combustion, through the production of non-flammable gas and inhibitors and refractive char [133].

#### 4.1.2. P–N bonded DOPO functionalized carbon-based nanostructures

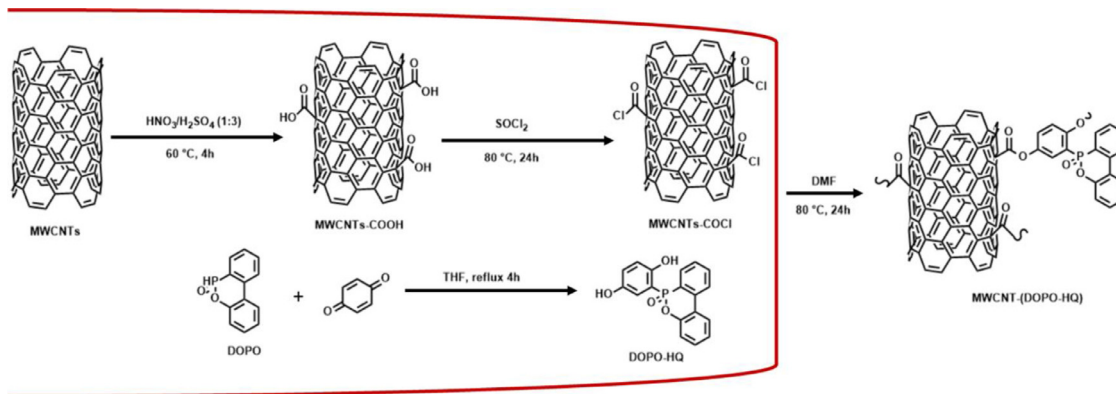
Guo et al. [135] reported the synthesis of a piperazine-based DOPO derivative phosphonamidate (PiP–DOPO) which was used to functionalize reduced graphene oxide to improve graphene dispersion in epoxy resin and flame retardancy of the polymer matrix and reduce its mechanical deterioration. GO was functionalized and reduced by piperazine simultaneously, and then incorporated into PiP–DOPO through *in situ* reaction, resulting in the formation of the hybrids (PD–rGO). Subsequently, the PD–rGO was incorporated into DGEBA epoxy resin cured with DDM to fabricate nanocomposite (Scheme 24).

With the addition of 4 wt% PD–rGO10 (10 wt% rGO in hybrid) in EP, the PHRR and THR values significantly decreased by





**Scheme 22.** Synthesis route and chemical structure CCD. CCD was synthesized by the condensation between cinnamaldehyde and chitosan, followed by the addition reaction with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide(DOPO) [132].



**Scheme 23.** Synthesis of MWCNT-(DOPO-HQ). Functionalized multi-walled carbon nanotubes (MWCNT) were synthesized by the reaction between acylated MWCNT and DOPO-HQ. Regarding DOPO-HQ, it was named ODOPB in the reference [133].

**Table 20**

Thermal and flame retardant properties of pure-epoxy resin and flame retardant epoxy nanocomposites [133].

Sample	P (wt%)	UL-94 rating	T <sub>g</sub> (°C)	Char yield at 600°C (wt%)	LOI (%)	PHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	CO <sub>2</sub> production (g/s)
<sup>a</sup> Epoxy resin	0	Unrated	161.2	25.4	25.0	/	/	/
<sup>b</sup> EC-1	0.078	V1	162.6	27.9	31.5	837.8	114.5	0.57
<sup>c</sup> EC-2	0.75	V1	172.7	23.3	36.5	603.3	83.2	0.38
<sup>d</sup> EC-3	1.00	V0	168.5	24.1	39.5	433.4	81.9	0.27
<sup>e</sup> EC-4	1.50	V0	180.2	27.5	41.2	367.3	56.5	0.20

<sup>a</sup> DGEBA resin

<sup>b</sup> DGEBA resin containing 1 wt% MWCNT-(DOPO-HQ)

