Recent Progress of DOPO-Containing Compounds as Flame Retardants for Versatile Polymeric Materials: Review

Qiuyue Wu[1], Rita de Cassia Siqueira Curto Valle[2], José Alexandre Borges Valle[2], Fabricio Bezerra Maestá[3], Xu Meng[4] and Manuel Jose Lis Arias[1,*]

[1]*INTEXTER-UPC, Colón, 15, 08222 Terrassa, Barcelona, Spain*

[2]*Department of Textile Engineering, Universidade Federal de Santa Catarina (UFSC), Blumenau, Santa Catarina, Brazil*

[3]*Tecnológica Textile Engineering (COENT), Universidade (UTFPR), Federal do Paraná Apucarana, Paraná, Brazil*

[4]*College of Textile and Garment, College of Life Science, Shaoxing University, Shaoxing, P.R. China*

Abstract: With the increasing awareness of environmental protection, the development and application of novel halogen-free flame retardants have attracted a lot of attention recently. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and its derivatives are regarded as one of the most promising and widely used halogen-free flame retardants among various phosphorus-containing compounds due to its superior reactivity, thermal stability and oxidation resistance. Accordingly, DOPO-containing compounds have been incorporated with versatile polymeric matrices and exhibited advanced flame retardancy performances in gaseous phase and condensed phase.

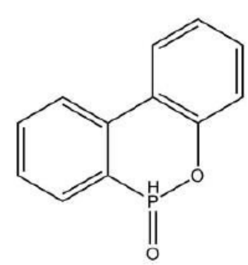
Keywords: 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, flame retardant, polymeric materials, application.

1. INTRODUCTION

Polymeric materials are widely used in buildings, textiles, electronic materials, furniture, transportation and many more application fields due to its light-weight and cost-effective properties, as well as excellent comprehensive performance. However, the limiting oxygen index (LOI) of most polymeric materials is less than 25%, which make them flammable or combustible, easily causing fire accidents, environmental hazards, personal injury and property losses. Therefore, flame-retardant (FR) addition in the treatment of polymeric materials, is highly valued by people, globally.

In order to accomplish with the environmental regulatory requirements, the development of phosphorus-containing flame retardants becomes increasingly popular, gradually edging out the halogen containing FRs. At present, because of the superior reactivity, thermal stability and oxidation resistance, DOPO and its derivatives have been the research focuses among the various phosphorus-containing compounds [1-4].

9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) (Scheme **1**) as a novel flame retardant intermediate, made from 2-phenylphenol and phosphorus trichloride, was synthesized and reported by Sanko Chemical Co., Ltd. for the first time in 1972 [5]. Owing to the high reactivity of O=P-H bond, DOPO could react with chemicals containing alkenes, schiff bases, ketone, carbonyls, etc., providing simple approaches to prepare multiple DOPO-derivatives [6]. In addition, it also enables DOPO-containing compounds to chemically modify the polymer matrix in a variety of types by covalent binding, for the purpose of improving the flame retardancy of polymeric materials (EP, Cellulose, PET, PBT, PA, etc.) (Scheme **2**).



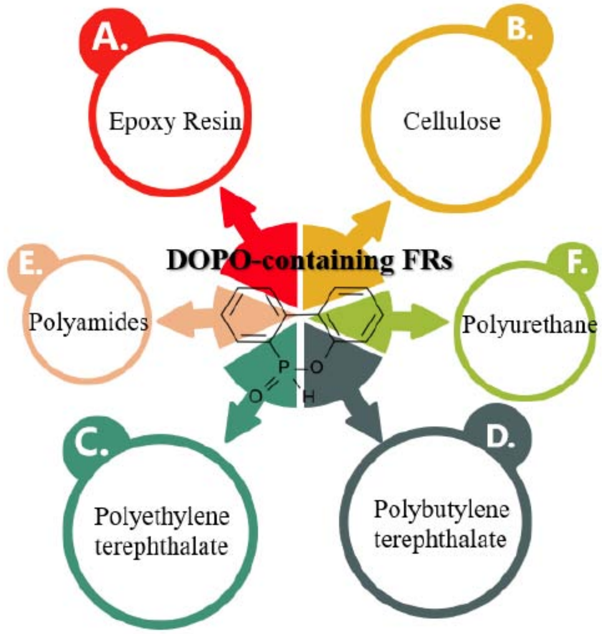
Scheme 1: Chemical structure of 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO).

2. FLAME RETARDANTS MECHANISM OF DOPO-CONTAINING COMPOUNDS

Under high temperature conditions, DOPO-containing compounds are decomposed and release PO• radicals, which are able to have quenching effect on the highly active H• and OH• radicals generated by

*Address correspondence to this author at the INTEXTER-UPC, Colón, 15, 08222 Terrassa, Barcelona, Spain;
E-mail: manuel-jose.lis@upc.edu

E-ISSN: 2415-5489/20



Scheme 2: The application of DOPO-containing FRs for versatile polymeric materials.

the pyrolysis of polymeric materials, thereby inhibiting the chain reaction and decreasing heat release in gas phase flame retarding [7,8]. Simultaneously, with the presence of decomposition products for DOPO-containing compounds in the combustion process, such as phosphoric acid that could dehydrate and carbonize the polymeric materials to form the char layer as a barrier on the surface, oxygen and heat are insulated from transferring inside to obtain the flame-retardant effect in condensed-phase [9].

Generally, when the modified DOPO contains nitrogen, silicon or other more retardant elements, it's supposed to produce the synergistic actions for further developing the thermal properties of polymeric materials [10,11].

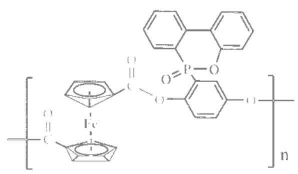
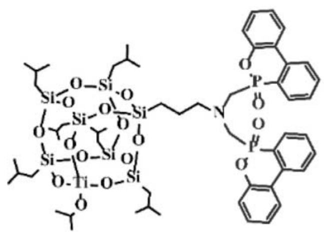
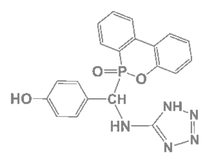
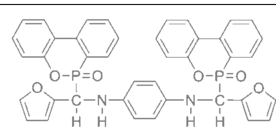
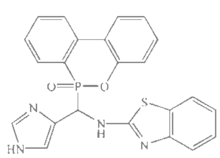
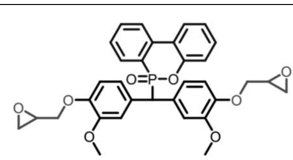
3. THE APPLICATION OF DOPO-CONTAINING FRS FOR POLYMERIC MATERIALS

3.1. Epoxy Resin (EP)

Epoxy resin (EP) with outstanding comprehensive properties, as one of the most important thermosetting polymers, has been commonly used in electronics, coatings, adhesives, aerospace industry, etc. Considering the intrinsic flammability, it's essential to develop the flame-retardant performance of EP [12] (Table **1**).

Diversified DOPO-containing compounds, DOPO–TMDS, DOPO–DMDP [13], DOPO-PHE [14], DOPO-PHM [15], DOPO-T [16], DOPO-THPO [17], etc. [18-27], have been used as flame retardants to modify epoxy resin for extensive application foreground. The mixture of DOPO and organoclay on EP was disclosed that it can contribute to reducing the decomposed products loss of DOPO, causing the synergic flame-retardant action of the gas barrier effects and condensed phase mechanism [28]. A silicon, phosphorous containing flame-retardant additive, 1,3,5,7-tetramethyl-1,3,5,7-tetra 2-(6-oxido-6-H-dibenzo(c,e) (1,2)oxaphosphorin-6-yl) ethylcyclotetrasiloxane (DOPO-SiD), was believed to effectively prevent the cycloaliphatic EP from dripping during combustion and further increase the thermal stabilities [29]. Wen *et al*. put forward a new thought for the molecular design of phosphorus and ferrocene-containing FRs. DOPO and ferrocene-based oligomer (PFDCHQ) was synthesized and applied in EP for improved thermal, thermo-oxidative stability and char yield [30]. CLEP–DOPO–POSS equipped with cage–ladder structure and epoxy groups could facilitate the uniform dispersion in the EP composites, enhancing the flame resistance and thermal stability of epoxy matrix by the presence of DOPO and POSS groups synergistically [31]. Not long afterward, an idea of ternary metal-silicon-phosphorus intramolecular hybrid for modified EP was provided by Wu *et al*. The EP/Ti-POSS-bisDOPO composites were proved with prominent fire retardance and comprehensive performances [32]. As the final morphology views of residues (Figure **1**) shows, the presence of Ti-POSS-bisDOPO (EP-2) was gained more chars that formed an intumescent and compact layer than untreated sample (EP-0) for restraining the transfer of heat and flammable gases after cone calorimetry test. By utilizing DOPO-based tetrazole derivative (ATZ), the initial degradation temperature and glass transition temperature (Tg) of the EP was decreased, whereas the char yield at high temperature was increased [33]. In addition, phosphorus-containing curing agent (FPD) gained through the addition reaction between Schiff-base C=N bond and P-H bond of DOPO, was used in epoxy thermoset for the excellent performance of toughness and flame retardancy [34]. Similarly, with the imine structure of DCAD (DOPO derivative FRs), it was bonded with the cross-linked network of EP without decreasing the crosslinking density of thermosets. As a consequence, the flame-retardant and physical-mechanical properties of EP were highly evaluated [35]. Zhang *et al*. proposed a DOPO-based reactive FRs (PBI) constructed by multiple heteroaromatic groups, which accelerated the crosslinking reaction of EP and were