<sup>c</sup> DGEBA resin containing 1 wt% MWCNT-(DOPO-HQ) and 2.92 wt% AlPi

<sup>d</sup> DGEBA resin containing 1 wt% MWCNT-(DOPO-HQ) and 3.67 wt% AlPi

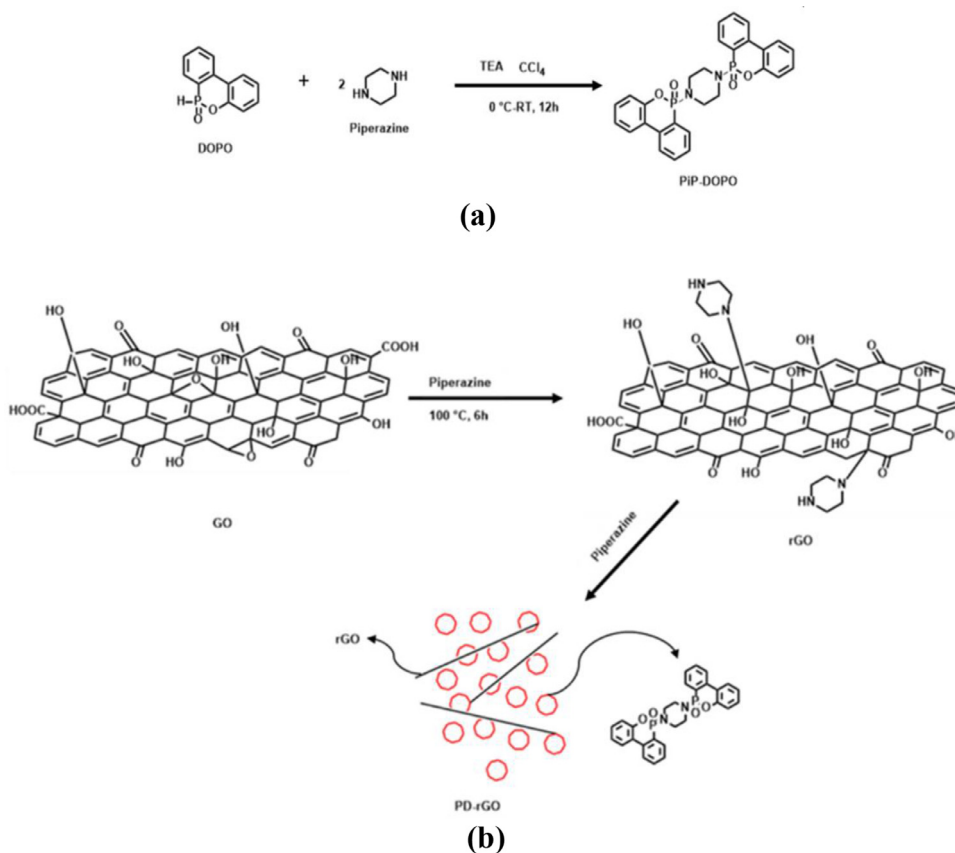
<sup>e</sup> DGEBA resin containing 1 wt% MWCNT-(DOPO-HQ) and 6.18 wt% AlPi

43.0% and 30.2% respectively, in comparison to neat EP. Besides, the epoxy composite containing 4 wt% PD-rGO5 (5 wt% rGO in hybrid) could pass the UL-94 V0 rating and achieve a LOI of 28.0% (where pure EP reported only 22%) [135]. The fire retardant mechanism of the PD-rGO hybrid was attributed to the synergism between two actions: PiP-DOPO degradation provided phosphorous radicals responsible for flame inhibition in UL-94 burning, while the presence of graphene guaranteed the formation of graphitized carbons and continuous char, which can work as efficient thermal shield and oxygen barrier [135,136].

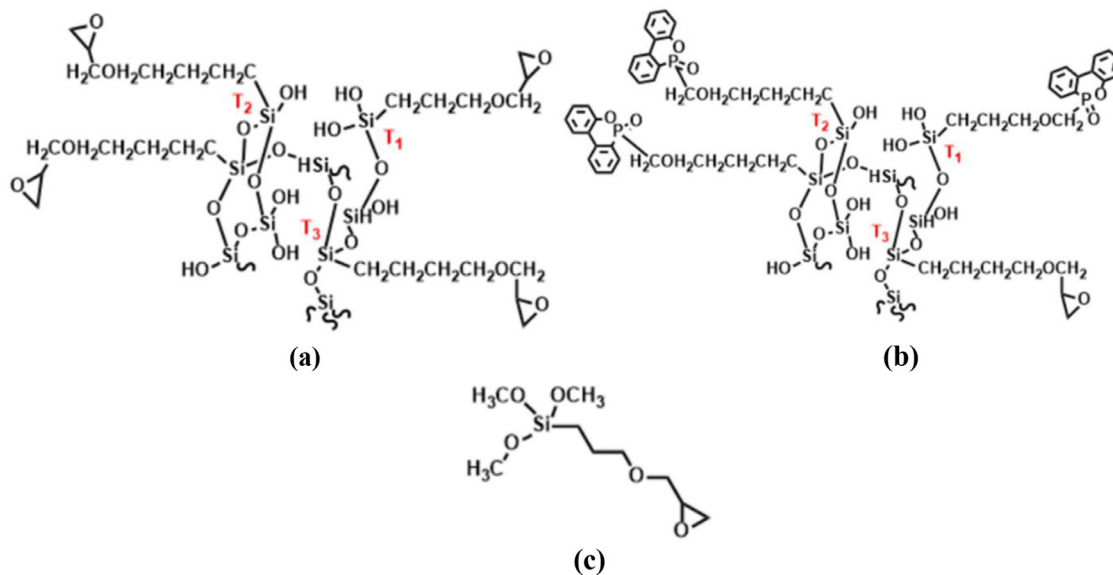
## 4.2. DOPO functionalized silica-based nanostructures

### 4.2.1. P-C bonded DOPO functionalized silica-based nanostructures

Yu et al. [137] prepared an epoxy modifier composed of a phosphorus-containing siloxane epoxide (DPS) with cyclic phosphorus groups in the SiO<sub>2</sub>-network. DPS was synthesized from the reaction of DOPO with polyhedral-oligomeric siloxanes T8 caged structures (POSS), this latter was obtained through the sol-gel reaction of GPTMS (Fig. 18) [38,138]. The use of this silane agent could improve the mechanical performances of the final sample



**Scheme 24.** (a) Synthesis route and chemical structure of piperazine-based DOPO derivative phosphonamidate (PIP-DOPO). (b) GO was functionalized and reduced by piperazine, and then incorporated into PIP-DOPO through *in situ* reaction, resulting in the formation of the hybrids (PD-rGO) [135].



**Fig. 18.** Structures of (a) polyhedral-oligomeric siloxanes (POSS), (b) phosphorus-containing epoxide siloxane (DPS) and GPTMS, adapted from [137].

and helped achieve a non-reactive DOPO derivative. DPS structure was confirmed by FT-IR and <sup>29</sup>Si NMR measurements, and then was used to modify E-54 bisphenol A epoxy resin at various ratios, with DDM as a curing agent.

The resulting organic-inorganic hybrid epoxy resins modified with DPS exhibited a high T<sub>g</sub>, good thermal stability, and high LOI values. In addition, the tensile strength of cured products was un-

affected [137,139,140]. The epoxy resin added with DPS exhibited higher char compared to the only DOPO-containing epoxy samples with the identical phosphorus contents (Tables 21 and 23). The influence of DPS on the char yield was mainly due to silica which could form in the char during the combustion process at high temperatures [43,44,137].

**Table 21**

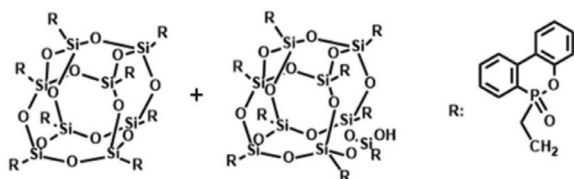
TGA data of cured epoxy resin, modified systems with DOPO and phosphorus-containing epoxide siloxane (DPS) [137].

Sample	<sup>a</sup> P content (wt%)	<sup>b</sup> Si content(wt%)	<sup>c</sup> T <sub>d</sub> 5% (°C)		Char yield at 720°C (wt%)		Tensile strength (MPa)
			N <sub>2</sub>	Air	N <sub>2</sub>	Air	
E-54 100*	0	0	341.9	338.2	17.8	17.8	45.1
E-54 98/DOPO 2**	0.3 <sup>a</sup>	0	336.5	330.8	18.0	18.0	46.5
E-54 96/DOPO 4	0.6 <sup>a</sup>	0	330.6	326.8	19.1	19.1	46.8
E-54 94/DOPO 6	0.9 <sup>a</sup>	0	325.2	315.9	21.5	21.5	47.1
E-54 90/DPS 10***	0.3 <sup>b</sup>	1.7	370.8	365.5	20.6	20.6	46.4
E-54 80/DPS 20	0.6 <sup>b</sup>	3.3	401.1	397.1	22.2	21.8	57.5
E-54 70/DPS 30	0.9 <sup>b</sup>	5.0	388.2	380.9	24.4	24.6	61.8

\* Pure epoxy resin

\*\* Sample composed by 98 wt% resin and 2 wt% DOPO

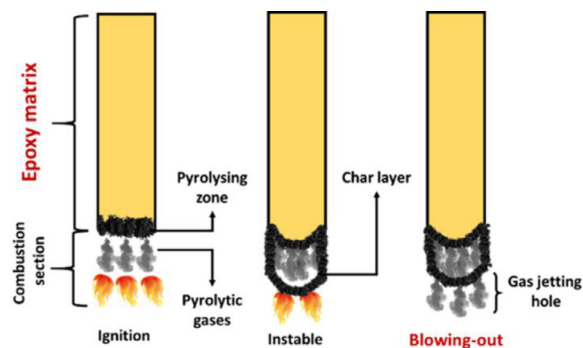
\*\*\* Sample composed by 90 wt% resin and 10 wt% DPS

<sup>a</sup> Calculated by the formula: (weight of DOPO/total weight of the system) x 14.34 wt% x 100%<sup>b</sup> Measured by the elemental analysis<sup>c</sup> Decomposition temperature at 5% of loss residual mass**Scheme 25.** Typical chemical structures of DOPO-POSS molecules. A mixture of perfect T<sub>8</sub> cage and an imperfect T<sub>9</sub> cage with one Si-OH group on it [141].

DPS-epoxy systems showed a higher tensile strength of 46.4–61.8 MPa, due to the establishment of hydrogen bonds between organic siloxane and hydroxyl groups of the crosslinked epoxy network.