Table 1: DOPO-Containing FRs for Epoxy Resins

FRs	Sturcture	Flame tests	Reference
PFDCHQ		LOI 32.0% UL-94 V-0	[30]
Ti-POSS-bisDOPO		LOI 31.7% UL-94 V-0	[32]
ATZ		LOI 33.7% UL-94 V-0	[33]
FPD		LOI 35.7% UL-94 V-0	[34]
PBI		LOI 34.6% UL-94 V-0	[36]
DGEBDB		LOI 30.2% UL-94 V-0	[38]

chemically bonded with EP matrix. Despite FR properties of EP system was notably improved with the incorporation of PBI, the existence of DMF in synthesis route may raise chemical safety issues and be banned for use in the manufacture in Europe [36]. A new nitrogen, phosphorus and boron ionic pair compound DTPA[AZB] was successfully synthesized from DOPO, boric acid, etc. It was introduced into an EP thermoset, playing a positive role in compatibility and flame retardancy, as well as mechanical properties [37]. From eco-friendly perspective, two lignin-derived compounds were combined with DOPO to obtain the bio-based flame retardant (DGEBDB) [38], which was of great benefit to flame retardation performance for EP. There is a disadvantage that the employed epichlorohydrin is still petroleum-based and toxic after all.

3.2. Cellulose

The cotton fibre is mainly composed of cellulose, which is the most abundant organic polymer on earth [39]. Due to the good characteristics of moisture permeability and comfort-dressing, cotton has been used in the textile industry with a long history [40]. On account of the high flammability and low thermal stability, it's meaningful to develop flame-retardant cotton for expanding application fields and reducing the fire hazards (Table **2**).

Hu *et al*. designed a route to synthesize the phosphorus-modified siloxanes (DIA) by DOPO, Isophorone diisocyanate (IPDI) and Aminopro-pyltriethoxysilane (AMEO). The organic–inorganic hybrid coating was formed on the surface of cotton

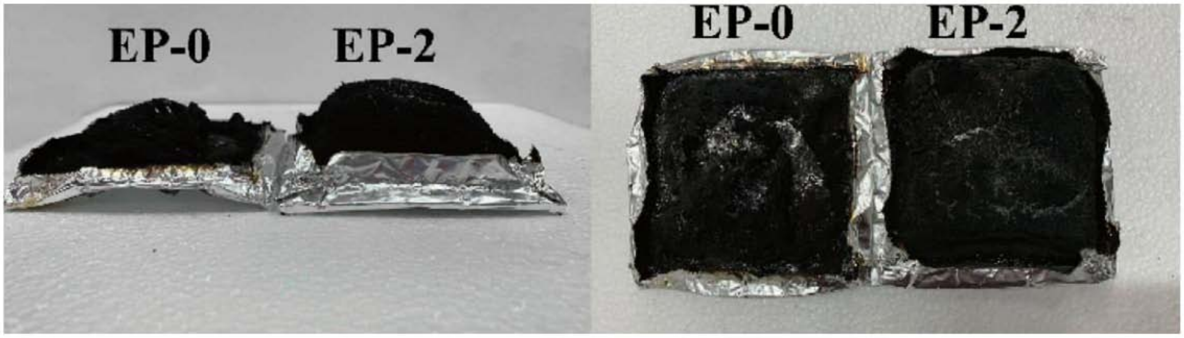
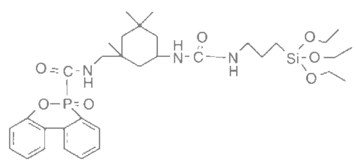
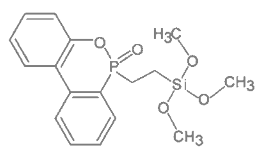
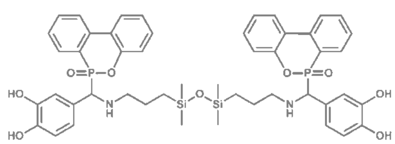
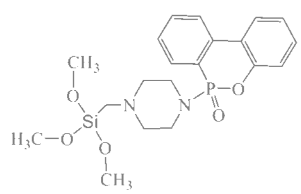


Figure 1: The comparison of morphology views of residues (from Ref. [32]).

Table 2: DOPO-Containing FRs for Cellulose

FRs	Sturcture	Flame tests	Reference
DIA		char residues increased from 1.82 to 9.38 wt% at 700℃	41
DOPO-VTS		LOI 23.5% char residues increased from 1.6 to 15.2 wt% at 800℃	42,43
BDD		LOI 27% PHRR decreased from 1050.1 to 644.9 kW/m^2	47
DOPO-PiP-Si		LOI 27.6% PHRR decreased from 230.8 to 161.1 kW/m^2	48

fabric after DIA treatment via sol-gel process, which increased the char layers and in turn led to improved thermal stability of cotton [41]. Coincidentally, both Vasiljevic [42] and Chernyy [43] *et al*. presented a method to synthesize the 10-(2-trimethoxysilyl-ethyl)-9-hydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO-VTS) nanosol coating solution for cotton textile [44]. Compared with pure DOPO finishing and untreated cotton, it can be viewed the synergetic effect of P and Si elements in condensed phase endows the cotton fibre with better thermal and oxidative stability. Based on these researches, Zhou [45] *et al*. further studied the flame-retardant mechanisms of DOPO containing SiO_2 hybrid sol on cotton fabrics by the preparation of SiO_2 sol, SiO_2-KH570 sol, DOPO, SiO_2-DOPO sol and SiO_2-KH570-DOPO sol respectively. Besides the synergistic effect, DOPO always played a positive role in dehydration and carbonation in the condensed phase during the combustion process. DOPO hybrid sol promoted the formation of three-dimensional microscopic gel coating to enhance the anti-flammable properties of cotton fabric. Chen *et al*. [46] suggested a method to introduce 9, 10-dihydro-9-oxa-10-phosphaphenanthrene 10-oxide (DOPO) and fluorine-silicon-containing polymer network on the surface of cotton fabric. The modified cotton

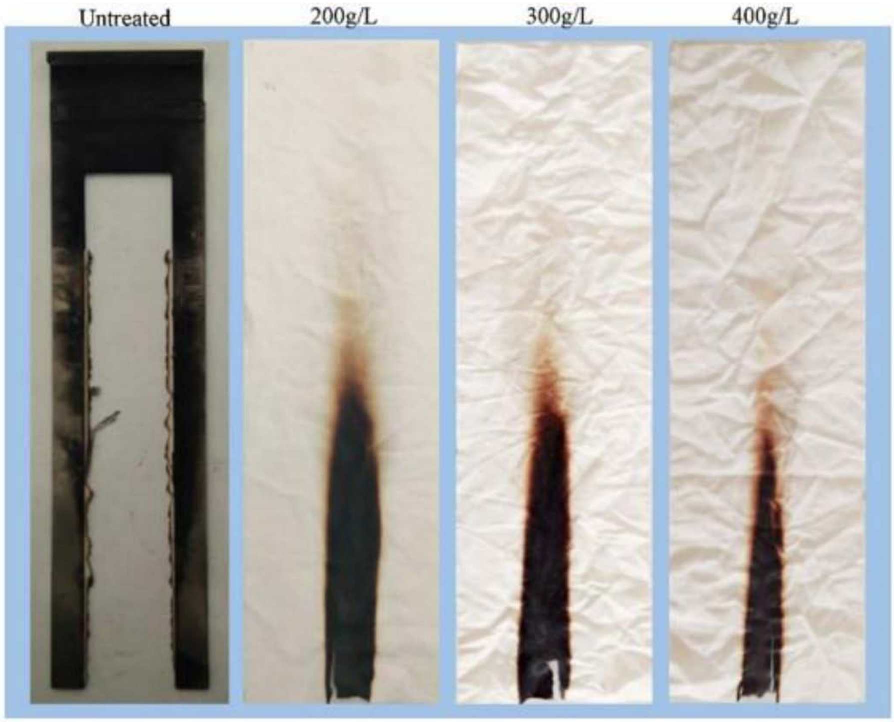


Figure 2: Different concentrations of DOPO-PiP-Si on cotton fabrics via vertical burning test (from Ref. [48]).

manifested both superhydrophobic and good heat resistance properties. Some research workers have provided an approach to make a phosphorus-nitrogen-silicone FRs (BDD) based on DOPO and Schiff Base (BD). Since BDD can act as the intumescent FRs on the cotton, working synergistically between gas phase and condensed phase, the modified cellulose membrane achieved the result of increased LOI and decreased PHRR [47]. Comparably, another Si/P/N flame retardant 1-(9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide)-4-(trimethoxysilyl-methyl) piperazine (DOPO-PiP-Si) was investigated and successfully applied to cotton fabric by Zhang *et al*. [48]. Through the vertical burning test, it can be intuitively seen that the corresponding fire resistance effects with different concentrations of DOPO-PiP-Si from Figure **2**. The treated cotton increased LOI value to 27.6% and lowered char length to 12.2 cm, simultaneously possessing high tensile strength. In order to reduce the water pollution, Liu [49] and co-workers innovatively conducted the flame retardant finishing of cotton with DOPO using supercritical CO in a self-built apparatus. The conclusion also revealed deceased combustibility and improved flame-retardant property for the treated cotton fibre.