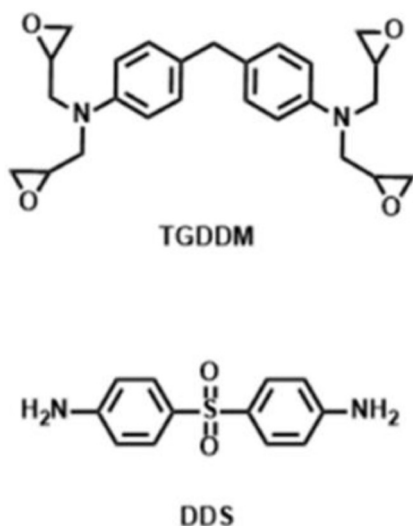
Zhang et al. [141] focused their attention on the use of a phosphorus-containing siloxane epoxide (DOPO-POSS) in DGEBA epoxy resin (EP-2.5) cured with *m*-phenylenediamine (*m*-PDA). DOPO-POSS was synthesized by addition reaction between DOPO and vinyl triethoxy silane (DOPO-VTES) and consequent hydrolytic condensation to polyhedral oligomeric silsesquioxanes [142]. Scheme 25 shows the structure of phosphorus-containing polyhedral oligomeric silsesquioxanes DOPO-POSS. Incorporation of 2.5 wt% DOPO-POSS into epoxy resin (EP/DPOSS-2.5) resulted in a LOI value of 30.2% and accomplished UL-94 V1 rating. Zhang et al. [141] observed during the UL-94 test the formation of pyrolytic gases from the sample together with the formation of a coherent char. The epoxy sample EP/DPOSS-2.5 exhibiting superior flame retardant performances showed the highest thermal stability and production of CO and CO<sub>2</sub> during the combustion process.

The blowing-out effect lowered the concentration of pyrolytic gases (combustible) in the flame zone, thus having a positive effect on the flame retardancy of DOPO-POSS/EP composites (Fig. 19), although it was not possible to achieve a V0 rating [141]. In order to deeply understand the principles of the “blowing-out effect”, Zhang et al. [144] developed and validated a method for the sampling of volatiles produced by polymer decomposition during UL-94 standard flammability tests, analyzing the composition of the fuel mixture feeding the flame in the real flaming scenario and conditions. For pristine DGEBA resin cured with DDS (DGEBA-DDS), the most abundant products were recognized as benzene, phenol, naphthalene and toluene, along with other minor aromatic products. The presence of DOPO-POSS at a low concentration (2.5 wt%) radically changed the composition of the aromatic volatile’s mixture, as no significant amount of benzene was produced, while phenol became the main product along with several tens of other products in lower concentrations (e.g. isopropyl phenol and bisphenol A). Thus, the addition of DOPO-POSS resulted in

**Fig. 19.** The model of the blowing-out effect. DOPO-POSS addition guaranteed the formation of a strong char layer which works as a thermal shield and oxygen barrier for the polymer matrix. The formation of this char layer (rigid char-brick) caused pyrolytic gases spurt through some holes, hence allowing a blowing-out effect in the flame zone and resulting in an intumescent char. The Figure was adapted from [143,144].

a modification of the fuel mixture feeding the flame and provided an explanation for the lower flammability of EP/DPOSS-2.5 as well the blowing out effect, which is mainly related to a physical thermal shielding effect [144].

Zhang et al. [143] also studied the fire retardant effect of DOPO-POSS in DGEBA resins cured with DDS and an aliphatic oligomeric polyamide 650 (PA650). The epoxy composites with DOPO-POSS showed different flame retardant properties depending on the type of hardener. During the UL-94 test it was observed that DGEBA/DDS, containing DOPO-POSS, exhibited a strong blowing-out effect, through vigorous emission of pyrolytic gases. The epoxy resin with 2.5 wt% of DOPO-POSS exhibited a LOI value of 27.1% and achieved a UL-94 V1 rating. In contrast, 10 wt% DOPO-POSS in the DGEBA/PA650 resulted in a LOI value of 25.9% and a UL-94 V1 rating. The modified DGEBA/DDS epoxy resin exhibited a lower value of PHRR and longer TTI than the DGEBA/PA650. DGEBA/DDS with only 2.5 wt% of DOPO-POSS was able to form a compact char, which kept pyrolytic gases at the boundary phase boosting the blowing-out effect. In contrast, 10 wt% of DOPO-POSS in DGEBA/PA650 was necessary to form char residue. Due to its aliphatic chains, PA650 did not easily produce a crosslinked structure in the condensed phase which can act as a thermal shield, oxygen barrier and construction for pyrolysis gas to the flame zone [143]. These studies revealed that the achievement of the blowing-out effect depended on the gas release rate, but the properties of the condensed phase were seemingly important for it [145,146]. Recently, Zhang et al. [147] investigated the fire behavior of an



**Fig. 20.** Chemical structure of tetraglycidyl diamino diphenyl methane (TGDDM) and DDS, adapted from [147].

epoxy monomer tetraglycidyl diamino diphenyl methane (TGDDM) containing DOPO-POSS and cured with DDS hardener (Fig. 20). Also, in this case, the blowing out effect during the UL-94 test was detected and samples containing 2.5 wt% of DOPO-POSS could achieve a V0 rating and LOI values of TGDDM/DDS resins were higher than 34%. The good flame retardancy of TGDDM/DDS composites containing DOPO-POSS was mainly attributed to an increase in melt viscosity, the formation of a swelling silicon-rich char and the accumulation of the pyrolytic gases in the condensed phase (Fig. 19) [147].