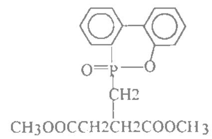
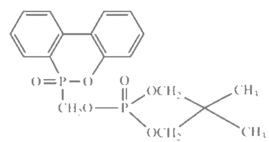
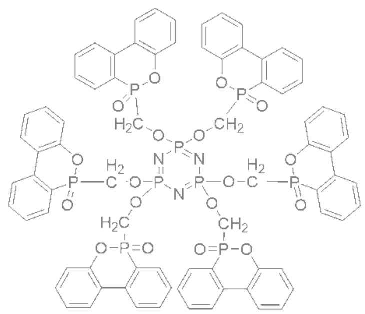
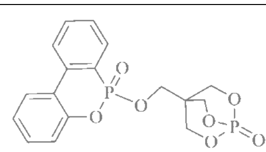
Additionally, cellulose is one of the main ingredients of wood. Chen *et al*. [50] reported a modified FRs called DOPO-cellulose acrylate (DCA), which was used as the cross-linked films and coatings to protect the flammable cellulose. However, when it was applied to dry manifold paper, corn husk and poplar chip, the durability of DCA films and coatings hasn't been discussed. It highly suggests checking the abrasion resistance of the films and coatings.

3.3. Polyethylene Terephthalate (PET)

Polyethylene terephthalate, considered as semi-crystalline thermo-plastic polymer, it owns good chemical stability, desirable physical-mechanical property and low costs [51]. To fulfil the application requirements of clothing, engineering plastic and decorative materials, flame retardant treatment is progressively crucial for PET (Table **3**).

Wang *et al*. early used 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) and dimethyl itaconate to prepare the compound ODOP-DI, working as a reactive flame retardant in poly(ethylene terephthalate) system. In virtue of the combination of the rigid structure of DOPO and pendant P groups, it exhibited higher char yield, improved thermal stability and flame retardancy [52]. Fang *et al*. proposed a carbon source containing DOPO-based flame retardant (DOPO–DOPC) to prepare PET/DOPO–DOPC composite [53]. Obviously, advanced retardancy performance of the composite was demonstrated by limiting oxygen index (LOI) and UL-94 test. From the

Table 3: DOPO-Containing FRs for PET

FRs	Sturcture	Flame tests	Reference
ODOP-DI		UL-94 V-0	52
DOPO–DOPC		LOI 42.8% UL-94 V-0	53
DOPO-TPN		LOI 42.7% UL-94 V-0	54
DOPO-PEPA		LOI 35.2% No melt drips	55,56

SEM images of the char surface of the untreated PET and PET/DOPO-TPN by roasting in the muffle furnace (Figure **3**), it's clear that the matrix structure become more continuous, compact and smooth after treatment, which greatly enhanced the retardancy effects in PET depending on gas-phase and condensed-phase actions [54]. Nonetheless, the synthesis reaction process is not extremely eco-friendly caused by formaldehyde, with a possibility to produce fume and toxic gas emission, too. Two types of DOPO derivatives, 6-[(1-oxido-2,6,7-trioxa-1-phosphabicyclo [2.2.2]oct-4-yl)methoxy]-, 6-oxide (DOPO-PEPA) and 3-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)propane-mide (AAM-DOPO) were synthesized in green chemistry principles and investigated by Salmeia *et al*. [55]. Compared with AAM-DOPO and a commercial FRs Aflammit PCO 960, the research data indicated that DOPO-PEPA was most compatible with polyethylene terephthalate (PET). Stable processing at high temperatures, the blends of PET and DOPO-PEPA was displayed the highest thermal-oxidative stability. Correspondingly, Gooneie *et al*. [56] also studied the DOPO-PEPA (DP) to modify PET, and indicated that the melt stability of composites at elevated temperatures was risen. Additionally, the modified-PET recyclability was developed due to synergistic behaviour of DP.

3.4. Polybutylene Terephthalate (PBT)

Polybutylene terephthalate (PBT), a common material used in electrical and electronics industries, belongs to a kind of thermoplastic engineering polymer. Some scholars have deeply studied the flame retardant of PBT for the reason that it's easily flammable with a limiting oxygen index approximately 21% [57] (Table **4**).

Sablong *et al*. developed a DOPO-containing diol (2-[4-(2-hydroxy-ethoxy)-3-(10-oxo-10-H9-oxa-10-l5-phospha-phenanthrene-10-yl)-phenoxy]-ethanol) (DOPO-HQ-GE), which was incorporated into PBT via solid state polycondensation. The flame retardancy properties of treated PBT was vastly improved. For specific performance of the combustion behaviour, it rendered enhanced char yields and LOI value, as well

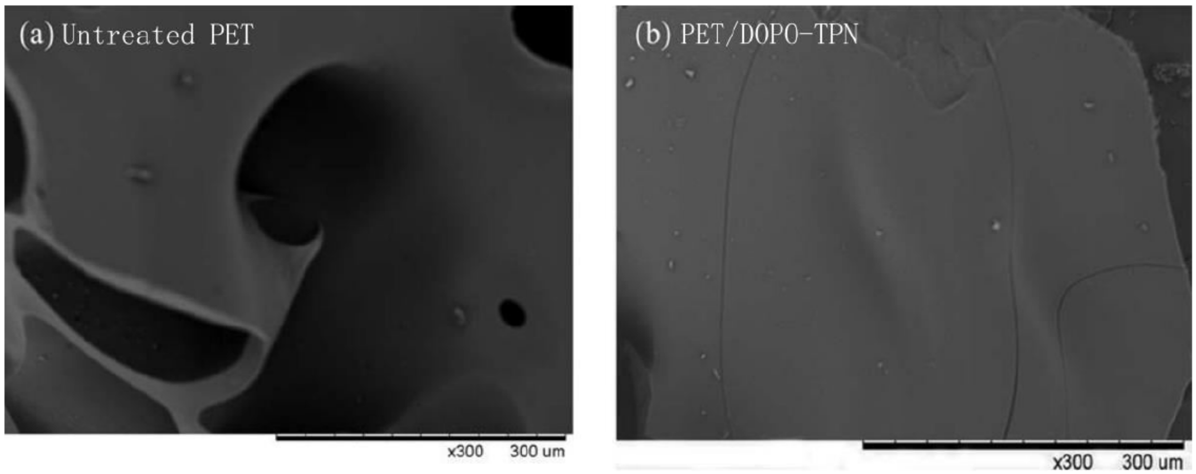
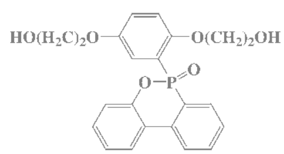
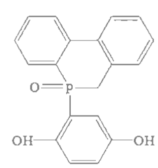
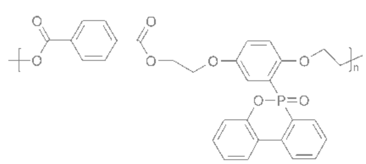
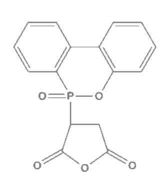


Figure 3: The SEM images of the char surface by roasting in the muffle furnace (from Ref. [54]).

Table 4: DOPO-Containing FRs for PBT

FRs	Sturcture	Flame tests	Reference
DOPO-HQ-GE		LOI 35%	58
DOPO–HQ		LOI 26.3% UL-94 V-2	59
PET-P-DOPO		LOI 39.3% UL-94 V-0	62
DOPO-MAH		LOI 25.7% UL-94 V-0	63

as extremely low heat release capacities with quite small amount of P-contents [58]. And He *et al*. [59] reported that the DOPO-HQ is a promising flame retardant for PBT. Although the LOI and CONE test exhibited a better result with the addition of 20% DOPO-HQ to PBT, it is worth noting that the incorporation of PBT and DOPO-HQ still leads to the flaming-dripping phenomenon. The author mentioned that the UL94 test rating can be upgraded from V2 to V0 when DOPO-HQ was applied with a compatibilizer, namely poly(ethylene– butylacry-late-glycidylmethacrylate) (PTW). Köppl *et al*. examined three phosphorus-containing polyesters, PET-P-DOPO, PET-P-DPPO and PET-P-DPhPO, as polymeric FRs introduced to PBT. By contrast with pure PBT, the FRs showed no significant influence on the dielectric properties, but with some changes of mechanical behavior [60]. PET-P-DOPO was also investigated by

Brehm *et al*. and compared with AlPi-Et that has already been proved with good flame retardancy properties in PBT. Objectively, PBT/PET-P-DOPO reflected the equal retardant efficiency yet better tensile strength than PBT/AlPi-Et under the same condition of phosphorus content. Thus, PET-P-DOPO was expected as a potential alternative material to the low-molecular-weight FRs [61,62]. With the help of addition reaction between DOPO and maleic anhydride (MAH), a derivative of DOPO with reactive anhydride groups known as DOPO-MAH can be synthesized and then melt-blended with PBT to acquire the PBT/ DOPO-MAH composites. Since DOPO-MAH can act as chain extender for the PBT matrix on the basis of Torque-time profile and intrinsic viscosity, not only upgraded the flame retardancy of PBT/ DOPO-MAH composites, but also strengthened the tensile and flexural properties [63]. By the melt-impregnation procedure, Zhang *et al*. prepared the long glass fibre-reinforced PBT composites filled with DOPO. According to thermal gravimetric analysis curves and LOI, the PBT composites acquired better thermal stability with longer ageing time. Meanwhile, the crosslinking and degradation of PBT molecular chains were considered the main reasons for thermo-oxidative ageing [64].

3.5. Polyamides (PA)

Polyamides (PA) containing repeating amide linkages (-CO-NH-) are one of the most important polymeric materials [65]. Among a variety of the synthetic polyamides, polyamide 6 (PA6) and polyamide 66 (PA66) are the most well known and widely used in automotive, textile industry, and consumer goods application [66]. Consequently, there is a growing concern about developing flame retardancy of Polyamides (Table **5**).

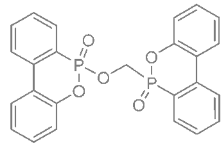
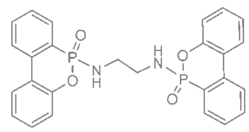
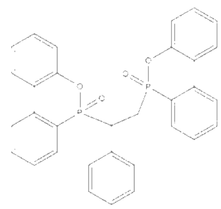
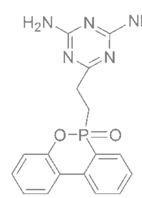
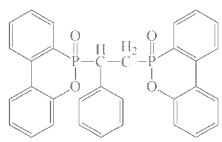
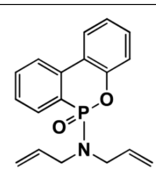
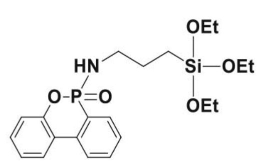
According to Liu's work, DOPO-containing compound was attributed to low initial decomposition temperature, heat insulating property and thermal stability for aromatic polyamides [67]. Two bridged DOPO-based FRs defined as DiDopoMeO and DiDopoEDA [68], as well as PHED [69], were all discovered performing good flame-retardant behaviour for PA6. In order to obtain the PA6 with excellent flame retardancy performance, DOPO-SiO_2 was successfully prepared in a one-step process by Li *et al.* [70]. With the presence of DOPO-VTS and TEOS precursors, Šehić *et al.* [71] evaluated the PA6 fibres with over and above preferable thermo-oxidative stability and anti-dripping properties. Also, the thermal performance of modified PA6 would remain stable even under the intensive washing condition. Butnaru *et al*. revealed a phosphorus-nitrogen-containing compound, 6-(2-(4,6-diamino-1,3,5-triazin-2-yl)ethyl)dibenzo[c,e][1,2]oxa-phosphinine 6-oxide (DTE-DOPO), whose flame retardant efficiency was comparable to a commercial additive Exolit® OP 1230 on PA6 [72]. As a result of the chain extending reaction between PA6 matrix and DOPO-TGIC, the complex viscosity of PA6 composites was increased, accompanied by improved mechanical and flame-retardant properties [73]. Polyamide 6T (PA6T) constructed by terephthalic acid and hexanediamine, is defined as a semi-aromatic nylon [74]. The incorporation of glass fibre-reinforced polyamide 6T (GFPA6T) and DOPO derivatives (PN-DOPO) was confirmed with highly-efficient flame retardancy, benefited from the charring effect of condensed phase flame inhibition effect in gaseous phase [75]. Yu *et al*. reported the synthesis of a DOPO-based phosphonamidite (DOPO-DAAM) via the reaction of DOPO and di-allyl amine. When DOPO-DAAM was introduced to PA66 by UV grafting method, it was found that self-sustained burning of PA66 composites was completely inhibited. Additionally, the flame-retardant properties of PA66/DOPO-DAAM composites was developed with increased char yield and decreased initial decomposition temperature [76]. Recently, Kundu *et al*. combined DOPO with two different silica compounds respectively, namely DOPO-APTES and DOPO-GPTMS [77], enabled PA66 fabric through the medium of sol-gel to enhance the flame-retardant and thermal stability properties with durability. In the meantime, it perfectly inhibited the melt-dripping of PA66.

3.6. Polyurethane (PU)

Polyurethane (PU) is a versatile class of polymers, most commonly derived from reaction between diisocyanates and polyols [78]. Rigid polyurethane foam (RPUF) and flexible polyurethane foam (FPUF), as two of the main categories of PUs, have widespread industrial application [79,80] in automotive interiors, packaging, furniture, surface coatings and sealants, etc. that demanding the build-up of flame retardancy influence (Table **6**).

Flexible polyurethane foam (FPUF) is highly flammable on the basis of its open cell structure, low density, and good air permeability [81]. König and Kroke made the synthesis of methyl-DOPO for FPUF and attained great flame retarding behaviour by reason of gas-phase action [82]. Dong *et al*. reported that TiO2-KH570-DOPO nanoparticles was successfully

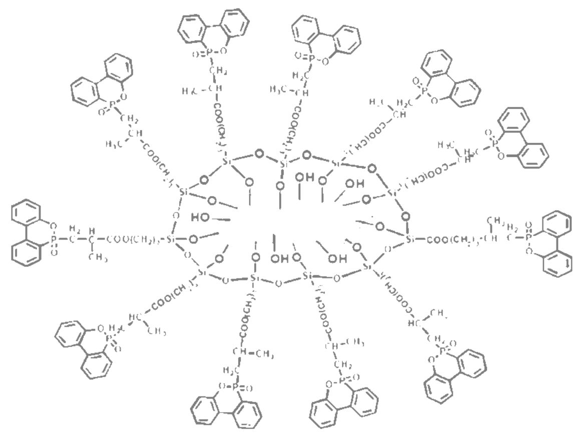
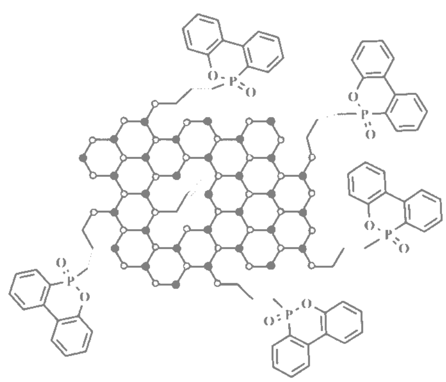
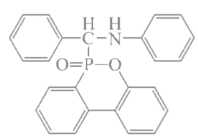
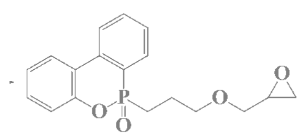
Table 5: DOPO-Containing FRs for PA

FRs	Sturcture	Flame tests	Reference
DiDopoMeO		LOI 29.8% UL-94 V-0	68
DiDopoEDA		LOI 31.7% UL-94 V-0	68
PHED		LOI 27.8% UL-94 V-0	69
DTE-DOPO		UL-94 V-0	72
PN-DOPO		UL-94 V-0 No melt drips	75
DOPO-DAAM		LOI 23% UL-94 V-0 No melt drips	76
DOPO-APTES		LOI 21.5% UL-94 V-1 No melt drips	77

prepared and applied in FPUF by supercritical carbon dioxide [83], which impart great fire performance for FPUF. Zhi *et al*. explored a synthesis route of MoS_2-DOPO hybrid via grafting DOPO on the surface of MoS_2 nanosheets, and thus deemed it the flame retardancy and smoke suppression performance of FPUF treated with MoS_2-DOPO was productively improved. The incorporation of DOPO and metal hydroxide can be inferred that there's a synergistic flame-retardant effect in bi-phase [84].