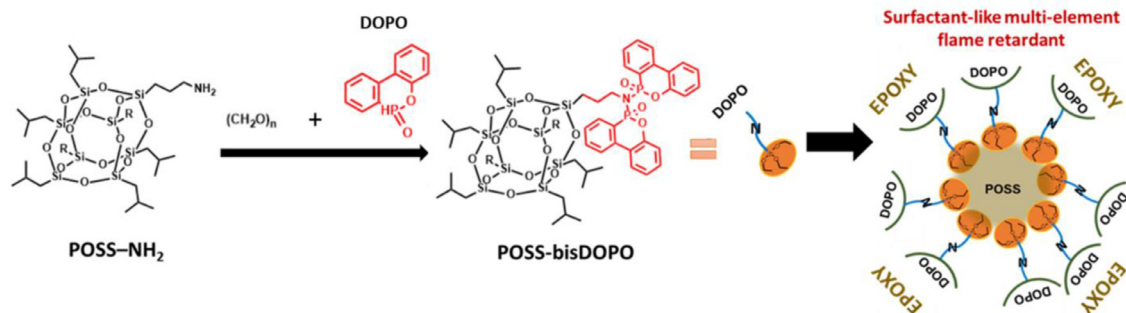
#### 4.2.2. P-N bonded DOPO functionalized silica-based nanostructures

Liu et al. [148] developed a multi-element flame-retardant system (POSS-bisDOPO) through the combination of DOPO, polyoxymethylene (POM) and POSS by using the classical Kabachnik-Fields reaction. The functionalization of POSS with DOPO molecule was obtained with the addition of a silica precursor APTS which worked as a coupling agent between the inorganic phase (POSS) and organic phase (DOPO) [149]. Besides, the amino modified POSS (POSS-NH<sub>2</sub>) could bond two DOPO molecules generating a multi-element structure where the flame retardant surrounded the silica phase. Since DOPO flame retardant contained aromatic rings, it could stabilize the POSS domains in the epoxy network, because of their chemical affinity. Liu et al. [148,150] disclosed that these domains were nanostructures (with a particle size of approximately 70 nm, and aggregates with wide distribution) of “surfactant-like

multi-element flame retardants” and surrounded by a shell of DOPO moieties. This surfactant-like multi-element flame retardant POSS-bisDOPO, with self-assembly capability in the polymer matrix, was added into a DGEBA epoxy resin (E51) cured with DDM (Scheme 26). The prepared epoxy composites containing POSS-bisDOPO appeared transparent and the excellent dispersion of the additive was proved by SEM.

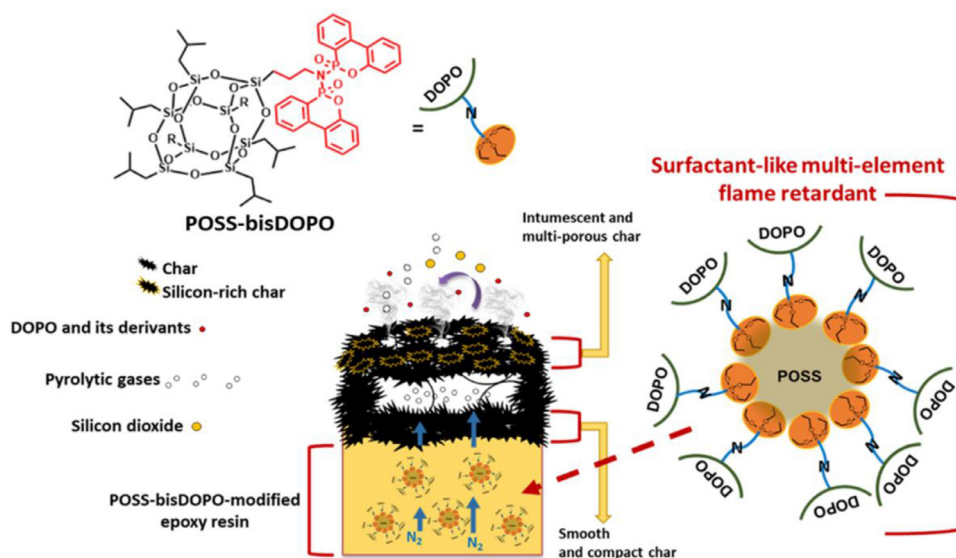
At 20 wt% loading of POSS-bisDOPO into the epoxy matrix, the sample still appeared transparent, and the LOI increased from 25.4% (pure DGEBA) to 34.5%. The TGA results of the composites showed that the char yield was strongly improved for cured epoxy samples containing POSS-bisDOPO (POSSbisDOPO/EP). FTIR results and SEM analyses indicated that the residual char had a compact and coherent appearance in the inner layer, while the outer structure was intumescent, silicon-rich and multi-porous. Therefore, the char played an important role by isolating heat and oxygen. The three-point bending test results showed that the mechanical strength of POSSbisDOPO/EP was higher than those of pure EP and epoxy composites containing POSS-NH<sub>2</sub> due to the outstanding reinforcement effect of the self-assembled hybrid nanostructure of POSS-bisDOPO in the EP matrix [148,151] (Fig. 21).

Liu et al. [148] demonstrated that POSS-bisDOPO could significantly increase the thermal stability and mechanical performance of DGEBA-based composites, because of its organic/inorganic characteristics which guaranteed an excellent dispersion of the additive in the epoxy network and the formation of a hybrid morphology. Although the use of POSS-bisDOPO helped decrease the LOI value, it was not possible to achieve self-extinguishing behavior. Thus, Zeng et al. [152] decided to combine the addition of the multi-element, synergistic, flame-retardant POSS-bisDOPO with tetrabutyl titanate (TBT) as co-additive to construct a phosphorous-silicon-titanium synergistic system for a DGEBA epoxy resin (E51). At first, TBT was dispersed in DGEBA by magnetic stirring at high temperature and then, the POSS-bisDOPO was added before cooling the mixture. The cured epoxy resins were obtained using a thermal curing process and using DDM as a hardener. Compared to pure EP, the char yield of the EP containing 5 wt% TBT and 5wt% POSS-bisDOPO (EP/PDT-5) was increased up to 42.4%. The LOI value and UL-94 ratings of EP/PDT-5 composites reached 31.0% and a V-0 classification, respectively. The PHRR and THR reduced to 28.4 W/g and 1.7 kJ/g, whereas for pure EP it was 430.2 W/g and 22.7 kJ/g, respectively. These results together with SEM analysis of residual char from cone calorimeter tests indicated a strong and efficient flame retardant activity of the phosphorous-silicon-titanium synergy (TBT/POSS-bisDOPO) in the condensed phase during the combustion process. In particular, the char of EP/PDT-5 composites showed an alveolate inner layer (this honeycomb structure char like was already observed in the case of DOPO-TMT and DOPO-VTMS) and continuous compact outer layer, which ef-



**Scheme 26.** Synthesis route of POSS-bisDOPO through a reaction between 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), polyoxymethylene (POM) and amino-functionalized polyhedral oligomeric silsesquioxane (POSS-NH<sub>2</sub>). The addition of POSS-bisDOPO into an epoxy system generated a surfactant-like multi-element flame retardant and thus hybrid composites with nanodomains of a well-dispersed inorganic phase [148].





**Fig. 21.** Route of the thermal decomposition mechanism. A hierarchical structure could be observed from the char with a smooth and compact inner layer and an intumescent and multi-porous layer on the outside. As a result, this char layer, mainly containing Si-O-Si (silicon-rich char) and aromatic structures, could protect the inner polymer matrix from further burning [148].

**Table 22**

LOI, UL-94, glass transition, char residue in a nitrogen atmosphere and cone calorimeter parameters of all the investigated epoxy samples [25].

Sample	UL-94 Rating	T <sub>g</sub> (°C)	LOI (%)	PHRR (kW/m <sup>2</sup> )	THR (MJ/m <sup>2</sup> )	Char yield at 700°C (wt%)
<sup>a</sup> EP-0	Unrated	152.0	25.0 ± 0.1	493.8 ± 9.8	23.6 ± 0.5	20.1
<sup>b</sup> EP-1	V1	162.4	27.0 ± 0.2	415.6 ± 8.3	20.8 ± 0.4	20.4
<sup>c</sup> EP-2	V0	172.4	29.2 ± 0.1	355.3 ± 7.1	18.1 ± 0.3	22.6
<sup>d</sup> EP-3	V0	173.4	37.5 ± 0.1	345.5 ± 6.9	17.9 ± 0.2	22.7
<sup>e</sup> EP-4	V0	163.8	39.2 ± 0.2	309.7 ± 6.1	17.1 ± 0.3	24.0