Incorporating the phosphorus-nitrogen FRs (DOPO-BA) into RPUF was verified that the modified-RPUF performed superior flame retarding without greatly altering their cell physical structure [85]. While the research group of Gaan proposed bis-DOPO phosphonamidate with better thermal stability than mono-DOPO phosphonamidate was conducive for PU industrial manufacturing [86]. Jia *et al*. investigated and compared the flame retarding effect of DOPO, e-DOPO, dimethyl methyl phosphonate and triethyl

Table 6: DOPO-Containing FRs for PU

FRs	Sturcture	Flame tests	Reference
TiO_2-KH570-DOPO		PHRR decreased from 657.0 to 519.2 W/g	83
MoS_2-DOPO		LOI 23.9% PHRR decreased from 356 to 209 kW/m^2	84
DOPO-BA		LOI 28.1%	85
e-DOPO		LOI 21.1% PHRR decreased from 274.46 to 209.48 kW/m^2	87

phosphate on RPUF [87]. In terms of related fire-testing results, e-DOPO-PUF composites exhibited the best general performances.

Moreover, some other researchers follow with interest the flame retardancy of lignin-based polyurethane (LPU) [88] and waterborne polyurethane (WPU) [89] by utilizing novel DOPO-containing FRs.

3.7. Other Polymeric Materials

To overcome the inflammability restricts of poly(lactic acid) (PLA), HPAPC [90], TGIC-DOPO [91], SEP-DOPO [92] and more DOPO-containing FRs have been investigated and studied. Three bis P-C bridged DOPO derivatives were synthetized and incorporated in PLA, imparting the prominent flame-retardant and thermal properties. Long *et al*. pointed out that the more aromatic groups contained in DOPO, it's more likely to form a cross-linked structure and improve the retardancy effect [93]. Jia and co-workers implied DOPO played a role of plasticizer through decreasing glass transition temperature and crystallinity, while DOPO-POSS could as a filler with a slight increase in crystallinity of PLA matrix, which both made the development of mechanical properties [94].

Polycarbonates (PC) as naturally high charring polymer is developed for higher flame retardancy

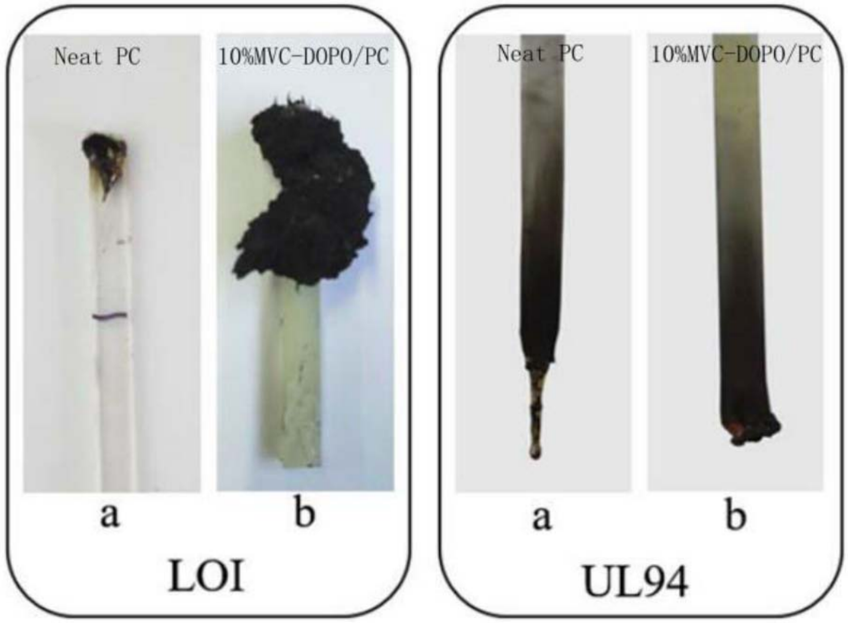


Figure 4: The comparison of residues in LOI and UL94 tests (from Ref. [96]).

efficiency by some academics. When Zhang *et al*. applied DOPO-POSS into PC matrix, it's indicated that DOPO-POSS could catalyse the thermal decomposition of PC but cut down on the release of flammable volatiles, associated with increased char residue [95]. A phosphorus/silicon flame retardant, MVC-DOPO, was synthetized and endowed DOPO-MVC/PC composites with suppression of burning intensity in the gas phase and formation of more viscous residue in condensed phase (Figure **4**) [96]. With an addition of only 3% DFPZ (DOPO derivative), Liu *et al*. also found the modified PC achieved a UL-94 V0 rating ultimately [97].

Further, there are more DOPO-containing compounds as flame retardants applying to several other kinds of polymeric materials, such as Polystyrene [98,99] and polypropylene [100,101].

4. SUMMARY AND PERSPECTIVES /CONCLUSION

With the increasing awareness of environmental protection, halogen flame retardants have already been phased out, while DOPO derivatives are regarded as one of the most promising and popular flame retardants on account of its excellent performance, high thermal and chemical stability. In recent years, the application of DOPO-containing FRs for different kinds of polymeric materials has attracted worldwide attention continuously.

With the objective to acquire the optimal flame retardancy of polymeric materials, the incorporation of DOPO and chemicals containing nitrogen, silicon or other elements for synergistic effect needs to be explored in depth. Besides flame resistance, it's also be interesting to develop other functional properties of polymeric materials simultaneously via the introduction of DOPO-containing FRs with multifunctional groups. Generally speaking, the required amount of halogen-free FRs is more than halogen FRs to achieve the same retardancy results. Accordingly, maintaining the flame-retardant effect, it's highly expected to minimize the dosage of DOPO-containing FRs, improve the compatibility, and diminish the negative effect on physical mechanical properties. Meanwhile, it will be more practical to reduce the difficulty of the synthesis process and meet the needs of large-scale industrial production. More importantly, the process of producing DOPO-containing FRs and applying it to polymeric materials tends to be in a green and ecological way.

ACKNOWLEDGEMENTS

The authors thank Marina Textil Inc. (Spain) for research grant support and supply of survey materials.

REFERENCES

[1] Liu Y, Zou M, Yang R, He J, Zhang W. Synthesis and Characterization of a Novel Metal–Organic Compound: 9,10-Dihydro-9-oxa-10-phosphaphenanthrene 10-Oxide (DOPO)–Mg. Chem Lett 2015; 44(6): 737-739. https://doi.org/10.1246/cl.141191

[2] Wang P, Cai Z. Highly efficient flame-retardant epoxy resin with a novel DOPO-based triazole compound: Thermal stability, flame retardancy and mechanism. Polymer Degradation and Stability 2017; 137: 138-150. https://doi.org/10.1016/j.polymdegradstab.2017.01.014

[3] Duan H, Ji S, Yin T, Tao X, Chen Y, Ma H. Phosphorus–nitrogen-type fire-retardant vinyl ester resin with good comprehensive properties. J Appl Polym Sci 2019; 136(39): 47997.
https://doi.org/10.1002/app.47997

[4] Liu S, Fang Z, Yan H, Chevali VS, Wang H. Synergistic flame retardancy effect of graphene nanosheets and traditional retardants on epoxy resin. Composites Part A: Applied Science and Manufacturing 2016; 89: 26-32.
https://doi.org/10.1016/j.compositesa.2016.03.012

[5] Wei Z, Gu X, Wu J, *et al.* Performance comparison of epoxy resins modified with diphenylphosphine oxide and DOPO. Fire and Materials 2019; 43(7): 892-902.
https://doi.org/10.1002/fam.2749

[6] Tang H, Zhu Z, Chen R, Wang J, Zhou H. Synthesis of DOPO-based pyrazine derivative and its effect on flame retardancy and thermal stability of epoxy resin. Polym Adv Technol 2019; 30(9): 2331-2339.
https://doi.org/10.1002/pat.4674

[7] Liu Y, He J, Yang R. The preparation and properties of flame-retardant polyisocyanurate–polyurethane foams based on two DOPO derivatives. Journal of Fire Sciences 2016; 34(5): 431-444.
https://doi.org/10.1177/0734904116662667

[8] Rakotomalala M, Wagner S, Döring M. Recent Developments in Halogen Free Flame Retardants for Epoxy Resins for Electrical and Electronic Applications. Materials 2010; 3(8): 4300-4327.
https://doi.org/10.3390/ma3084300

[9] Hergenrother PM, Thompson CM, Smith JG, *et al.* Flame retardant aircraft epoxy resins containing phosphorus. Polymer 2005; 46(14): 5012-5024.
https://doi.org/10.1016/j.polymer.2005.04.025

[10] Lu H, Song L, Hu Y. A review on flame retardant technology in China. Part II: flame retardant polymeric nanocomposites and coatings. Polym Adv Technol 2011; 22(4): 379-394.
https://doi.org/10.1002/pat.1891

[11] Morgan AB, Gilman JW. An overview of flame retardancy of polymeric materials: application, technology, and future directions: An overview of flame retardancy of polymeric materials. Fire Mater 2013; 37(4): 259-279.
https://doi.org/10.1002/fam.2128