<sup>a</sup> DGEBA resin

<sup>b</sup> DGEBA resin containing 1.5 wt% Ti-POSS-bisDOPO

<sup>c</sup> DGEBA resin containing 3 wt% Ti-POSS-bisDOPO

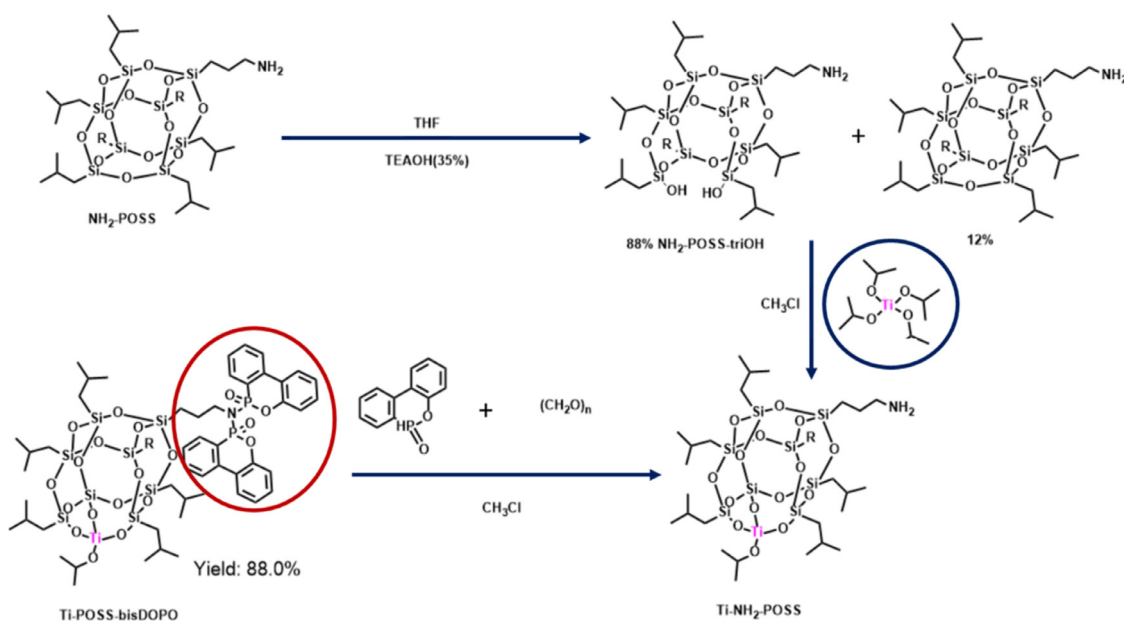
<sup>d</sup> DGEBA resin containing 4.5 wt% Ti-POSS-bisDOPO

<sup>e</sup> DGEBA resin containing 6 wt% Ti-POSS-bisDOPO

ficiently worked as a physical barrier to hinder the oxygen and heat penetration responsible for further combustion of the polymer [32,97,152]. The addition of a single component of TBT into epoxy increased the T<sub>g</sub> from 155.1 to 179.6 °C, because TBT could react with oxirane groups of epoxy and serve as the crosslinking agent for the resin. This effect of TBT on the crosslinking density of the matrix helped retain the glass transition temperature of the TBT/POSS-bisDOPO, unlike the reduction in T<sub>g</sub> observed by Liu et al. [148] for samples containing POSS-bisDOPO. The flame retardant efficiency of TBT/POSS-bisDOPO could be attributed to the synergistic effect of phosphorous, silicon and titanium. The presence of (i) phosphorous accelerated the formation of char, (ii) silicon formed a ceramic-like layer to keep the char from undergoing thermal degradation, and (iii) TBT strongly enhanced the char formation by catalyzing the dehydrogenation during polymer thermal degradation [152,153].

Wu et al. [25] synthesized a metal-POSS compound N,N'-bis(methylene)-bis(dibenz[C,E][1,2]-oxaphosphorin6-oxide)-propylisobutyl-amino-titanium-polyhedral oligomeric silsesquioxanes, namely Ti-POSSbisDOPO, through a three-step process including the corner-opening, corner-capping and Kabachnik-Fields reactions. In detail, the POSS-bisDOPO additive was modified by embedding one titanium atom into the POSS cage framework, forming an organic-inorganic-metal ternary intramolecular hybrid system (Scheme 27). Ti-POSSbisDOPO was used as a flame retardant for improving the fire behavior of a DGEBA resin cured with DDM hardener. This DOPO derivative was characterized by the