[12] Müller P, Morys M, Sut A, Jäger C, Illerhaus B, Schartel B. Melamine poly(zinc phosphate) as flame retardant in epoxy resin: Decomposition pathways, molecular mechanisms and morphology of fire residues. Polymer Degradation and Stability 2016; 130: 307-319.
https://doi.org/10.1016/j.polymdegradstab.2016.06.023

[13] Ding J, Tao Z, Zuo X, Fan L, Yang S. Preparation and properties of halogen-free flame retardant epoxy resins with phosphorus-containing siloxanes. Polym Bull 2009; 62(6): 829-841.
https://doi.org/10.1007/s00289-009-0052-0

[14] Zhao J, Dong X, Huang S, *et al.* Performance comparison of flame retardant epoxy resins modified by DPO–PHE and DOPO–PHE. Polymer Degradation and Stability 2018; 156: 89-99.
https://doi.org/10.1016/j.polymdegradstab.2018.08.007

[15] Xie C, Zeng B, Gao H, *et al.* Improving thermal and flame-retardant properties of epoxy resins by a novel reactive phosphorous-containing curing agent. Polym Eng Sci 2014; 54(5): 1192-1200.
https://doi.org/10.1002/pen.23642

[16] Yang S, Hu Y, Zhang Q. Synthesis of a phosphorus–nitrogen-containing flame retardant and its application in epoxy resin. High Performance Polymers 2019; 31(2): 186-196.
https://doi.org/10.1177/0954008318756496

[17] Wang J, Ma C, Wang P, Qiu S, Cai W, Hu Y. Ultra-low phosphorus loading to achieve the superior flame retardancy of epoxy resin. Polymer Degradation and Stability 2018; 149: 119-128.
https://doi.org/10.1016/j.polymdegradstab.2018.01.024

[18] Wang X, Song L, Xing W, Lu H, Hu Y. A effective flame retardant for epoxy resins based on poly(DOPO substituted dihydroxyl phenyl pentaerythritol diphosphonate). Materials Chemistry and Physics 2011; 125(3): 536-541.
https://doi.org/10.1016/j.matchemphys.2010.10.020

[19] Wang P, Yang F, Li L, Cai Z. Flame-retardant properties and mechanisms of epoxy thermosets modified with two phosphorus-containing phenolic amines. J Appl Polym Sci 2016; 133(37).
https://doi.org/10.1002/app.43953

[20] Wu H, Hu R, Zeng B, *et al.* Synthesis and application of aminophenyl- s -triazine derivatives as potential flame retardants in the modification of epoxy resins. RSC Adv 2018; 8(66): 37631-37642.
https://doi.org/10.1039/C8RA07450J

[21] Xu M-J, Xu G-R, Leng Y, Li B. Synthesis of a novel flame retardant based on cyclotriphosphazene and DOPO groups and its application in epoxy resins. Polymer Degradation and Stability 2016; 123: 105-114.
https://doi.org/10.1016/j.polymdegradstab.2015.11.018

[22] Huo S, Wang J, Yang S, *et al.* Synthesis of a novel reactive flame retardant containing phosphaphenanthrene and piperidine groups and its application in epoxy resin. Polymer Degradation and Stability 2017; 146: 250-259.
https://doi.org/10.1016/j.polymdegradstab.2017.10.015

[23] Huo S, Liu Z, Li C, Wang X, Cai H, Wang J. Synthesis of a phosphaphenanthrene/benzimidazole-based curing agent and its application in flame-retardant epoxy resin. Polymer Degradation and Stability 2019; 163: 100-109.
https://doi.org/10.1016/j.polymdegradstab.2019.03.003

[24] Qian L-J, Ye L-J, Xu G-Z, Liu J, Guo J-Q. The non-halogen flame retardant epoxy resin based on a novel compound with phosphaphenanthrene and cyclotriphosphazene double functional groups. Polymer Degradation and Stability 2011; 96(6): 1118-1124.
https://doi.org/10.1016/j.polymdegradstab.2011.03.001

[25] Chen R, Dai S, Guo T, Tang H, Fan Y, Zhou H. Transparent low-flammability epoxy resins with improved mechanical properties using tryptamine-based DOPO derivative. Polym Eng Sci 2019; 59(10): 2008-2015.
https://doi.org/10.1002/pen.25199

[26] Qiu Y, Qian L, Xi W. Flame-retardant effect of a novel phosphaphenanthrene/triazine-trione bi-group compound on an epoxy thermoset and its pyrolysis behaviour. RSC Adv 2016; 6(61): 56018-56027.
https://doi.org/10.1039/C6RA10752D

[27] Qian L, Qiu Y, Sun N, *et al.* Pyrolysis route of a novel flame retardant constructed by phosphaphenanthrene and triazine-trione groups and its flame-retardant effect on epoxy resin. Polymer Degradation and Stability 2014; 107: 98-105.
https://doi.org/10.1016/j.polymdegradstab.2014.05.007

[28] Weng Z, Senthil T, Zhuo D, Song L, Wu L. Flame retardancy and thermal properties of organoclay and phosphorous compound synergistically modified epoxy resin. J Appl Polym Sci 2016; 133(18).
https://doi.org/10.1002/app.43367

[29] Li Y-J, Gu X-Y, Zhao J, Jiang P, Sun J, Wang T. Flame retardancy effects of phosphorus-containing compounds and cationic photoinitiators on photopolymerized cycloaliphatic epoxy resins. J Appl Polym Sci 2014; 131(7).
https://doi.org/10.1002/app.40011

[30] Wen Y, Cheng Z, Li W, *et al.* A novel oligomer containing DOPO and ferrocene groups: Synthesis, characterization, and its application in fire retardant epoxy resin. Polymer Degradation and Stability 2018; 156: 111-124.
https://doi.org/10.1016/j.polymdegradstab.2018.08.010

[31] Li S, Zhao X, Liu X, *et al.* Cage-ladder-structure, phosphorus-containing polyhedral oligomeric silsesquinoxanes as promising reactive-type flame retardants for epoxy resin. J Appl Polym Sci 2019; 136(23): 47607. https://doi.org/10.1002/app.47607

[32] Wu H, Zeng B, Chen J, *et al.* An intramolecular hybrid of metal polyhedral oligomeric silsesquioxanes with special titanium-embedded cage structure and flame retardant functionality. Chemical Engineering Journal 2019; 374: 1304-1316. https://doi.org/10.1016/j.cej.2019.06.027

[33] Wang P, Chen L, Xiao H. Flame retardant effect and mechanism of a novel DOPO based tetrazole derivative on epoxy resin. Journal of Analytical and Applied Pyrolysis 2019; 139: 104-113. https://doi.org/10.1016/j.jaap.2019.01.015

[34] Yao Z, Qian L, Qiu Y, Chen Y, Xu B, Li J. Flame retardant and toughening behaviors of bio-based DOPO-containing curing agent in epoxy thermoset. Polym Adv Technol 2020; 31(3): 461-471. https://doi.org/10.1002/pat.4782

[35] Jin S, Liu Z, Qian L, Qiu Y, Chen Y, Xu B. Epoxy thermoset with enhanced flame retardancy and physical-mechanical properties based on reactive phosphaphenanthrene compound. Polymer Degradation and Stability 2020; 172: 109063. https://doi.org/10.1016/j.polymdegradstab.2019.109063

[36] Zhang Q, Yang S, Wang J, *et al.* A DOPO based reactive flame retardant constructed by multiple heteroaromatic groups and its application on epoxy resin: curing behavior, thermal degradation and flame retardancy. Polymer Degradation and Stability 2019; 167: 10-20. https://doi.org/10.1016/j.polymdegradstab.2019.06.020

[37] Tang H, Zhou H. A novel nitrogen, phosphorus, and boron ionic pair compound toward fire safety and mechanical enhancement effect for epoxy resin. Polym Adv Technol 2020; 31(4): 885-897. https://doi.org/10.1002/pat.4823

[38] Liu J, Dai J, Wang S, Peng Y, Cao L, Liu X. Facile synthesis of bio-based reactive flame retardant from vanillin and guaiacol for epoxy resin. Composites Part B: Engineering 2020; 190: 107926. https://doi.org/10.1016/j.compositesb.2020.107926

[39] Klemm D, Heublein B, Fink H-P, Bohn A. Cellulose: Fascinating Biopolymer and Sustainable Raw Material. Angew Chem Int Ed 2005; 44(22): 3358-3393. https://doi.org/10.1002/anie.200460587

[40] Zhao B, Liu Y-T, Zhang C-Y, Liu D-Y, Li F, Liu Y-Q. A novel phosphoramidate and its application on cotton fabrics: Synthesis, flammability and thermal degradation. Journal of Analytical and Applied Pyrolysis 2017; 125: 109-116. https://doi.org/10.1016/j.jaap.2017.04.011

[41] Hu S, Hu Y, Song L, Lu H. Effect of modified organic–inorganic hybrid materials on thermal properties of cotton fabrics. J Therm Anal Calorim 2011; 103(2): 423-427. https://doi.org/10.1007/s10973-010-1093-1