presence of two DOPO moieties with flame retardant properties linked to an aminopropyl substituent group on the corner of the POSS silicious cage. Ti-POSSbisDOPO still preserved the capability to self-assemble into a nanoparticle, which was already observed by Liu et al. [148] for POSS-bisDOPO. As Ti-POSS-bisDOPO contains a non-polar POSS unit and a polar DOPO segment it can behave like an amphiphilic surfactant. Therefore, SEM analysis of epoxy samples containing Ti-POSS-bisDOPO (EP/Ti-POSS-bisDOPO) revealed that the flame retardant could achieve very good dispersion in the matrix with a particle size varying from 150 nm to 1.5 μm. Compared to the pure EP, EP/Ti-POSS-bisDOPO composites showed a remarkable increase in both limited oxygen index and char yield, by 50% and 13% respectively, at a 4.5 wt% loading (Table 22). As previously reported, Liu et al. [148] used POSS-bisDOPO to flame retard a DGEBA resin cured with DDM. At 20 wt% loading of POSS-bisDOPO, a LOI value of 34.5% could be achieved, though it was not possible to achieve any UL-94 classification. By contrast with thermosets containing unmodified POSS-bisDOPO, EP/Ti-POSS-bisDOPO composites could achieve self-extinguishing capability with only 3.0 wt% loading. Meanwhile, the corresponding PHRR and THR values of EP/Ti-POSS-bisDOPO were all reduced with respect to pristine resin (Table 22). It was observed that the interior layers of the residues after the cone calorimeter test showed a honeycomb-like multilayer structure and the exterior layers were compact (Fig. 1, Section 2.1), which could effectively hinder the heat transfer and gas diffusion by working as a barrier and thermal shield. Besides, Wu et al. [25] investigated in detail



**Scheme 27.** Synthesis route of Ti-POSS-bisDOPO. NH<sub>2</sub>-POSS was obtained through the reaction of POSS with APTS as reported in the literature, and then NH<sub>2</sub>-POSS-triOH was prepared via the corner opening reaction of completely condensed POSS. Finally, Ti-NH<sub>2</sub>-POSS was acquired through the corner-capping reaction and the Kabachnik-Fields reaction was adopted to complete the synthesis to produce Ti-POSS-bisDOPO [25,154].

**Table 23**

The flame retardancy performance of epoxy-containing hybrid DOPO nanostructures.

Flame retardant (FR)	Polymer matrix	Hardener	FR content (wt%)	Phosphorous content (wt%)	UL-94 rating	Ref.
DOPO-rGO	DGEBA	DDM	5	NA	V0	[118]
DOPO-rGO	Mesogenic epoxy resin	NA	15	0.57	V0	[120]
PD-rGO	DGEBA	DDM	4	NA	V0	[135]
PFDCHQ	DGEBA	m-PDA	5	NA	V0	[127]
CCD	DGEBA	DDM	10	NA	V0	[132]
MWCNT-(DOPO-HQ)	DGEBA	DDM	1	1	V0	[133]
AlPi			3.67			
DOPO-POSS	TGDDM	DDS	2.5	NA	V0	[147]
POSS-bisDOPO	DGEBA-based epoxy	DDM	5	NA	V0	[152]
TBT	resin(E-51)		5			
Ti-POSS-bisDOPO	DGEBA	DDM	3	NA	V0	[25,154]

\*NA= Not Available in the literature

the composition of residues and the evolved gaseous products. It was found that when Ti was doped into the vertex of the siliceous cage, it acted as a catalyst by promoting char formation, producing thermodynamically stable TiO<sub>2</sub> in a ceramic layer. Finally, the non-flammable gas and the PO<sub>2</sub>· and HPO<sub>2</sub>· radicals released from the pyrolysis of EP/Ti-POSS-bisDOPO could promote a flame inhibition effect.

The flame-retardant performance of the most effective DOPO functionalized carbon- and silica based nanostructures mentioned in this review are summarized Table 23.

## 5. Summary and perspectives

This review covers the use of non-reactive DOPO-based derivative flame retardants currently available or under design and development for application in epoxy resins. The non-reactive DOPO compounds have demonstrated a hybrid activity in gas and condensed phases that occurs during the combustion of epoxy composites, without showing an adverse effect on their mechanical properties compared to the similar systems containing pristine DOPO. Thus, mono-, multi and hybrid DOPO derivatives do not negatively affect the epoxy crosslinking process and improve

the flame retardancy of the polymer matrix. In particular, DOPO-triazine and DOPO-phosphazene derivatives promote dehydration reaction and thus the production of a highly effective protective char. Furthermore, the release of nitrogen leads to intumescence and a delay in the time to ignition. Finally, DOPO functionalized carbon- and silica based nanostructures provide inorganic phases acting as heat insulators or act as charring agents and allow the tailoring of the interphase between filler and polymer matrix, hence improving both the flame retardancy and the mechanical performances. Despite the remarkable flame retardant effect of non-reactive DOPO-compounds in epoxy systems, self-extinguishing capability and smoke suppression are mostly achieved via the incorporation of aromatic hardeners, which are responsible for the formation of toxic species during the disposal of composites or their combustion. Therefore, in order to obtain a balance of toxicity, fire, and mechanical performances for epoxy systems containing non-reactive DOPO-based derivative flame retardants, it is necessary to develop new strategies to achieve excellent fire behavior with the use of aliphatic curing agents. This target is fundamental to move future research toward the development of more sustainable materials with low impact on the environment and human health.

## Author contributions

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

## Declaration of Competing Interest

The authors declare no conflict of interest. We confirm that this submission is original, it is not published elsewhere and not under consideration for the publication elsewhere.

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