[42] Vasiljević J, Jerman I, Jakša G, *et al.* Functionalization of cellulose fibres with DOPO-polysilsesquioxane flame retardant nanocoating. Cellulose 2015; 22(3): 1893-1910. https://doi.org/10.1007/s10570-015-0599-x

[43] Chernyy S, Ulah S, Sørensen G, Tordrup SW, Pedersen PB, Almdal K. DOPO-VTS-based coatings in the realm of fire retardants for cotton textile. J Appl Polym Sci 2015; 132(19). https://doi.org/10.1002/app.41955

[44] Peng C, Li J, Wu Z, Peng W, Zhou D. Investigating into the liquid oxygen compatibility of a modified epoxy resin containing silicon/phosphorus and its mechanical behavior at cryogenic temperature. RSC Adv 2016; 6(44): 38300-38309. https://doi.org/10.1039/C6RA06033A

[45] Zhou S, Huangfu W, You F, Li D, Fan D. Flame Retardancy and Mechanism of Cotton Fabric Finished by Phosphorus Containing SiO_2 Hybrid Sol. In: 2019 9th International Conference on Fire Science and Fire Protection Engineering (ICFSFPE). IEEE; 2019: 1-5. https://doi.org/10.1109/ICFSFPE48751.2019.9055847

[46] Chen T, Hong J, Peng C, *et al.* Superhydrophobic and flame retardant cotton modified with DOPO and fluorine-silicon-containing crosslinked polymer. Carbohydrate Polymers 2019; 208: 14-21. https://doi.org/10.1016/j.carbpol.2018.12.023

[47] Li N, Ming J, Yuan R, *et al.* Novel Eco-Friendly Flame Retardants Based on Nitrogen–Silicone Schiff Base and Application in Cellulose. ACS Sustainable Chem Eng 2020; 8(1): 290-301. https://doi.org/10.1021/acssuschemeng.9b05338

[48] Zhang Z, Dong C, Liu J, Kong D, Sun L, Lu Z. Preparation of a synergistic reactive flame retardant based on silicon, phosphorus and nitrogen and its application to cotton fabrics. Cellulose 2020; 27(3): 1799-1815. https://doi.org/10.1007/s10570-019-02900-4

[49] Liu G, Han Y, Zhao Y, Zheng H, Zheng L. Development of CO2 utilized flame retardant finishing: Solubility measurements of flame retardants and application of the process to cotton. Journal of CO2 Utilization 2020; 37: 222-229. https://doi.org/10.1016/j.jcou.2019.12.015

[50] Chen Z, Xiao P, Zhang J, *et al.* A facile strategy to fabricate cellulose-based, flame-retardant, transparent and anti-dripping protective coatings. Chemical Engineering Journal 2020; 379: 122270. https://doi.org/10.1016/j.cej.2019.122270

[51] Horrocks AR. Flame retardant challenges for textiles and fibres: New chemistry versus innovatory solutions. Polymer Degradation and Stability 2011; 96(3): 377-392. https://doi.org/10.1016/j.polymdegradstab.2010.03.036

[52] Wang CS, Shieh JY, Sun YM. Synthesis and properties of phosphorus containing PET and PEN (I). : 6.

[53] Fang Y, Zhou X, Xing Z, Wu Y. Flame retardant performance of a carbon source containing DOPO derivative in PET and epoxy. J Appl Polym Sci 2017; 134(12). https://doi.org/10.1002/app.44639

[54] Fang Y, Zhou X, Xing Z, Wu Y. An effective flame retardant for poly(ethylene terephthalate) synthesized by phosphaphenanthrene and cyclotriphosphazene. J Appl Polym Sci 2017; 134(35): 45246. https://doi.org/10.1002/app.45246

[55] Salmeia KA, Gooneie A, Simonetti P, *et al.* Comprehensive study on flame retardant polyesters from phosphorus additives. Polymer Degradation and Stability 2018; 155: 22-34. https://doi.org/10.1016/j.polymdegradstab.2018.07.006

[56] Gooneie A, Simonetti P, Salmeia KA, Gaan S, Hufenus R, Heuberger MP. Enhanced PET processing with organophosphorus additive: Flame retardant products with added-value for recycling. Polymer Degradation and Stability 2019; 160: 218-228. https://doi.org/10.1016/j.polymdegradstab.2018.12.028

[57] Yang W, Hu Y, Tai Q, Lu H, Song L, Yuen RKK. Fire and mechanical performance of nanoclay reinforced glass-fiber/PBT composites containing aluminum hypophosphite particles. Composites Part A: Applied Science and Manufacturing 2011; 42(7): 794-800. https://doi.org/10.1016/j.compositesa.2011.03.009

[58] Sablong R, Duchateau R, Koning CE, *et al.* Incorporation of a flame retardancy enhancing phosphorus-containing diol into poly(butylene terephthalate) via solid state polycondensation: A comparative study. Polymer Degradation and Stability 2011; 96(3): 334-341. https://doi.org/10.1016/j.polymdegradstab.2010.07.001

[59] He M, Zhang D, Zhao W, Qin S, Yu J. Flame retardant and thermal decomposition mechanism of poly(butylene terephthalate)/DOPO-HQ composites. Polym Compos 2019; 40(3): 974-985. https://doi.org/10.1002/pc.24772

[60] Köppl T, Brehme S, Pospiech D, *et al.* Influence of polymeric flame retardants based on phosphorus-containing polyesters on morphology and material characteristics of poly(butylene terephthalate). J Appl Polym Sci 2013; 128(5): 3315-3324. https://doi.org/10.1002/app.38520

[61] Brehme S, Köppl T, Schartel B, *et al.* Phosphorus Polyester - an Alternative to Low-Molecular-Weight Flame Retardants in Poly(Butylene Terephthalate)? Macromol Chem Phys 2012; 213(22): 2386-2397. https://doi.org/10.1002/macp.201200072

[62] Brehme S, Schartel B, Goebbels J, *et al.* Phosphorus polyester versus aluminium phosphinate in poly(butylene terephthalate) (PBT): Flame retardancy performance and mechanisms. Polymer Degradation and Stability 2011; 96(5): 875-884. https://doi.org/10.1016/j.polymdegradstab.2011.01.035

[63] Liu P, Liu M, Gao C, *et al.* Preparation, characterization and properties of a halogen-free phosphorous flame-retarded poly(butylene terephthalate) composite based on a DOPO derivative. J Appl Polym Sci 2013; 130(2): 1301-1307. https://doi.org/10.1002/app.39318

[64] Zhang D, He M, He W, Zhou Y, Qin S, Yu J. Influence of Thermo-Oxidative Ageing on the Thermal and Dynamical Mechanical Properties of Long Glass Fibre-Reinforced Poly(Butylene Terephthalate) Composites Filled with DOPO. Materials 2017; 10(5): 500. https://doi.org/10.3390/ma10050500

[65] Song L, Zhu T, Yuan L, *et al.* Ultra-strong long-chain polyamide elastomers with programmable supramolecular interactions and oriented crystalline microstructures. Nat Commun 2019; 10(1): 1315. https://doi.org/10.1038/s41467-019-09218-6

[66] Garth K, Döring M, Kraemer R, Roth M, Thomas C. Novel phosphinate-containing zinc polyacrylate and its utilization as flame retardant for polyamides. J Appl Polym Sci 2019; 136(22): 47586. https://doi.org/10.1002/app.47586

[67] Liu Y. Synthesis and properties of new organosoluble aromatic polyamides with cyclic bulky groups containing phosphorus. Polymer 2002; 43(21): 5757-5762. https://doi.org/10.1016/S0032-3861(02)00473-1

[68] Buczko A, Stelzig T, Bommer L, Rentsch D, Heneczkowski M, Gaan S. Bridged DOPO derivatives as flame retardants for PA6. Polymer Degradation and Stability 2014; 107: 158-165. https://doi.org/10.1016/j.polymdegradstab.2014.05.017

[69] Vasiljević J, Čolović M, Čelan Korošin N, Šobak M, Štirn Ž, Jerman I. Effect of Different Flame-Retardant Bridged DOPO Derivatives on Properties of in Situ Produced Fiber-Forming Polyamide 6. Polymers 2020; 12(3): 657. https://doi.org/10.3390/polym12030657

[70] Li M, Zhong Y, Wang Z, *et al.* Flame retarding mechanism of Polyamide 6 with phosphorus-nitrogen flame retardant and DOPO derivatives. J Appl Polym Sci 2016; 133(6). https://doi.org/10.1002/app.42932

[71] Šehić A, Tomšič B, Jerman I, Vasiljević J, Medved J, Simončič B. Synergistic inhibitory action of P- and Si-containing precursors in sol‑gel coatings on the thermal degradation of polyamide 6. Polymer Degradation and Stability 2016; 128: 245-252. https://doi.org/10.1016/j.polymdegradstab.2016.03.026

[72] Butnaru I, Fernández-Ronco M, Czech-Polak J, Heneczkowski M, Bruma M, Gaan S. Effect of Meltable Triazine-DOPO Additive on Rheological, Mechanical, and Flammability Properties of PA6. Polymers 2015; 7(8): 1541-1563. https://doi.org/10.3390/polym7081469

[73] Xu M, Liu H, Ma K, Li B, Zhang Z. New strategy towards flame retardancy through design, synthesis, characterization, and fire performance of a chain extender in polyamide 6 composites. Polym Eng Sci. Published online December 13, 2018: pen.25030. https://doi.org/10.1002/pen.25030

[74] Huang W, He W, Long L, *et al.* Highly efficient flame-retardant glass-fiber-reinforced polyamide 6T system based on a novel DOPO-based derivative: Flame retardancy, thermal decomposition, and pyrolysis behavior. Polymer Degradation and Stability 2018; 148: 26-41. https://doi.org/10.1016/j.polymdegradstab.2018.01.008

[75] Huang W, He W, Long L, *et al.* Thermal degradation kinetics of flame-retardant glass-fiber-reinforced polyamide 6T composites based on bridged DOPO derivatives. Polym Bull 2019; 76(4): 2061-2080. https://doi.org/10.1007/s00289-018-2437-4

[76] Kundu CK, Yu B, Gangireddy CSR, *et al.* UV Grafting of a DOPO-Based Phosphoramidate Monomer onto Polyamide 66 Fabrics for Flame Retardant Treatment. Ind Eng Chem Res 2017; 56(6): 1376-1384. https://doi.org/10.1021/acs.iecr.6b04188

[77] Kundu CK, Song L, Hu Y. Sol-gel coatings from DOPO-alkoxysilanes: Efficacy in fire protection of polyamide 66 textiles. European Polymer Journal 2020; 125: 109483. https://doi.org/10.1016/j.eurpolymj.2020.109483

[78] Yuan Y, Ma C, Shi Y, Song L, Hu Y, Hu W. Highly-efficient reinforcement and flame retardancy of rigid polyurethane foam with phosphorus-containing additive and nitrogen-containing compound. Materials Chemistry and Physics 2018; 211: 42-53. https://doi.org/10.1016/j.matchemphys.2018.02.007

[79] Randall D, Lee S. The Polyurethanes Book. John Wiley & Sons New York; 2002.

[80] Zhou Y, He W, Wang N, *et al.* Thermoplastic polyurethane/ polytetrafluoroethylene/bridged dopo derivative composites: Flammability, thermal stability, and mechanical properties. Polym Eng Sci 2019; 59(8): 1593-1602. https://doi.org/10.1002/pen.25157

[81] König A, Kroke E. Flame retardancy working mechanism of methyl-DOPO and MPPP in flexible polyurethane foam. Fire Mater 2012; 36(1): 1-15. https://doi.org/10.1002/fam.1077

[82] König A, Kroke E. Methyl-DOPO-a new flame retardant for flexible polyurethane foam. Polym Adv Technol 2011; 22(1): 5-13. https://doi.org/10.1002/pat.1728

[83] Dong Q, Chen K, Jin X, *et al.* Investigation of Flame Ret-ardant Flexible Polyurethane Foams Containing DOPO Immo-bilized Titanium Dioxide Nanoparticles. Polymers 2019; 11(1): 75. https://doi.org/10.3390/polym11010075

[84] Zhi M, Liu Q, Zhao Y, Gao S, Zhang Z, He Y. Novel MoS_2 –DOPO Hybrid for Effective Enhancements on Flame Retardancy and Smoke Suppression of Flexible Polyurethane Foams. ACS Omega 2020; 5(6): 2734-2746. https://doi.org/10.1021/acsomega.9b03346

[85] Zhang M, Luo Z, Zhang J, Chen S, Zhou Y. Effects of a novel phosphorus–nitrogen flame retardant on rosin-based rigid polyurethane foams. Polymer Degradation and Stability 2015; 120: 427-434. https://doi.org/10.1016/j.polymdegradstab.2015.08.001

[86] Gaan S, Liang S, Mispreuve H, Perler H, Naescher R, Neisius M. Flame retardant flexible polyurethane foams from novel DOPO-phosphonamidate additives. Polymer Degradation and Stability 2015; 113: 180-188. https://doi.org/10.1016/j.polymdegradstab.2015.01.007

[87] Jia D, He J, Yang R. The synthesis and characterization of a DOPO derivative bearing an active terminal epoxy group: e-DOPO and its application in rigid polyurethane foam. Journal of Fire Sciences 2019; 37(1): 47-66. https://doi.org/10.1177/0734904118812227

[88] Zhang YM, Zhao Q, Li L, *et al.* Synthesis of a lignin-based phosphorus-containing flame retardant and its application in polyurethane. RSC Adv 2018; 8(56): 32252-32261. https://doi.org/10.1039/C8RA05598J

[89] Wang H, Wang S, Du X, Wang H, Cheng X, Du Z. Synthesis of a novel flame retardant based on DOPO derivatives and its application in waterborne polyurethane. RSC Adv 2019; 9(13): 7411-7419. https://doi.org/10.1039/C8RA09838G

[90] Jiang P, Gu X, Zhang S, Wu S, Zhao Q, Hu Z. Synthesis, Characterization, and Utilization of a Novel Phosphorus/Nitrogen-Containing Flame Retardant. Ind Eng Chem Res 2015; 54(11): 2974-2982. https://doi.org/10.1021/ie505021d

[91] Xi W, Qian L, Qiu Y, Chen Y. Flame-retardant behavior of bi-group molecule derived from phosphaphenanthrene and triazine groups on polylactic acid: Flame Retardant Polylactic Acid with Bi-Group Molecule. Polym Adv Technol 2016; 27(6): 781-788. https://doi.org/10.1002/pat.3714

[92] Jiang P, Zhang S, Bourbigot S, Chen Z, Duquesne S, Casetta M. Surface grafting of sepiolite with a phosphaphenanthrene derivative and its flame-retardant mechanism on PLA nanocomposites. Polymer Degradation and Stability 2019; 165: 68-79. https://doi.org/10.1016/j.polymdegradstab.2019.04.012

[93] Long L, Chang Q, He W, *et al.* Effects of bridged DOPO derivatives on the thermal stability and flame retardant properties of poly(lactic acid). Polymer Degradation and Stability 2017; 139: 55-66. https://doi.org/10.1016/j.polymdegradstab.2017.03.016

[94] Jia L, Zhang W-C, Tong B, Yang R-J. Crystallization, Mechanical and Flame-retardant Properties of Poly(lactic acid) Composites with DOPO and DOPO-POSS. Chin J Polym Sci 2018; 36(7): 871-879. https://doi.org/10.1007/s10118-018-2098-7

[95] Zhang W, Li X, Yang R. Flame retardant mechanisms of phosphorus-containing polyhedral oligomeric silsesquioxane (DOPO-POSS) in polycarbonate composites. J Appl Polym Sci 2012; 124(3): 1848-1857. https://doi.org/10.1002/app.35203

[96] Ni P, Fang Y, Qian L, Qiu Y. Flame-retardant behavior of a phosphorus/silicon compound on polycarbonate. J Appl Polym Sci 2018; 135(6): 45815. https://doi.org/10.1002/app.45815

[97] Liu C, Yao Q. Design and Synthesis of Efficient Phosphorus Flame Retardant for Polycarbonate. Ind Eng Chem Res 2017; 56(31): 8789-8796. https://doi.org/10.1021/acs.iecr.7b01915

[98] Sun Y, Wang Y, Qing Y, Wu X, Shi Z. A DOPO-base Schiff derivative used as a flame retardant for polystyrene. J Appl Polym Sci 2020: 49224. https://doi.org/10.1002/app.49224

[99] Wang Y, Qing Y, Sun Y, Zhu M, Dong S. A study on preparation of modified Graphene Oxide and flame retardancy of polystyrene composite microspheres. Designed Monomers and Polymers 2020; 23(1): 1-15. https://doi.org/10.1080/15685551.2020.1720934

[100] Dong Q, Liu M, Ding Y, *et al.* Synergistic effect of DOPO immobilized silica nanoparticles in the intumescent flame retarded polypropylene composites: Synergistic effect of SIO2-DOPO in PP/IFR composite. Polym Adv Technol 2013; 24(8): 732-739. https://doi.org/10.1002/pat.3137

[101] Yuan G, Yang B, Chen Y, Jia Y. Synthesis of a novel multi-structure synergistic POSS-GO-DOPO ternary graft flame retardant and its application in polypropylene. Composites Part A: Applied Science and Manufacturing 2019; 117: 345-356. https://doi.org/10.1016/j.compositesa.2018.12.006

Received on 28-10-2020 Accepted on 17-11-2020 Published on 03-12-2020

DOI: https://doi.org/10.31437/2415-5489.2020.06.7